

Modification of Scots Pine with Activated Glucose and Citric Acid: Physical and Mechanical Properties

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An eco-friendly agent mainly consisting of activated glucose (AG) and citric acid (CA) was investigated for its potential wood modification applications. Scots pine (*Pinus sylvestris* L.) sapwood was treated with AG and CA both individually and in combination. The treatments with the combined agent resulted in an increase in the weight percent gain and decrease in the leaching ratio, which suggested a synergy between the two components for their fixation in wood. The dynamic vapor sorption behavior indicated an increased sorption at a higher AG concentration. Compared with the AG treatment, the CA treatment more effectively improved the dimensional stability of the wood. The modulus of elasticity was not influenced by the treatments, and the modulus of rupture was slightly reduced. Incorporation of AG in the CA inhibited the decrease in impact strength of wood compared to treatment with CA alone, which was a result of reduced crosslinking from the CA within the wood matrix. Fourier transform infrared (FTIR) spectroscopy revealed an enhanced absorbance, indicating development of ester bonds due to the treatment.

Keywords: Activated glucose; Citric acid; Physical and mechanical properties; Wood modification; FTIR

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INTRODUCTION

Wood is a popular material because of its natural characteristics, such as a high stiffness, high toughness, aesthetic quality, good machinability, renewability, and others. However, wood exhibits some additional issues, such as a low dimensional stability in an environment with changing humidity levels and susceptibility to biological degradation (Popescu *et al.* 2014). These disadvantages result in a reduced service life and limited utilization. Chemical modification methods, including acetylation, furfurylation, and impregnation with low-molecular weight resins, can improve the dimensional stability and anti-biodegradation ability of wood (Militz 1993; Esteves *et al.* 2011; Huang *et al.* 2013; Klüppel and Mai 2013; Rowell and Dickerson 2014). Several methods have been commercially introduced to the wood market at various scales.

In the Chinese market, urea- and phenolic-formaldehyde resin treatments are the most widely used techniques in wood modification because of their low cost and effective ability to improve the quality of plantation-grown wood. However, formaldehyde emissions have led to problems and complaints from both producers and end users. Related enterprises have been listed as pollution generators by the Chinese government. Low-cost

green modification techniques need to be developed because of environmentally motivated legislation.

Citric acid (CA) is a low-cost and readily available chemical that is used in the food, beverage, and cosmetics industries, as well as in the textile and paper industries to improve wrinkle resistance and wet strength (Doll *et al.* 2006). Several trials using CA as a wood modification agent have revealed an improved dimensional stability, modulus of elasticity (MOE), compression strength, and biological durability; meanwhile, increased brittleness of the treated wood most likely resulted from enhanced crosslinking within the cell wall polymers (Hasan *et al.* 2007; Despot *et al.* 2008; Xie *et al.* 2013; Feng *et al.* 2014). Impregnating wood with the combinative agents of CA and polyhydroxy compound was reported to improve the dimensional stability and biodegradation resistance of wood benefiting from the formation of polyesters (L'Hostis *et al.* 2017; Larnøy *et al.* 2018).

Glucose (Glc) is a natural compound that is continuously generated by photosynthesis in plants. The introduction of Glc to wood does not change the chemical elements of the wood. However, the fixation of Glc in wood can be a challenge. This issue has been clarified in a study to improve the fixation of Glc in cellulosic material by pre-activation with Fenton's reagent. The fixation ratio was increased from 0% to approximately 48% by pre-activation. Glucose was oxidized into aldehydes and carboxylic acids accompanied with the cleavage of C-C because of activation. However, 40% of the feeding Glc was retained in the solution in an optimum procedure (Guo *et al.* 2019). He *et al.* (2016) reported that CA can help fix the Glc in wood by acting as a crosslink between the Glc and polymers of the wood cell wall. Therefore, the combined CA and activated Glc (AG) agent was applied in the current study to further improve the fixation of AG in wood by fixing the residual Glc and other hydroxyl-containing compounds found in the solution.

This study aimed to evaluate the feasibility of modifying wood by the combination of AG and CA. The interaction between these two components was determined. The chemical fixation and its effect on the dimensional stability, hygroscopicity, and mechanical strength of modified Scots pine were evaluated.

EXPERIMENTAL

Materials and Methods

Chemicals

The chemicals D-(+)-glucose monohydrate (CAS no. 14431-43-7) and H₂O₂ (CAS no. 7722-84-1, 35 wt%) were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). The citric acid monohydrate (CAS no. 5949-29-1) was supplied by AppliChem GmbH (Darmstadt, Germany). The compound Fe(II) sulfate heptahydrate (FeSO₄ × 7H₂O, CAS no. 7782-63-0) was provided by Sigma-Aldrich Laborchemikalien GmbH (Seelze, Germany). Sodium hypophosphite monohydrate (CAS no. 10039-56-2) was supplied by Honeywell Fluka™ (Seelze, Germany). All of the chemicals were used as received.

Activation of the Glc

The activation process was conducted in an Erlenmeyer flask in a water bath. A 500-g solution containing 110 g of Glc monohydrate and 54 g of H₂O₂ (35 wt%) were preheated to 30 °C. A FeSO₄ solution was prepared by dissolving 0.62 g of FeSO₄ × 7H₂O in 5 mL of deionized water. Activation was initiated by adding pre-dissolved Fe(II) and then stopped when the H₂O₂ decayed completely. The activation procedure was repeated

50 times, and the resulting solutions were mixed by stirring. The typical compounds in the AG solution were previously detected by gas chromatography-mass spectrometry. The composition of the AG is listed in Table 1.

Table 1. Proportions of the Compounds Detected in the Activated Glucose (%)*

Compound	Proportion (%)
Formic Acid	16.0
Oxalic Acid	0.4
Dihydroxymaleic Acid	1.3
(E)-2,3-Dihydroxy-2-butenedioic Acid	1.4
Furfural	12.3
Furoic Acid	1.2
5-Hydroxymethyl-2-furaldehyde	1.1
Levogluconone	6.2
2,5-Dicarboxaldehydefuran	1.5
Unidentified	9.1

*In the activation process, 40% of the feeding glucose was not converted according to the previous result of high-performance liquid chromatography

Wood treatment

Sapwood from Scots pine (*Pinus sylvestris* L.) (Niedersachsen, Germany) was cut into various sizes for different tests. The density of the wood was $0.49 \pm 0.03 \text{ g cm}^{-3}$. The samples were impregnated under vacuum ($5 \times 10^{-3} \text{ MPa}$ for 1 h), which was followed by a pressure step (1.2 MPa for 1 h). The impregnated samples were dried in air for two weeks. Subsequently, the samples were dried according to the following sequence: 40 °C for 12 h, 80 °C for 12 h, and 120 °C for 24 h. Table 2 shows the composition of the impregnation solutions and their pH values.

Table 2. pH Values of the Impregnation Solutions

Impregnation Solution	pH at 22 °C
18 wt.% Glc	3.58
8.2 wt.% CA	1.69
4.5 wt.% AG	2.22
9 wt.% AG	1.89
18 wt.% AG	1.62
4.5 wt.% AG + 8.2 wt.% CA	1.63
9 wt.% AG + 8.2 wt.% CA	1.59
18 wt.% AG + 8.2 wt.% CA	1.50

Impregnation solutions involving CA contained 1 wt% sodium hypophosphite as the catalyst

Leaching test

Samples with the dimensions 10 mm × 25 mm × 25 mm (L × R × T) underwent a leaching test. The mean densities of the samples per treatment were grouped to be homogeneous. The cured samples were conditioned at room temperature for 24 h, which was followed by soaking in tap water for 10 d with daily water changes. The samples were then air-dried for 5 d on tissue paper, with the top surface covered. Afterwards, the tissue paper was removed and the samples were air-dried for another 2 d. The air-dried samples were then dried in an oven with an increasing temperature: 40 °C, 60 °C, 80 °C, and 103 °C for 24 h at each temperature. The leaching-drying cycle was repeated five times. The

mass and cross-sectional area of each sample were measured in the wet and oven-dry states, respectively. A total of 15 replicates per treatment were initially prepared. Samples that showed cracks over the five cycles were removed during the test and excluded from the evaluation. The weight percent gain (WPG), leaching ratio (LR), bulking coefficient (BC), and anti-swelling efficiency (ASE) for each cycle were calculated. The LR was calculated using Eq. 1,

$$\text{LR (\%)} = (M_{\text{BL}} - M_{\text{AL}}) \times 100\% / (M_{\text{AC}} - M_{\text{BT}}) \quad (1)$$

where M_{BL} is the oven-dry mass (g) of the wood before the specific leaching cycle, M_{AL} is the oven-dry mass (g) after the specific leaching procedure, M_{AC} is the dry mass (g) after curing, and M_{BT} is the oven-dry mass (g) before treatment.

To determine whether the interaction between the AG and CA is synergistic for fixation in wood, the increment ratio in the weight percent gain (IWPG, %) and reduction ratio in the leaching ratio (RLR, %) compared with the predicted values after the first leaching process were calculated using Eqs. 2, 3, 4 and 5, respectively,

$$\text{WPG}_{\text{Pred}} (\%) = \text{WPG}_{x\% \text{AG}} + \text{WPG}_{8.2\% \text{CA}} \quad (2)$$

$$\text{IWPG (\%)} = (\text{WPG}_{x\% \text{AG} + 8.2\% \text{CA}} - \text{WPG}_{\text{Pred}}) \times 100\% / \text{WPG}_{\text{Pred}} \quad (3)$$

$$\text{LR}_{\text{Pred}} (\%) = (x \times \text{LR}_{x\% \text{AG}} + 8.2 \times \text{LR}_{8.2\% \text{CA}}) \times 100\% / (x + 8.2) \quad (4)$$

$$\text{RLR (\%)} = (\text{LR}_{\text{Pred}} - \text{LR}_{x\% \text{AG} + 8.2\% \text{CA}}) \times 100\% / \text{LR}_{\text{Pred}} \quad (5)$$

where WPG_{Pred} is the predicted accumulated WPG of the wood treated with x wt.% AG and 8.2 wt.% CA, $x\%$ is the AG concentration (wt.%) in the solution treatment, $\text{WPG}_{x\% \text{AG}}$ is the WPG of the wood treated solely with x wt.% AG, $\text{WPG}_{8.2\% \text{CA}}$ is the WPG of the wood treated solely with 8.2 wt.% CA, $\text{WPG}_{x\% \text{AG} + 8.2\% \text{CA}}$ is the WPG of the wood treated with x wt.% AG and 8.2 wt.% CA, LR_{Pred} is the predicted accumulated LR of the deposited chemicals in the wood treated with x wt.% AG and 8.2 wt.% CA, $\text{LR}_{x\% \text{AG}}$ is the LR of the chemicals in the wood treated solely with x wt.% AG, $\text{LR}_{8.2\% \text{CA}}$ is the LR of the chemicals in the wood treated with 8.2 wt.% CA, and $\text{LR}_{x\% \text{AG} + 8.2\% \text{CA}}$ is the LR of the chemicals in the wood treated with x wt.% AG and 8.2 wt.% CA.

Dynamic water vapor sorption

Sorption isotherms were measured for wood particles in a dynamic vapor sorption (DVS) apparatus (DVS Advantage, Surface Measurement Systems, London, UK). Specimens with different WPG levels and treated with different modification agents were milled and mixed in a cutting mill (SM2000, Retsch GmbH, Haan, Germany) with a mesh size of 2 mm. Approximately 20 mg of wood particles were used for each measurement and placed on the sample holder of the DVS. Sorption experiments were run at a constant temperature of 25 °C. The relative humidity (RH) was first reduced to 0% to determine the initial dry weight of the sample and then incrementally increased as follows: 0%, 5%, 15%, 25%, 35%, 45%, 55%, 65%, 75%, 85%, and 95%. A constant RH was maintained until the weight change of the sample per minute (dm/dt) was less than 0.002%/min over a period of 10 min. The equilibrium weight (W_{E}) at each RH step was used to calculate the equilibrium moisture content (EMC) following Eq. 6,

$$\text{EMC (\%)} = (W_{\text{E}} - W_{\text{E0}}) \times 100\% / W_{\text{E0}} \quad (6)$$

where W_{E} is the equilibrium weight of the sample at a given RH, and W_{E0} is the equilibrium weight at a 0% RH.

To eliminate the influence of the additional weight from the modification chemical, the corrected equilibrium moisture content (EMC_c) of the sample was calculated with Eq. 7,

$$EMC_c (\%) = EMC \times (1 + WPG / 100) \quad (7)$$

where WPG is the weight percent gain (%) of the specific specimen after the two-cycle leaching procedure before the dynamic sorption test.

The EMC_c ratio was calculated at each RH step using Eq. 8 (Wentzel *et al.* 2018),

$$EMC_c \text{ ratio} = \text{sample } EMC_c / \text{reference } EMC \quad (8)$$

where the *sample* EMC_c is the EMC_c of the respective modified sample at a given RH, and the *reference* EMC is the EMC of the unmodified sample measured at the same RH.

Mechanical properties tests

The three-point bending tests were conducted on a universal testing machine (ZwickRoell Zmartpro, ZwickRoell, Ulm, Germany). The span width was 150 mm, and the load was applied in the transversal direction with a testing speed of 6 mm/min. Samples were loaded to the point of fracture and then unloaded after a decrease of 20% in the maximum force. The MOE and modulus of rupture (MOR), both expressed in MPa, were determined in accordance with the modified standard DIN 52186 (1978). The Charpy impact test was performed on an impact tester (Resil Impactor, CEAST, Martinsried, Germany). The span width was 105 mm. The tests were performed on samples with the dimensions 180 mm × 10 mm × 10 mm (L × R × T). The samples were not subjected to the leaching procedure after the treatment. They were conditioned at 20 °C and a 65% RH to a constant mass prior to testing. The corrected moisture content (MC_c) of each sample was determined several seconds before loading. A total of 30 replicates per treatment were evaluated for the MOE, MOR, and impact bending strength.

Statistical analysis

The statistical comparison of mechanical properties between untreated and treated groups was based on the two sample t-test using OriginLab 9.0 (OriginLab Corporation, Northampton, MA, USA).

FTIR spectroscopy

The untreated and treated Scots pine were milled and mixed as previously described. The oven-dried particles were analyzed by FTIR spectroscopy (ATR mode, 4 cm^{-1} resolution averaging 32 scans), (Nicolet 6700, Thermo Fisher Scientific Inc., Waltham, MA, USA). The normalization of the spectra was performed with Omnic 8.2 (Thermo Fisher Scientific Inc., Waltham, MA, USA)

RESULTS AND DISCUSSION

Weight Percent Gain and Chemical Fixation Stability

The WPG of the Scots pine before leaching ranged from 5.8% to 40.0%. A steep reduction in the WPG after the first leaching cycle indicated severe leaching from unfixed chemicals and degraded wood components (Fig. 1a). In subsequent leaching cycles, the WPG decreased slowly.

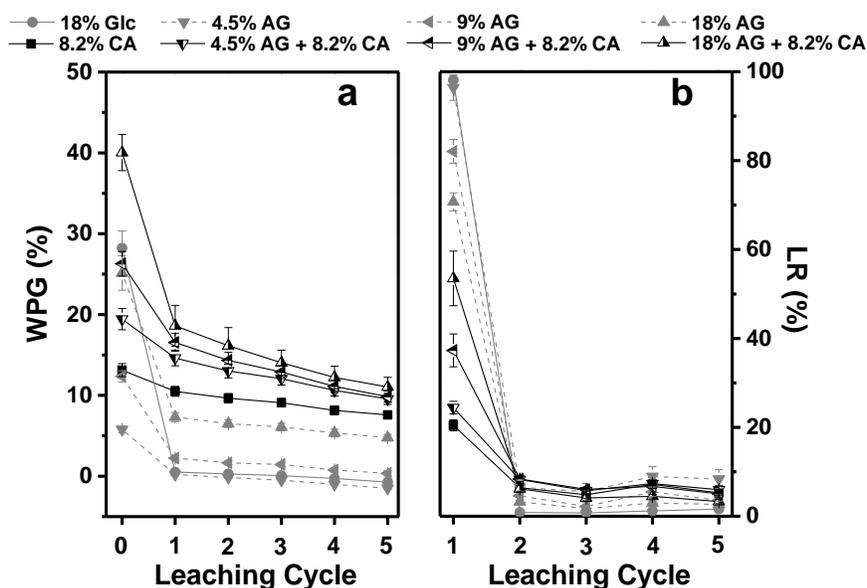


Fig. 1. (a) WPGs and (b) LR of the deposited chemicals over five leaching cycles in the Scots pine treated individually with Glc (18 wt.%), AG (4.5 wt.%, 9 wt.%, and 18 wt.%), or CA (8.2 wt.%) solutions, or solutions containing 8.2 wt.% CA combined with 4.5 wt.%, 9 wt.%, and 18 wt.% AG

The LR of the deposited chemicals in the wood treated with Glc was 98% (Fig. 1b), which indicated the almost complete loss of Glc by cold-water leaching. A lower LR was obtained by activating the Glc, and the LR declined with the AG concentration. Previous analysis of the AG solution revealed that approximately 40% of the feeding Glc was not activated (Table 1). A highly concentrated AG solution with a lower pH (Table 2) can facilitate the fixation of unconverted Glc by the formation of water-insoluble polymers (Hu *et al.* 2011). Wood treated solely with CA had an LR of 20.4% in the first leaching cycle. However, higher LRs were obtained in the wood treated with AG and CA combined because of the lower fixation ability of AG compared with that of CA. With a constant CA concentration, the increase in the AG concentration led to an increase in the LR. This occurrence was attributed to the stronger dilution effect exerted on the CA at higher AG dosages because of the decreased CA percentage in the solute. Unfixed chemicals were leached out in the first cycle. In the subsequent leaching cycles, a constant LR of less than 10% was observed, possibly attributed to a moderate leaching from wood components and/or remnant chemicals.

Synergy Between the AG and CA for Fixation

The synergistic effect between the AG and CA on their fixation in wood was evaluated. A greater synergistic effect was observed at a lower AG concentration with respect to both the WPG and LR (Fig. 2). Their synergy caused the WPG to increase by up to approximately 37% and the LR to decrease by up to approximately 48%, compared with the accumulated predicted values from the results in the individual treatment. The interaction between the two components was explained by two factors. The first was that the CA could act as a crosslinker between the wood polymers and hydroxyl-containing compound in the AG solution (He *et al.* 2016). Second, the pH of the solution containing both AG and CA was lower than that of the solution containing only one of the two

components, which facilitated the fixation of the chemicals in the wood. The decreased contribution of the synergistic effect at increased AG dosage suggested that CA crosslinking was a dominant factor.

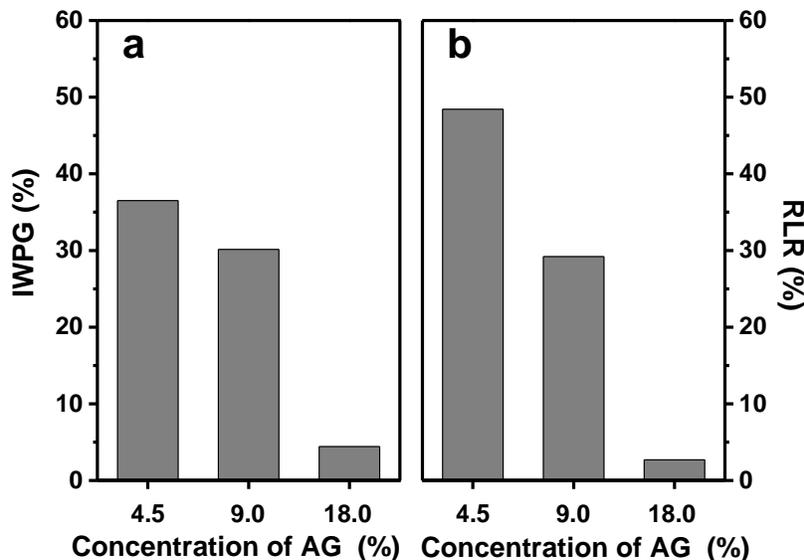


Fig. 2. (a) IWPG and (b) RLR of deposited chemicals in the Scots pine treated with 8.2 wt.% CA combined with 4.5 wt.%, 9 wt.%, and 18 wt.% AG, separately, which resulted from the synergy between the CA and AG

Cell Wall Bulking

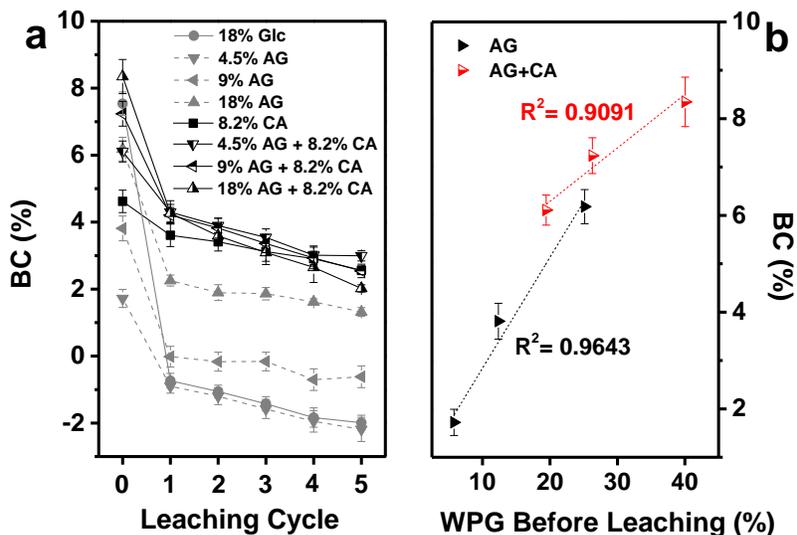


Fig. 3. (a) BC over five leaching cycles of Scots pine treated with Glc (18 wt.%), AG (4.5 wt.%, 9 wt.%, and 18 wt.%), or CA (8.2 wt.%) solution individually or the solutions containing 8.2 wt.% CA combined with 4.5 wt.%, 9 wt.%, and 18 wt.% AG, and (b) linear fitting results of the relationship between the BC and WPG before leaching

The BC of the treated wood decreased remarkably after the first leaching process (Fig. 3a) because of the leaching of unfixed chemicals and degraded wood constituents

from the cell wall. An almost complete removal of Glc was observed in the first leaching cycle (Fig. 1b); however, the BC kept decreasing in the following cycles, which was explained by shrinkage of the cell wall with repeated wet-dry cycles. Additionally, this shrinkage accounted for the downward trend of the BC over the cycles for other treatments, besides the continuous leaching out of chemicals. For the treatments combining CA and AG, the BC decreased at a higher rate with a higher AG concentration, which was attributed to a severe acidic degradation of the cell wall because of the lower pH. A positive bulking effect remained after five wet-dry cycles, where the wood was treated with 18 wt.% AG alone or with CA. For both chemicals, the BC linearly increased with the increasing chemical load (Fig. 3b).

Dimensional Stability

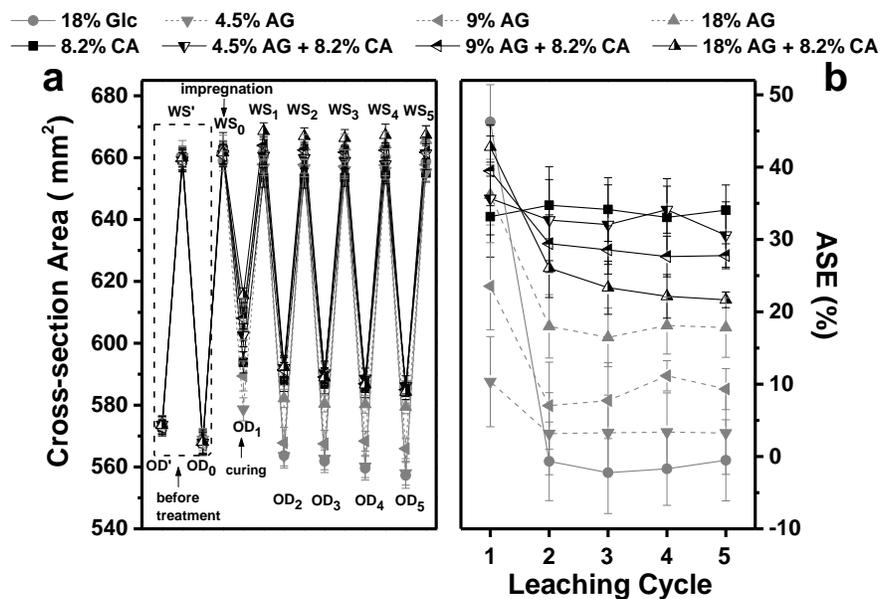


Fig. 4. (a) Series of cross-sectional areas of the Scots pine in the oven-dried and water-saturated states before, during, and after the treatments, and (b) the ASE of the treated Scots pine over five leaching cycles

The overlapping values of the cross-sectional area of the sample before the treatment verified the uniform distribution of the sample density among all of the groups (Fig. 4a). The change in the cross-sectional area could represent a change in the wood volume because of the negligible changes in the longitude over the wet-dry cycles. A decrease in the oven-dry volume before the treatment and after a wet-dry cycle was observed, which indicated shrinkage of the cell wall between the successive two oven-dry states. This occurrence should be considered when evaluating the dimensional stability of treated wood. After treatment, the oven-dry volumes of all of the samples increased, which was attributed to the bulking effect of the deposited chemicals. In the subsequent wet-dry cycles, the decreasing trend in the oven-dry volume was consistent with that of the BC, as was previously described. The water saturation volume of the treated wood increased with the increasing AG concentration because of the severe damage to the cell wall (Ohmae *et al.* 2002; Hill 2006). The reduced wet volume of the wood treated with AG at a low

concentration (*e.g.*, 4.5%) or 8.2 wt.% CA, compared with that of the untreated wood, indicated an enhanced crosslinking within the wood matrix (Vukusic *et al.* 2006).

The ASE of CA-treated wood remained stable around 34% over the dry-wet cycles (Fig. 4b). With regard to other treatments, the ASE decreased in the second cycle because of a reduced bulking effect. The ASE of the wood treated with CA-containing reagents exhibited no positive relationship with the bulking coefficient since the second dry-wet cycle and decreased with AG concentration. CA could crosslink the cell wall polymers, effectively inhibiting cell wall swelling. With increasing the AG concentration, CA has a higher probability to react with AG, thereby reducing the degree of crosslinking within the cell wall polymers by CA. After the fifth leaching, the wood treated solely with AG increased in ASE from 3.2% to 17.8% as AG concentration increased from 4.5% to 18%; meanwhile, ASE decreased from 30.6% to 21.7% under the treatment with combined AG and CA.

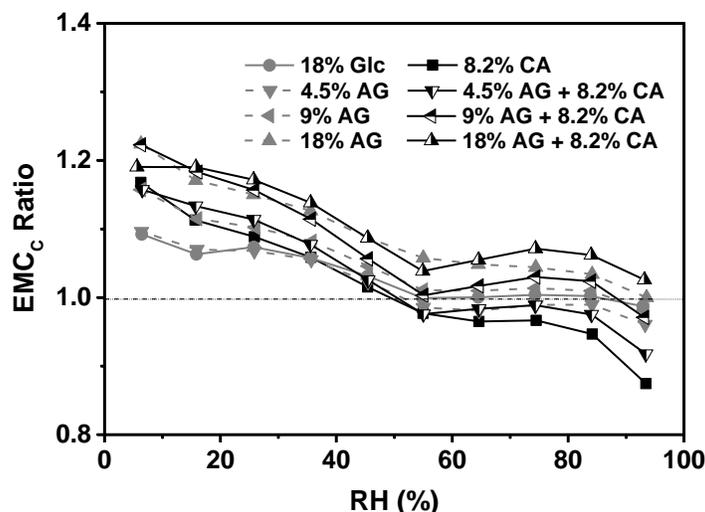


Fig. 5. EMC_c ratio, as a function of the RH, of the treated Scots pine; the samples underwent two leaching cycles before the moisture sorption test was conducted

Hygroscopicity

The change in the hygroscopicity of the Scots pine after different treatments was expressed as the EMC_c ratio. An EMC_c ratio of 1 denotes no difference in the EMC_c between the untreated and treated wood. Thus, the water vapor uptake and release were almost not affected by the modification chemical. A deviation from an EMC_c ratio of 1 indicates either an increase in the EMC_c caused by the treatment (EMC_c ratio > 1) or a decrease (EMC_c ratio < 1) compared with the untreated control samples (Wentzel *et al.* 2018). Over the RH range of 0% to 45%, all of the treatments showed an EMC_c greater than 1, which indicated an increase in the number of sorption sites (OH-groups; Fig. 5). This increased amount of easily available, low RH sorption sites was attributed to the incorporated chemicals bearing more than one hydroxyl groups or the exposure of new sorption sites in the cell wall matrix because of the hydrolytic degradation of cell wall polymers catalyzed by acid. At a RH greater than 55%, the wood treated with 4.5 wt.% AG or 8.2 wt.% CA, individually or in combination, showed a reduced sorption compared with the untreated wood, due to degradation of hemicellulose and/or the enhanced crosslinking between the cell wall matrix. The wood exhibited an increased sorption when treated with

AG at higher concentrations, either alone or in combination with CA. When treated with only AG, the treated wood had a higher BC at higher AG concentrations, which implied that the sorption of the treated wood at a high RH was affected by the hygroscopicity of the chemicals and degree of damage in the cell wall, rather than the degree of bulking.

Mechanical Properties

The lowest MOE and MOR values of the Scots pine were obtained with the treatment using 18 wt.% Glc, which was attributed to the higher moisture content from the hygroscopicity of the deposited Glc (Figs. 6a, 6b, and 6d). An increase in the moisture content below the fiber saturation point led to decreases in the MOE and MOR (Gerhards 1982; Winandy and Rowell 2005; Xie *et al.* 2013). The statistical analysis revealed no significant difference of MOE between untreated wood and wood treated with AG, CA, and their combination (Table 3), while significant difference of MOR was obtained, regardless of the wood treated with 18 wt.% AG and 8.2 wt.% CA (Table 3). However, the relative variations of the mean values of MOR between untreated and treated wood were less than 10%, except for the wood treated with 18 wt.% Glc. The acidity of the impregnation solution led to enhanced degradation of the cell wall polymer during curing, which reduced the tensile strength (data not shown) of the wood. Regardless, the improved density from the deposition of chemicals in the cell wall and lumen was expected to increase the compression strength of the wood, which could to a certain extent compensate for the loss in the tensile strength during the static bending test (Xiao *et al.* 2010).

Table 3. Statistical Comparison of MOE, MOR and Impact Strength between Untreated and Treated Scots Pine based on Two Sample t-Test

Treatment	t Statistic		
	MOE	MOR	Impact strength
18 wt.% Glc	5.610*	7.233*	1.512
8.2 wt.% CA	-0.251	3.384*	11.910*
4.5 wt.% AG	2.572	4.914*	3.739*
9 wt.% AG	-0.132	4.656*	5.647*
18 wt.% AG	-0.975	3.545*	7.618*
4.5 wt.% AG + 8.2 wt.% CA	-0.012	3.989*	12.348*
9 wt.% AG + 8.2 wt.% CA	-0.654	2.864*	10.659*
18 wt.% AG + 8.2 wt.% CA	-2.167	-1.253	9.584*

Significant difference ($\alpha = 0.01$) were marked with an asterisk (*)

In contrast with the minor change in the MOE and MOR, the impact strength of the wood treated with AG, CA, or a combination of the two was reduced by up to 54% (Fig. 6c). Empirically, the embrittlement of the wood caused by hydrolytic chemical treatments was attributed to the loss of the ability of the hydrolyzed cell wall polymers to dissipate strain energy away from localized stress concentrations (Winandy 1995; Winandy and Rowell 2005). Also, the enhanced crosslinking within the cell wall matrix contributed to the embrittlement. Crosslinking reagents, such as CA, furfuryl alcohol, formaldehyde, glutaraldehyde, formaldehyde-based low-molecular weight resins, and 1,3-dimethylol-4,5-dihydroxyethyleneurea, have been frequently reported to lead to the severe embrittlement of wood, which is explained by the formation of a rigid crosslinking network (Xiao *et al.* 2010; Xie *et al.* 2013; Feng *et al.* 2014). Under the treatment with solely AG, the reduced impact strength at increased AG concentrations resulted from the severe degradation of cell wall polymers. Meanwhile, under the treatments of AG and CA combined, the improved

impact strength with increased AG concentrations was attributed to the reduced crosslinking of the cell wall by CA, given that a larger portion of CA was consumed by AG, instead of the cell wall polymers, at a higher AG dosage.

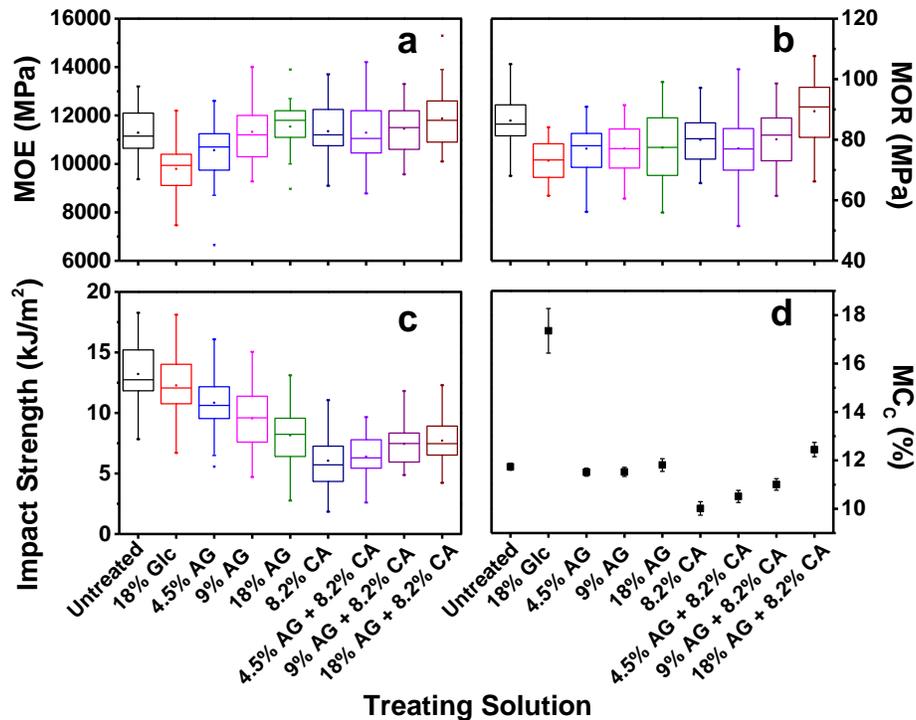


Fig. 6. (a) MOE, (b) MOR, (c) impact strength, and (d) MC_c of the untreated and treated pine

FTIR spectroscopy

The absorbance at 1730 cm^{-1} ($\text{C}=\text{O}$ in xylans) of wood treated with 4.5 wt.% AG was reduced (Fig. 7) due to the degradation of hemicellulose (L'Hostis *et al.* 2017).

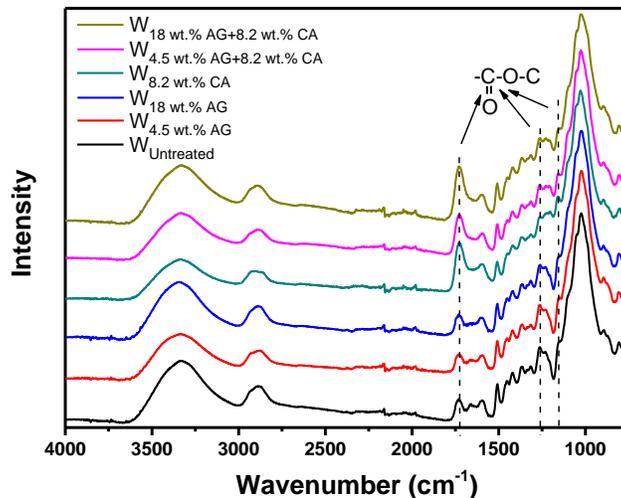


Fig. 7. FTIR spectra of Scots pine untreated ($W_{\text{Untreated}}$) and treated with AG (4.5 wt.% and 18 wt.%, defined as $W_{4.5\text{ wt.\%AG}}$ and $W_{18\text{ wt.\%AG}}$, respectively), or CA (8.2 wt.%, $W_{8.2\text{ wt.\%CA}}$) solution individually or the solutions containing 8.2 wt.% CA combined with 4.5 wt.% and 18 wt.% AG ($W_{4.5\text{ wt.\%AG}+8.2\text{ wt.\%CA}}$ and $W_{18\text{ wt.\%AG}+8.2\text{ wt.\%CA}}$, respectively)

This band increased in wood treated with 18 wt.% AG, indicating that the esterification took place during the modification. A similar trend was observed in the treatment combining AG and CA. Both the formation of polyesters and the esterification of the wood cell wall polymer may intensify the absorbance. It is still unclear which factor makes the dominant contribution based on the FTIR results (Noël *et al.* 2015; L'Hostis *et al.* 2017).

CONCLUSIONS

1. A synergistic effect between the activated glucose (AG) and citric acid (CA) contributed to their improved fixation in the wood, and this effect weakened at higher AG dosages.
2. The bulking coefficient (BC) of the treated wood confirmed the penetration of the AG and CA into the wood cell wall. The dimensional stability of the wood after leaching was improved by up to approximately 30% because of the treatment.
3. The dynamic moisture behavior revealed an increased sorption at higher AG concentrations.
4. The treatments involving AG and/or CA did not influence the modulus of elasticity (MOE) of the wood, while the MOR was slightly reduced (variation less than 10%); however, the impact strength decreased by up to approximately 54%. The AG could partly compensate for the brittleness of the wood caused by the CA treatment.

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