Effect of Delignification Pretreatment and Furfurylation on Practical Properties of Alder Wood (*Alnus spp.*)

Sayed Mohammad Hossein Yahyaee, Foroogh Dastoorian,* Maryam Ghorbani, and Seyed Majid Zabihzadeh

Partial delignification of alder wood specimens was performed with alkaline sulfite and peracetic acid (PAA) methods, and subsequently the delignified samples were saturated with furfuryl alcohol, as an eco-friendly chemical. The aim of delignification before furfurylation was to facilitate the penetration of furfuryl alcohol into the cell wall, in order to overcome the weak mechanical properties and hydrophilicity of alder wood as a fast growing species. The results showed that alkaline delignification removed a lower percentage of lignin despite more significant mass loss as compared to peracetic acid delignification method, which indicates more carbohydrates degradation in alkaline delignification. Infrared spectroscopy also confirmed more retention of carbohydrates in the sample delignified with peracetic acid. The polymerization of furfuryl alcohol in the cell cavities decreased the access of water molecules to the hydroxyl groups of the cell wall, increased the contact angle, and decreasing surface wettability. This effect was more noticeable in the PAA-delignified samples. Mechanical tests revealed that the delignified samples with peracetic acid had higher mechanical strength and modulus, compared to the alkaline sulfite delignified samples. This was attributable to the maintenance of carbohydrates during the delignification process.

DOI: 10.15376/biores.19.4.9169-9190

Keywords: Peracetic acid delignification; Alkaline delignification; Mechanical properties; Physical properties; Contact angle

*Contact information: Sari Agricultural Sciences and Natural Resources University, Dep. of Wood and Cellulosic Products Engineering; *Corresponding author: f.dastoorian@sanru.ac.ir*

INTRODUCTION

Wood, as one of the most sustainable “green” building materials on Earth, has been widely used from ancient times to the modern day (Akpan *et al.* 2021; Ding *et al.* 2022). In addition to advantages such as naturalness, acceptable specific strength, ease of use, and renewability (Dogu *et al.* 2016), wood has also several disadvantages, such as moisture absorption, dimensional instability, and the possibility of biodegradation (Navi and Heger 2004). With increasing population growth and development of wood demand, the supply of natural forests has decreased sharply (Karadeniz *et al.* 2009). Therefore, fast-growing species such as eucalyptus, poplar, and alder, having short growth periods, can be considered as alternatives to slow-growing species (Yahyaee *et al.* 2022). Caucasian alder (*Alnus subcordata*) is one of the native fast-growing trees in the forests of northern Iran and Caucasus, which reaches its maximum growth at the age of 50. Due to its high biomass production (with volume growth of 10 to 15 cubic meters per hectare), this species is suitable for wood cultivation to rebuild and rehabilitate deforested areas. Undesirable properties of *Alnus* spp. wood such as low density (385 to 535 kg/m^3), low hardness, low mechanical strength, high moisture absorption, and mediocre natural durability (Bakhshi, 2022; Reh *et al*. 2024), limit the use of these fast-growing species (Tu *et al.* 2014). To overcome these limitations, various modifying methods, such as mechanical, thermal, and chemical treatments, can be used. The chemical modification leads to reaction of a chemical with cell wall components (cellulose, hemicellulose, and lignin), changes the nature of cell wall macromolecules, which in turn leads to higher dimensional stability and natural durability (Hill 2006). In recent years, the chemical modification of wood by the furfurylation method has been regarded considerably (Yao *et al*. 2017; Yang *et al*. 2019; Li *et al*. 2020). Furfuryl alcohol is one of the furfural derivatives (Fig. 1). Furfural is a low price, bio-derived product of pentose-rich agricultural residues such as bagasse and rice husk. Due to its high polarity and solubility in water, furfuryl alcohol can penetrate the wood cell wall and form a polymer (Kong *et al.* 2018). According to previous reports, the amount of volatile organic compounds and aromatic hydrocarbons resulted from the burning of the furfurylated wood is meager (Lande *et al.* 2004), and the toxicity of this substance has not been reported so far. Therefore, furfuryl alcohol can be used as an eco-friendly chemical for wood modification to increase its dimensional stability, biological durability, and significantly improves mechanical properties (Lande *et al.* 2008). Because of these valuable properties and environmental benefits, the commercial production of furfurylated wood has been initiated since 2004, by Kebony Products in Norway. The resulting wood has been utilized for laboratory countertops, parquet flooring, knife handles, decking, siding, and walkways in acid plants (Schneider 2007; Lande *et al.* 2008).

In addition to reacting with lignin and hemicellulose, furfuryl alcohol is also capable of self-condensing and can form polymers in the cell wall cavities and wood lumens (Lande *et al.* 2008; Gerardin 2016; Li *et al.* 2016). Partial lignin removal before furfurylation can facilitate the penetration of furfuryl alcohol into the cell wall by increasing the porosity and the possibility of reacting with carbohydrates. Likewise, covalent bonding between residual lignin and furfuryl alcohol/poly furfuryl alcohol (Fig. 2) probably occurs more easily as a result of partial delignification due to the development of more porosity. This study aimed to evaluate the effect of partial replacement of cell wall lignin with polyfurfuryl alcohol on the mechanical and hydrophilic properties of alder wood.

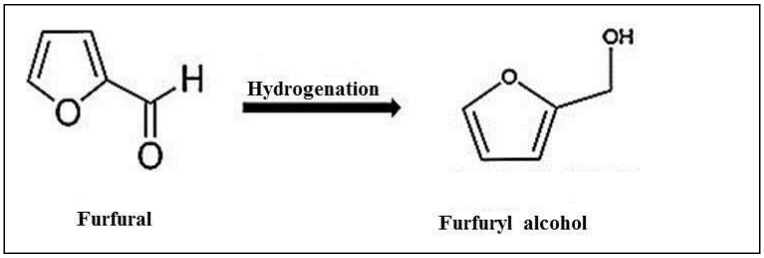

Fig. 1. Conversion of furfural to furfuryl alcohol

Previous research has shown that furfuryl alcohol can form covalent bonds with lignin (Fig. 2) and occupy lignin-rich areas *i.e.*, the middle lamella and corners of the wood cells (Nordstierna *et al.* 2008; Thygesen *et al.* 2010). Because of the similarity of polyfurfuryl alcohol with lignin structure, it may play a similar role in the cell wall.

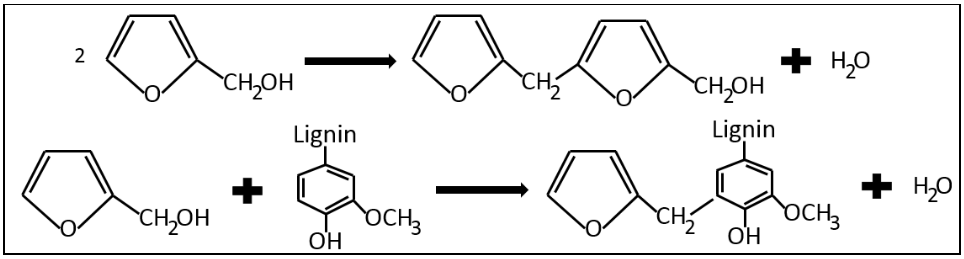

Fig. 2. Self-condensation reaction of furfuryl alcohol and its reaction with lignin (Gerardin 2016)

Lignin removal with sodium hydroxide, known as the soda method, is a prevalent delignification technique that causes substantial degradation of hemicellulose and also, to some extent, cellulose (Song *et al.* 2018). In previous studies, delignification using sodium hydroxide-sodium sulfite was performed at variable temperatures and times, which reduced density, increased porosity, and simplified impregnation with different resins (Naseeruddin *et al.* 2013; Frey *et al.* 2019). Further research by Keplinger *et al* (2018) showed that it is possible to fabricate a composite by impregnating wood with epoxy resin following the delignification pretreatment, while maintaining the structure of fibers similar to natural wood. This process considerably increased the mechanical strength and decreased the moisture absorption. Maturana *et al*. (2022) evaluated alkaline sulfite partial delignification depends on three tropical hardwood samples. They found morphological structures affect the flow of the alkaline solution and subsequently the efficiency of the delignification process.

Peracetic acid delignification leads to less degradation of carbohydrates (Zhao *et al.* 2010) and consumes far less energy than the conventional processes such as soda and kraft. In addition, because this process is free of inorganic chemicals and the cooking organic acids are completely recyclable using distillation technology, it is considered as an environmentally friendly process (Zhao *et al.* 2010; Palamae *et al.* 2014). Investigations that have been conducted so far in the field of wood furfurylation have confirmed the positive effect of this treatment on the significant improvement of water absorption, thickness swelling, and wettability of surfaces, and that by increasing the amount of furfurylation, the physical properties will be greatly improved. But on the other hand, increasing the furfurylation level weakens the mechanical strength. The research conducted by Yang *et al*. (2019) showed that lignin removal facilitates the saturation of furfuryl alcohol. In the current research, delignification with an organic peracetic acid solvent, which leads to less degradation of carbohydrates, was compared with alkaline sulfite delignification relative to the physical and mechanical properties of furfurylated alder wood. According to the investigations, no research has been reported on the effect of delignification with organic solvent on the physical and mechanical properties of furfuryl wood.

EXPERIMENTAL

Materials

Alder (*Alnus spp.*) wood veneers with a thickness of 1.5 mm were prepared from Nekachoob Co. (Mazandaran province, Iran), peeled tangentially from the sapwood of a 65-cm diameter log. The chemicals were furfuryl alcohol (purity of ≥98%wt), hydrogen peroxide, sodium sulfite, citric acid (Merck Co., Germany), sodium hydroxide (Mojallali Co., Iran), and acetic acid (AsiaPahohesh Co. Iran).

Delignification

Sodium hydroxide-sodium sulfite delignification

An aqueous solution containing 400 g of water, 20 g of sodium hydroxide, and 10.1 g of sodium sulfite was prepared. Then, wood specimens were immersed in the prepared solution (L/W = 0.10 by weight) and heated in an oven at temperature of 103 °C for 6 h. Afterward, the samples were removed from the solution and washed with boiled, distilled water until a colorless washing was obtained.

Peracetic acid delignification

Alkaline peroxide was prepared according to Misson *et al*. (2009). Peracetic acid (PAA) was prepared by mixing 600 mL of refrigerated acetic acid with 400 mL of alkaline hydrogen peroxide. Sulfuric acid (15 mL) was added as a catalyst, and the reagents were stirred at room temperature (35 °C) for 72 h. The wood samples were immersed in water and peracetic acid solution by 1:15 weight ratio. Delignification was performed for 2 h in an oven at 75 °C. Afterward, the samples were removed from the solution and washed with boiling water. The Klason lignin content was measured according to the TAPPI T222 om-02 (2002) on three replications from both PAA and alkaline sulfite delignified powdered samples. The percentage of delignification was calculated as Eq. 1,

$$\textit{delignification}\ (\%) = ((L_c - L_t)/L_c) \times 100 \tag{1}$$

where L_c and L_t denote Klason lignin values of the control and delignified samples, respectively.

The amount of mass loss (*ML*) after delignification was calculated according to Eq. 2, where, m_o and m_t denote oven-dry mass values before and after delignification respectively.

$$ML\ (\%) = ((M_0 - M_t)/M_0) \times 100 \tag{2}$$

Fluorescence Microscopy

Transverse sections of 5 µm were prepared using a microtome (Did sabz Co, Iran) and placed on a microscope slide. In order to examine the residual lignin distribution in fiber's cell wall regions of the partially delignified samples, a fluorescence microscope (Smart 300, Canada Smart Co. Newmarket, Canada) equipped with an ultra-pressure mercury lamp was used. Because of its autofluorescence property, lignin can be excited with blue light (wavelength of 488 nm) and emission occurs at wavelength of 495 to 600 nm. Therefore, lignin rich fractions would be appeared as luminescent regions (Ji *et al*. 2013; Donaldson 2020).

Furfurylation

First, a 50:50 mixture of furfuryl alcohol (FA) and deionized water was prepared at ambient temperature, and then 10% citric acid was added as a catalyst. The delignified samples were immersed in the mixture, and the saturation process was performed for 30 min at intervals of 5 min under 0.8 MPa vacuum. Then, the samples were covered with aluminum foil and placed in an oven at 120 °C for 8 h. In order to complete the polymerization process, the samples were removed from the foil and placed in an oven at 70 °C for 24 h. The percentage of weight gain (*WPG*) due to furfurylation was calculated according to Eq. 3. The specified codes for different treated samples and their density are presented in Table 1,

$$WPG\ (\%) = ((M_1 - M_0)/M_0) \times 100 \quad (3)$$

where M_0 and M_1 are the oven-dry mass values before and after impregnation, respectively.

Table 1. The Specified Codes of Different Samples

Code	Treatment	Density (g/cm^3)
Control	Untreated	0.51
FA	Impregnated by Furfuryl Alcohol	0.64
Alk Sulfite/FA	Delignified By Naoh-Na_2SO_3 And Subsequently Impregnated by Furfuryl Alcohol	0.66
PAA/FA	Delignified By Peracetic Acid and Subsequently Impregnated by Furfuryl Alcohol	0.71

Fourier Transform Infrared Spectroscopy

Infrared spectroscopy was carried out in the Attenuated Total Reflectance (ATR) mode, using a Cary 630 spectrometer (Agilent, USA), equipped with a ZnSe diamond crystal and a deuterated triglycine sulfate (dTGS) detector. A 10×10 mm^2 sample was placed in contact with the ATR crystal to absorb the evanescent waves. Spectra of three different points of a sample were recorded, and an average spectrum was obtained. The spectra of all samples were determined in the range of 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were averaged, and baseline corrected using SpectraGryph software.

Water Absorption Test

The water absorption test was conducted according to ASTM D 570 (1998) on specimens with the size of 1.5×60×60 mm^3 (R × T × L). Measurements of water uptake (*WA*), anti-swelling efficiency (*ASE*), and water-repellent efficiency (*WRE*) were carried out with ten replicates at intervals of 2, 4, 6, 12 and 24 h and then every 24 h until a constant water absorption and thickness swelling was obtained.

The water absorption (*WA*), anti-swelling efficiency (*ASE*), and water-resistant efficiency (*WRE*) were calculated with Eqs. 4 to 6,

$$WA\ (\%) = ((M_t - M_0)/M_0) \times 100 \quad (4)$$

where M_o and M_t denote the oven-dried mass before and after water soaking, respectively.

$$ASE\ (\%) = ((S_u - S_t)/S_u) \times 100 \quad (5)$$

In Eq. 5, S_u and S_t stand for swelling of the control and the treated samples respectively.

$$WRE\ (\%) = ((WA_c - WA_t)/WA_c) \times 100 \quad (6)$$

In Eq. 6, WA_c is the water absorption of the control samples and WA_t is the water absorption of the treated ones.

Tensile Strength Parallel to Grain

Tensile test was conducted according to ASTM D638 (2003), on dumbbell-shaped type V test specimens, by using a universal testing machine (Santam Co., Iran) at speed of 5 mm/min, in 5 replications.

Bending Properties

The bending test was performed according to ASTM-D790 (2017) by the SANTAM test machine on test specimens of 50.8 mm length by 12.7 mm width on a 25.4 mm support span, at displacement rate of 1.2 mm/min, in 5 replications.

Contact Angle Analysis

The contact angles of water droplets were determined using a Digidrop contact angle measuring device equipped with an image processing system, according to the ASTM- D7334-08 (2013). A deionized water droplet was released onto the sample's surface (10×20 mm^2), and the contact angle was measured from the droplet profile until 140 s of exposure using Dino-Lite software.

RESULTS AND DISCUSSION

Mass Loss and Delignification Efficiency

As shown in Fig. 3, for the alkaline sulfite delignified samples, the mass loss was 30%, while this parameter was 25% for the delignified sample with PAA. Furthermore, Klason lignin content showed 45% of lignin removal in the alkaline process, but this value for the PAA-delignified sample was calculated as 52%. It can be concluded that in the typical delignification process (*i.e.*, alkaline delignification), lignin, cellulose, and especially hemicellulose are largely destroyed and removed, while in the PAA delignification, despite lower mass loss, higher lignin destruction and removal was observed, which indicates the concentration of PAA on removal of lignin and other cell wall polymers (cellulose and hemicellulose) have remained essentially unchanged (Zhao *et al.* 2011).

During alkaline delignification at temperatures below 170 °C, at the reducing end group of a cellulose molecule, glucose units are progressively detached one by one, which is known as peeling or unzipping (Loon and Glaus 1997; Knill and Kennedi 2003; Li *et al*. 2017). In the present research, delignification at 103 °C for 8 h probably led to peeling and shortening of cellulose molecules, especially at the amorphous parts. Hemicelluloses, as low molecular weight carbohydrates, are extensively prone to dissolution/degradation in alkaline solutions, even at ambient temperature (Wigell *et al*. 2007). In PAA delignification, hydroxonium ions (OH+) produced by peracetic acid, attack the electron-rich moieties of lignin, cleave ether bonds between lignin monomers, and produce phenolic compounds (Ma *et al*. 2016). Aromatic ring hydroxylation leads to its demethoxylation and subsequently aromatic ring opening, which makes the oxidized lignin soluble (Barros *et al*. 2010). Kumar *et al*. (2003) reported that cellulose reducing ends had no alteration during peracetic acid delignification.

Another advantage of the PAA delignification process, considering energy consumption, compared to the alkaline one, is lower process temperature and a shorter time (Palamae *et al.* 2014). Kundu *et al*. (2021) found that the delignification of biomass at temperature of 90 °C for 5 h resulted in the effective removal of lignin with a negligible loss of carbohydrates.

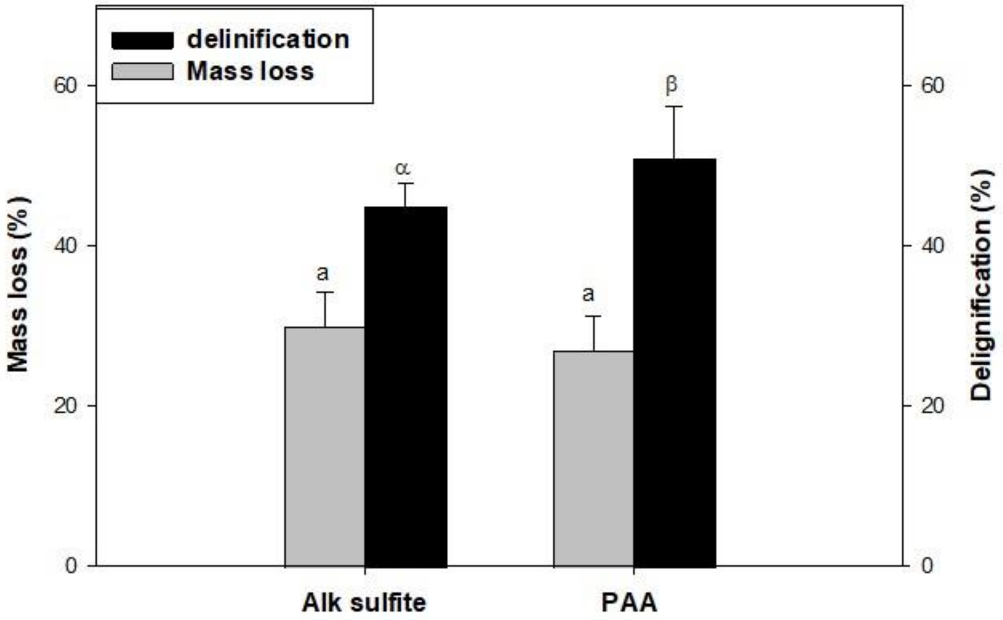

Fig. 3. Comparison of mass loss and lignin removal percentage of peracetic acid (PAA) and alkaline sulfite (Alk sulfite) delignification processes.

Fluorescence Microscopy

The fluorescence microscopic method was used to examine the distribution of lignin in fiber's cell wall regions in the control and delignified samples, as a function of lignin autofluorescence. The observations indicated delignification, leading to bulking of the cell wall structure caused by hydrophilicity of the residual sulfonated lignin in the alkaline sulfite delignified sample (Fig. 4b), and also may be attributed to more carbohydrate ratio in the PAA delignified sample (Fig. 4c).

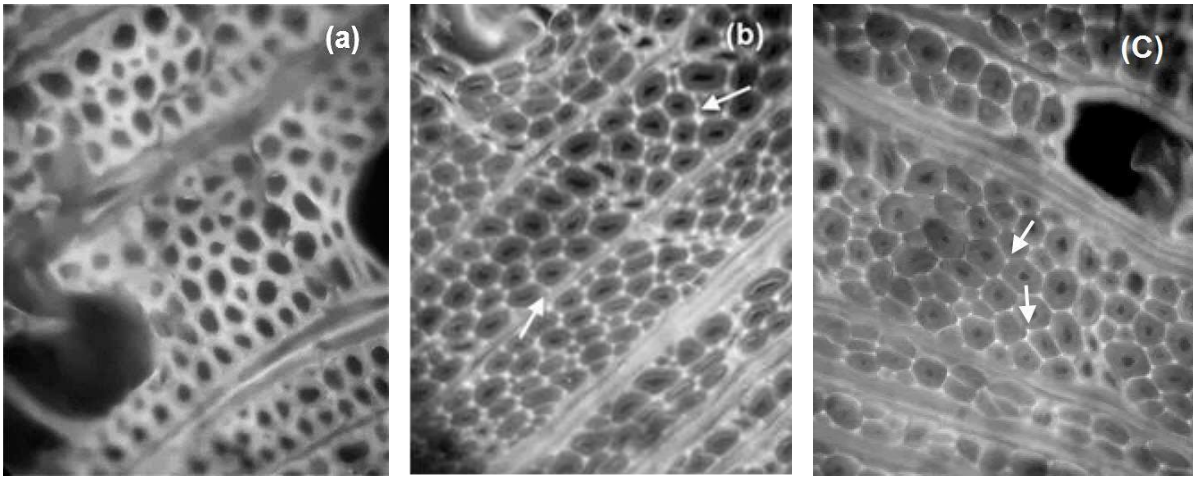

Fig. 4. Fluorescence microscopic images of transverse section of the control (a); Alk-sulfite delignified (b); and PAA-delignified samples (c)

In the alkaline sulfite sample, lignin in the cell corners and middle lamella, shown by white arrows in Figs. 4b and 4c, appeared with a thicker luminescent layer compared to the PAA sample. Concerning the higher lignin removal of PAA delignified samples (Fig.

3), it can be concluded that in alkaline delignified samples, the major lignin removal occurred between the cell wall microfibrils. At first stages of Alk-sulfite delignification, up to 50% of lignin removal, major delignification occurs in the cell wall, while in organosolv PAA-delignification, major lignin removal occurs in middle lamella and the cell wall lignin remains almost intact (Albrecht 1971; Behera 1985; Sjostrom 1987).

Weight Percentage Gain

Comparing the weight percentage gain (WPG) after furfurylation in FA, Alk-sulfite/FA, and PAA/FA samples (Fig. 5), a significant difference was observed between the FA sample and the two delignified ones (P-value = 0.00). The WPG values of Alk-sulfite/FA and PAA/FA samples (83% and 85%, respectively) were almost threefold of the FA sample (27%). It can be concluded that the delignification pretreatment led to higher permeation of furfuryl alcohol. In PAA pretreatment, lignin removal was slightly higher than Alk sulfite pretreatment (Fig. 3). However, WPG values of PAA/FA samples and Alk sulfite/FA samples were statistically insignificant. In PAA delignified samples, the major lignin removal occurred in middle lamella and cell corners (Fig. 4c). Therefore, FA can penetrate more easily into them and because of adequate space, FA self-condensation reaction and grafting with residual lignin (Fig. 2) could take place. Xu *et al*. (2022) stated that methylene bridge linkage between lignin and PFA was created in the middle lamella and cell corners. In Alk sulfite delignified samples, as a result of more lignin removal from cell wall, FA can penetrate between the cell wall microfibrils and may just deposit on them without crating linkage (Ehmcke *et al*. 2017).

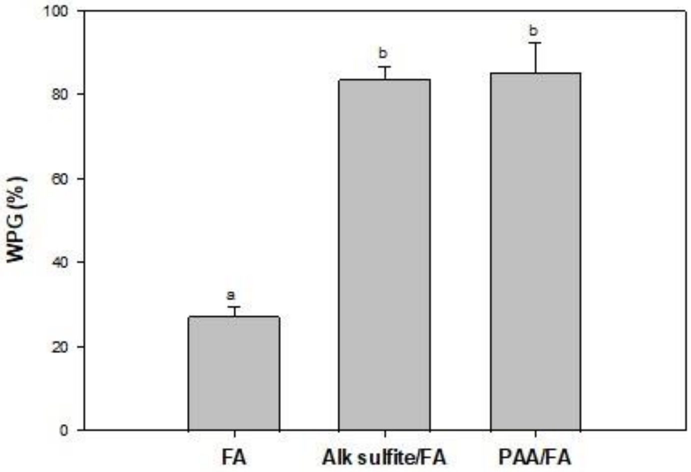

Fig. 5. Percentage of weight gain due to furfurylation in FA, Alk-sulfite/FA, and PAA/FA samples.

Attenuated Total Reflectance FTIR Analysis

The results of infrared spectroscopy for the control sample, Alk-sulfite, and PAA-delignified samples are shown in Fig. 6. The results showed that the peaks due to C=C or C=O stretching vibrations in the aromatic ring of lignin (1528 to 1626 cm^{-1}) were observed strongly in the control sample and almost disappeared for the delignified ones. The peak associated with the C=O stretching vibration of acetyl or carboxylic acid groups of lignin and hemicellulose (1734 cm^{-1}) was observed only in the control sample. The peak related to the alcoholic hydroxyl groups appeared in the control sample (3291 to 3490 cm^{-1}) and with the highest intensity in the PAA delignified sample (3334 cm^{-1}), while the peak disappeared in the alkaline delignified samples. Due to the preservation of carbohydrates, the delignified sample with PAA had a higher peak intensity and bandwidth compared to the control sample. Also, the peak related to C-O stretching vibration in carbohydrates (1027 to 1031 cm^{-1}) was more intense in the PAA-delignified sample, which confirms the preservation of carbohydrates in this method. Appearance of three new peaks in Alk-sulfite delignified samples, at wave numbers of 1403, 1031 and 874 cm^{-1}, assigned to S=O stretching vibration, implies the presence of remaining lignosulfonate. The peak in the range of 2860 to 3000 cm^{-1} corresponding to asymmetric C-H stretch vibration of alkane appeared with the lowest intensity in Alk sulfite sample, may be attributed to more degradation of carbohydrates in addition to lignin removal.

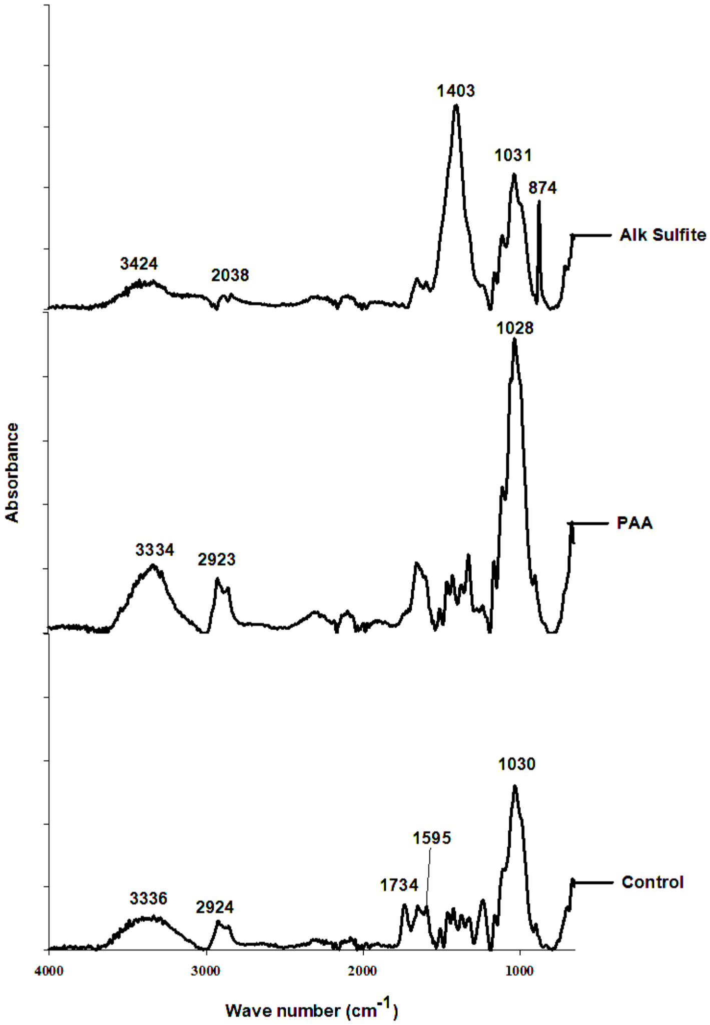

Fig. 6. FTIR spectra of control and delignified samples with alkaline sulfite (Alk sulfite) and peracetic acid (PAA)

Figure 7 presents the FT-IR spectra of untreated and furfurylated samples. The absorption band at 2850 to 2950 cm^{-1} related to the stretching C-H vibrations of alkanes (methoxyl group and methyl or methylene groups) while alkenes and aromatic compounds show a C-H band at 3020 to 3080 cm^{-1} (Liu 2021). The highest peak intensity in the range of 2850 to 2950 cm^{-1} was found in Alk sulfite/FA samples. This can be related to the free hydroxymethyl groups of FA monomers deposited between microfibrils (as described in WPG section). The lowest peak intensity belonged to PAA/FA samples, which is attributable to more polymerization of FA in middle lamella and cell corners. This creates methylene linkage between FA monomers or residual lignin and FA monomers and leads to band broadening slightly higher than 3000 cm^{-1} (indicated in Fig. 7 by a red circle).

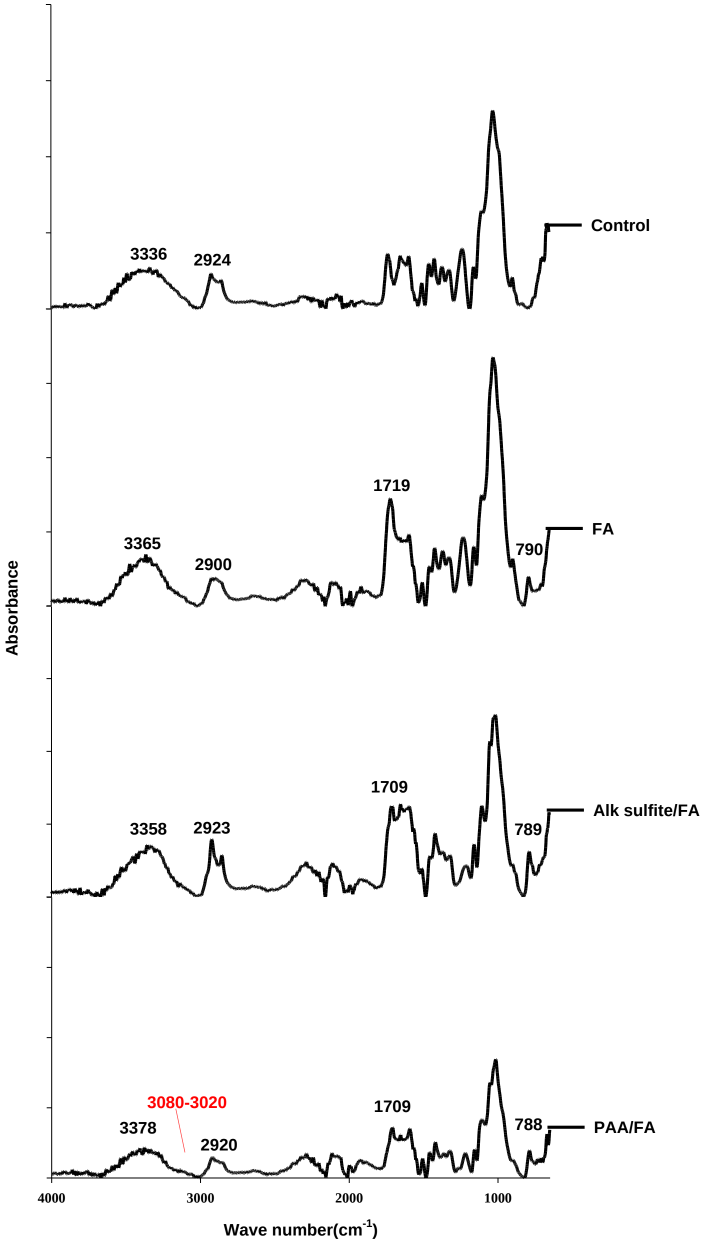

Fig. 7. FTIR spectra of furfurylated (FA), alkali delignified and furfurylated (Alk sulfite/FA) and the PAA delignified and furfurylated (PAA/FA) samples

The intensity of the peak related to hydroxyl groups (3300 to 3600 cm^{-1}) in furfurylated samples did not change appreciably compared to non-furfurylated one. This phenomenon implies no reaction between the hydroxyl groups of the cell wall and furfuryl alcohol. The lower peak intensity in PAA/FA samples compared to the Alk Sulfite/FA samples could be related to more FA polymerization. Beck *et al*. (2019) and Alvarez *et al*. (2021) reported similar results. The appearance of a new peak in treated samples at 787 to 790 cm^{-1} attributed to skeletal vibration of furan ring of FA structure (Alvarez *et al*. 2021) was observed, with the highest intensity in Alk-sulfite one demonstrating polymerization of FA in the cell cavities. The peak around 1707 to 1719 cm^{-1} in FA treated samples was attributable to C=O stretching of γ-diketons formed by some furan ring opening in the polymerized FA structures (Pranger *et al.* 2008; Lems *et al.* 2019; Li *et al.* 2020).

Water Absorption and Thickness Swelling

The water absorption values of the test specimens as a function of immersion time and the correlation curve between WPG and water absorption at 96 hours of immersion are shown in Figs. 8a and 8b. The highest amount of water absorption was related to the control sample, and the lowest was related to the PAA/FA, Alk sulfite/FA, and FA samples, respectively. Comparing Figs. 8a and 8b shows a direct relationship between the WPG and decrease of water absorption (Dong *et al.* 2015). Furfurylation causes polymer formation in the lumen and cell wall and prevents water from entering the pores. In the delignified samples, due to the more significant penetration of FA into the wood structure and subsequently its polymerization in the pores, a significant decrease in water absorption was observed, especially in the PAA-delignified samples. Also, as shown in Fig. 9, the highest water resistance efficiency was found in PAA-delignified samples, which is due to the reduction of available spaces for water absorption, which in turn, increases the water resistance efficiency (Thygesen *et al.* 2010). On the other hand, the presence of furan compounds in phenolic structures (confirmed by IR spectrum, Fig. 7) that could form a chemical bond with cell wall lignin in middle lamella (Thygesen *et al.* 2010), decreases the accessibility of hydroxyl groups of carbohydrates to water molecules.

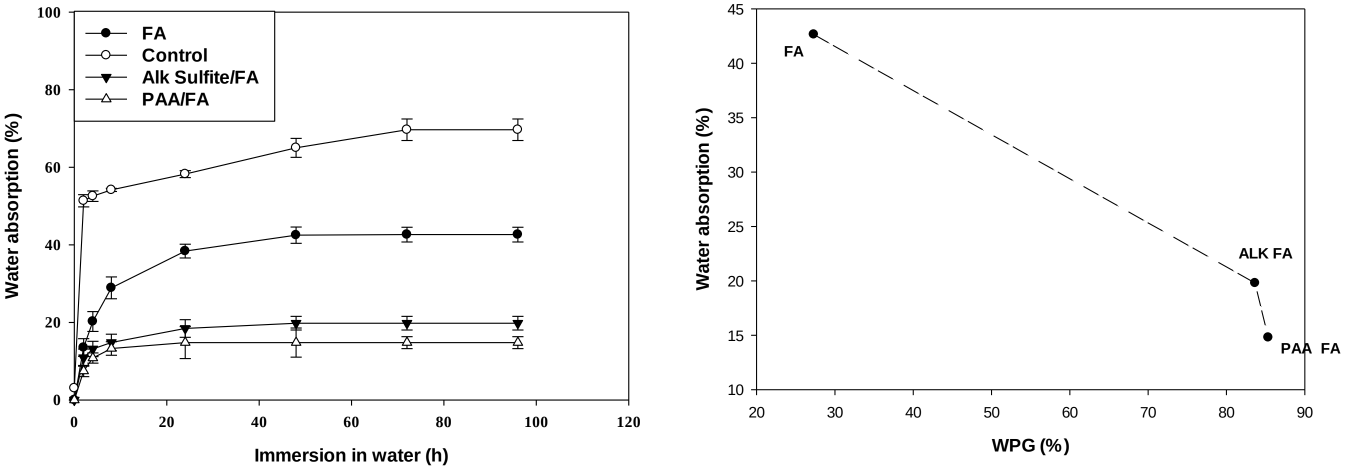

Fig. 8. Water absorption of the control and treated samples (a), Correlation curve of water absorption values after 96 hours and WPG (b)

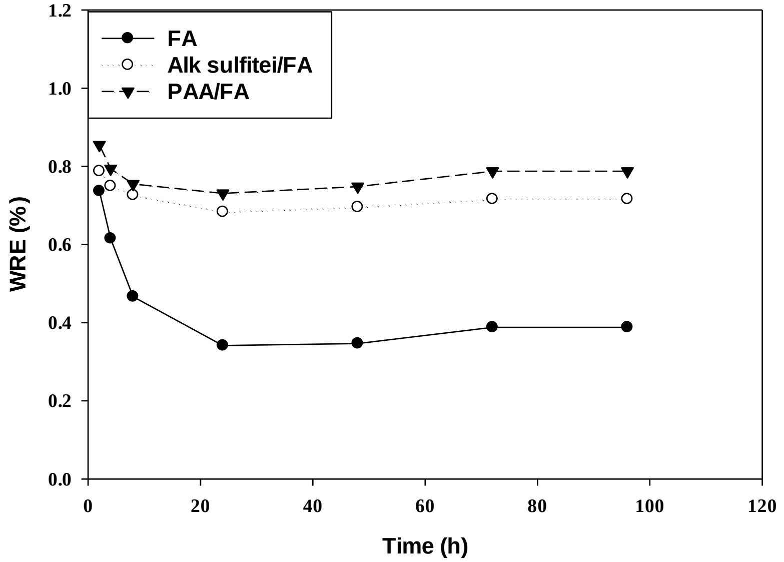

Fig. 9. Water resistance efficiency of FA, Alk sulfite /FA, and PAA/FA

As can be seen in Fig. 10, thickness swelling of the control sample was significantly higher than the furfurylated samples. The furfurylated samples showed shrinkage of about 2% due to the filling of the pores with the hydrophobic poly furfuryl alcohol, as discussed in ATR-FTIR section and shown in Fig. 7 (Li *et al.* 2015).

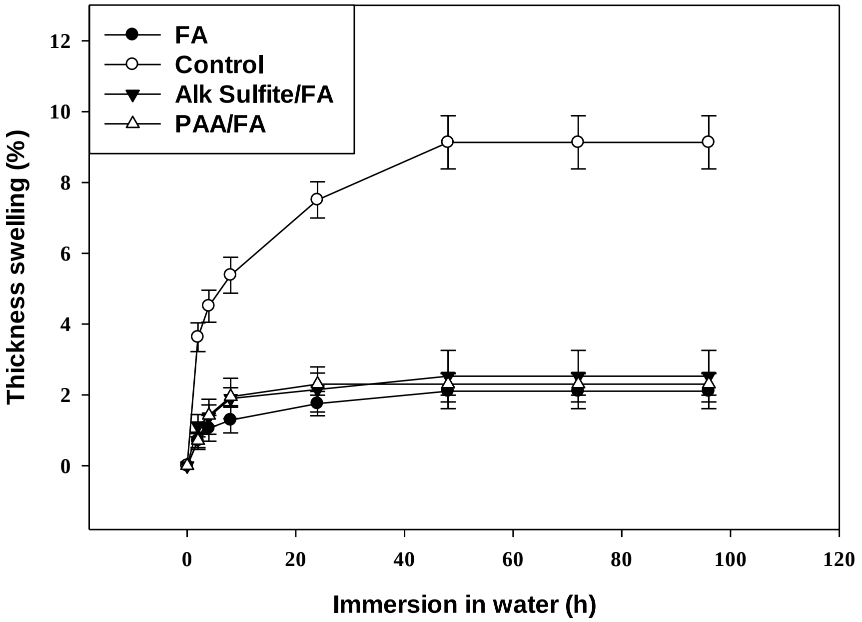

Fig. 10. Thickness swelling of control, FA, Alk sulfite /, and PAA/FA

Despite higher WPG values of delignified samples, there was no significant difference between the thickness swelling values of delignified and non-delignified furfurylated samples, although the water absorption values had a direct correlation with WPG (Fig. 8b). Furfuryl alcohol polymerization or deposition in the lumen and cell wall acts as a physical barrier and decreases the accessibility of hydroxyl groups of carbohydrates to water molecules, so the thickness swelling of all furfurylated samples was almost the same, while the amount of water absorption was dependent to WPG.

The results of FTIR spectroscopy (Fig. 7) did not show any change in the intensity of hydroxyl groups, which are the hydrophilic positions of the cell wall. Gaitán-Alvarez *et al*. (2021) acknowledged that the formation of polyfurfuryl alcohol in the cell wall and cavity acts as a barrier to accessing the hydroxyl groups of the cell wall and enhances the dimension stability. Also, as can be seen in Fig. 11, the anti-swelling efficiency of the furfurylated samples was almost the same and above 70% due to polymerization of furfuryl alcohol and filling of the pores in the structure (Dong *et al.* 2015). Lande *et al* (2004) reported that even small amounts of furfurylation can significantly improve the anti-swelling efficacy.

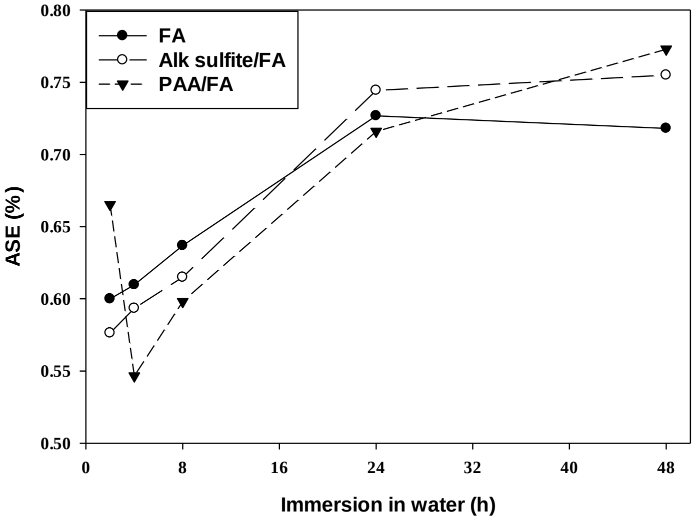

Fig. 11. Anti swelling efficiency of FA, Alk sulfite /, and PAA/FA

Tensile Properties Parallel to Grain

Figure 12 illustrates the tensile strength and tensile modulus values of the control, FA, Alk sulfite/FA, and PAA/FA samples. The results of the analysis of variance indicated a significant difference between the average tensile strength values of the samples (P value = 0.00). The lowest strength was related to the Alk sulfite/FA sample (27 MPa), which can be attributed to the destruction of a significant part of the hemicellulose and the amorphous part of the cellulose (peeling) during the alkaline delignification process (Lu *et al.* 2020). The 30% decrease in the tensile strength of the FA sample compared to the control sample. Li *et al*. (2020) found that the enhancement of mechanical properties of furfurylated wood was dependent on the wood species because of different morphological structures, affecting the resin distribution and also FA concentration. They reported that higher FA concentration (>15%), had a destructive influence on the mechanical properties, and attributed this phenomenon to the cell wall bulking caused by excess FA infiltration, which unfavorably affect the integrity of cell walls.

No significant difference was observed between the strength properties of the PAA/FA and the control samples, which indicates the superiority of the peracetic acid delignification process over the alkaline delignification process due to the preservation of cellulose during delignification. In addition, the removal of lignin from the middle lamella and the substitution of furfuryl alcohol, in PAA delignified samples, do not cause a decrease in the tensile strength of fibers. In contrast, the lignin removal from the cell wall, in alkaline delignified samples, weakens the connection between cellulose microfibrils. Therefore, FA can easily penetrate into the cell wall. It just creates deposits between microfibrils without linkage and reduces the tensile strength.

The highest amount of tensile elasticity modulus was related to the PAA/FA sample, and the lowest tensile modulus was related to the Alk/FA sample. Wimmer and Lucas (1997) found that the Young's modulus of lignin in the middle lamella is 50% lower than that of the secondary wall lignin. Degradation of middle lamella lignin as a result of PAA delignification, as depicted in Fig. 4a, and substitution of poly-furfuryl alcohol improved the tensile modulus, but in the alkaline-sulfite delignified samples, the tensile modulus decreased drastically due to the destruction of cell wall lignin (Fig. 4b). Also, lower mass loss and higher lignin removal in the PAA delignified samples (Fig. 3), implies maintaining the cellulose, which could be another reason for increasing the tensile modulus of the PAA/FA sample.

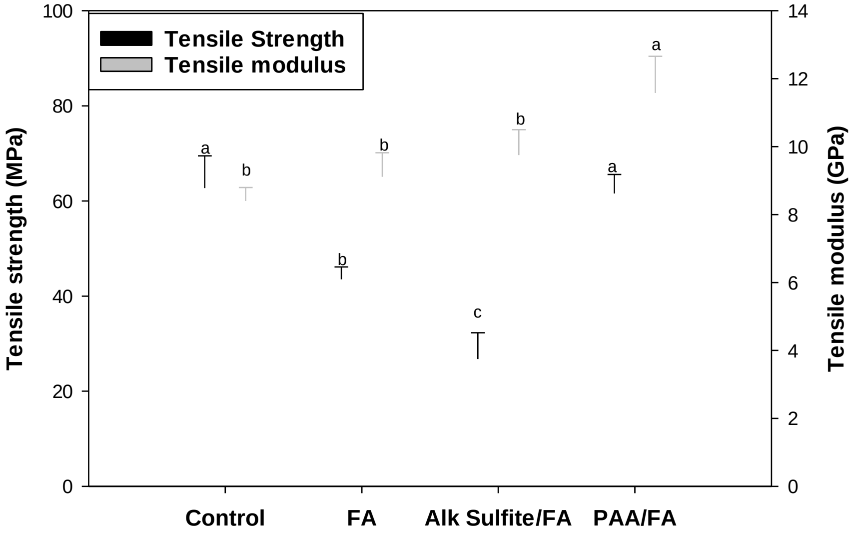

Fig. 12. Tensile Strength and modulus of the control, FA, Alk sulfite/FA, PAA/FA samples

Bending Properties

Figure 13 illustrates the bending strength and bending modulus of the samples. The highest amount of bending strength was related to the PAA/FA sample (132.3 MPa), control (104.2 MPa), FA (100 MPa), and Alk sulfite/FA (72.5 MPa), respectively. However, no significant difference was observed between the bending strength values of the control sample and the FA sample. Similar results were reported by Esteves *et al.* (2011). The comparison between Alk sulfite/FA and PAA/FA samples showed a significant decrease of bending strength in alkaline delignified sample, while no statistical difference was observed between PAA/FA and the control sample. The reason can be attributed to more lignin removal from the middle lamella as a result of PAA delignification and substitution of furfuryl alcohol. Li *et al* (2020) mentioned the positive effect of furfurylation on the bending strength of Chinese fir and poplar wood at concentration of 15%. But by increasing the concentration of furfuryl alcohol up to 70%, the bending strength decreased. The probable cause of this phenomenon was attributed to the entry of furfuryl alcohol into the cell wall at a high concentration, the bulking of the cell wall, and subsequently the disruption of the integrity of the cell wall. There was no significant difference between the flexural modulus values of the control samples (8.33 GPa), FA

(7.41 GPa), and Alk sulfite/FA (6.73 GPa). However, the flexural modulus of the PAA/FA sample (12.31 GPa) was significantly higher than other ones. The cause of this phenomenon can be related to the lower role of lignin in the middle lamella on improving the modulus (Wimmer and Lucas 1997), which is destroyed by peracetic acid during the delignification process and replaced by poly-furfuryl alcohol. While in the alkali delignification process, most of the lignin is removed from the secondary wall. Also, maintaining the crystalline areas of cellulose in delignification with organic solvent is another reason for increasing the modulus of the PAA/FA sample.

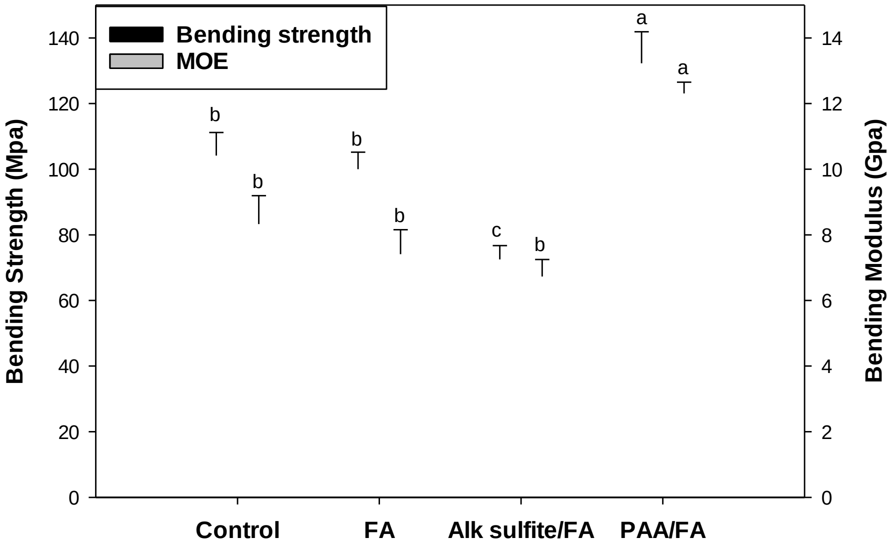

Fig. 13. Bending Strength and bending modulus of the control, FA, Alk sulfite/FA, and PAA/FA samples

Contact Angle

As can be seen in Fig. 14, in the control sample, the contact angle at the moment of drop formation was 65º, and after about 30 s, the drop was entirely absorbed and disappeared. In the FA sample, the contact angle at the moment of drop impact was 125.5º; in the Alk-sulfite/FA sample, it was 125º; and in the PAA/FA sample, it was 144º. The comparison of drop behavior after 140 s also showed that the highest contact angle values belonged to the PAA/FA, Alk sulfite/FA, and FA samples, respectively. With the increase in WPG caused by furfurylation, the polymerization of furfuryl alcohol in cell cavities and cell walls increased, leading to blocking of cell lumens and cell wall pores, and decreasing access to hydroxyl groups, which increased contact angle and decreased surface wettability.

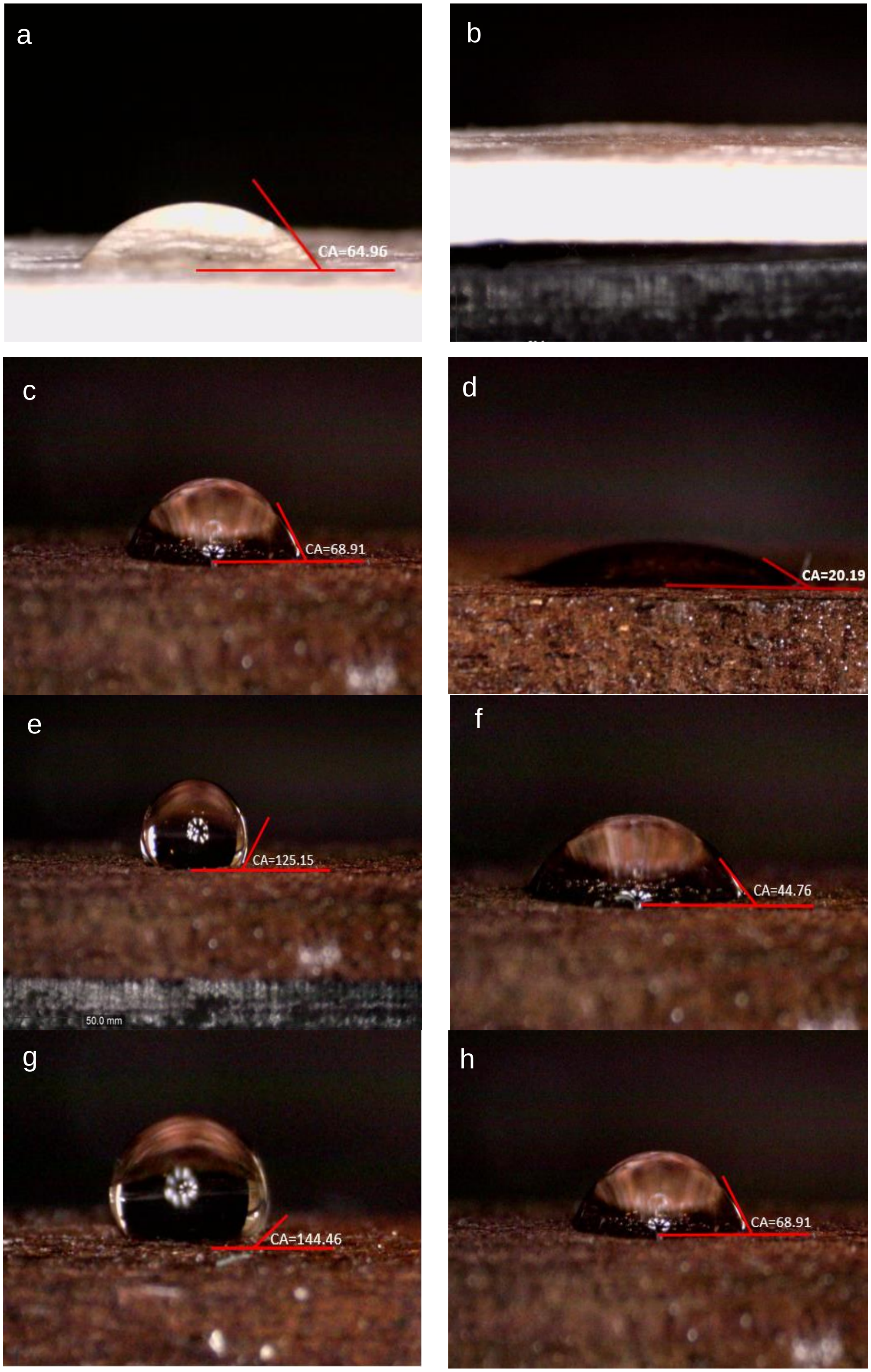

Fig. 14. Contact angle images in the first second and after 140 s of control samples (a and b), FA (d and c), Alk sulfite/FA (e and f), and PAA/FA (g and h)

CONCLUSIONS

In this work, partial delignification of alder wood specimens was done by alkaline sulfite and peracetic acid methods, and the delignified specimens were then impregnated by furfuryl alcohol. In general, peracetic acid (PAA) delignification pretreatment led to higher stiffness, higher flexural strength, and higher water repellency of furfurylated alder wood. Investigating the effect of partial replacement of lignin with poly-furfuryl alcohol on mechanical properties and hydrophilicity showed that:

1. The amount of lignin removal in the alkaline-sulfite delignified and PAA-delignified samples (45% and 52%, respectively) compared to their corresponding mass loss (30% and 25%), indicated more degradation of carbohydrates in the alkaline-sulfite delignified samples.
2. The fluorescence microscopic observations indicated that in alkaline sulfite delignified sample, lignin in the cell corners and middle lamella appeared with a thicker luminescent layer while in the PAA delignified sample; the major lignin removal occurred between the cell wall microfibrils.
3. The results of Fourier-transform infrared (FTIR) spectroscopy confirmed the retention of carbohydrates in the PAA-delignified samples. Skeletal vibration of furan ring of furfuryl alcohol (FA) structure, observed with the highest intensity in alkaline sulfite sample demonstrating polymerization of FA in the cell cavities.
4. Poly-furfuryl alcohol polymerization in the lumen and cell wall decreased the access of water molecules to the hydroxyl groups of wood, increased the contact angle, and decreased surface wettability. This effect was more noticeable in the PAA-delignified samples.
5. The tensile strength values of PAA/FA and control samples were almost the same and the bending strength values of PAA/FA was significantly higher than the control sample, related to cellulose preservation during PAA delignification. Alk sulfite/FA sample had the lowest tensile and bending strengths as a result of cellulose peeling during delignification. The 30% decrease in the tensile strength of FA sample compared to the control one was attributed to the cell wall bulking caused by excess FA infiltration, which unfavorably affect the integrity of cell walls.
6. The highest and lowest tensile modulus values were related to PAA/FA and Alk/FA samples, respectively.
7. The flexural modulus of the PAA/FA sample was significantly higher than other samples while, was no significant difference between the flexural modulus values of control, FA, and Alk sulfite/FA samples.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Dr. Friedrich Menges for providing the SPECTRAGRYPH open-source software. The author would like to thank Sari Agricultural Sciences and Natural Resources University for financial support of this research under contract number “04-1399-11”. The authors would like to acknowledge the Central laboratory staff at Sari Agricultural Sciences and Natural Resources University (SANRU), for their help and support in FTIR analysis and fluorescence microscopy.

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Article submitted: June 14, 2024; Peer review completed: July 4, 2024; Revisions received and accepted: September 22, 2024; Published: October 15, 2024.
DOI: 10.15376/biores.19.4.9169-9190