

Combined effect of acetylation and heat treatment on the physical, mechanical and biological behavior of jack pine (*Pinus banksiana*) wood

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Abstract: A comparative study on the combined effect of heat treatment and acetylation on jack pine wood properties has been undertaken and the results were compared with those of each treatment carried out individually. The dimensional stability and mechanical property of wood with different treatments were examined and statistically analyzed. The results demonstrated that combined acetylation of jack pine wood with acetic anhydride and heat treatment at 190 °C has a positive effect on the dimensional stability. Results also suggested that the dimensional stability was affected more than the modulus of rupture (MOR) and modulus of elasticity (MOE) by both heat and acetylation treatments under the experimental conditions used. In addition, the hardness increases after high temperature modification but decreases slightly after acetylation. A comprehensive investigation of the effects of heat treatment and acetylation separately and together (combination treatment) on the fungal durability of jack pine wood against a brown rot fungus, *Poria placenta* (pp), and a white rot fungus, *Trametes versicolor* (tv) has also been performed. The results indicated that the weight loss caused by fungi is reduced by both modifications. It was also found that combination of heat treatment and acetylation offers additional bioprotection. FTIR results indicated that the heat and acetylation treatments have a significant influence on the chemical properties, but less influence on their structures.

1. Introduction

Wood is one of the most appropriate and versatile materials for a common use in a variety of fields due to its properties (Jebrane et al. 2011; Xie et al. 2013). However, two shortcomings of unprotected wood, namely biological degradation and dimensional variations, when exposed to fluctuating humidity of its surroundings, restrict its wider use. Different types of modifications are used to improve wood properties mentioned above and consequently increase the service life of wood materials, which is well documented in the literature (Ashori et al. 2013; Epmeier et al.

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2004; Homan and Jorissen 2004; Poncsák et al. 2006; Rowell 2006; Rowell et al. 2009; Shi et al. 2007; Temiz et al. 2006; Xie et al. 2013). With increased environmental awareness, new environmentally friendly wood modification methods and technologies without the use of toxic chemicals need to be developed for wood preservation (Rowell et al. 2009).

Heat treatment of wood has been studied for many years and been used commercially during the last decade (Chen et al. 2012; Lekounougou and Kocaefe 2014a; Mburu et al. 2007; Poncsák et al. 2006; Rowell et al. 2009). This technology is eco-friendly and does not require the use of chemicals. The heat treatment of wood at temperatures from 160 °C to 220 °C causes the degradation of wood chemical composition of hemicelluloses and lignin (Lekounougou and Kocaefe 2014a; Poncsák et al. 2006). Consequently, this process leads to increased decay resistance and improved dimensional stability (Chen et al. 2012; Lekounougou and Kocaefe 2014a; Mburu et al. 2007; Poncsák et al. 2006; Shi et al. 2007). These attractive properties of heat-treated wood bring wider utilization and new business opportunities for North American wood such as jack pine. However, the strength properties of the wood are affected by heat treatment (Poncsák et al. 2006; Rowell et al. 2009), which restricts the utilization of heat-treated wood as engineering material. The need for high strength in heat-treated wood products requires the development of new technology which will preserve or improve its mechanical properties while maintaining the advantages of the heat treatment.

Until now, considerable effort has been devoted to chemical modification of wood to improve the properties of wood materials (Ashori et al. 2013; Epmeier et al. 2004; Kartal 2006; Rowell 2006; Xie et al. 2013). Acetylation is one of the chemical modification methods which occurs between the hydroxyl groups of wood and the acetic anhydride molecule (Jebrane et al. 2011). The chemical bond forming between the wood material and acetic anhydride reduces the hydroxyl groups in wood, which consequently prevents the interaction of water with wood (Rowell et al. 1998). The acetylation, which is ecofriendly, was found to efficiently improve the dimensional stability and the biological resistance against fungal decay (Brelid 2002; Brelid and Simonson 1999; Jebrane et al. 2011; Larsson Brelid et al. 2000; Larsson and Simonson 1994; Mohebbi and Militz 2010; Ohkoshi et al. 1999; Pu and Ragauskas 2005; Rafidah et al. 2006; Ramsden et al. 1997; Rowell and Dickerson 2014; Rowell et al. 2009; Temiz et al. 2006). In addition, numerous investigations have been conducted on the influences of acetylation on wood mechanical properties (Papadopoulos and Pougioula 2010; Ramsden et al. 1997; Rowell 2015; Xie et al. 2013). The results reported in literature on effect of acetylation on mechanical properties of wood seem to depend on wood species and treatment methods (Xie et al. 2013). However, there is no common consensus. Moreover, there are also a few reported studies on the chemical structure (Gilarranz et al. 2001; Mohebbi 2008) and the physical microstructure (Sander et al. 2003) of the acetylated wood.

As it was stated previously, studies reported in the literature focus on the heat treatment and acetylation treatment of wood separately. The comparison of these two wood treatment techniques was documented and concluded that both are environmental friendly and might lead to increased decay resistance and improved dimensional stability of wood to different extents

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(Rowell et al. 2009). The study of heat treatment followed by acetylation of Scots pine wood was first reported by Rowell (Rowell 2014; Rowell 2015). He pointed out that the WPG due to acetylation for heat-treated wood was lower than that of untreated wood, which was attributed to the degradation of hemicellulose during heat treatment. However, the complete report is not available in the literature regarding the combined effect of heat treatment and acetylation modification on the fungal resistance and physical property of jack pine wood. Moreover, the effect of these two methods on the mechanical properties of jack pine has not been compared. The acetylation treatment improves the properties of wood. However, the color of wood is not as attractive as that of the heat treatment. Heat treatment improves the wood properties with the exception of mechanical properties if the treatment is carried out at relatively high temperatures (above 200 °C). If the combination treatment (heat treatment up to a certain temperature followed by the acetylation) can preserve all the improvements of both treatments and prevent their adverse effects, this will result in better quality and ecofriendly wood product. Consequently, the purpose of this study was: (i) to examine the efficacy that acetylation modification may have on the physical properties, mechanical strength and biological resistance of heat-treated wood against the brown and white rot basidiomycete fungi, (ii) to investigate the effect that the types of anhydride on the properties of wood heat-treated at different temperatures, (iii) to study the molecular reasons behind the improvement of the resistance of heat-treated wood with and without acetylation against fungal attack.

In this study, jack pine (*Pinus banksiana*) was heat-treated at different temperatures in the prototype furnace of University of Quebec at Chicoutimi (UQAC). Untreated and heat-treated jack pine samples were acetylated with acetic anhydride under the same conditions and their properties were compared. The effect of combined heat and acetylation treatments on the physical, chemical, mechanical, biological properties of jack pine was studied. FT-IR analysis of wood samples was carried out before and after the acetylated modification. Moreover, the by-product, acetic acid, of the acetylation performed with acetic anhydride, is hard to remove from wood after reaction (Jebrane et al. 2011). Preliminary study suggested acetic acid causes strength losses of wood (Brelid 2002; Homan and Jorissen 2004), but further work is needed to clarify this point. In the present paper, a comparative study on the reaction with vinegar (VIN) and the acetylation with acetic anhydride (AA) of heat-treated and untreated wood is also proposed. The results would promote the understanding of the effect and mechanism of acetylation on heat-treated wood and also provide a scientific basis for the development of environmentally friendly wood products. The combined treatment, if successful, may have the potential to widen the use of wood. There is acetic acid left in acetylated wood after acetylation with acetic anhydride. The acetic acid may not react with wood but it could extract some soluble material in cell wall. The treatment with vinegar was designed to investigate the influence of acetic acid on the fungal resistance and other properties of wood. If the improvement of wood properties with vinegar is possible, the cost of the combination wood treatment process will decrease, consequently, this facilitates its application at the industrial scale.

2. Experimental

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2.1 Heat treatment of wood

Jack pine (*Pinus banksiana*), which is commonly used for outdoor applications in North America, was studied. Kiln dried wood with the final moisture content of about 12% was obtained from a local sawmill in Saguenay-Lac-St-Jean (Quebec, Canada) and studied. Wood boards of approximately $2100 \times 100 \times 40 \text{ mm}^3$ were heat-treated in the prototype furnace of UQAC. Table 1 shows the conditions used during the heat treatment. Heat treatment was carried out at two different maximum temperatures (165°C and 190°C). Wood boards were heated to maximum temperature with a heating rate of 15°C/h in a humid and inert gas, and were kept at that temperature for one hour. Specimens were arbitrarily selected for a complete statistical randomization. They were stored in a room at 20°C and 40% relative humidity (RH) until they were acetylated. After, the characterization tests were carried out. The details of combined treatment and the characterization tests are described in the following sections.

The wood boards heat-treated in the prototype furnace were heavy and it was not possible to measure the weight loss precisely. Thus, the weight losses of the samples of $145 \times 38 \times 38 \text{ mm}^3$ were investigated in a thermogravimetric analysis (TGA), including a vertical tube furnace and a balance installed above the furnace, with controlled and constant flow of nitrogen. The sample weight can be recorded continuously at each 30 seconds. The heat treatments were carried out with a ramp rate of 15 °C/h to maximum temperature 165 °C and 190 °C, sacking time of 1h and naturally cooling down to room temperature. To simulate the heating process in the prototype furnace, kiln-dried wood samples with moisture content of about 12% were used in the weight loss test. Therefore, the obtained total weight loss was due to the removing of moisture and the loss of the wood components. To study the weight loss due to decomposition, the complete oven-dried wood samples at 100 °C were also heat treated in the TGA with the same hearing process, and the weight loss was recorded. The weight loss results are presented in Figure 1 (a) and (b).

2.2 Acetylation of wood

Heat-treated wood samples were subjected to acetylation treatment using different solutions. Untreated, pre-dried wood boards, which have a final moisture content of about 12%, were also impregnated with the same solutions along with specimens heat-treated at high temperatures for comparison purposes.

2.2.1 Wood pretreatment

Specimens of $35 \times 35 \text{ mm}^2$ cross-section on tangential surface and 200 mm long were cut from sapwood of heat-treated and untreated wood, and then planed to smooth their surfaces. All samples were conditioned at a temperature of $20 \pm 2 \text{ °C}$ and relative humidity (RH) of $65 \pm 2 \%$ for three weeks and then weighted prior to acetylation. Thereafter, all samples were oven-dried for 24 h at 105 °C to reduce the moisture content to about 4%.

2.2.2 Acetylation

The wood samples were placed in a glass container and impregnated with two different acetylation solutions (acetic anhydride and vinegar) which resulted in different percentage of

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weight gain in different samples. Commercial vinegar (10% acetic acid) was employed in this study to investigate its effect on the fungal resistance and other properties of wood. Excess acetic anhydride was drained off, and the wood samples were then kept at a desired temperature for 6 to 24 h to facilitate the acetylation reactions, depending on the acetylation solution used. The reaction temperatures were 50°C and 110 °C. Table 3 summarizes the condition used for acetylation. After acetylation, the samples were soaked in de-mineralized water to convert acetic anhydride to acetic acid within few days. Afterwards, samples were again oven dried at 105 °C until their weight remained constant to remove the remaining acetic acid. Finally, samples were conditioned at a temperature of 20±2 °C and RH of 65%±2% for three weeks and then weighed. The weight percent gain (WPG) was calculated using the following equation:

$$\text{WPG (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

(1)

where W_0 and W_1 are the conditioned weight of the wood samples in grams before and after the acetylation treatment.

2.3 Characterization of treated wood

2.3.1 Chemical analysis of wood components

Untreated and wood samples heat-treated up to 165 °C and 190 °C in TGA underwent chemical characterization analyses, by means of determination of extractives soluble in acetone and ethanol, lignin, pentosane, and holocellulose content. The detailed methods of chemical analysis for wood components are described in a previous publication (Huang et al. 2012). Chemically characterized results in this experiment are shown in Table 2.

2.3.2 Water absorption and dimensional stability

The dimensional stability tests were carried out to determine the effect of heat treatment temperature and acetylation with different solutions on the dimensional stability, and the results were compared. In this study, the methodology used to perform dimensional stability of wood has been adapted from ASTM D-1037 standard (ASTM International 2004). Wood samples of each experimental set with dimensions of 35 × 35 × 35 mm³ in radial, tangential and axial directions were prepared. The size of wood samples was reduced according to the limitation of acetylation container in this study, which provided the smaller samples. A minimum of 10 samples were tested in each case. All specimens were conditioned at a temperature of 20±2 °C and RH of 65%±2% prior to testing. Prior to the tests, specimens were weighed with SARTORIUS GW7201 analytic balance (precision ± 0.1g), and their average dimensions were measured for more than 6 times in radial, tangential, and longitudinal directions, respectively. During the tests, the samples were kept immersed in distilled water at constant temperature of 20 ± 1°C for 24 h. The samples were removed from the water and weighted directly. Then, their dimensions were also measured.

The amount of absorbed water (A) was calculated using the following equation:

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$$A (\%) = \frac{M_1 - M_0}{M_0} \times 100$$

(2)

where M_0 and M_1 are the weight of samples in grams before and after the test, respectively.

The changes in dimension (D) in tangential, radial, and longitudinal directions were determined using the following equation:

$$D (\%) = \frac{D_1 - D_0}{D_0} \times 100$$

(3)

where D_0 and D_1 are the dimension of wood samples before and after tests, respectively.

2.3.3 Mechanical properties

Three-point bending and hardness tests were carried out to determine the effect of thermal modification and acetylation and their combination on the modulus of rupture (MOR), modulus of elasticity (MOE) and hardness of modified wood. The results were compared and statistical analysis was carried out. The tests were performed using MTS ALLIANCE RT 100 Universal Mechanical Test Machine. All specimens were conditioned at an ambient temperature of 20 ± 2 °C and RH of 65% \pm 2% prior to testing.

Three-point static bending tests were performed according to ASTM D-143 standard (ASTM International 2004). Due to the dimension limitation of the experimental setup for acetylation, the sample size for mechanical tests was reduced to 12 mm \times 12 mm \times 200 mm. Then, they were tested at a crosshead speed of 1.3×10^{-3} m/min and span of 0.1524 m. The obtained load deformation data were analyzed to determine the MOR and the MOE as described in literature (Poncsák et al. 2006). Tests were repeated more than ten times for each treatment condition.

The penetration hardness (H) tests were carried out in accordance with ASTM D-1037 standard (ASTM International 2004). More than five wood specimens with dimensions 35 \times 35 \times 200 mm³ were tested for each set of parameters. A maximum force of 400 N was used during the tests. The diameter of the ball was 12.7 mm and the penetration rate was 1.3×10^{-3} m/min. Tests were repeated six times on the radial and tangential faces for each sample.

2.3.4 Fungal Durability

Poria placenta (FTK120E), a brown rot fungus, and *Trametes versicolor* (FTK105D), a white rot fungus, purchased from FPInnovations FORINTEK, Québec, Canada were used in this study. Stock cultures of fungi were maintained on malt-agar stored at 4°C. In this study, the methodology used to perform solid state cultures on wood has been adapted from EN-113 (1986) standard. Wood samples with dimensions of 15 \times 5 \times 35 mm³ in radial, tangential and axial directions were prepared. The size of wood samples was reduced to facilitate fungal degradation and also reduce the testing duration from 16 weeks to 7 weeks (Lekounougou and Kocafe 2014a). Untreated wood was used as reference for biological durability. 20 ml of sterile medium was prepared by dissolving 40 g malt and 30 g agar in 1 L of distilled water and petri dishes of 9 cm in diameter were filled with this medium, inoculated with fungus, and incubated for two weeks at a temperature of 22 °C \pm 1°C and a relative humidity of 70% \pm 4% so that the mycelium can colonize. Nine sets of each wood sample (untreated (UN), UN-VIN, UN-AA, 165 °C, 165

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°C-VIN, 165 °C-AA, 190 °C, 190 °C-VIN, 190 °C-AA) were placed in different petri dishes. Three repeats were carried out for each experiment to ensure the reproducibility of the results. Incubation was carried out under controlled temperature and humidity ($22^{\circ}\text{C} \pm 1^{\circ}\text{C}$, $70\% \pm 4\%$ relative humidity) in climatic chamber of Conviron. At the end of each test period, mycelia were removed and the samples were oven dried at $103^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 48 h. Finally, the percent of weight loss caused by the fungal decay (W) was determined using Equation (4) given below:

$$W (\%) = \frac{m_0 - m_1}{m_0} \times 100 \quad (4)$$

where m_0 and m_1 are the oven dried mass of wood samples before and after fungal tests, respectively.

2.4 Statistical analysis

An analysis of variance (ANOVA) was used to determine the effect of each treatment on the physical, mechanical and biological properties. When the ANOVA indicated a significant difference among factors and levels, a comparison of the mean values was done to identify the groups that were significantly different from others at 95% confidence levels. All data were analysed with Statistica software.

2.5 FTIR analysis

Infrared spectroscopy is a highly useful tool for obtaining rapid information on the chemical structure of wood constituents and chemical changes taking place due to various treatments. In this study, the effect of acetylation and heat treatment on cellulose crystallinity and the chemical compositions of both cellulose and lignin on wood surface were studied using Fourier transform infrared spectroscopy (FTIR NICOLET 6700). The main objective was to identify the new bond formation in wood sample after acetylation and heat treatment which could potentially be used for improving their fungal resistance. IR spectra were collected in the wave number range of $400\text{--}4000\text{ cm}^{-1}$, and all the spectra were recorded at 4 cm^{-1} resolution. Each time, 64 scans were carried out prior to the Fourier transformation. All spectra were collected using a KBr technique (Perkin Elmer Instrument, Spectrum one), and the results considered were the average of two experiments. The samples were mixed with KBr at a ratio of 1:100. Then, the mixture was pressed to a pellet form for FTIR analysis. The effective depth of the surface scanning is 0.5-5 microns. All spectra were analyzed using spectra manager software. The IR spectra for each treatment and fungal test were transformed into absorbance spectra. The FTIR serve only for qualitative comparison in the discussion of the results.

3. Results and discussion

To assess significant differences for different variability sources, a multivariate analysis of data was carried out by means of tests for orthogonal square sums.

3.1 Weight percentage gain

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Untreated and heat-treated jack pine wood samples at a temperature of 165°C and 190°C were chemically treated with acetic anhydride and vinegar in a reactor for the same time and at a desired temperature (see Tables 1 and 3). Figure 2 shows the effect of different chemical modifications on the weight percentage gain (WPG) of untreated and heat-treated wood. It can be seen from this figure that WPG of wood samples treated with acetic anhydride were all significantly ($p < 0.05$) higher (more than 15%) than those of the vinegar treated wood samples as expected. The contribution of vinegar treatment to WPG is not obvious ($< 2\%$). There is no significant ($p > 0.05$) effect of the heat treatment on WPG of wood due to both acetic anhydride and vinegar, when maximum temperatures are less than 190 °C.

The weight gain is an indication of the degree of acetylation since the increase in wood volume is equal to the volume of chemical added and reacted during the acetylation process (Rowell et al. 1976). The differences in the contribution to WPG of wood samples modified by acetic anhydride and vinegar indicate the different degree of acetylation. Similarly, the degrees of acetylation are similar for wood samples treated with the same chemical. Rowell (Rowell 2014, 2015) reported that Scots pine (*Pinus sylvestris* L.) wood heat treated at 220 °C for 2 h had a WPG of 13.1% due to acetylation, while the control un-heat-treated wood had a WPG of 19.7%. In their study, the weight loss due to heat treatment was 9.3% with a major loss of arabinose and xylose, but no loss of cellulose and lignin. It was also shown that 50% hemicellulose was esterified during acetylation (Rowell 2015). The degradation of hemicellulose explained that decrease in WPG due to acetylation for heat-treated wood at 220 °C. Slight decrease in WPG of sample wood heat-treated at maximum temperature of 190 °C due to acetylation of acetic anhydride can be observed in Figure 2, compared to wood which was not heat-treated.

In the heat treatment process of the present study, the size of the wood sample was big ($2100 \times 100 \times 30 \text{ mm}^3$), so the samples were heavy and it was not possible to measure the weight loss precisely for the sample heat-treated in the prototype furnace. Thus, the weight losses of the smaller samples were investigated in a thermogravimetric analysis (TGA) using similar heat treatment conditions to those in the prototype furnace as shown in Table 1. The weight loss results for kiln-dried samples of 12 % moisture content and complete oven-dried samples are presented in Figure 1 (a) and (b). It can be observed that the weight losses of kiln-dried samples were 5.63% and 6.22% for temperature of 165 °C and 190 °C, respectively. However, when the oven-dried samples were used, the weight losses reduced to 0.34% and 0.63%. Therefore, the major weight loss of kiln-dried sample during heat treatment was due to moisture loss, and this loss continues up to the final temperature as shown in the weight loss curve in Figure 1 (a). Dos Santos et al. (2014) reported weight losses of 0.34% and 0.29 % for Cedro-marinhoiro and Cedroarana when they were subjected to the temperature of 160 °C, while they increased to 6.59 % and 1.58 % when using a maximum temperature of 220 °C. It can be inferred that the weight loss of oven-dried sample due to heating at temperatures of 165 °C and 190 °C in this study is lower than that heat-treated at 220 °C.

To investigate the changes in different components of jack pine wood during the heat treatment at a temperature of 165 °C and 190 °C as well as their influence on the acetylation, quantitative

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analyses of the components of untreated and heat-treated jack pine at 165 °C and 190 °C were carried out. The results are presented in Table 2. Pentosan decreased from 9.09% to 8.22% and 7.38%, and holocellulose reduced from 63.81% to 63.04% and 62.27% for samples heat-treated at 165 °C and 190 °C, respectively. The higher loss of pentosans than that of holocellulose indicated that the degradation by heat treatment on hemicellulose was more serious than on cellulose. However, lignin increased from 28.95 % to 30.09% and 31.91 %, which means the lignin did not increase in mass and it became higher since there was a loss of carbohydrate. The weight loss during heat treatment is the result of the change in the quantity of different components mentioned above. The data of component changes agreed with the very little weight loss in the heat treatment at a temperature less than 190 °C.

In addition, the amorphous regions of cellulose are degraded, though cellulose is a more stable component of jack pine wood than hemicellulose during heat treatment (Huang et al. 2012). It was reported that 100% of the hemicellulose hydroxyl groups and certain amount of hydroxyls in the amorphous regions of cellulose were substituted when wood reacted with acetic anhydride at an acetyl weight gain of 16-19% (Papadopoulos and Pougoula 2010; Rowell 1982). Therefore, the reduction in hemicellulose and amorphous cellulose content results in the loss of the reactive hydroxyls of cell wall polymers which can react with acetic anhydride. This explains the difference of WPG due to heat treatment modification compared to untreated wood. The jack pine wood samples were heat-treated at maximum temperature of 190 °C in this study. Therefore, the degradation degree of hemicellulose by heat treatment at this temperature was lower than that heat-treated at 220 °C in literature (Rowell 2014). The degree of acetylation shows lower in this study. The wood composition may not be significantly degraded by a temperature less than 190 °C. Thus, the difference in WPG of heat-treated wood with untreated wood is slight.

Both untreated and heat-treated samples were slightly darker after acetylation compared to the color of the non-acetylated wood, which is in agreement with the results reported in literature for untreated wood (Ramsden et al. 1997). The samples after vinegar treatment became slightly gray for both untreated and heat-treated samples. It is possible that reaction of the cell wall occurs due to the application of acetic acid in vinegar over an extended period of time, which causes a change in wood color.

3.2 Water absorption and dimensional stability

Water absorption of wood is a good performance indicator of susceptibility to fungal attack for wood materials (Ashori et al. 2013). The results of water absorption tests are presented in Figure 3, where the highest water absorption corresponds to the untreated wood specimen, and the lowest value of water absorption is observed for the combination of heat-treatment at 190 °C and acetylation by acetic anhydride. All wood samples treated only by high temperature or only by acetylation absorbed less water than the untreated control wood (61.7%). Wood samples heat-treated at different temperatures of 165 °C and 190 °C were 7.9% and 19.3% lower than that of the control wood, respectively. The difference between the untreated wood and heat-treated wood in absorbing water became more significant with increasing temperature, ($p < 0.05$ for 190 °C heat treatment). This trend is in agreement with the results reported in literature (Temiz et al.

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2006). Scots pine wood heat-treated at the temperature of 240°C showed lower water absorption (24.7%) than the untreated wood (Temiz et al. 2006). This value is much lower than the results in this study, 56.8 % for 165 °C and 42.8% for 190 °C heat-treated woods respectively, which confirms the treatment with higher temperature reduce more water absorption. This might be attributed to the thermal degradation of the hygroscopic polymer in the wood cell wall: hemicellulose and amorphous region of cellulose (Poncsák et al. 2006). It can be also seen from Figure 3 that water absorption of woods treated with acetic anhydride were all significantly ($p < 0.05$) lower than those of the non-acetylated woods both for untreated and heat-treated woods. While untreated control specimen absorbed 61.7% of water, the samples acetylated with acetic anhydride absorbed about 35.7% water. The considerable decrease in water absorption of treated wood is due to the hydrophobic characteristic of acetyl groups, which reduce the availability of sites for hydrogen bonding in the cell wall and lumens leading to reduction in reaction rate between wood and water, consequently, water penetration into wood. The difference in water absorption among untreated and heat-treated wood samples after acetylation is not obvious ($p < 0.05$). The effect of acetylation on reducing of water absorption (from 61.7% to 35.7 %) is higher than that of heat treatment at 190 °C (from 61.7% to 42.8%) in this study. However, it was reported that heat treatment at maximum temperature of 240°C was found to be more effective than acetylation with 26% weight gain by acetic anhydride on Scots pine wood (Temiz et al. 2006). Therefore, the efficiency in changes of water absorption of wood depends on the heat-treatment temperature and degree of acetylation, which is in agreement with the results of WPG as stated above. The heat treatment followed by acetylation with acetic anhydride was the most effective treatment choice for reducing water absorption. The water absorption values of vinegar-treated wood are, in most cases, similar to those of non-acetylated woods, which means the contribution of vinegar treatment to water absorption is not obvious. This is also in agreement with the results of WPG stated previously.

The evaluation of the dimensional stability is especially important for the application of bio-based materials. Hence the measurement of changes in dimension of wood after heat treatment and acetylation was carried out. The properties of wood vary with respect to the three mutually perpendicular axes of the material (radial, tangential, and longitudinal) (Winandy and Rowell 2005). The differences in the dimensions of wood samples after immersing them in water for 24 h were investigated in three different directions and are presented in Figure 4 (a). The changes in dimension of treated samples were lower than that of the control sample in radial and tangential longitudinal surface regardless of the type and condition of treatment, demonstrating that both heat treatment and chemical modification with vinegar and acetic anhydride increase wood dimensional stability to different extents. Similar to water absorption, shrink efficiencies of acetylation on heat-treated wood are lower compared with those before heat treatment. The anti-shrink efficiency results were reported by Brelid and Simonson (1999), where ASE of 65 % was obtained for acetylated pine with 20.0% weight gain. The ASE of heat-treated wood was reported to be 52%, sample after heat treatment and acetylation with a weight gain of 13.1% has an ASE of 76.4% (Rowell 2015). The changes in dimension are lower on axial surfaces than on

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longitudinal surfaces. The differences in the values on axial surfaces are not significant between untreated samples and treated samples (Figure 4 (a)). It is easier to observe the influence of one factor on changes in dimension when the one-way factorial analysis was carried out (Figure 4 (b-d)). Reduction in dimensional change varied from 2.8 % to 1.9% and 1.1% for vinegar and acetic anhydride, respectively (Figure 4 (b)). The variation of change in dimension due to heat treatment is smaller than that due to acetylation (Figure 4 (b) with Figure 4 (c)). Different directional surface is also a variable with a significant influence on changes in dimension (see Figure 4 (d)). The contributions of different variables are compared in Figure 4 (e), which indicates that level of acetylation in this study is more effective than heat treatment of 160 °C to 190 °C on dimension stability modification. However, less than 1.5% of changes in dimension for both radial and tangential directions were reported for black spruce heat-treated at a maximum temperature of 210 °C (Lekounougou and Kocaefe 2014b). Similar results were also obtained for jack pine when it was treated at intensive temperature conditions (Poncsak et al. 2011). Thus, the dimensional stability (less than 15%) obtained with higher temperature is better than those treated with acetylation in this study (see Figure 4 (a)). The change in dimension has positive correlation with water absorption for the same treatment conditions. The acetylation of hydroxyl sites during acetylation process in wood induces wood cell wall bulking and volume increases to close to its original value (Ramsden et al. 1997). This cell wall bulking and volume increase minimized the additional dimension change due to absorption of water when acetylated wood was immersed in water. In addition, the reduction in the availability of sites for hydrogen bonding restricts reaction with water and leads to an increase in the dimensional stability of acetylated woods. The degradation of hemicellulose and amorphous region of cellulose during heat treatment reduce the free OH groups, and thus affect the water affinity and dimensional change. The high value shown in Figure 4 (e) is due to the difference between longitudinal and transverse surface as a result of different number of hydroxyl sites present in these directions.

3.3 Mechanical properties

Figure 5 shows the hardness for unmodified, heat-treated, and acetylated wood on both tangential and radial surfaces, since the mechanical characterization on these two surfaces is more important than axial surface according to the wood utilization (Winandy and Rowell 2005). As can be seen from one-way ANOVA analysis results (Figure 5 (d)), different surfaces do not have significant influence on hardness ($P=0.888$), though hardness changes differently depending on different modifications and surfaces (see Figure 5 (a)). Thus, static bending strength was characterized only on tangential surface.

The hardness of most samples after heat treatment at 190 °C was found to be higher compared to that before heat treatment under the same chemical modification condition except the tangential surface of acetylated wood (see Figure 5 (a)). Statistical analysis revealed that this improvement is significant at 95 % confidence level; while there is no significant difference for the hardness of

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wood heat-treated at 165 °C compared with the control (see Figure 5 (b)). It is known that the exothermic reactions start at a temperature around 160°C for birch and its hardness increases slightly with temperature above 200 °C (Poncsák et al. 2006). Decreased amounts of bound water, at moisture contents from oven-dry to fiber-saturation point, increase the possibility to form hydrogen bonding between the organic polymers of the wood cell wall, which increases the strength of wood (Winandy and Rowell 2005). It is well known that the moisture content of heat-treated wood is lower than its untreated control (Lekounougou and Kocaeffe 2014a). Therefore, it seems that the lower moisture content of heat-treated wood might be attributed to the enhancement in hardness. The hardness was decreased in both directions for the acetylated specimens except the one heat-treated at 190 °C, which shows slightly higher value after acetylation, as compared with the unacetylated specimens. The reduction in hardness is probably related to the effect of acetic acid. This can be indicated from the decrease in hardness of vinegar-treated samples compared to the unmodified ones (see Figure 5 (c)). Those observations are not in accordance with the literature (Larsson and Simonson 1994), reporting hardness increases slightly due to acetylation. The analysis of factorial importance implies that the contribution to hardness changes proceeds in the order acetylation > heat treatment temperature > surface direction (see Figure 5 (e)).

The effect of acetylation with acetic anhydride and vinegar and heat treatment on static bending strength of wood is presented in Figures 5 and 6. It can be seen from Figure 6 that the MOR values of modified woods with all the acetic anhydride are higher than the value of non-acetylated wood and therefore, it can be concluded that acetylated modification with 15% WPG increases the MOR strength to a different extent for untreated and heat-treated wood, respective of the temperature used. Statistical analysis revealed that this improvement is significant, at 95% confidence level, for all the acetylated wood with acetic anhydride compared with the control ($p=0.003 < 0.05$ and see Figure 6 (c)). It was also reported that pine and spruce showed a slight increase in MOR and compression strength at the levels of acetylation lower than 16.4 WPG (Brelid and Simonson 1999; Papadopoulos and Pougoula 2010). A decrease in equilibrium moisture content at a given relative humidity can be a result of acetylation treatment (Rowell et al. 2009). This consequently reduces the amounts of bound water and in turn increases hydrogen bonding between wood polymeric substance of the cell wall and yields an increase in the mechanical properties of wood (Ramsden et al. 1997). A closer look at the data presented in Figure 6 (a), shows that as the temperature increases, the magnitude of the improvement in MOR is decreased. According to the statistical analysis, the differences of MOR for wood heat-treated at temperature of 190 °C between before and after acetylation were not significant. The possible reason proposed for this behavior may be the reduction of free hydroxyl groups due to the degradation of hemicellulose and cellulose during heat treatment which might decrease the potential for reaction with acetic anhydrides. From Figure 6 (a) and (c), it can be seen that vinegar treatment of wood resulted in a decrease of MOR for untreated and heat-treated woods to different degrees, where specimens heat-treated at 190°C after vinegar treatment had the lowest value. This indicates the presence of acetic acid can contribute to the reduction of MOR. It can be proposed that the acetic acid generated as a by-product in the cell wall (Hill 2006) and thermal degradation during heat treatment evened out the strength the MOR gained due to

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acetylation. The importance of acetylation contribution to MOR (1) is more influential than that of the heat treatment temperature (0.6) as shown in Figure 6 (d).

Figure 7 shows the influence of the acetylation and heat treatment on MOE. It can be seen from Figure 7 (a), the MOE strength of heat-treated specimens without acetylation decreases significantly (see Figure 7 (b)) with the temperature increasing, which is similar to the tendencies reported in literature (Poncsák et al. 2006). Heat treatment shows negative effect also on the MOE for acetylated and vinegar-treated specimens. On the other hand, acetylation with acetic anhydride enhances the MOE while vinegar decreases slightly the MOE for all specimens. Although, the influence of acetylation on the MOE is not significant statistically (see Figure 7 (c)), it can be observed from Figure 7 (a) that the extent of the improvement in the MOE decreased as the temperature is increased. The importance of acetylation contribution to MOE (0.58) is less compared to that of heat treatment temperature (1) as shown in Figure 7 (d). According to the model of the relationship between strength and wood composition (Winandy and Rowell 2005), when the load is applied to a piece of wood beyond the elastic limit (namely elastic strength), initially, hydrogen bonds between and within individual polymer chains such as adjacent microfibrils of wood are reforming, sliding (uncoiling), and subsequently breaking. Then the covalent C-C and C-O bonds between lignin and hemicellulose copolymers, hemicellulose and amorphous cellulose not only become distorted within the ring structures but also break. Furthermore, the crystalline cellulose failure occurs, which means the main framework of wood is disintegrating. At the limit of range of elasticity, with the same displacement of wood sample center, the needed load is more when the MOE is higher. It seems therefore, the amount of hydrogen bonds between and within wood composition is attributed to the needed load. Thus, higher content of hydrogen bonds between and within wood components provide rigidity (higher MOE) to wood via stress transfer and allow the molecule to absorb shock by subsequently breaking and reforming (Winandy and Rowell 2005). Degradation of hemicellulose and amorphous region of cellulose by heat treatment results in the reduction of hydrogen bonds and cleavage of C-C and C-O bondage, which induces the lower levels of strength loss in woody materials. Another result of thermal degradation is high lignin content present in heat-treated wood (Huang et al. 2012). The reactivity of cell wall polymers with acetic anhydride proceeds in the order of lignin > hemicelluloses > cellulose (Xie et al. 2013). It is assumed that 100% of the lignin hydroxyl groups are substituted (Rowell 1982) and no cellulose hydroxyl substituted when heat-treated wood was reacted with acetic anhydride. The acetylated lignin acts as an encrusting agent on and around the carbohydrate fraction, and thereby limits the influence of water and acetic anhydride on that carbohydrate fraction (especially cellulose). Thus, the strength of heat-treated wood after acetylation is due in part to the hydrophobic (water-repelling) ability of acetylated lignin to limit the access of water to the carbohydrate moiety and thereby lessen the influence of water on the hydrogen bonded structure of cellulose (Winandy and Rowell 2005).

Two possible reasons may explain the increase in the mechanical properties of heat-treated wood after acetylation: increased density and reduced moisture content (Xie et al. 2013). However, the acetyl groups are situated as side groups on the existing wood polymers (Brelid and Simonson

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1999) but do not polymerize themselves or cross-link the cell wall polymers and forming a stiff network (Tsoumis 1991). Therefore, the increase in density of wood due to acetylation may not substantially improve the strength properties. A decrease in wood equilibrium moisture content due to acetylation of heat-treated wood might be the only reason for the increase in strength properties. The richness of lignin of heat-treated wood strengthens this influence. There are several factors which influence negatively the mechanical strength properties of heat-treated wood during acetylation. Firstly, decrease in some mechanical properties may be explained by swelling of wood (both untreated and heat-treated wood). Swelling of cell wall reduce the fiber amount per volume, resulting in fewer load-bearing fibers within a given cross-sectional area (Winandy and Rowell 2005). In addition, swelling tends to plasticize wood and reduce its strength properties (Winandy and Rowell 2005). In general, the greater the material swells, the greater its strength loss. Acetylation swells the wood; therefore, the strength of heat-treated wood after acetylation, such as hardness in this study, decreases accordingly. Secondly, the by-product acetic acid of acetylation may cause a certain degree of heat-treated wood degradation resulting in strength reduction. Finally, it is pointed out that the hydrolysis of lignocelluloses at high temperatures during the acetylation process may affect the strength of wood without heat treatment (Homan and Jorissen 2004). However, the effect of high temperature might be less on heat-treated wood due to the hydrolysis of lignocelluloses during heat treatment. This may explain the high value in hardness on the radial surface of 190 °C heat-treated specimens after acetylation (see Figure 5 (a)). Since all these factors combine and interact, it might be possible that during the acetylation of heat-treated wood, an increase in strength due to the reduction in moisture content evened out strength losses caused by acidic degradation and swell.

3.4 Fungal Durability

Modified samples were exposed to the white rot fungus *Trametes versicolor* and the brown rot fungus *Poria placenta*. Weight loss is an important parameter for assessing fungal decay of solid wood; for this reason the discussion will only focus on the percentage of wood weight loss during acetylation and heat-treatment and the results will also be compared with those of untreated control. The biological behavior of specimens during different treatments is presented in Figure 8. Figure 8 presents the weight loss (%) of wood specimens after 7 weeks of incubation with fungi. It can be observed that brown rot fungus showed more decay than white rot fungus on all the wood specimens for the same treatment (see Figure 8 (a)). This difference is significant statistically when only fungal type is considered as variable (see Figure 8 (b)). The result from this study is in line with the observation made earlier as far as the effect of fungal type upon the weight loss of wood. The resistance of heat-treated *Pinus banksiana* against four wood decaying fungi was evaluated including three brown rot fungi and a white rot fungus. Results showed that the untreated wood samples lost more weight when exposed to *P. placenta* (brown rot fungus) compared to the weight loss observed in case of *T. versicolor* (white rot fungus) (Lekounougou and Kocafe 2014a). Similar result was reported by Ohkoshi et al. (1999) that the decay power of white-rot fungus was lower than that of brown-rot fungus showing that the mass loss of the nonacetylated wood was just 23.0% due to white-rot fungus and 72.8 % due to brown-rot fungus. White rot fungi degrade extensive amounts of lignin and they also degrade cellulose and

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hemicellulose simultaneously, whereas brown rot fungi are characterized by extensive degradation of polysaccharides (cellulose and hemicellulose) but limited degradation of lignin (Blanchette 1990). It was reported in a previous study that jack pine wood contains 60.21 % holocellulose (cellulose and hemicellulose) prior to treatment (Huang et al. 2012). The highest weight loss was recorded on the untreated control wood sample in this study (22.4% for white rot fungus and 60.3% for brown rot fungus). 75 % of lignin content percentage left in the wood decayed by brown rot fungus was reported in literature (Ohkoshi et al. 1999), which is much less than 100%. Therefore, it can be inferred from the results and the information from literature that 60.3% of weight loss due to brown rot fungus is not just the degradation of polysaccharides, since the lignin content percentage left in the wood decayed by brown rot fungus should be nearly 100%. This is not correct according to the results of 75 % of lignin content reported in the literature (Ohkoshi et al. 1999). This means the degradation of polysaccharides by brown rot fungus is accompanied by a reduction in lignin of wood. In other words, the brown rot fungus needs to decompose lignin to survive. It was pointed out that cellulose activity is observed only after lignin has been removed by white rot fungus (Blanchette 1990), and part of lignin (23.1%) is left after degradation of white rot fungus (Ohkoshi et al. 1999). Thus, the weight loss due to white rot fungus is attributed to the degradation of lignin and hemicellulose. It can also be observed from Figure 8 (e) that the contribution of fungal type to weight loss of biological decay is the most important in the three variables studied in this research.

Heat treatment improved resistance of wood against decay fungi (see Figure 8 (c)) when the heat treatment temperature was the only variable considered as shown by one-way statistical analysis. This is in agreement with previous studies on the number of other decay fungi and wood systems (Lekounougou and Kocaefe 2014a; Mburu et al. 2007; Shi et al. 2007). As previously discussed, both white and brown rot fungi degrade hemicellulose and lignin of wood. However, a closer look at the data presented in Figure 8 (a), shows that the magnitudes of the improvement in decay resistance are different depending on different fungal types and chemical modifications. For white rot decay, wood modified with heat treatment at 165°C and 190 °C showed similar resistance (around 10% weight loss). White rot fungi degrade wood by preferentially degrading lignin. The enhancement of lignin content due to high temperature treatment (Huang et al. 2012), which may increase the resistance against white rot fungi. Wood samples modified with vinegar and acetic anhydride have shown much less attack (weight loss < 4.2 %) than unmodified wood. There was no significant difference in weight loss for chemically modified woods with wood heat-treated at different temperatures suggesting that heat treatment did not offer additional protection to vinegar and acid anhydride modified wood at least during their search period of 7 weeks against white rot decay. Therefore, the vinegar treatment without heat treatment may be a choice to protect jack pine wood against white rot decay (see right arrow in Figure 8 (a)). However, it was reported that 1.5% weight loss by degradation of white rot of 12 weeks could be reached for jack pine heat-treated at maximum temperature of 210 °C (Lekounougou and Kocaefe 2014a). This weight loss value is lower than that of acetylated and vinegar-treated samples in this study. Moreover, the vinegar-treatment has vinegar acidic smell and the gray aging color, which are the disadvantages from this treatment. In the case of brown rot decay, it can be seen that the weight loss values of modified woods with both solutions and heat treatment temperature mentioned above separately are lower than the value of unmodified wood and

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therefore, it can be concluded that both thermal and chemical modifications increase the resistance against brown rot fungus, irrespective of the chemicals and temperature used. Statistical analysis revealed that this improvement is significant, at 95% confidence level, for all the treatment used compared with the untreated sample. Wood modified by heat treatment at 190°C combined with acetic anhydride showed the greatest resistance (16.6 %). Overall, chemical modification with vinegar and acid anhydrides afforded substantial bio-protection on both untreated and heat treated jack pine against brown rot decay. In other words, the combination of heat treatment and acid anhydrides acetylation offers additional protection, which might be attributed to the combination effect of these two treatments.

Figure 9 shows the FTIR spectra between the spectral region of 2000-500 cm^{-1} on untreated wood and samples acetylated with acetic anhydride and vinegar. Differences due to reaction with the different liquid can be clearly seen in the infrared spectra in the band shapes. The bottom two spectra in Figure 9 show similar features in infrared spectra for untreated and vinegar-treated samples. However, the infrared spectra in the studied region had uniform features for acetylated samples. Upon analysis of the spectra, it can be seen that the relative intensity of band at 1730 cm^{-1} which was characteristic of C=O bond in hemicelluloses, increased significantly after acetylation. This increase of groups in hemicelluloses indicates the change of hemicellulose by acetylation process. Another peak which has to be taken into consideration is the increase in the peak at 1169-1300 cm^{-1} which is characteristic of CO Guaiacyl ring breathing with CO-stretching in lignin or esters (Huang et al. 2012). This indicated that acetylation of lignin also occurs during reaction with acetic anhydride, which can also be confirmed by the increase of the relative intensity at 1373 cm^{-1} which was assigned to C-H bond in lignin carbohydrate complexes. The FTIR results indicate the formation of ester bond during acetylation process occurs with acetic anhydride but not in vinegar solution. This is similar to the infra-red spectra results found in literature (Papadopoulos et al. 2010). The arabinose sugar in the hemicelluloses, an L-pentose sugar, are the only sugars in a strained five-membered ring (Tsoumis 1991). This sugar might be the most unstable sugar of wood polymer and might be attacked first during the fungal degradation process. As a result, the hemicellulose becomes the most fungal sensitive polymer. Therefore, hemicelluloses degradation during heat treatment modification may reduce the availability of nutrient for fungi (Lekounougou and Kocaefe 2014a). In addition, this degradation can reduce the hygroscopicity and moisture of wood since hemicellulose is the most hydrophilic compound. The similar phenomenon can be caused by the substitution of hydroxyl group by acetyl group during acetylation process. Certain moisture content is essential for the hydrolysis by fungal enzymes and the development of fungal growth (Rowell et al. 1987). Therefore, the decrease in moisture content of the heat-treated and acetylated wood is too low to support fungal attack. The white rot fungi require more moisture than the brown rot fungi to achieve their optimal performance (Zabel and Morrell 1992). This might explain the higher improvement of heat treatment against brown rot fungi than white rot fungi (Figure 8 (a)). Furthermore, it was proposed that fungal enzyme penetration may be prevented by physical blocking of the covalently bonded acetyl group in the cell wall of acetylated wood (Hill et al. 2005; Papadopoulos et al. 2010). The results reported by Papadopoulos et al. (2010) indicate that the degree of cell wall bulking caused by the adduct, rather than the chemical/biochemical in

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substrate is the mechanism of protection against soft rot decay, since the type of anhydride employed has little influence on the degradation.

4. Conclusion

The purpose of this paper was to examine the effect that acetylation modification may have on the physical, mechanical, and bio-resistance properties of heat-treated wood and to investigate the effect that the by-product of acetylation acetic acid may have on the properties of wood. It was found that acetylation did not result in a significant increase of the mechanical strength of heat-treated wood, compared to the non-acetylated wood. Both heat treatment and acetylation reduce water absorption and improve significantly the additional dimensional stability for untreated wood. The combination of heat treatment and acid anhydrides acetylation offers significant additional protection against white rot fungus and brown fungus.

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Table 1 Conditions of heat treatment

English name	Maximum temperature	Heating Rate (°C/h)	Holding Time (h)
Jack pine	Untreated (120 °C)	-	-
Jack pine	165 °C	15	1
Jack pine	190 °C	15	1

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Table 2 Quantitative analysis of the components of heat-treated jack pine

	Extractive (%)		Lignin (%)	Pentosan (%)	Holocellulose (%)	Total weight loss (%)	Component loss (%)	Moisture loss (%)
	Acetone	Ethanol						
Untreated	5.10	1.81	28.95	9.09	63.81	/	/	/
165 °C	4.94	1.29	30.09	8.22	63.04	5.63	0.34	5.29
190 °C	4.87	1.08	31.91	7.38	62.27	6.22	0.63	5.58

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Table 3 Conditions of acetylation

Heat treatment	Reaction temperature (°C)	Reaction time (h)	Solution
Untreated	110	6	Acetic anhydride
165°C	110	6	Acetic anhydride
190°C	110	6	Acetic anhydride
Untreated	50	24	Vinegar
165°C	50	24	Vinegar
190°C	50	24	Vinegar

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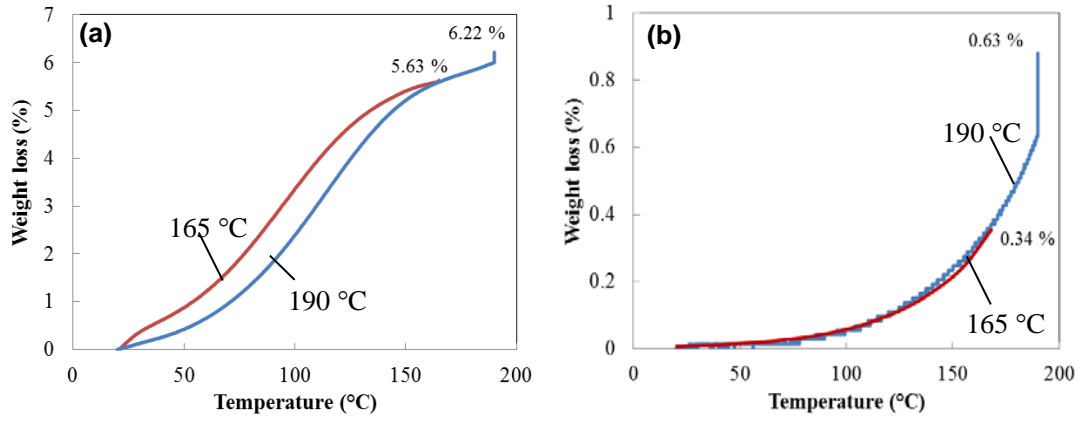


Figure 1 Weight loss during heat treatment of kiln-dried (a) and oven-dried wood (b) at different maximum temperatures

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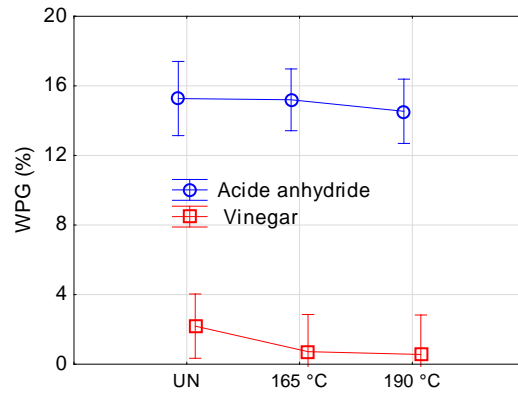


Figure 2 Weight percentage gain (WPG) of untreated and heat-treated jack pine wood after acetylation with different solutions (UN: sample without heat treatment)

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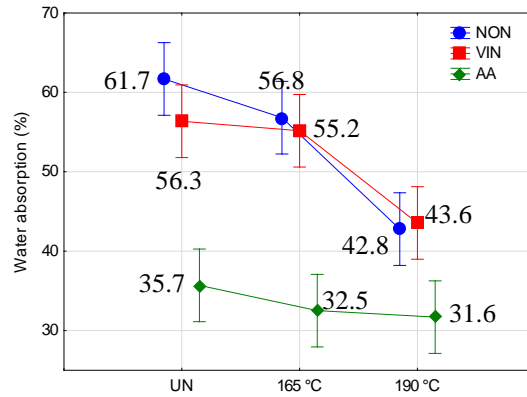


Figure 3 Water absorption of untreated and heat-treated jack pine wood before and after acetylation with different solutions (UN: sample without heat treatment, NON: Non-acetylated sample
VIN: acetylated with vinegar, AA: acetylated with acetic anhydride)

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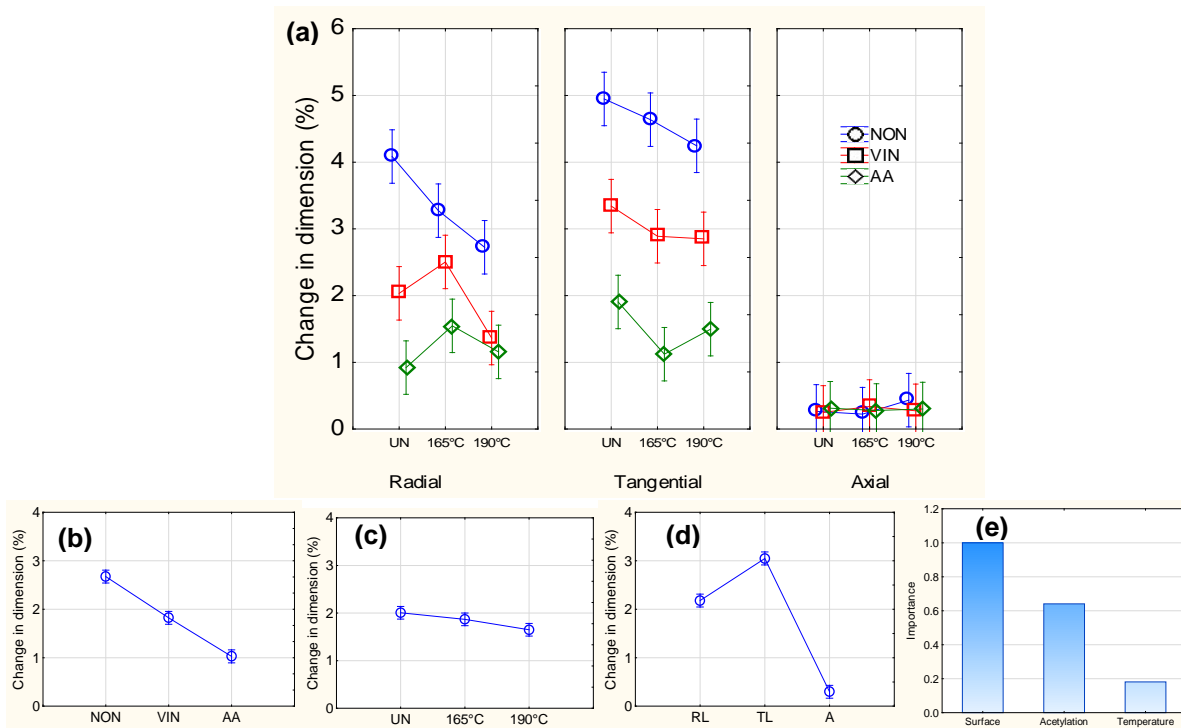


Figure 4 ANOVA analysis on impact of heat-treatment temperature and acetylation on dimensional stability of jack pine (a) Factorial ANOVA analysis, (b) one-way ANOVA analysis of heat-treated temperature, (c) one-way ANOVA analysis of acetylation, (d) one-way ANOVA analysis of surface, (e) impact importance of different factors (UN: sample without heat treatment, NON: Non-acetylated sample, VIN: acetylated with vinegar, AA: acetylated with acetic anhydride, RL: radial longitudinal surface, TL: tangential longitudinal surface, A: axial surface)

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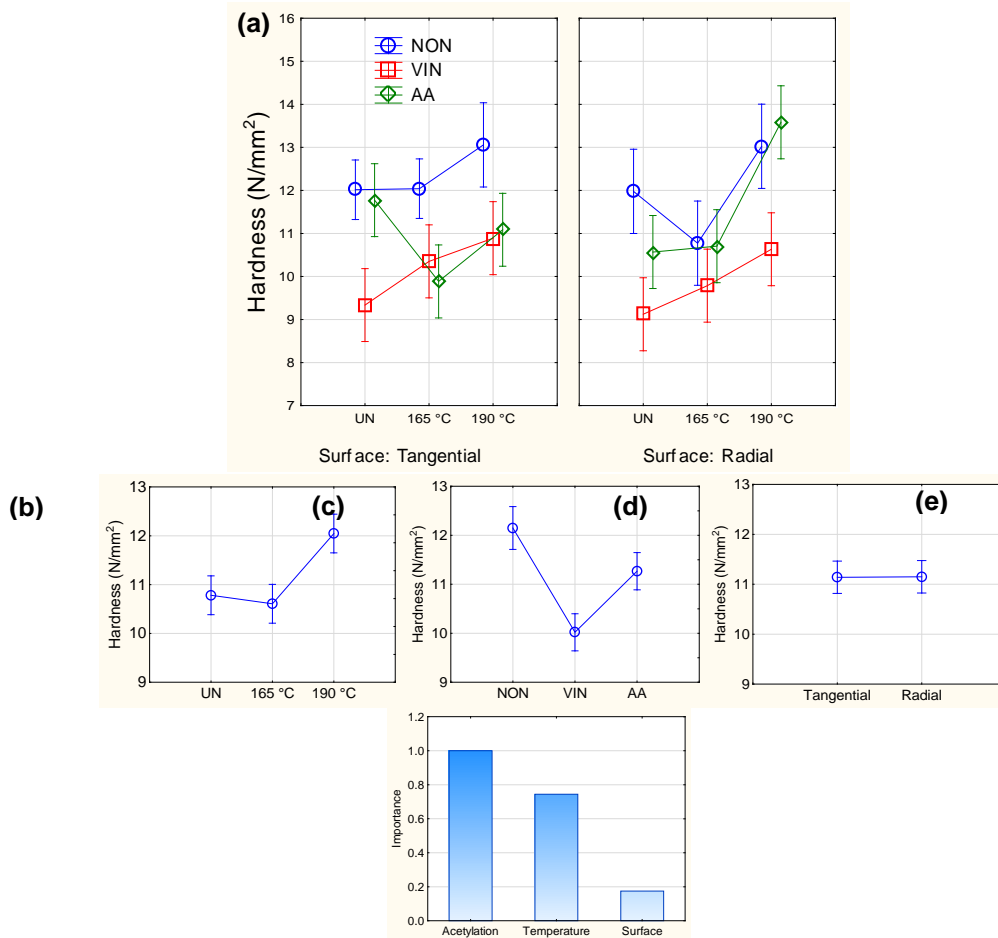


Figure 5 ANOVA analysis on impact of heat-treated temperature and acetylation on hardness of jack pine (a) Factorial ANOVA analysis, (b) one-way ANOVA analysis of heat-treated temperature, (c) one-way ANOVA analysis of acetylation, (d) one-way ANOVA analysis of surface, (e) importance of impact of different factors (UN: sample without heat treatment, NON: Non-acetylated sample, VIN: acetylated with vinegar, AA: acetylated with acetic anhydride)

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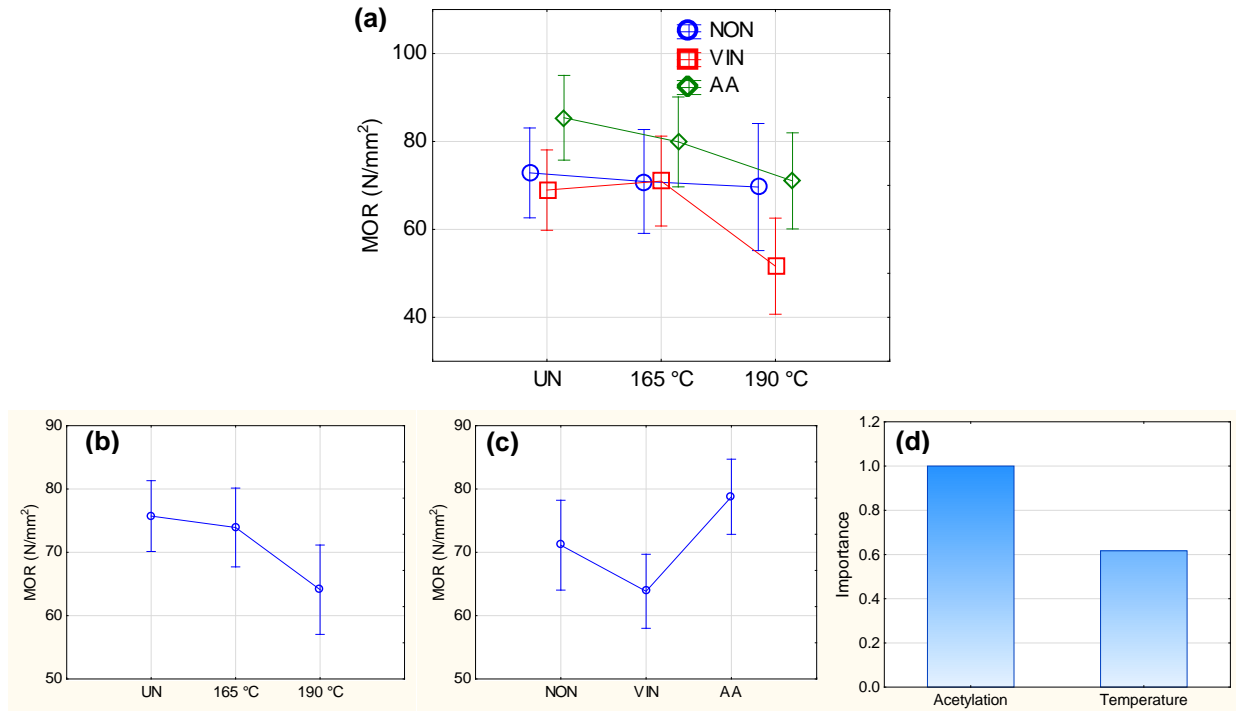


Figure 6 ANOVA analysis on impact of heat-treated temperature and acetylation on MOR of jack pine (a) Factorial ANOVA analysis, (b) one-way ANOVA analysis of heat-treatment temperature, (c) one-way ANOVA analysis of acetylation, (d) impact importance of different factors (UN: sample without heat treatment, NON: Non-acetylated sample, VIN: acetylated with vinegar, AA: acetylated with acetic anhydride)

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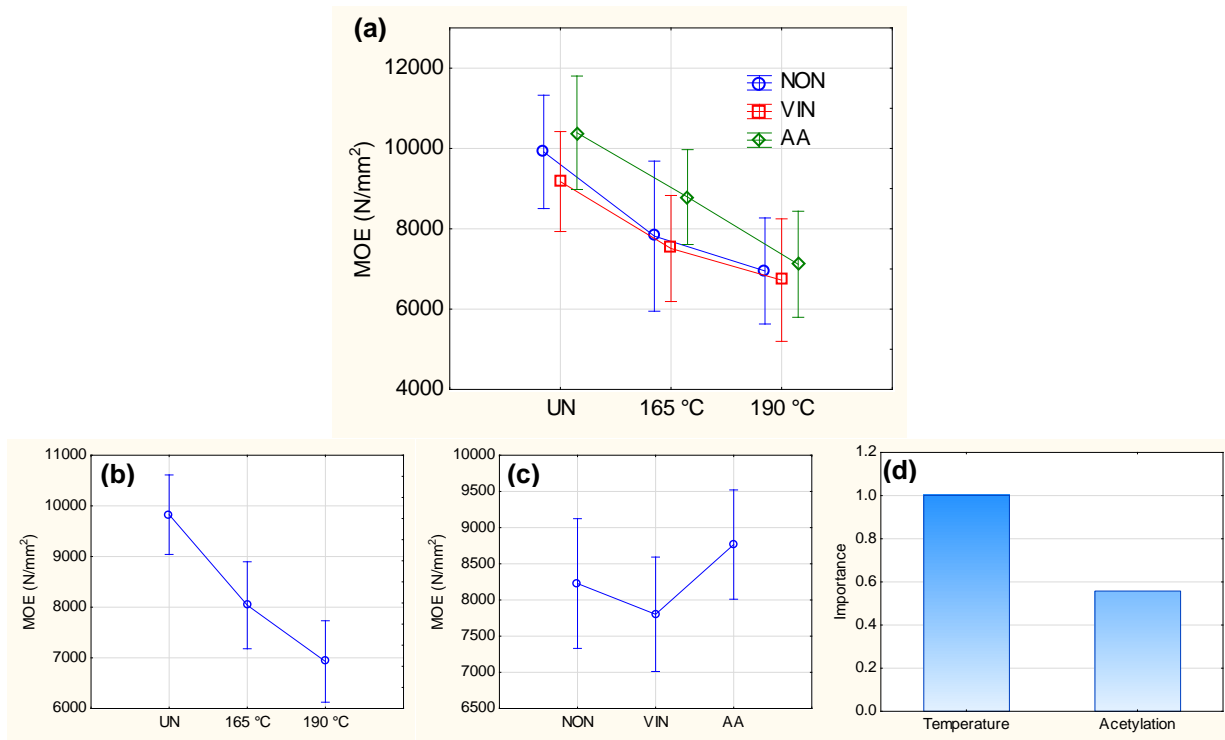


Figure 7 ANOVA analysis on impact of heat-treated temperature and acetylation on MOE of jack pine (a) Factorial ANOVA analysis, (b) one-way ANOVA analysis of heat-treated temperature, (c) one-way ANOVA analysis of acetylation, (d) impact importance of different factors (UN: sample without heat treatment, NON: Non-acetylated sample, VIN: acetylated with vinegar, AA: acetylated with acetic anhydride)

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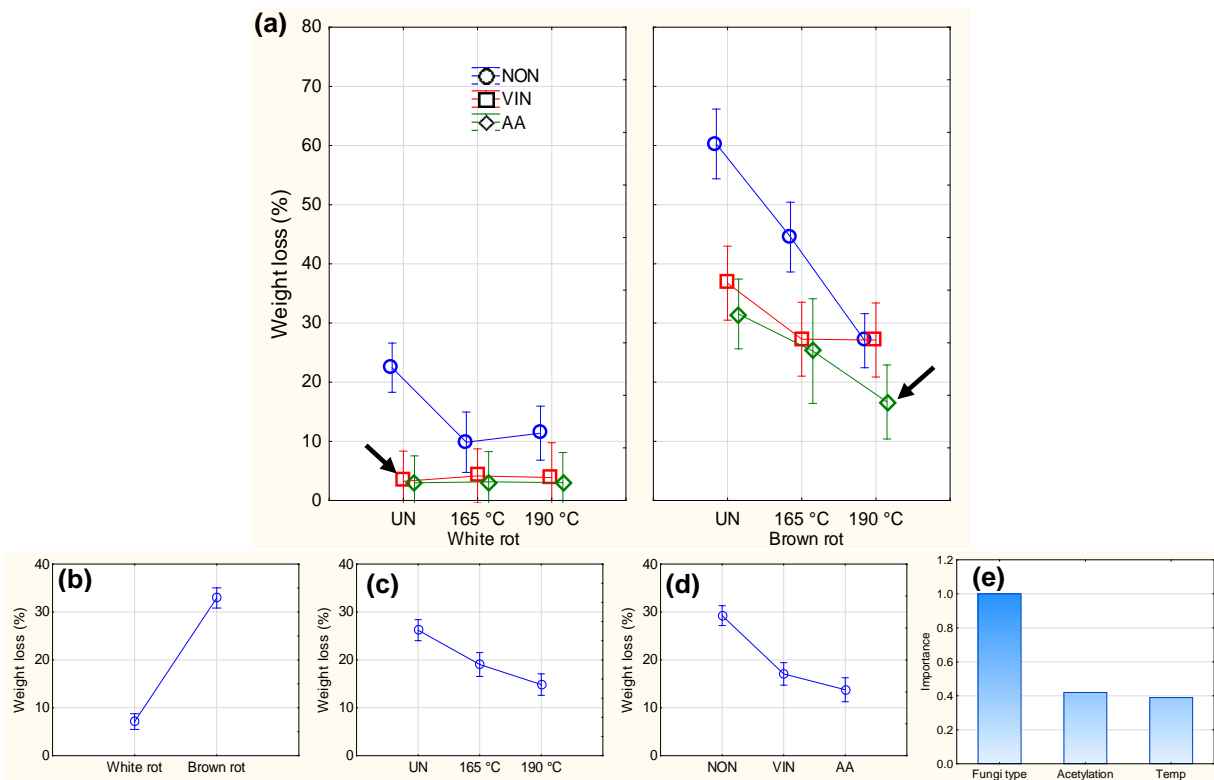


Figure 8 ANOVA analysis on impact of heat-treatment temperature and acetylation on fungal durability of jack pine (a) Factorial ANOVA analysis, (b) one-way ANOVA analysis of fungal type, (c) one-way ANOVA analysis of heat-treated temperature, (d) one-way ANOVA analysis of acetylation, (e) impact importance of different factors (UN: sample without heat treatment, NON: Non-acetylated sample, VIN: acetylated with vinegar, AA: acetylated with acetic anhydride)

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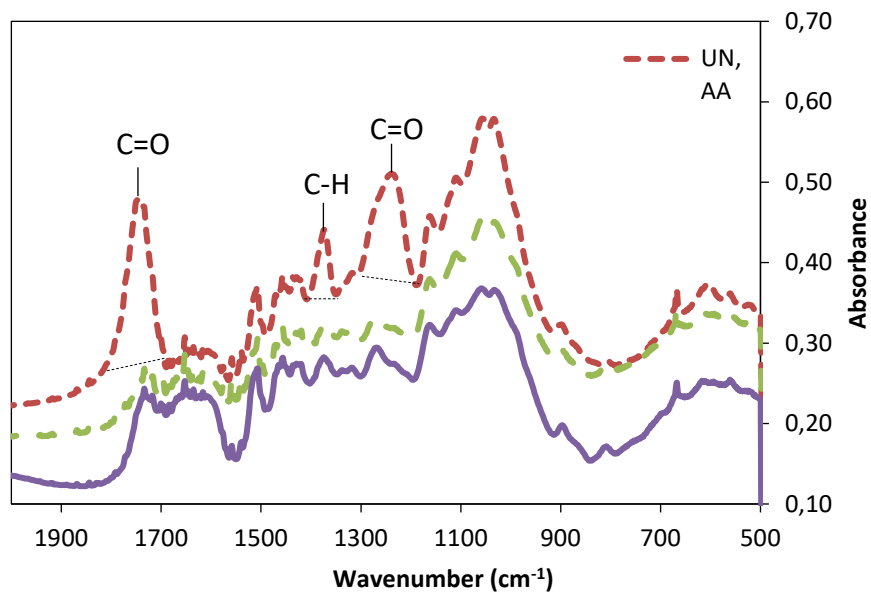


Figure 9 FTIR spectra of esterified and control untreated wood: untreated (UN), modified with vinegar (VIN), and modified with acetic anhydride (AA)

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