Pine Wood Treated with a Citric Acid and Glycerol Mixture: Biomaterial Performance Improved by a Bio-byproduct

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Wood material is a good reservoir for biogenic carbon storage. The use of wood material for outdoor products such as siding in the building construction sector presents limits. These limits are bound to the nature of wood material (hygroscopic property and anatomical structure). They are responsible for the dimensional variation associated with moisture content variations. Fungal attacks and coating layers adhesion on wood surface, are other problems. This research investigated the feasibility of impregnation with environmentally friendly chemicals, *i.e.*, a citric acid-glycerol mixture (CA-G). The anti-swelling efficiency (ASE), hardness, biodegradation, and coating adhesion tests were performed on softwood specimens. ASE results were up to 53%. The equilibrium moisture content of the treated specimens was less than half of the untreated ones. FTIR spectroscopy showed bands at 1720 to 1750 cm^{-1}, indicating the presence of ester bonds, and scanning electron microscopy images confirmed the polymerization and condensation of treatment solution inside the wood structure. Hardness and decay resistance were increased; however, treatment reduces coating adhesion. In conclusion, CA-G represents a promising eco-responsible solution for improving the technical performance of outdoor wood products.

Keywords: Wood impregnation; Citric acid; Glycerol; Wood technical performance; Environmentally friendly treatment; By-product valorization

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INTRODUCTION

Outdoor solid wood siding is one of a number of wood products used in residential and nonresidential construction. In an exterior environment, wood products are subjected to various conditions that cause durability issues, such as dimensional instability (Chang and Chang 2001; Hill 2006; Ross 2010; Teaca *et al.* 2013) warping induced by internal tensions (Siau 1984), fungal attacks (Panshin *et al.* 1964; Van Acker *et al.* 1999), and photodegradation and pollutants (Hill 2006; Rosu *et al.* 2015).

In recent decades, various treatments of wood have been demonstrated. Heat treatment and oleo-thermal treatment with air-steam and oil as the thermal vector, respectively, are two of them. Treatments using chemicals are the most frequently investigated. Chemical modification is a very effective way of improving wood properties (Rowell 1984; Sèbe and De Jéso 2000; Hill 2006; Essoua E. *et al.* 2015). Indeed, several studies have focused on etherification and esterification reactions between treatment chemical solutions and wood hydroxyl groups: formaldehyde resins (Goldstein *et al.* 1959; Inoue *et al.* 1993; Lukowsky 2002), dimethyloldihydroxyethyleneurea (DMDHEU) (Weaver *et al*. 1960; Van Acker *et al.* 1999); furfural alcohol (Westin *et al.* 2004); maleic acid and glycerin (Uraki *et al.* 1994); and citric acid (Hasan *et al.* 2012). In addition to these reactions (etherification and esterification), bulking of the wood cell walls with hydrophobic polymers has been found to improve dimensional stability using organosilicone or alkoxysilane molecules (Sèbe and De Jéso 2000; Sèbe *et al.* 2004).

Among other factors, the use of petrochemical products, the complexity of the treatment process, the cost of chemical products, and human and environmental toxicity of the treatment solutions have limited the industrialization of these processes conducted in laboratories. Given the weight of environmental issues in current political and industrial decisions, the scientific community has called for environmentally and industrially applicable solutions. The development of new using and valorization of biodiesel industry byproduct is a good beginning (Guerrero *et al.* 2015). Glycerol is a byproduct of the biodiesel refining process based on a vegetal renewable resource. The amount of crude glycerol produced represents 10% of the biodiesel production (Maminski *et al.* 2011; Yang *et al.* 2012; Wen 2012). Expansion of biodiesel production in the previous decade has created a surplus of crude glycerol in the market. For example, worldwide crude glycerol from biodiesel production increased from 200,000 tonnes in 2000 (Pagliaro and Rossi 2008) to 1.224 million tonnes in 2008 (Yang *et al.* 2012). Crude glycerol production in 2016 is estimated to be approximately 12.6 million tonnes (Anand and Saxena 2011). Therefore, development of novel and sustainable use and valorization of this raw material is imperative to maintain the sustainability of biodiesel production (Guerrero *et al.* 2015).

Glycerol is a trifunctional compound that can react with carboxylic acids (*i.e.*, citric acid) to form the corresponding ester bonds. Under the effect of heat, with or without a catalyst, the citric acid-glycerol mixture (CA-G) produces resistant polymers. The temperature and reaction time are two parameters that are most important in this process. In the same conditions (without catalyst), at lower temperature (90 °C) the number of OH groups that react to form esters bonds with citric acid is lower than in the high temperature condition as 130 °C (Halpern *et al.* 2013). The reason for this is that, at lower temperature, the water formed in the reaction remains in the mixture for a longer time. In the case of high temperature treatment, this formed water evaporates and the reaction rate increases (Budhavaram and Barone 2008). At the same temperature, different reaction time produce polymers with different properties. At 110 °C, polymers produced at different reaction times (5 h, 8 h, 12 h, and 24 h) present different hydrolyzation times in water (2 days, 12 days, 34 days, and 50 days), respectively (Trenkel-Amoroso 2008). The reaction of carboxylic acid groups is a nucleophilic substitution reaction on the acyl carbon. Carboxylic groups of citric acid present lower reactivity to the acyl carbon than anhydride carboxylic groups (Bender 1960). Esterification of the citric acid and glycerol mixture has been shown to yield polymer networks of varying complexity, depending on the ratio and esterification parameters used (Pramanick and Ray 1988; Halpern *et al.* 2013). The structure of the acid, the extent of the reaction, and the crosslinking density influence the properties in the resulting material (Holser *et al.* 2008).

As a partial solution, this study explored several technical aspects of the performance of outdoor softwood treatment with a citric acid and glycerol (CA-G) mixture. For a better understanding of the work, this paper has been divided into four sections. The first section focuses on demonstrating that the proposed treatment improved dimensional stability in terms of anti-swelling efficiency (ASE-a), anti-shrinkage efficiency (ASE-b), and water sorption isotherms. The second section discusses the ability of the treatment to improve wood hardness and successively increase density. The third section relates to decay tests, followed by the fourth section, which examines coating adhesion to the wood substrate, comparing treated and untreated specimens. To analyze these results, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and density profiles were performed.

EXPERIMENTAL

Materials

White pine (Wp) (*Pinus strobus* L.) and lodgepole pine (Lp) (*Pinus contorta* D.) wood specimens used in this work were supplied by Maibec Inc., Saint-Pamphile, Quebec, Canada.

Chemicals used were anhydrous citric acid (CA_A) and hydrochloric acid (HCl), obtained from Sigma-Aldrich Co., St Louis, MO. Glycerol (G) was obtained from Rothsay Biodiesel, Ville Ste-Catherine, Québec, Canada. For the decay test, the fungi strain 103 A of *Irpex lacteus* (IL), for white rot, and strain 120 AM of *Postia placenta* (PP), for brown rot, were obtained from FPInnovations, Canada.

Specimen preparation

The wood planks selected were free of sapwood, knots, and resin pockets. Planks were planed and specimens were cut to size in the tangential fiber direction. Then they all were conditioned at 20 ± 2 °C and 40 ± 4% relative humidity (RH). The dimensions of wood specimens were selected considering the standards used in this study. Table 1 shows the specimen dimensions used for each test. All specimens were free of knots, resin pockets, or any other defects.

Table 1. Specimen Dimensions for Various Tests

Test and analysis	Length (mm)	Width (mm)	Thickness (mm)
Swelling (α) and shrinkage (β)	20	20	10
FTIR	25	25	10
SEM	25	25	10
Hardness	50	20	20
Density profile	50	50	20
Fungal decay	25	25	10
Pull-off	60	60	10

Preparation of treatment solution

The total mass of the solution was divided into five parts in a ratio of 3:1:1 by weight: three parts CA_A, one part G, and one part distilled water. The catalyst (HCl) made up 2% of the total mass of the solution. Figure 1 represents schematically the different steps involved in the preparation process and the respective proportions of the ingredients.

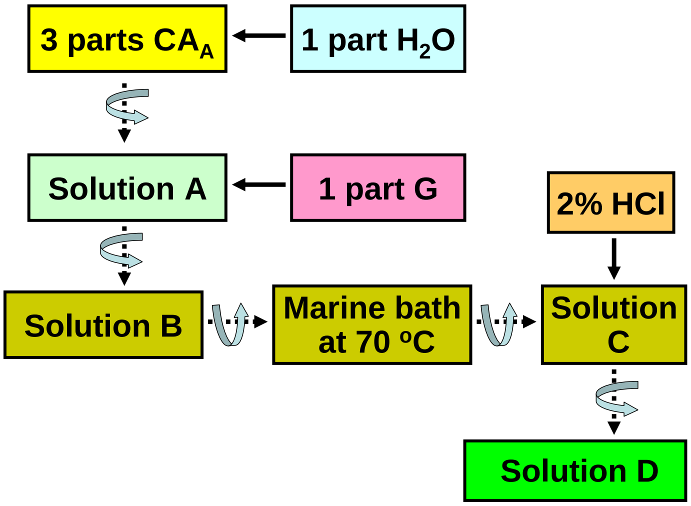

Fig. 1. Schematic representation of the solution preparation process; [1] stirring

Methods

Impregnation parameters

Solution D contained a mixture of CA-G-H_20 plus 2% catalyst (HCl). The wood specimens were impregnated with Solution D inside a pressure reactor vessel, Model 4522 from Parr Instrument Company, Illinois, USA. The reactor was connected to a vacuum pump and to a bottle of N_2, which was used to apply pressure. The use of different pressure and time values served to determine the effects of these parameters on wood modification at the core of the specimens. Preliminary tests were performed to identify suitable impregnation parameters. These parameters were set according to specimen size and wood species. A vacuum of 72 kPa was applied to the specimens of both species, with the time being 0.5 h for Wp and 0.75 h for Lp specimens. The pressure values that led to the best impregnation results for Wp and Lp wood are presented in Table 2.

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

Dimensions (mm)	White pine		Lodgepole pine	
	Pressure (kPa)	Time (h)	Pressure (kPa)	Time (h)
20 x 20 x 10	1378.952	2	2068.428	2
25 x 25 x 10	1378.952	2.5	2068.428	3
60 x 60 x 10	2068.428	3	2757.904	3.5
50 x 20 x 20	2068.428	3	2757.904	3.5
50 x 50 x 20	2068.428	4	2757.904	4.5

Wood treatment

The wood specimens were sized in accordance with the standards used in the study. The specimens were placed inside the reactor shell in the fiber direction most appropriate for impregnation. Impregnation conditions were as shown in Table 2. The specimens were first impregnated with the treatment solution using a vacuum and pressure process. Pressure was applied as described in Fig. 2. *In-situ* polymerization was achieved in an oven at 180 °C for 2 to 4 h, the time being related to the specific specimen dimensions.

Impregnation to the core increased specimen width and thickness. During the esterification and condensation reactions occurring in the oven, the specimens lost part of the solution as they shrank. Immediately after the reaction, they were placed inside a desiccator containing phosphorus pentoxide (P_2O_5) for cooling. The cooling time varied according to the specimen dimensions, with a minimum of 30 min. Following the cooling step, the layer of polymerized CA-G product remaining on specimen surfaces was removed by sawing to eliminate surface roughness and restore right angles, as required for accurate swelling and shrinkage measurements. Measurement accuracy was 0.001 mm, as determined with a digital micrometer from Insize CO., Ltd., China.

At the end of the cleaning operation, all the specimens were conditioned to a constant mass at 20 ± 2 °C and 40 ± 4% RH. For each wood species, five treated and five untreated specimens were taken randomly as controls.

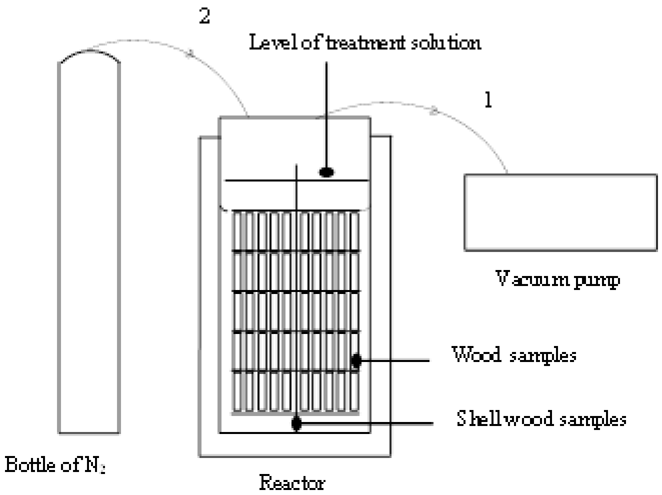

Fig. 2. Impregnation process diagram: (1) indicates first step followed by (2) second step (Essoua Essoua *et al.* 2015)

Swelling, shrinkage, anti-swelling, and anti-shrinkage efficiency measurements

The impregnated 20 x 20 x 10-mm specimens were tested through three cycles of water immersion (three days at ambient temperature for each cycle) and oven drying at 103 ± 2 °C for 24 h. Specimen widths and thicknesses were measured before each test. Swelling (α) of treated and untreated specimens was measured in the radial (α_R) and tangential (α_T) directions, and calculated with Eqs. 1 and 2,

$$\alpha_R\,(\%) = [(R_1-R_0)/R_0] \times 100 \qquad (1)$$

$$\alpha_T\,(\%) = [(T_1-T_0)/T_0] \times 100 \qquad (2)$$

where R_0 and R_1 are the radial dimensions of the specimens respectively, before and after the swelling test, while T_0 and T_1 are the corresponding tangential dimensions.

Radial shrinkage (β_R) and tangential shrinkage (β_T) were also measured in the radial and tangential directions with the same device and calculated with Eqs. 3 and 4:

$$\beta_R\,(\%) = [(R_1-R_0)/R_1] \times 100 \qquad (3)$$

$$\beta_T\,(\%) = [(R_1-R_0)/R_1] \times 100 \qquad (4)$$

The swelling and shrinkage results in the radial and tangential direction coefficients were added up to determine the swelling or shrinkage coefficients (Eqs. 5 and 6). As confirmed by many authors in the literature, longitudinal swelling and shrinkage before and after immersion in water can be neglected, as they do not vary significantly in that direction (Panshin *et al.* 1964; Norimoto *et al.* 1992; Sèbe and De Jéso 2000; Hill 2006; Ross 2010).

$$\alpha\ (\%) = (\alpha_R + \alpha_T) \tag{5}$$

$$\beta\ (\%) = (\beta_R + \beta_T) \tag{6}$$

The specimen swelling (α) and shrinkage (β) coefficients were used to calculate the anti-swelling efficiency (ASE-a) and anti-shrinkage efficiency (ASE-b) (Eqs. 7 and 8). It is worth noting that the swelling and shrinkage of the regular wood specimens were calculated by reference to the same specimens before and after the test, while the ASE of treated specimens was calculated by reference to the untreated specimens.

$$\text{ASE-a}\ (\%) = [(\alpha_{ut} - \alpha_t)/\alpha_{ut}] \times 100 \tag{7}$$

$$\text{ASE-b}\ (\%) = [(\beta_{ut} - \beta_t)/\beta_{ut}] \times 100 \tag{8}$$

where α_t and β_t, respectively, represent the swelling and shrinkage coefficients of treated (t) wood specimens, while α_{ut} and β_{ut}, respectively, represent the swelling and shrinkage coefficients of untreated (ut) specimens.

Water vapor sorption isotherm test

Studies on the adsorption and desorption of wood examine the relationship between equilibrium moisture content (EMC) and relative humidity (RH) at constant temperatures (isotherm) (Siau 1984; Hill 2006). In this research, adsorption and desorption tests served to determine the effect of the impregnation treatment on the EMC of both wood species. Heat treatments at 180 °C without chemical impregnation were used to single out the effect of temperature on the EMC of the specimens. The reduced equilibrium moisture content (EMCr) is generally used as a reference to calculate the effect of a chemical treatment on a treated wood specimen. It was calculated using Eq. 9. For the sorption test, the specimens' dimensions were 3 x 3 x 3 mm, and a VTI-SA + vapor sorption analyser was used (TA Instruments, USA). RH was ramped up from 0% to 95% at a constant temperature in the environment test,

$$\text{EMCr}\ (\%) = [(M_2 - M_1)/ M_0] \times 100 \tag{9}$$

where M_0 is the oven-dry weight of the specimen before modification, M_1 is the oven-dry weight of the specimen after modification, and M_2 is the weight of the modified specimen at equilibrium with the atmosphere at a given RH.

Fourier transform-infrared spectroscopy (FTIR) analysis

Chemical analyses of the treated and untreated wood specimens were performed with FTIR. The purpose was to confirm the presence of ester bonds in the structure of the treated wood. Such bonds result from chemical reactions between acid carboxylic groups (COOH) in the citric acid and hydroxyl groups (OH) in the glycerol. Ester bonds also result from reactions between acid carboxylic groups (COOH) in the citric acid and hydroxyl groups (OH) in wood macromolecules. Specimen spectra were recorded with a FTIR spectrophotometer equipped with an Attenuated Total Reflectance (ATR) crystal (model spectrum 400, Perkin Elmer, UK). The parameters used for all analyses were: 4 cm^{-1} resolution, 64 scans, wavenumber range 4000 to 500 cm^{-1}, and absorbance mode. Prior to analysis, the treated and untreated specimens were conditioned at 20 ± 2 °C and 40 ± 4% RH. The treated specimens were analyzed on their external surface and half way through their thickness. After analysis of external surfaces, the specimens were cut half-way through the thickness (Fig. 3). Four repetitions were performed to confirm the effective presence of ester bonds and a reduction in the presence of wood OH groups.

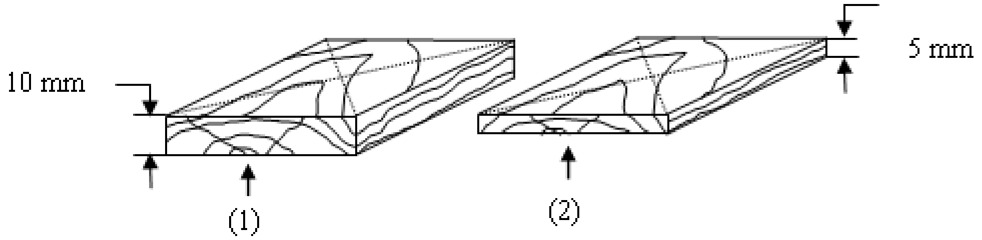

Fig. 3. Specimen surfaces analyzed with Fourier transform infrared spectroscopy: (1) external surface and (2) middle surface half-way through the thickness

Scanning electron microscopy (SEM)

SEM analysis using a JSML-6360LV (JEOL Corporation, Japan) was performed to investigate and compare the morphology of the treated and untreated wood specimens. Four 10 x 10 x 10-mm treated specimens (longitudinal-transversal-radial) and the same number of untreated specimens were selected randomly for each wood species and immersed in distilled water for a few days to facilitate wood surface preparation with a microtome (Leica SM 2400, Germany). The setting parameters were as follows: acceleration voltage, 30 kV; spot size, 46; vacuum mode, high vacuum (HV); and signal, SEI. Images were obtained from transversal sections at low magnification (x600) to evaluate a broad surface area.

Hardness test

This test was performed according to the general guidelines of ISO 1534 (2000). In the Brinell hardness definition the diameter “*d*” (in millimeters) of the residual indentation was measured by the operator with a digital caliper. As this measurement was not very accurate, the Brinell hardness equation was not used. The load Applied on the specimen surface was used to determine the surface hardness of wood specimen.

Instead, three parameters were fixed as follows: surface detection load, 10.000 N; high extension limit, 1.00 mm; and initial speed, 2.00 mm/min. The parameters were the same for treated and untreated specimens of both wood species. The applied load required to produce 1.00 mm of extension at a speed of 2.00 mm/min was deemed to represent the hardness of specimens. The ball diameter (*D*) was 10 mm.

All the specimens were prepared for tangential and radial surface tests. Six 1220 x 140 x 35-mm specimens of each wood species were conditioned at 20 ± 2 °C and 40 ± 4% RH to a constant mass. They were planed and sawed to 50 x 20 x 20 mm (longitudinal x tangential x radial), and then conditioned under the same conditions. Treated wood specimens were sawed clean and then conditioned again at 20 ± 2 °C and 40 ± 4% RH.

Two indentations were performed per specimen: one on the tangential face and one on the radial face. The load was applied perpendicularly to the specimen surface at the intersection point of the two diagonals. A template was prepared to facilitate specimen positioning in the test machine. The tests involved 40 treated and 20 untreated specimens for each wood species. Testing was performed with a Material Testing System QTest/5KN (MTS, USA). Ambient room conditions during the test were kept at 20.1 ± 0.2 °C and 61.4 ± 0.3% RH.

Density profiles

Density profiles were obtained to determine the effectiveness of the modification treatment at various depths. This test was performed with an X-ray densitometer system, QDP-01X (Quintek Measurement Systems Inc, USA) on the same specimens before and after treatment. Six 50 x 50 x 20-mm (length x width x thickness) specimens of each wood species were analyzed. Before analysis, all the specimens were identified so that they could be placed in the same position inside the equipment. The test was performed according to the general guidelines of the ASTM D2395 (2014).

Decay test

Resistance to the decay was tested through a method inspired by AWPA E10 (2012). Six 25 x 25 x 10-mm (length x width x thickness) treated and two untreated specimens for each species were tested in every repetition, with six repetitions being performed under the same test conditions. In each repetition, the eight specimens were divided into two groups. Each group was exposed to one fungus strain of Basidiomycete, *i.e.*, strain 103 A of *Irpex lacteus* for white rot, and strain 120 AM of *Postia placenta* for brown rot.

Anhydrous specimen weights (W_0) were determined before exposure to the inoculated environment. To prepare the culture environment, a Malt-Agar solution was introduced into a sterilized environment, and V-form glass stalks were placed inside the bottle. After three days, the culture environment was inoculated with the fungal strains. At the end of 14 days, the sterilized specimens at about 20% MC were exposed to a fungal attack for 10 weeks.

At the end of the 10 weeks, the specimens were removed from the bottle, and fungal growth was carefully removed with a brush from the wood surfaces. The specimens were weighed (W_1) and dried for 72 h in a vacuum oven at 40 °C and 30 in Hg. After drying, the specimens were weighed (W_2) one more time. W_1 provided an indication of specimen MC (Eq. 10), an important factor in the assessment of fungal activity.

$$\text{MC (\%)} = [(W_1-W_2)/W_2] \times 100 \qquad (10)$$

The weight loss caused by fungal activity was calculated using Eq. 11:

$$\text{Weight loss (\%)} = [(W_0-W_2)/W_0] \times 100 \qquad (11)$$

FTIR analyses were performed before and after fungal exposure to determine whether the chemical composition had changed. This approach has been extensively studied (Pandey and Pitman 2003; Li *et al.*, 2011; Shang *et al.* 2013). Different spectrum peaks were studied for holocellulose (cellulose and hemicellulose). Peaks were observed at 1734 to 1719 cm^{-1} for unconjugated C=O stretching (hemicellulose) in the case of holocellulose (cellulose and hemicellulose); 1644 to 1638 cm^{-1} for C=C of holocellulose;

approximately 1454 cm^{-1} for an H-C-H vibration of cellulose and lignin; and 1170 to 1153 cm^{-1} and 897 cm^{-1}, respectively, for O-H and C-O-C vibrations of cellulose and hemicellulose. For the lignin component, peaks were observed at 1515 to 1504 cm^{-1} and 1260 to 1234 cm^{-1} for aromatic skeletal vibration and O-H stretching, respectively (Owen and Thomas 1989; Bodîrlau and Teaca 2009; Li *et al.* 2011).

Adhesion Tests

This part of the paper describes wood surface preparation, coating application and drying, and pull-off strength testing.

Wood surface preparation

To eliminate blemishes and produce smooth and uniform surfaces, the treated and untreated specimens were sanded with sandpaper (aluminum oxide type, Sia abrasives Inc., Switzerland) mounted on a Costa belt sander (model 36 CCK 1150 Costa & Grisson Machinery CO Inc., Italy). The feed speed was 8 m/min. A first pass at 80 grit was followed by passes at 120 and 150 grit.

Coating application and drying

The white opaque coating used to finish the specimens was a self-crosslinking water-based acrylic for exterior applications manufactured by Cabot (USA).

The coating was applied with a high-volume low-pressure (HVLP) spray gun following supplier instructions. The viscosity of the coating was measured at 23 °C with a Brookfield viscometer (model RVDVI+ Brookfield Eng Labs Inc, USA) and a No. 1 RV spindle set. Viscosity was found to be 951 cP at 27 RPM. Three layers of the 59.1% solids coating were applied on one wood surface. The wet film thickness was found to be 2 mils (as measured with a comb) for the first and second layers and 3 mils for the third layer. Thickness was measured at three different points in the same diagonal on the wood coating surface. Coated specimens were then air dried in a room at 21.7 °C and 23.7% RH for 12 h.

Pull-off strength test

The finished specimens were tested quantitatively and qualitatively for coating adhesion. The quantitative tests were performed were adapted from ASTM D4541 (2009). This standard recommends using a portable machine, but in this work, a QTest/5kN machine was used. After the coating had dried, the specimens were conditioned to a constant weight at 20 ± 2 °C and 60 ± 4% RH. All surfaces were manually cleaned with a dry wipe to remove any dust before the aluminum dollies were glued onto the specimens.

The 20-mm aluminum dollies were from DeFelsKo Corporation, Ogdensburg, NY. They were cleaned to remove dust, and a 1-to-2 mm layer of marine epoxy adhesive (from Henkel Canada Corporation, Mississauga, ON) was placed on their surface. Care was taken to ensure that the adhesive components did not affect coating properties. The two components constituting the adhesive, hardener, and epoxy resin, were mixed correctly without air bubbles, and then applied onto the dolly surface with a wood spatula. The dolly was pasted at the center of the specimen surface with low manual pressure applied in a circular movement to remove air bubbles from the adhesive. Each coated specimen had one dolly placed at the center of its surface. The wood specimens with their dollies were cured in a conditioning chamber at 20 ± 2 °C and 60 ± 4% RH for 24 h.

After curing, the coating and any excess adhesive around each dolly were removed with a cutting tool (20.63-mm internal diameter) mounted on an automatic drill (model 75-150-M1; imported by General International MFG. CO. Ltd) to ensure that the pull-off load was applied to the exact surface of the dolly. The pull-off testing machine (Material Testing System (MTS), QTest/5kN model from MTS Systems Corporation, Eden Prairie, MN) allowed for constant and repeatable tests. This machine was used for the same purpose by Hernandez and Cool (2008) and Nkeuwa *et al.* (2014). The dollies were placed in the machine and a load (F) was applied perpendicularly to the dolly at a specimen displacement rate of 2 mm/min. The maximum load ($F_{\max}$) was expressed in Newtons (N) and served to calculate adhesion strength as per Eq. 12,

$$\text{Adhesion strength (MPa)} = 4\, F_{\max}/\pi d^2 \qquad (12)$$

where "*d*" is the dolly diameter (mm).

Testing was performed on 30 treated and 30 untreated specimens for each wood species. Laboratory environmental conditions during testing were kept at 20.1 ± 0.2 °C and 61.4 ± 0.3% RH.

The failures induced by pull-off tests occurred at different levels: 1) at the dolly/coating interface; 2) between two different coating layers; and 3) at the coating/wood interface (Nelson 1995; Nkeuwa *et al.* 2014). Failure modes were determined according to ISO 4624 (2002), section 9.5.2. For each specimen set (treated and untreated for both species), the failure mode was determined, as was the average percentage of the total dolly surface area covered by material. Cross sections of coated specimens were subjected to SEM analysis to determine the level of coating anchored to the wood structure.

RESULTS AND DISCUSSION

The weight percent gain (WPG) resulting from the impregnation treatment was on the order of 30% to 35% in both wood species.

Swelling (α), Shrinkage (β), and Anti-Swelling Efficiency and Anti-Shrinkage Efficiency Measurement

ASE (a-b) values, shown in Fig. 4, were calculated by reference to the untreated specimens. They clearly indicate that polymerization of the treatment solution occurred in the wood structure, with bonds forming between hydroxyl groups in the wood macromolecules and carboxylic groups from the citric acid. In the swelling test, ASE-a loss between the first and third cycles was lower with the Lp wood specimens than with the Wp specimens. The opposite was observed in the shrinkage test. The Lp ASE-b values after the third cycle were 60.17% for swelling and 59.12% for shrinkage. For the Wp specimens, they were 53.41% for swelling and 54.37% for shrinkage. Yang *et al.* (2013) impregnated European aspen specimens with oxidized carbohydrates to improve their dimensional stability. The anti-swelling efficiency (ASE-a) of this treatment was around 35% to 45%. ASE-a results obtained after wood treatment with maleic anhydride and glycerol or maleic anhydride only were also less than those obtained in this section, at approximately 48% (Roussel *et al.* 2001; Essoua Essoua *et al.* 2015).

Sorption isotherms illustrated the effect of the treatment on moisture uptake. Treated specimens picked up less water than untreated specimens and specimens heated to 180 °C. The EMC of Lp and Wp treated specimens was only half that of untreated ones at 95% RH. As indicated by the isotherms of Wp specimens, the EMC of specimens heated to 180 °C was approximately 19%; this value was 18% for untreated specimens and 8% for treated specimens (Fig. 5). Regarding Lp specimens, nearly the same values were measured. These confirm that dimensional stability does not result from heat exposure but from the chemical reaction between the treatment product and hydroxyl groups from wood. The average values of EMCr after treatment were 52.39% and 53.54% for Lp and Wp, respectively.

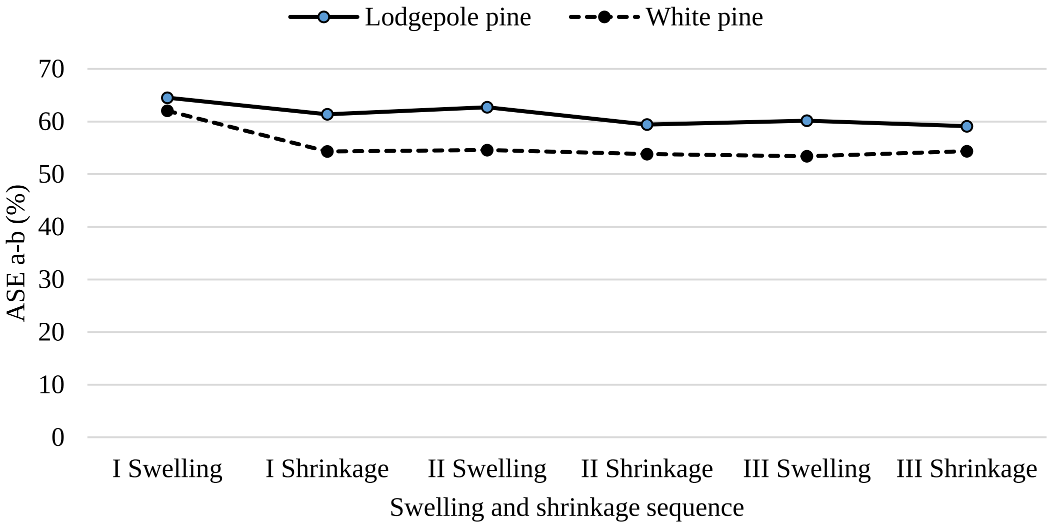

Fig. 4. Average ASE a-b values observed after 1, 2, and 3 cycles

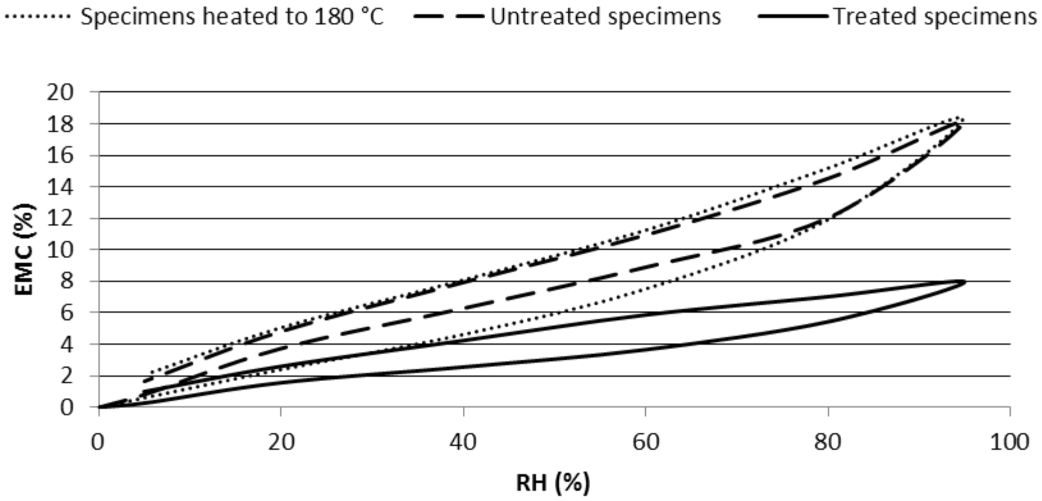

Fig. 5. Adsorption and desorption isotherm of Wp specimens

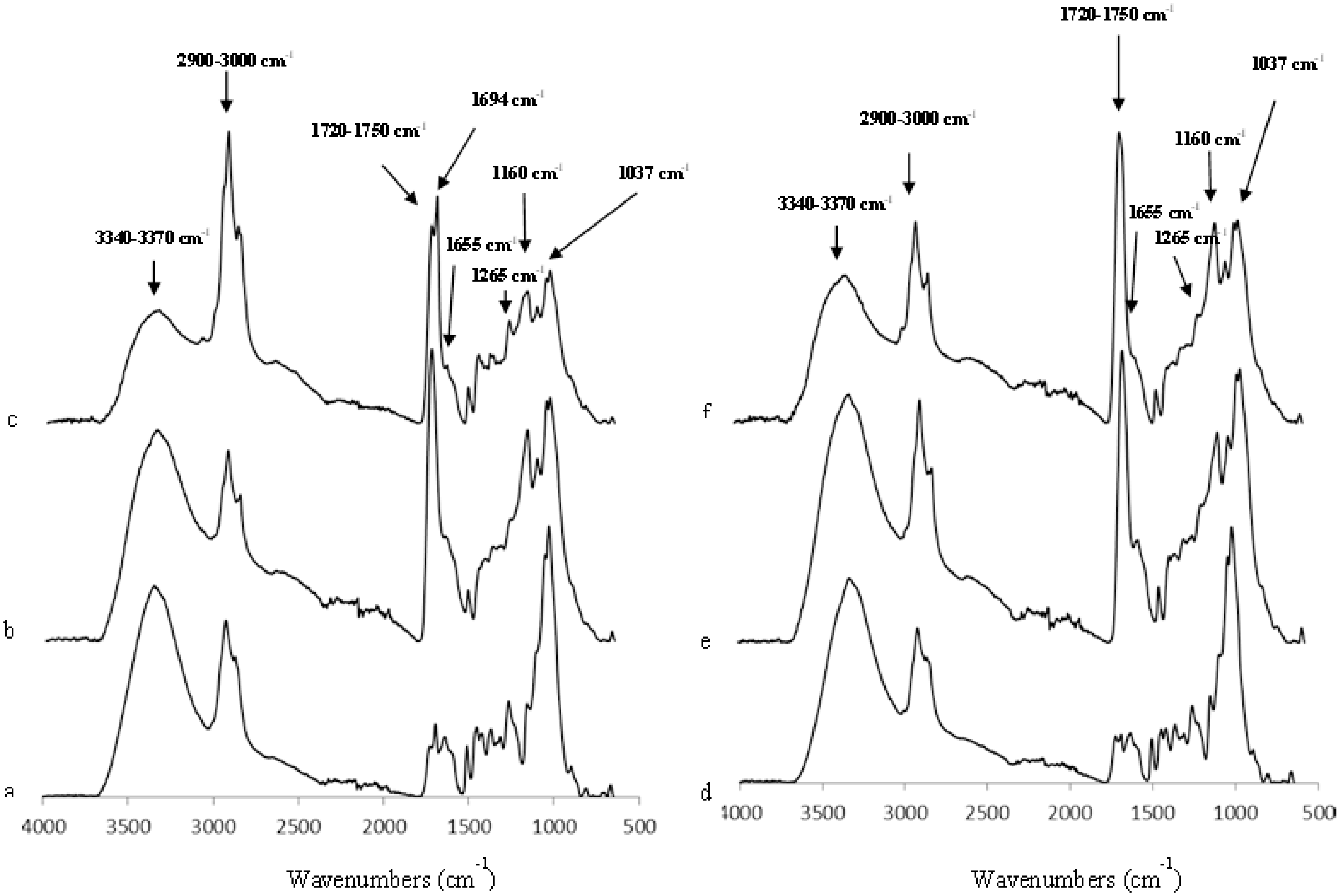

Fig. 6. FTIR spectra of untreated and treated Lp and Wp specimens. Letters a, b, and c, respectively represent the spectra of the outer faces of untreated specimens and the outer and middle faces of treated specimens of Lp wood, while d, e, and f represent the same spectra for Wp wood specimens.

Regarding the chemical analyses by Fourier transform infrared spectroscopy (FTIR), the spectra of all treated specimens (Fig. 6) presented peaks between 1720 and 1750 cm^{-1} corresponding to ester bonds (Paukszta *et al.* 2014). Ester groups resulted from polymerization reactions between glycerol and citric acid molecules, and between the carboxylic groups of citric acid and wood hydroxyl (OH) groups (monoester and/or diester linking). A broad O-H absorption elongation vibration occurs in the region of 3600 to 3200 cm^{-1} (Holser *et al.* 2008; Yong *et al.* 2010). This OH group peak is due to glycerol, citric acid, and wood molecules. This wavenumber was characterized by low absorbance intensity in the case of treated specimens. The presence of these ester bonds indicates a reduction in wood hydroxyl groups able to react with water molecules, which explains why the treated specimens picked up less liquid water or vapor than their untreated counterparts.

FTIR spectra in absorbance mode showed peaks in the 2950 to 2855 cm^{-1} region, indicating C-H elongation vibration of citric acid (Brioude *et al.* 2007). With both wood species, higher intensities were observed in the middle of the specimens (half thickness) than on outer faces. The peak at 1165 cm^{-1} was indicative of (CO) linking, and the peak near 1037 cm^{-1} was attributed to glycerol (Barone and Arikan 2007). Bands at 1655 cm^{-1} and 1265 cm^{-1} were a sign of higher intensity in the spectrum of the middle faces than those on the outer faces of the treated specimens, which can be explained by incomplete reactions in the middle of Lp specimens.

SEM images of treated wood cross sections present cell lumens and cell walls filled with polymer (Fig. 7, (b) and (d)), while this was not the case with the untreated specimens (Fig. 7, (a) and (c)). The presence of polymer inside the wood structure influenced the physical and chemical properties of the wood, one effect being reduced swelling and shrinkage.

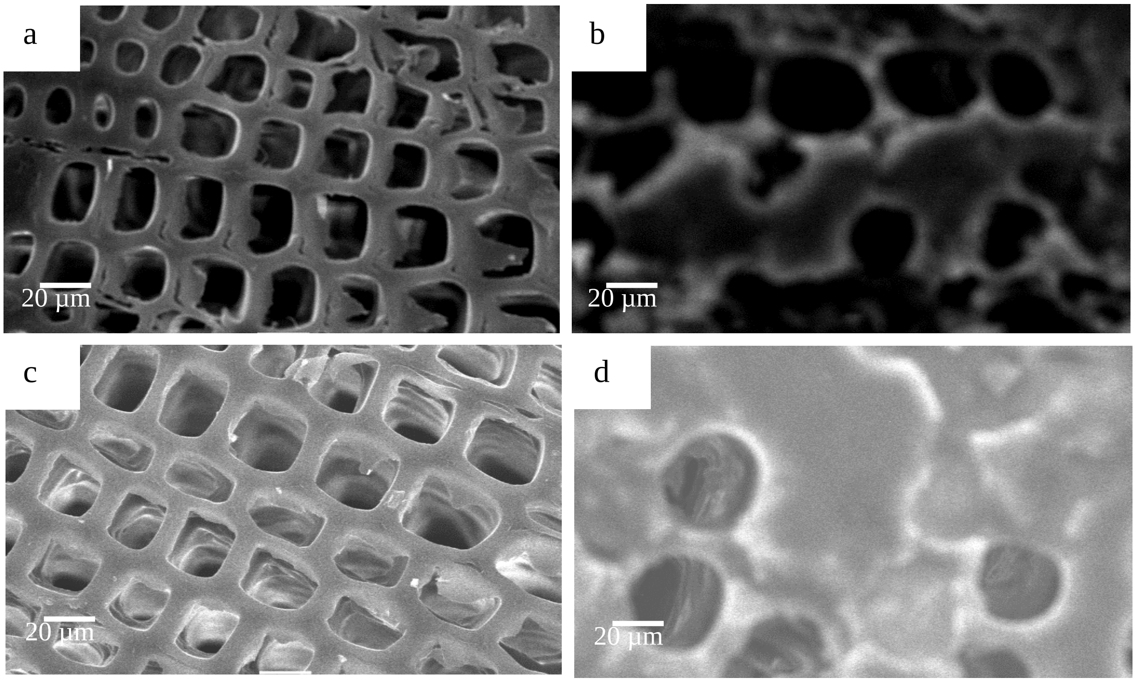

Fig. 7. SEM images of wood cross sections. (a) and (b): untreated and treated Lp; (c) and (d): untreated and treated Wp

Hardness

For both studied wood species, the hardness varied with fiber direction. According to Green *et al.* (2006), Lp and Wp woods are harder in the tangential than in the radial direction. This was confirmed by measurements from this study. By filling the empty spaces in the wood structure with a solid material, a polymer treatment increases specimen hardness in both directions (Cai 2007). The surface hardness of treated specimens was higher in the tangential direction than in the radial direction (Korkut *et al.* 2008). As shown in Fig. 8, the load applied to produce 1.00 mm of extension on treated Lp specimens was 534.09 N in the radial direction and 742.98 N in the tangential direction, with equivalent values of 500.10 N and 602.29 N for Wp. The average load values applied (average of radial and tangential values) of all specimens, treated and untreated were 406.25 N and 633.61 N for Lp and 352.21 N and 535.35 N respectively. Treatment solution became solid in wood structure after heating at 180 °C, and this increased specimen surface hardness.

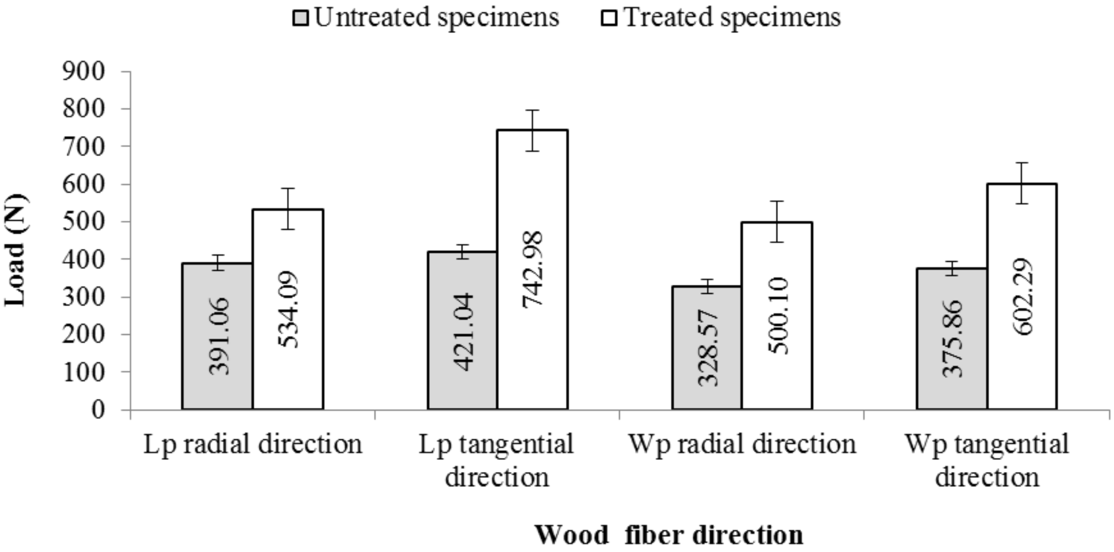

Fig. 8. Average load values applied on Lp and Wp specimens in the radial and tangential directions

SEM analyses of treated specimens help to explain why specimens increase density after treatment. Density profiles for Lp and Wp specimens before and after treatment are shown in Figs. 9 and 10.

Regarding the fiber direction, Fig. 9 presents a specimen profile that is more regular than the one presented in Fig. 10. This is because, in Fig. 9, growth rings were parallel to the X-ray emissions of the machine test, while in Fig. 10, growth rings were perpendicular to the X-rays. The peaks in Fig. 10 correspond to late wood and provide information about the density variation inside growth rings.

As can be seen from Table 3, the density of all specimens of both species was greater after treatment, with average increases of 200 kg/m^3 for Lp and 180 kg/m^3 for Wp. Filling the empty spaces in the wood structure with solid material increased the specimen density.

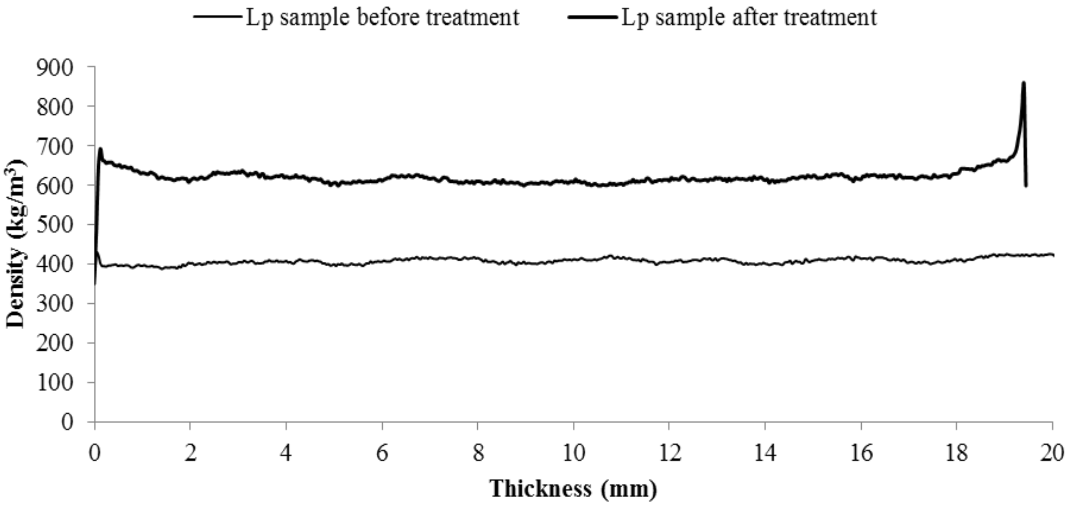

Fig. 9. Density profile of Lp specimens in the radial fiber direction

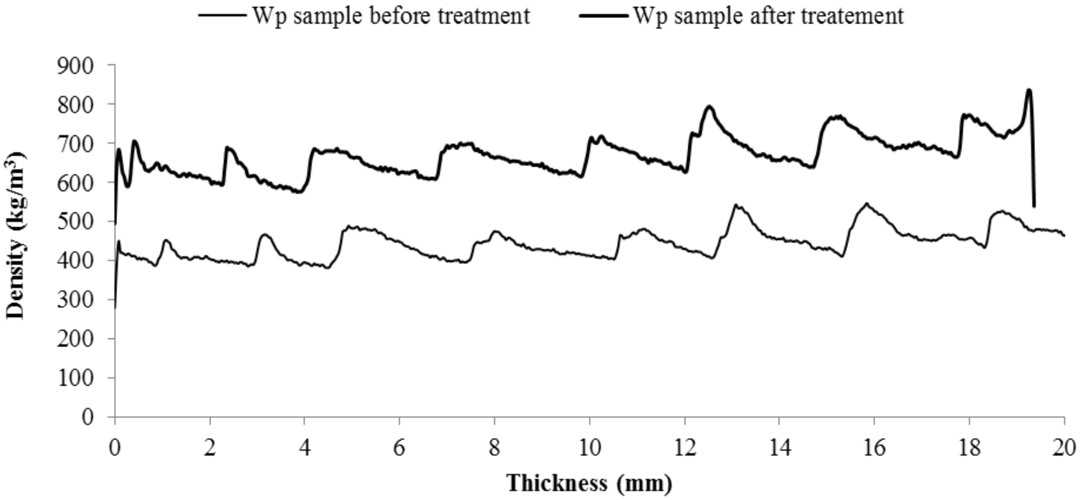

Fig. 10 Density profile of Wp specimens in the tangential fiber direction

Table 3. Average Density Values of Specimens Before and After Treatment for Both Wood Species

Specimen N°	Specimen density of Lp before treatment (kg/m^3)	Specimen density of Lp after treatment (kg/m^3)	Specimen density of Wp before treatment (kg/m^3)	Specimen density of Wp after treatment (kg/m^3)
1	436.13	563.13	443.88	670.23
2	506.97	600.56	444.07	669.69
3	511.50	739.36	435.21	663.57
4	433.49	732.62	446.95	589.06
5	439.95	743.57	450.71	581.64
6	407.98	620.60	438.09	592.29
Average values	456.00	666.64	443.15	627.75

Decay Test

The average values of weight loss (WL) resulting from fungal activity, shown in Fig. 11, demonstrated greater WL in untreated than in treated specimens of both wood species. The PP strain proved more aggressive than the IL strain, with average WLs of 39.67% and 36.36% for untreated Lp and Wp specimens, as compared with 3.64% and 1.74% for IL. With the treated specimens, WL was much lower with both fungal strains, with average values of 0.72% and -3.54% for Lp and Wp, respectively, in the case of PP, and -0.43% and -4.09% for IL. A possible explanation for the weight gains observed would be the liberation of sorption water (hydroxyl groups) from the wood or polymer structure because of fungal action. For a better understanding of this phenomenon, fungal resistance tests should be conducted separately on the biopolymer.

Visual observation of the specimens confirmed the superior resistance to decay of the treated wood, which had suffered far less degradation and deformation than the untreated material.

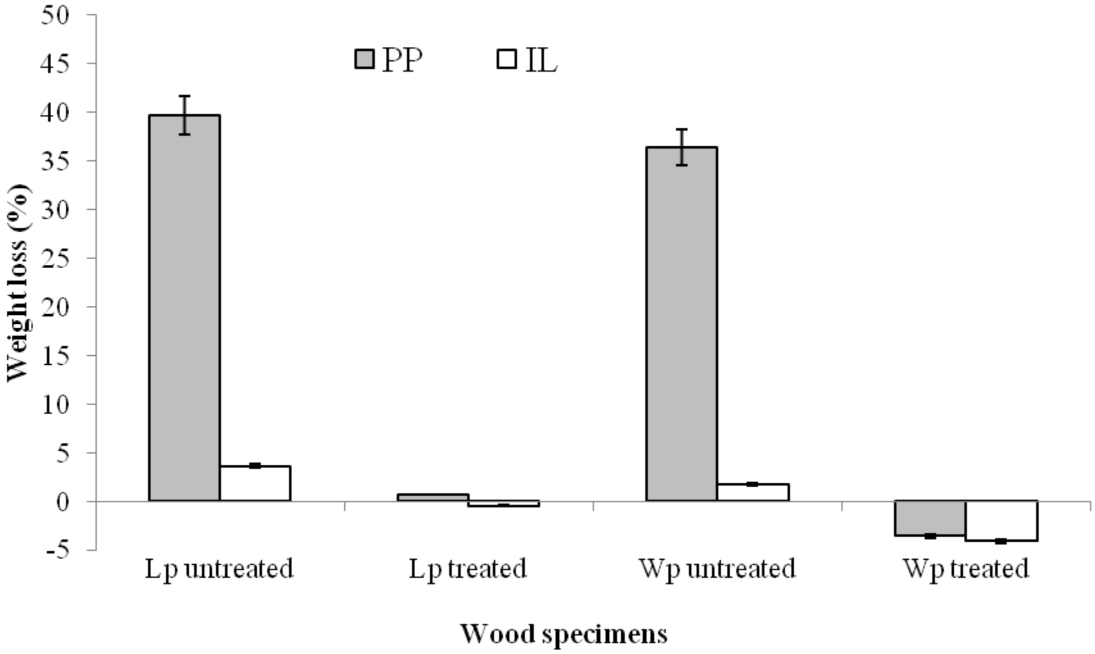

Fig. 11. Average WL values following exposure to *Postia placenta* (PP) and *Irpex lacteus* (IL) fungi

The FTIR-ATR spectroscopy results also supported these observations. The relative intensities of the holocellulose (cellulose and hemicellulose) and lignin bands revealed differences between exposed and unexposed specimens (Fig. 12) with both species and both fungi. With untreated Lp and Wp, the relative intensities of holocellulose (1740 to 1730, 1454, 1260 to 1234, 1170 to 1153, and 897 cm^{-1}) decreased with fungal exposure, while the lignin bands presented the same intensities before and after exposure. In treated specimens, the holocellulose and lignin bands (1260 to 1234 cm^{-1}) increased in intensity after fungal exposure. For the band 1515 to 1504 cm^{-1}, intensity increased for the treated Wp specimens exposed to the IL strain but decreased with the PP strain.

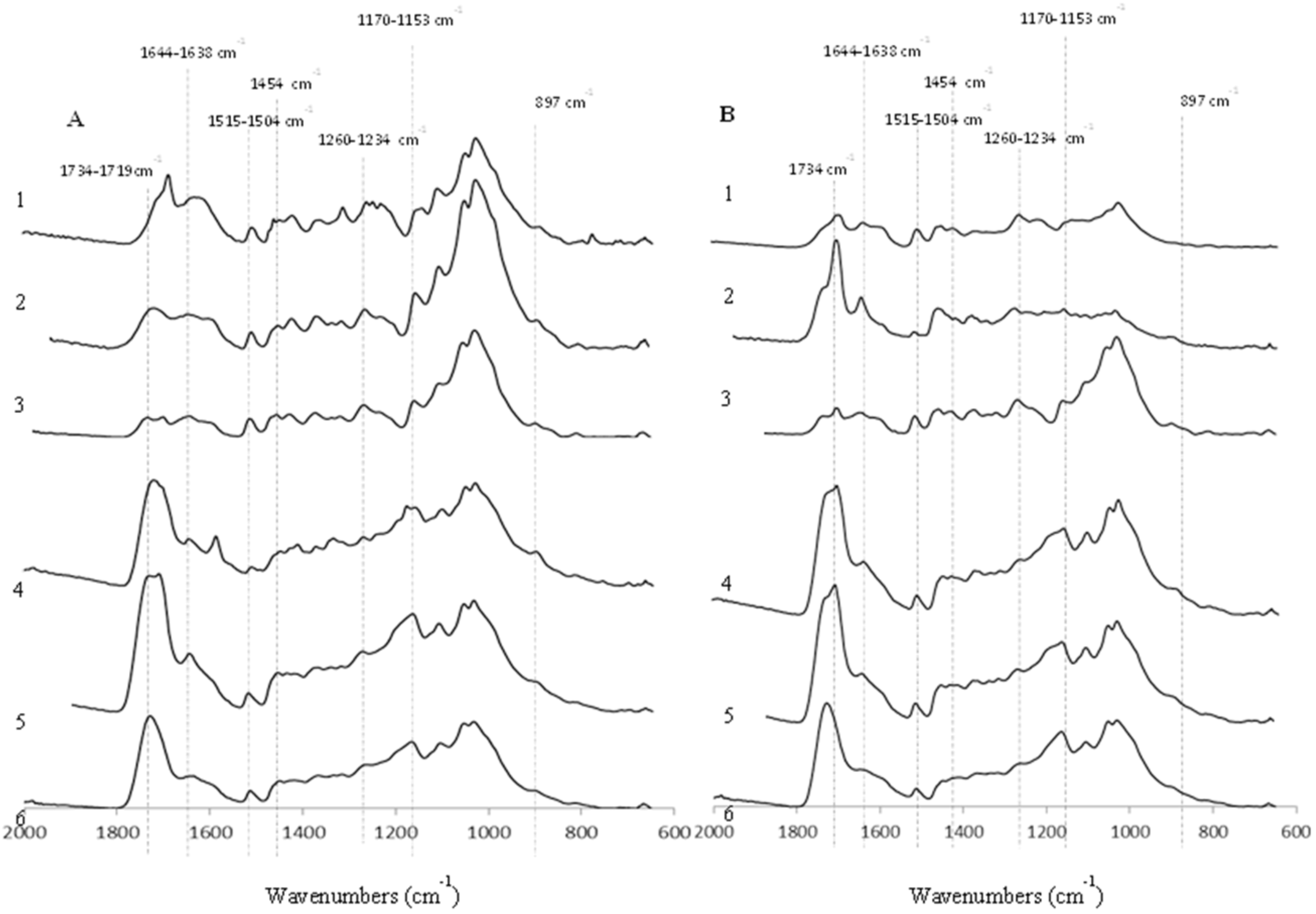

Fig. 12. FTIR spectra of Lp and WP specimens exposed to PP and IL fungus strains

These results suggest that the PP strain is more aggressive than the IL in its interaction with the wood macromolecules under testing. The presence of free citric acid in the wood structure has been identified with carbonyl groups (C=O) near 1694 cm^{-1} (Brioude *et al.* 2007; Budhavaram and Barone 2008) (Fig. 6), which would limit fungal action.

All the spectra shown in Fig. 12 were normalized at the wavelength 1510 cm^{-1}, which corresponds to the lignin (aromatic skeletal) wood component. Columns A and B show the spectra for Wp and Lp, respectively (Fig. 12). The spectra No. 3 to 1 in each column apply to untreated specimens: spectrum 3 for unexposed specimens, spectrum 2 for specimens exposed to the IL strain, and spectrum 1 for specimens exposed to the PP strain. Spectra 6 to 4 applied to treated specimens in the same order: spectrum 6 for unexposed specimens, spectrum 5 for specimens exposed to the IL strain, and spectrum 4 for specimens exposed to the PP strain.

Pull-off Tests

Pull-off tests provide a measure of the adhesion performance of a coating over a wood substrate. The average results presented in Fig. 13 showed that the adhesion strength was much greater with untreated specimens than with their treated counterparts, *i.e.*, 3.41 and 3.44 N/mm^2 for untreated Lp and Wp, respectively, as compared with 2.58 and 2.67 N/mm^2 for the corresponding treated specimens. These results can be explained by differences in the morphology of the wood surface as affected by the treatment.

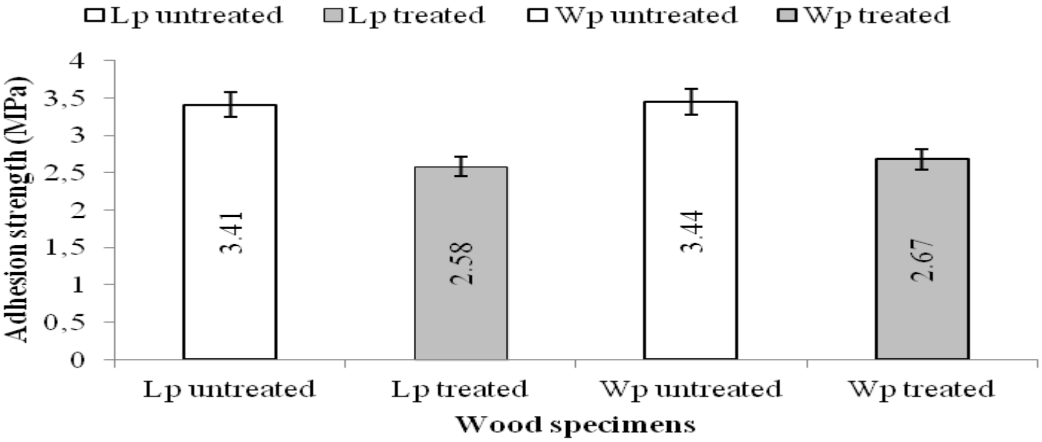

Fig. 13. Average adhesion strength of untreated and treated wood (Lp and Wp)

Observation of the wood/coating interface confirmed that the untreated surface offered better mechanical anchoring for the coating (Fig. 14).

The geometry of the interface line proved more irregular in the case of untreated specimens; it was also thinner, even though the coating was applied at the same rate. This indicates that coating penetration into the wood structure was better with untreated than with treated substrates.

SEM analyses confirm that the cell lumens of the treated wood were filled with polymer deposits. The SEM images of tangential surfaces shown in Fig. 15 clearly indicate that surfaces were smoother in treated than in untreated specimens. This contributes to a weaker bond for coatings on treated specimens. These observations were also reported by other authors (Hernandez and Cool 2008; Podgorski *et al.* 2010; Vistosyté *et al.* 2012;

Ozdemir *et al.* 2015). The treatment modifies wood surface properties and surface structure, as observed by Arnold (2010).

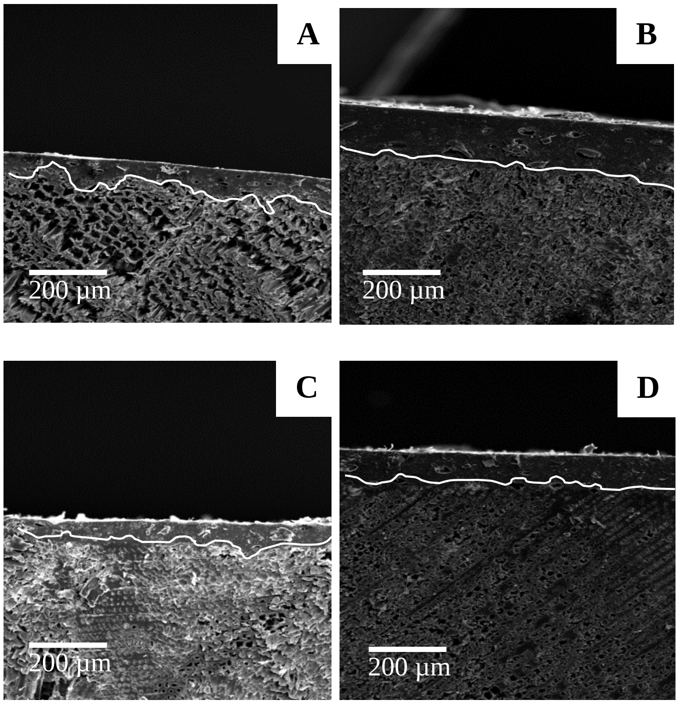

Fig. 14. SEM images of wood/coating interfaces for untreated and treated specimens of Wp (A,B) and Lp (C,D)

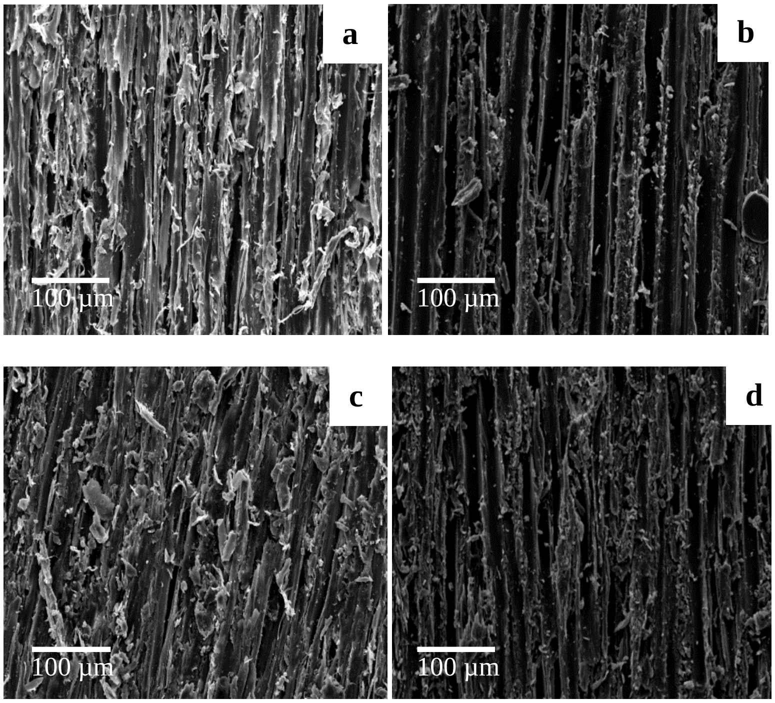

Fig. 15. SEM images of untreated and treated specimen surfaces for Wp (a, b) and Lp (c, d) in the tangential direction

Failure modes were assessed through visual observation of the dolly and wood surfaces (Table 4). With both Lp and Wp, a greater percentage of torn wood fiber was observed on the dollies with untreated than with treated wood. The treated specimens presented a higher percentage of failures between the wood and the first coating layer than the untreated specimens.

Table 4. Failure Modes between Wood and Dolly Surfaces

Wood specimens	Type of fracture		
	A[1] (%)	A/B[2] (%)	B/C[3] (%)
Lp untreated	79.61	4.44	15.94
Lp treated	73.63	26.36	-
Wp untreated	67.00	11.77	21.22
Wp treated	54.50	45.50	-

1. “A”: wood failure;
2. “A/B”: failure at the wood/first coating layer interface
3. letters “B/C”: failure between the first and second coating layers

As already indicated, these results can be explained by weaker coating anchoring in the wood structure resulting from the increase in wood fiber cohesion and reduced penetration of the coating material into the wood structure caused by the treatment. Future work to solve this problem could include the use of less viscous coating materials.

CONCLUSIONS

1. Crude glycerol was used to improve the technical performance of outdoor softwood siding as another way to valorize byproducts of the biodiesel industry. Mixture with citric acid was a new wood treatment solution that is also renewable, eco-responsible, and eco-friendly compared with previous petrochemical solutions.
2. Treatment enhanced the technical performance of outdoor softwood siding. These improvements come from ester bonds formed between solution components (polymerization that filled wood structure) and between solution and wood structure. Treatment improved dimensional stability, and this result was supported by sorption isotherms. The hardness properties of treated specimens increased, giving them a technical advantage over untreated wood. Decay tests demonstrated that the treatment improved the resistance of wood to fungal degradation. Irpex lacteus is not the good testing fungi for softwood.
3. Adhesion and density tests, however, showed that the treatment had a negative effect. For the first, it was attributed to reduced penetration of the coating into the treated wood structure, combined with a reinforcement of wood fiber internal cohesion. For the second one, increased product density is not a benefit for truck transport.
4. Future work is needed to solve these problems. An optimization of the impregnation program could be an avenue to explore.
5. With improving technical performance of softwood outdoor products, it possible to increase wood’s service life and keep biogenic carbon sequestered in the building for a long period of time. A life cycle analysis on the impregnated product should be considered to analyze the impact of the mixture, the process itself, and the new lifespan on the environmental footprint of the suggested solution.

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