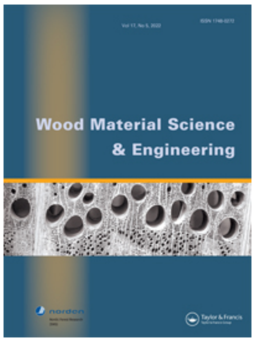

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ORIGINAL ARTICLE

Vacuum-heat treatment of Scots pine (*Pinus sylvestris* L.) wood pretreated with propanetriol

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ABSTRACT

Scots pine sapwood was pretreated with two levels of propanetriol (20% and 40% w/w glycerol), and then subjected to vacuum-heat treatment (VHT) at 180°C and 200°C. The treated samples were examined with respect to their weight and volumetric changes, mechanical properties, colour changes, and dynamic water vapour sorption. The weight of the samples after VHT did not change with increasing the temperature, but it was increased in glycerol pretreated samples. Combination of glycerol pretreatment and VHT decreased the maximum swelling. Total colour change was significantly higher during VHT at a higher temperature, while no obvious trend observed in the samples pretreated with glycerol. Modulus of elasticity (MOE) and modulus of rupture (MOR) were not affected by solely VHT, but strongly decreased after glycerol pretreatment. The equilibrium moisture content (EMC) of the samples decreased by VHT. The glycerol pretreatment caused a reduction in EMC values at a relative humidity (RH) below 60%, but considerably increased the moisture sorption in the RH above 75%. VHT slightly reduced the sorption hysteresis compared to untreated wood, but an apparent reduction in hysteresis observed by glycerol pretreatment. This indicates that the flexibility of the wood cell wall polymers increases due to glycerol pretreatment, which results in decreased MOE and sorption hysteresis values.

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Bulking; colour change; dynamic vapour sorption; glycerol; vacuum-heat treatment

Introduction

Wood is one of the most commonly used renewable materials in the building and furniture sectors. However, the utilisation of many wood species is limited to indoor applications due to their hygroscopicity, low durability and weathering performances. Wood modification, such as chemical modification, resin impregnation, and thermal modification, is an established technology to overcome the issues related to the susceptibility of wood against abiotic and biotic damages, and thus prolonging its lifecycle (Brischke *et al.* 2006). Thermal treatment of wood is an environmentally friendly method that has been widely studied and even applied on the industrial scale (Militz 2002, Weiland and Guyonnet 2003, Esteves *et al.* 2008, Calonego *et al.* 2010, Lekounougou and Kocaefe 2014, Hosseinpourpia and Mai 2016). The treatment can be performed at temperatures that usually range between 180 °C to 260 °C in air, in a vacuum, or under an inert atmosphere (Sivrikaya *et al.* 2019). Heat treatment alters the chemical structure of wood by the initial release of acetic acid from hemicelluloses due to deacetylation, followed by liberation of formaldehyde, furfural, and other aldehydes (Tjeerdsma *et al.* 1998). The latter compounds may react with phenolic nuclei of lignin and change its chemical structure (Hosseinpourpia *et al.* 2017). The released acetic acid degrades the amorphous regions of cellulose and increases its crystallinity index (Sivonen *et al.* 2002). Previous studies reported that the reversible and irreversible chemical and structural changes of wood due to thermal modification reduced its hygroscopicity and mechanical strength and improved the resistance to microbiological degradation (Poncsak *et al.* 2006, Rowell *et al.* 2009, Mohareb *et al.* 2012, Sandberg *et al.* 2013, Endo *et al.* 2016). Reduction in mechanical properties has always been one of the main drawbacks for thermally treated wood (Tjeerdsma and Militz 2005), which is mainly due to the degradation of hemicelluloses, relative increases in the amount of crystalline cellulose, and irreversible stiffening of the cell wall matrix (Tjeerdsma *et al.* 1998, Esteves and Pereira 2009, Suchy *et al.* 2010a, 2010b). On the other hand, the treatment process affects the wood properties. According to Wentzel *et al.* (2019) chemical composition of thermally modified wood, strongly correlated with the mechanical properties, was more affected by a closed system under high pressure than the modifications in the open system. Willems and Altgen (2020) introduced the hygrothermolytic(HGT) process to be a potential method with independent and continuous process variable and improved material properties and improved process characteristics.

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Development of industrial kiln for thermal wood modification with an initial vacuuming step was developed by Silvaprodukt (Rep *et al.* 2012). Termovuoto® (WDE Maspell s.r.l., Terni, Italy) is however patented an alternative technology recently for thermal modification of wood under vacuum condition to avoid wood pyrolysis or combustion. The process consists of a semi-industrial prototype plant, made of stainless steel cylinder with an internal diameter of 1.7 m and operates at higher temperatures up to 250° C, with the fan speed ranges from 635 r $\min^{-1}$ to maximum speed of 1930 r $\min^{-1}$ at vacuum pressure of 200 mbar (Ferrari *et al.* 2013, Sandak *et al.* 2015). Due to the constant removal of volatile compounds from the reactor by vacuum pump, their contribution to the degradation of the cell wall polymers is limited, and thus the reduction in mechanical strength of treated wood is not as significant as the other thermal modification methods (Allegretti *et al.* 2012, Ferrari *et al.* 2013). Norway spruce and fir treated with the vacuum-heat process showed higher dimensional stability and durability against brown-rot and white-rot fungi as compared to untreated samples (Allegretti *et al.* 2012). In addition, the weight loss of the wood samples treated with the vacuum-heat systems was considerably lower than the ones treated according to Thermowood process (Pockrandt *et al.* 2018). Most recently, Sivrikaya *et al.* (2019) quoted that Scots pine wood samples treated with the vacuum-heat process showed lower weight loss, higher lightness, and lower colour changes in comparison with that from solely a heat treatment method. The equilibrium moisture content (EMC) of wood treated with the vacuum-heat process was considerably reduced as a result of the degradation of the carbonyl groups in xylan and the loss of carbonyl group linked to the aromatic skeleton in lignin due to the treatment (Sun *et al.* 2017).

Pretreatment of wood in combination with heat treatment became attractive in recent years to make the process more economical and to reduce the negative impact of the process on some of the wood properties (Hong *et al.* 2013, Zhu *et al.* 2014, Wang *et al.* 2015, Qu *et al.* 2019). Propanetriol compound, which is the IUPAC (International Union of Pure and Applied Chemistry) name for glycerol, is a major by-product of biodiesel production. Glycerol has been widely used as a splasticiser for edible and/or biodegradable films (Vieira *et al.* 2011) to improve mechanical properties, and reduce the fragility and brittleness. The effect of glycerol pretreatment on material properties of heat-treated wood has been reported recently (Yan and Morrell 2014, 2019, Salman *et al.* 2016, 2017, Liu *et al.* 2018, Mubarok *et al.* 2019). Yan and Morrell (2014) reported that the dimensional stability of Douglas fir heartwood improved by glycerol pretreatment followed by heat treatment, while the modulus of rupture (MOR) of the treated samples decreased with increasing the intensity of heat treatment, e.g. treatment duration and temperature. The modulus of elasticity did not show significant changes under the treatment conditions. Pretreatment of beech samples with glycerol or polyglycerol, in the presence of glycidyl methacrylate or maleic anhydride, and then heat treatment at 150, 200, or 220°C improved the dimensional stability (approximately 80%), and resistance to fungal and termite degradation, while modulus of elasticity (MOE) and MOR were reduced considerably by approximately 30% and 60%, respectively (Mubarok *et al.* 2019). The authors quoted that the degradation of cell wall polymers was accelerated by glycerol pretreatment under elevated temperature, and this resulted in a strong reduction of mechanical strength of modified wood.

The catalytic effect of glycerol during thermal modification of wood facilitates the degradation of cell wall polymers, and thus result in alteration of wood properties at relatively lower temperatures, which makes the process more economically viable. Pretreatment of wood with glycerol and followed by vacuum-heat treatment however provides a relatively milder condition than the ones under heat treatment process, and thus reducing the risk of undesirable changes on wood properties. In addition, it is expected that glycerol delivers extra hydroxyl groups to form a three-dimensional network and stabilise the wood cell wall polymers (Roussel *et al.* 2001, Soulounganga *et al.* 2004). Therefore, the present study was conducted to establish the effect of vacuum-heat treatment on mechanical properties, swelling performance and water vapour sorption behaviour of wood pretreated with glycerol. The treated samples were also evaluated via their weight changes and colour alterations, and compared with those untreated, solely vacuum-heat treated or pretreated with glycerol.

Experimental

Sample preparation

Scots pine (*Pinus sylvestris* L.) sapwood with the annual ring width of 1.56 mm and density of 543 kg/m^3, free from knots and defects was collected from Sawmill in Bartın province, Turkey. Propanetriol, so-called glycerol (GL), anhydrous with 92.1 g/mol and 1.26 g/cm^3 density was purchased from Merck KGaA, Darmstadt, Germany. The samples were vacuum impregnated (0.08 MPa) for 60 min with 20% and 40% (w/w) of glycerol dissolved in water. After impregnation, the samples were dried at 103°C for 48 h. Then, vacuum-heat treatment was performed by direct exposure of dried samples to 180°C and 200°C for 2 h using a vacuum oven (JEIO TECH OV-12; Jeio Tech Co., Ltd., Daejeon, Korea; 65 L, vacuum range: 0–0.1 MPa) under mild vacuum condition (0.08–0.09 MPa). The cross-sections of the treated samples were then observed and maximum penetration depth was confirmed visually. The weight of the samples was recorded before (w_0) and after each treatment (w_1) to assess the weight gain, due to glycerol treatment, and the weight loss, due to vacuum-heat treatment. The volumes of the samples were also recorded before (V_0) and after treatments (V_1).

Weight and dimensional changes

The leaching test was performed to remove the unreacted chemicals, by following a method described previously

(Mubarak *et al.* 2019). In details, six untreated and treated samples measuring 20 × 20 × 10 mm^3 (L × R × T) were initially oven-dried and then subjected to periodic leaching process by submerging in 72 ml of distilled water over 1, 2, 4, 8, 16, and 48 h under continuous shaking (175 linear shakes min^{-1}) at 20°C. After the leaching test, samples were dried at 103°C for 48 h and reweighed (w_3). The weight changes of the wood samples due to different treatment steps and leaching process were then assessed according to the following equation:

$$\Delta w(\%) = 100 \times (w_1 \text{ or } w_2 \text{ or } w_3 - w_0)/w_0 \tag{1}$$

where Δw is the weight change of treated or untreated wood samples before or after treatments and/or leaching test, w_0 is the oven-dry weight before treatment, w_1 is the dry weight of the wood samples after sole glycerol treatment at 103°C or sole vacuum-heat treatment at the higher temperatures (180°C or 200°C), w_2 is the dry weight of the wood samples after glycerol pretreatment and then vacuum-heat treatment, and w_3 is the oven-dry weight of the treated and untreated wood samples after leaching test.

The volumetric changes of the wood samples due to different treatment processes were calculated according to the following equation:

$$\Delta v = (v_1 \text{ or } v_2 - v_0)/v_0 \tag{2}$$

where Δv is the volumetric changes of treated wood samples after treatments, v_0 is the oven-dry volume before treatment, v_1 is the dry volume of the wood samples after sole glycerol treatment at 103°C or sole vacuum-heat treatment at the higher temperatures (180°C or 200°C) and v_2 is the dry volume of the wood samples after glycerol pretreatment and then vacuum-heat treatment.

Maximum swelling (S_{max}) was also determined as described previously (Xiao *et al.* 2010, Mubarok *et al.* 2019), according to the following equation:

$$S_{\max} = (a_w - a_d)/a_d \tag{3}$$

where S_{max} is the percentage of wood swelling, a_d is the dry area (radial × tangential) of the wood sample, a_w is the wet area of the wood sample.

Colour measurement

The colour changes in wood samples before and after treatments were measured by a Konica Minolta CM-700d spectrophotometer (Konica Minolta, Inc., Tokyo, Japan) according to the CIE L*a*b system with five replicates, as described previously (Sivrikaya *et al.* 2019). Based on the *L**, *a**, *b** colour coordinate system, *L** represents lightness, *a** presents red/green opponent colour, *b** reveals the yellow/blue opponent colour. The colour change (ΔE) was calculated based on the differences in colour parameters before and after treatment according to following Equation 4:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{4}$$

Mechanical properties

A three-point bending test was performed according to ASTM D143-14 (2014) standard using a universal testing machine (MTS 810 Material Test System, 100 kN, MTS Systems Corporation, Eden Prairie, MN, USA). Prior to test, 15 wood samples with dimensions of 10 × 10 × 200 mm^3 (*R* × *T* × *T*), from each treatment category, were conditioned at 20°C and 65% RH, until constant weight. The distance between the supports (span) was 180 mm and the testing speed was 10 mm/min. Modulus of elasticity (MOE) and modulus of rupture (MOR) were determined from Equations 5 and 6,

$$\mathrm{MOR}(\mathrm{N/mm^2}) = \frac{3Fls}{2bh^2} \tag{5}$$

$$\mathrm{MOE}(\mathrm{N/mm^2}) = \frac{\Delta Fl^3}{\Delta f 4bh^3} \tag{6}$$

where *F* is the maximum force (N), ΔF is the difference at 10% and 40% of maximum load in elastic deformation area, Δf is the increment of deflection difference at the mid-length of the test piece corresponding to ΔF, *l* is the span length (mm), *b* is the width (mm), and *h* is the height (mm).

Dynamic vapour sorption

The water vapour sorption behaviour of the wood samples was determined using an automated vapour sorption (AVS) apparatus (Q5000 SA, TA Instruments, New Castle, DE, USA), as reported previously (Hosseinpourpia *et al.* 2016, 2019). Approximately 8 mg of untreated and treated wood powder (passed through a 20-mesh sieve) were used for each measurement. The wood samples were exposed to relative humidity (RH) that increased from 0% to 90% in step sequences of 15% and of 5% from 90% to 95% RH, decreasing to 0% RH in a reverse order, at a constant temperature of 25°C. The instrument maintained a constant target RH until the mass change in the sample (dm/dt) was less than 0.01% per minute over a 10 min period. The equilibrium moisture content (EMC) of the untreated and treated wood samples was calculated based on their equilibrium weight at each given RH step throughout the sorption run measured by the sorption balance device.

Statistical analysis

Properties differences of treated samples were analysed using the statistical software package IBM SPSS Version 23 (IBM Corporation, Armonk, NY, USA). A 5% level of significance was used during ANOVA analysis. One-way analysis of variance (ANOVA) was applied to determine whether measured properties were significantly different among treated samples categories. A 5% level of significance was used to detect differences and when a significant difference was found, a Tukey HSD post-hoc test was performed.

Table 1. Mean values (± standard deviations) of weight and volumetric changes of wood samples due to different treatment processes.

Code	Treatment Step 1	Treatment Step 2	Δw (%) Before leaching	Δw (%) After leaching	Δv (%)	$S_{\max}$ (%)
Untreated	–	–		0.2 ± 0.2(a)	–	17.1 ± 0.7(a)
GL-20	20% glycerol	–	23.2 ± 1.1(d)	19.0 ± 0.7(f)	16.5 ± 1.4(d)	17.0 ± 0.7(a)
GL-40	40% glycerol	–	53.0 ± 2.2(f)	34.9 ± 0.8(g)	22.1 ± 1.0(e)	16.4 ± 0.7(a)
VHT180	–	Vacuum-heat-180°C	−0.5 ± 0.4(a)	1.9 ± 0.3(b)		16.9 ± 0.6(a)
VHT200	–	Vacuum-heat-200°C	−0.4 ± 0.4(a)	1.2 ± 0.3(ab)		16.2 ± 0.4(a)
GL-20 + VHT180	20% glycerol	Vacuum-heat-180°C	13.2 ± 1.2(b)	7.5 ± 1.1(d)	6.9 ± 0.9(ab)	16.5 ± 0.6(a)
GL-20 + VHT200	20% glycerol	Vacuum-heat-200°C	16.4 ± 0.7(c)	4.3 ± 0.5(c)	5.7 ± 0.6(a)	16.4 ± 0.6(a)
GL-40 + VHT180	40% glycerol	Vacuum-heat-180°C	29.7 ± 1.1(e)	8.0 ± 0.5(d)	7.4 ± 0.5(b)	16.05 ± 0.4(a)
GL-40 + VHT200	40% glycerol	Vacuum-heat-200°C	28.4 ± 1.3(e)	10.2 ± 1.6(e)	9.7 ± 0.9(c)	15.9 ± 0.7(a)

Notes: GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment; Mean values followed by different lower case letter within a column indicate that there is a significant difference ($p \leq 0.05$) as determined by ANOVA and Tukey HSD *post-hoc* test.

Results and discussion

Weight and dimensional changes

Weight and dimensional changes of Scots pine samples due to different treatments are presented in Table 1. The Δw for samples treated with glycerol at 20% and 40% concentration were ranged between 23% and 53%, respectively. The weight gain of wood samples after impregnation with glycerol corresponds to its deposition in the wood cell walls and/or lumens (Berube *et al.* 2018).

Treatment of wood samples at high temperatures under vacuum caused a slight change in samples weight, as it is reflected by Δw before leaching (Table 1). The low Δw of wood samples due to vacuum-heat treatment was reported previously (Allegretti *et al.* 2012, Kutnar *et al.* 2013), which is mainly due to the removal of volatile compounds (Pockrandt *et al.* 2018). Combined treatment of wood samples with glycerol pretreatment and vacuum-heat treatment caused a significant change in Δw values. A direct comparison of Δw changes in sole glycerol-treated samples, and sole vacuum-heat treated samples with combined treated ones illustrates an obvious decrease of glycerol in combined treated samples. The highest Δw value was obtained by the pretreated samples with 40% glycerol and post-treated under the vacuum-heat condition. This is in accordance with reports of other authors (Yan *et al.* 2011, Luo *et al.* 2014, Liu *et al.* 2018, Mubarok *et al.* 2019), and can be attributed to: (a) degradation of glycerol molecules by exposure to high temperature, and (b) acceleration of the degradation of wood polymers in the presence of glycerol (Yan *et al.* 2011, Luo *et al.* 2014).

For leaching test, among different treatments, a dramatic reduction observed in Δw value of glycerol-treated wood cured at 103°C, which indicates that significant glycerol amounts were not fixed at this temperature. The vacuum-heat treatment of glycerol pretreated wood at higher temperatures, e.g. 180°C and 200°C, however, decreased the Δw values considerably. Comparable results were reported most recently by Mubarok *et al.* 2019. The bulking value (Δv) was increased after glycerol treatment, and it was more increased by increasing the glycerol concentrations from 20% to 40%, i.e. the Δv value was about 6% higher in GL-40 than GL-20. Although, a similar trend was observed in combined treated wood samples, smaller bulking values were obtained in these samples, which might be due to the possible degradation of glycerol induced at high temperature Evaluation of glycerol kinetics in wood at elevated temperatures were also showed a complete stress relaxation and high activation energy between 120–180°C (Yan *et al.* 2011). The $S_{\max}$ values (at the cycle II) decreased with increasing glycerol concentration and with the combined treatments. The sole glycerol or vacuum-heat treatments slightly decreased the $S_{\max}$ values. A similar trend observed in the samples after combined treatments, although there were not statistically in comparision with untreated control. The samples pretreated with 40% glycerol and followed with vacuum-heat treated exhibited the lowest $S_{\max}$ values, and thus the highest dimensional stability. As stated previously by Yan and Morrell (2014) and Mubarok *et al.* (2019), glycerol pretreatment combined with heat treatment increase the dimensional stability of wood due to the formation of covalent bonds between glycerol and wood polymers.

Colour changes

The effect of glycerol and the combination of glycerol and vacuum-heat treatments on colour changes of the wood samples is given in Table 2. Glycerol pretreatment slightly enhanced the darkness of the samples. The blackish hue increase with increasing temperatures due to vacuum-heat treatments, i.e. there were respectively −10.17 and −17.78 at 180°C and 200°C. When the glycerol pretreatment followed by vacuum-heat treatment, the darkness decreased from −5 to −17. Bekhta and Niemz (2003) quoted that the darkness accelerates when the treatment temperature exceeded approximately 200°C. Yan and Morrell (2019) reported that

Table 2. Mean values (± standard deviations) of change of ΔL^*, Δa^*, and Δb^* in different treated samples.

Treatment	ΔL^*	Δa^*	Δb^*
GL-20	−6.9 ± 0.7 (cd)	3.0 ± 0.7 (cd)	3.6 ± 1.9 (cd)
GL-40	−9.4 ± 1.9 (bcd)	3.1 ± 0.6 (cd)	3.3 ± 0.7 (cd)
VHT180	−10.2 ± 3.3 (bc)	3.6 ± 0.7 (d)	4.6 ± 1.6 (d)
VHT200	−17.8 ± 2.2 (a)	5.2 ± 0.7 (e)	3.4 ± 1.5 (cd)
GL-20 + VHT180	−8.6 ± 1.3 (bcd)	1.3 ± 0.2 (ab)	−0.8 ± 0.6 (ab)
GL-20 + VHT200	−12.6 ± 1.6 (b)	1.9 ± 0.2 (abc)	−2.3 ± 1.6 (a)
GL-40 + VHT180	−5.3 ± 0.9 (d)	0.7 ± 0.7 (a)	0.8 ± 1.4 (bc)
GL-40 + VHT200	−17.6 ± 2.9 (a)	2.4 ± 0.9 (bcd)	−1.8 ± 1.4 (ab)

Notes: GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment; Mean values followed by different lower case letter within a column indicate that there is a significant difference ($p \leq 0.05$) as determined by ANOVA and Tukey HSD *post-hoc* test.

the glycerol pretreatment did not significantly change the *L** of Douglas fir heartwood, but the darkness value decreased considerably by the treatment temperature and duration. The darkness hue on the heat-treated wood is attributed to the formation of degradation products from hemicellulose (Sundqvist 2004). For instance, quinones from the oxidation products could be the reason for colour change (Mitsui *et al.* 2001). The Δ*a** values of the samples treated with 20% and 40% glycerol were 3.0 and 3.1, respectively. The wood samples treated with glycerol and the combination of glycerol and vacuum-heat treatment showed the lowest Δ*a** values. Sole glycerol treatment enhanced the yellowness (Δ*b**) of the wood samples. In contrast, the combination of glycerol and vacuum-heat treatments exhibited a blue characteristic according to colour coordinate system. In general, treatments increased the Δ*a** value, while Δ*b** value decreased for the combinations of glycerol with vacuum-heat treatments. Additionally, Δ*a** increased with increasing temperature, whereas Δ*b** decreased with increased temperature. Most recently, Yan and Morrell (2019) reported that the *a** value decreases by increasing treatment temperature in glycerol-treated Douglas fir, while *b** values are initially increased but then decreased with increasing treatment time or temperature.

The colour changes (Δ*E**) of the wood samples were increased due to the treatment and they were more pronounced in higher temperatures, e.g. 200°C (Figure 1). This is in accordance with Brischke *et al.* (2007) and Tuong and Li (2010), who reported a strong correlation between colour change and heat treatment intensities. Slight colour changes were observed for the glycerol-treated samples at 20% (8.52) and 40% (10.47) weight concentrations. The lowest Δ*E** value of 5.56 was obtained by the samples treated with the combination of 40% glycerol and vacuum-heat treatment at 180°C. The Δ*E** was much more influenced by Δ*L** than Δ*a** and Δ*b**, and thus, it can be said that the Δ*L** was a major contributor to the total colour change. Similar results were reported by González-Peña and Hale (2009), who suggested that the colour changes in heat-treated wood mainly originate from chemical changes in the lignin polymers than in the polysaccharides.

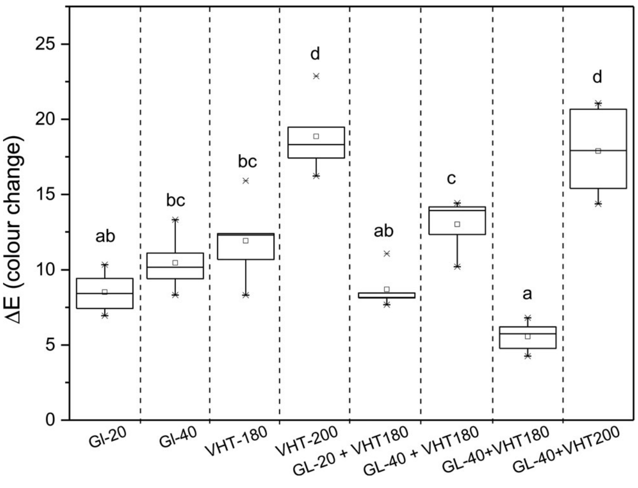

Figure 1. Total colour change (Δ*E**) of the wood samples after treatment with glycerol, combined glycerol and vacuum-heat treatments. GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment. Box-plots with whiskers from the minimum to the maximum; the box represents 25%, 50% and 75% quartile; the mean value of each data set is depicted as quadrate inside the box. Different lower case letter indicated that there was a significant difference ($p \leq 0.05$) as determined by ANOVA and Tukey HSD *post-hoc* test.

Table 3. Mean values (± standard deviation) of MOE and MOR of different treated samples.

Treatments	MOR (N/mm^2)	Change in MOR (%)	MOE (N/mm^2)	Change in MOE (%)
Control	94.2 ± 6.5 (de)	–	11,945 ± 838 (fg)	–
GL20	55.6 ± 6.7 (ab)	−40	8832 ± 745 (ab)	−26
GL40	54.7 ± 9.2 (ab)	−45	8696 ± 734 (ab)	−27
VHT-180	98.8 ± 10.2 (de)	5	11,559 ± 814 (fg)	−3
VHT-200	99.6 ± 10.4 (e)	6	12,360 ± 896 (g)	3
GL20-VHT180	76.9 ± 6.8 (c)	−18	10,527 ± 547 (de)	−12
GL20-VHT200	72.2 ± 8.9 (c)	−23	10,364 ± 1004 (cde)	−13
GL40-VHT180	48.8 ± 6.5 (ab)	−48	8380 ± 791 (a)	−30
GL40-VHT200	49.7 ± 7.4 (ab)	−47	8668 ± 844 (ab)	−27

Notes: GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment; Mean values followed by different lower case letter within a column indicate that there is a significant difference ($p \leq 0.05$) as determined by ANOVA and Tukey HSD *post-hoc* test.

Mechanical strength of treated wood

The MOE and MOR, of untreated and treated samples, are shown in Table 3. The MOR in all cases were more affected by the treatment process than MOE.

Treatment of wood samples with glycerol at 20% and 40% showed considerably lower bending strength than untreated control samples. Vacuum-heat treated samples illustrated comparable MOR and MOE values as untreated ones. Bending properties of thermally treated wood were extensively studied previously and different results due to the treatment process, temperature, duration, and wood species were reported (Bekhta and Niemz 2003, Johansson and Morén 2006, Poncsak *et al.* 2006, Esteves *et al.* 2007, Shi *et al.* 2007, Korkut *et al.* 2008, Behr *et al.* 2018). Allegretti *et al.* (2012) quoted insignificant changes in bending strength and stiffness of wood samples after vacuum-heat treatment. The treatment processes carried out in this study were initiated by a drying step at 103°C and then it was followed by direct exposure to the target temperature. This approach caused therefore minor weight changes in vacuum-heat-treated samples, and subsequently, a slight alteration in bending strength of the treated samples was observed as compared with controls.

Like sole glycerol treatment, a combination of glycerol pretreatment with vacuum-heat treatment significantly reduced the MOR and MOE. Although, the combined treatments, e.g. glycerol pretreatment and vacuum-heat treatment, strongly reduced the MOR and MOE, the reduction was almost half in the samples with a combined treatment containing 20% of glycerol as compared with the sole glycerol pretreated ones at a similar level. The combined modification with higher glycerol content, e.g. 40%, however, exhibited an identical reduction in MOR and MOE as those pretreated with sole glycerol. The results indicate that the effect of vacuum-heat treatment to provide a mild treatment condition is compensated with a presence of higher concentration of glycerol.

Thermal degradation analysis of crude glycerol showed remarkable weight loss at temperatures between 240°C and 255°C (Castelló *et al.* 2009, Almazrouei *et al.* 2017). Treatment of wood samples at elevated temperatures such as 180°C and 200°C provides an acidic condition and the existence of a high concentration of glycerol may accelerate the degradation of wood polymers, as shown by the increase in WL value. These results are in-accordance with the Yan and Morrell (2014) who found a reduction in bending properties of heat treated wood samples after pretreatment with glycerol. Nevertheless, the MOR and MOE reduction due to glycerol pretreatment and vacuum-heat treatment are still considerably lower than the values were reported previously with a combination of glycerol and heat-treatment (Mubarok *et al.* 2019).

Automated vapour sorption (AVS) analysis

The water vapour sorption of untreated and treated wood samples during adsorption and desorption processes are shown in Figure 2(a,b). It should be noted that due to a strong effect of combined treatment at 180°C on the mechanical strength, the samples treated at this temperature were selected for AVS analysis. Sorption curves showed that EMC of the control and treated samples increased in the range of 0–95% RH with the increase in RH. Glycerol treatment resulted in higher EMC value than the other treatments. This can be explained by extra hydroxyl groups that have been delivered by glycerol, i.e. glycerol monomer contains three hydroxyl groups. According to Xie *et al.* (2011), an increase in moisture content leads to swelling of viscoelastic cell walls and thus accommodation of more water. Therefore, due to the excess amount of hydroxyl groups in glycerol-treated samples, the elasticity of the wood cell wall may have been further increased, and that might have led to the accommodation of more water molecules at higher RH. It should be notified that for a direct comparison of the treatment effect on moisture sorption of wood samples, the influence of the additional weight of glycerol treatment has not been considered in this study. A significant upward bend was observed in EMC of control and treated samples, especially from 75% RH. This can be due to the relaxation of cell wall polymer, resulting in the accommodation of more water molecules (Hosseinpourpia *et al.* 2019). All treated samples (expect for GL40) showed lower EMC than the control at RH below 60%, but the EMC was sharply increased above 75% RH, where the highest EMC value at 95% RH was obtained by GL40-treated sample and followed by GL20 and GL20-VHT180. A similar trend was observed during the desorption process. The EMC value of HVT180 at 95% RH was 17.6%, while the control sample showed an EMC of 22.3% at 95% RH. The moisture increment and decrement of untreated and treated samples are presented in Figure 3(a,b). Sole glycerol treatment, i.e. GL20 and GL40, showed considerably higher moisture increment and decrement pattern than the other treatments. The moisture increment constantly increased with increasing RH from 15% to 95% in glycerol-treated samples as well as the combination of glycerol and vacuum-heat-treated samples, i.e. GL20, GL40, and GL20-HVT180. The HVT180-treated wood showed the lowest changes in moisture increment and decrement, and this was comparable with the changes in the untreated control.

Treatment of wood samples considerably changed the sorption hysteresis over the whole hygroscopic range in comparison with untreated control (Figure 4). Control samples exhibited a hysteresis maximum at 75% RH. The treated wood samples showed lower sorption hysteresis than control. The glycerol-treated samples, such as GL20 and GL40, illustrated the lowest hysteresis as compared with other treated and untreated samples. Sorption hysteresis was previously explained by the flexibility of cell wall

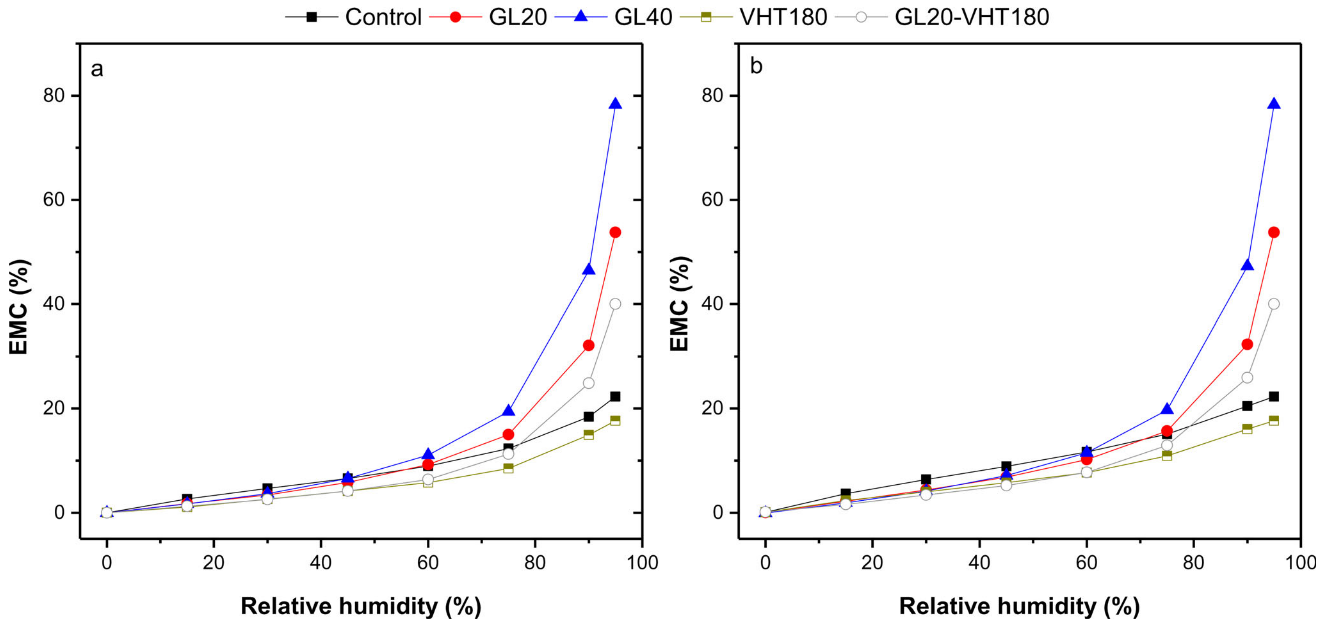

Figure 2. Adsorption (a) and desorption (b) isotherms of untreated and treated wood for the whole range of RH. GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment.

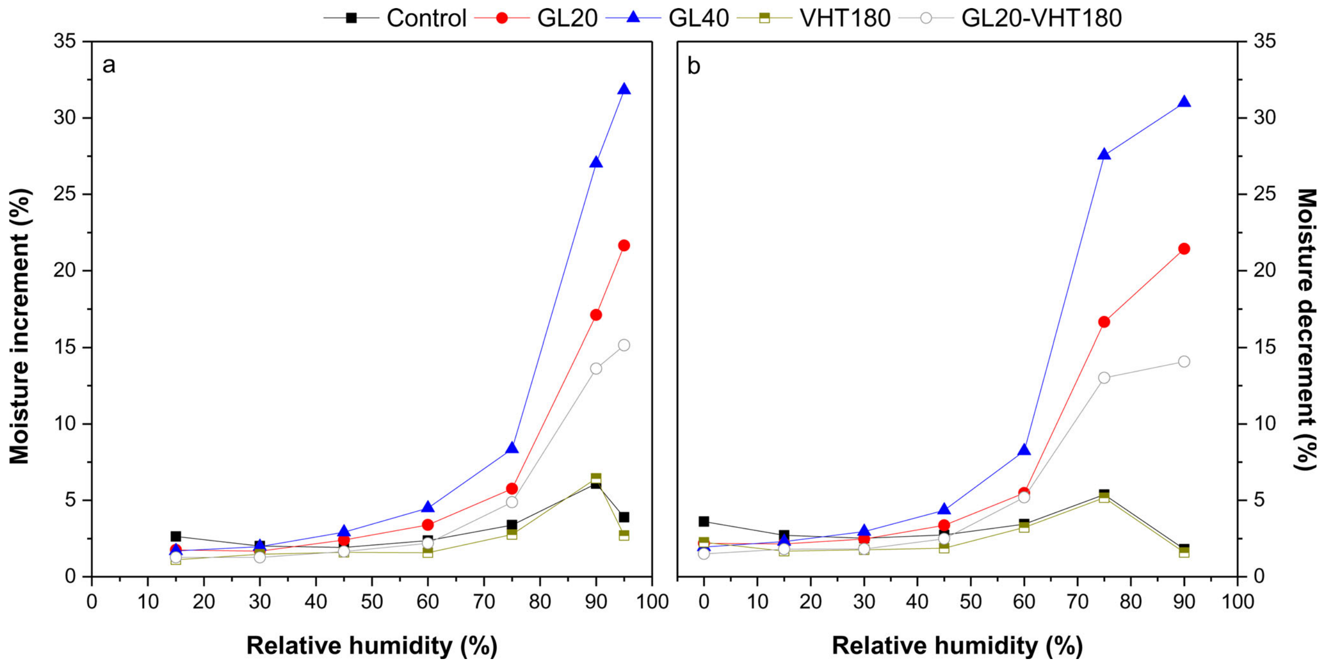

Figure 3. Moisture increment during adsorption (a) and decrement during desorption (b) of untreated and treated wood at each given RH over the full RH range. GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment.

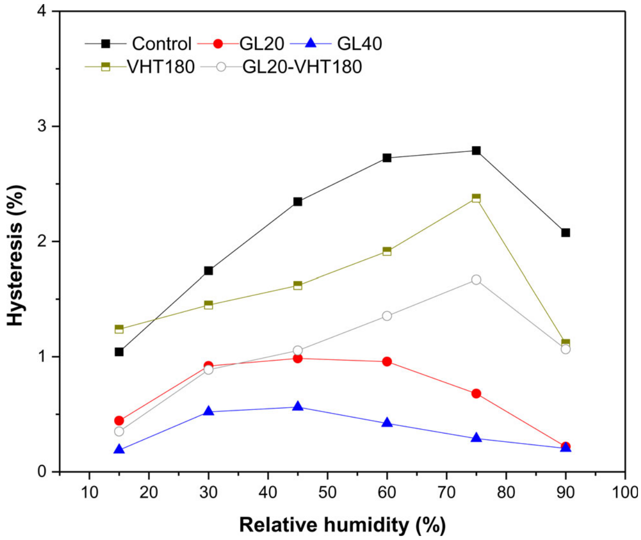

Figure 4. Hysteresis of untreated and treated wood at each given RH level during the sorption run (obtained by subtraction of EMC between desorption and adsorption at the same RH level, according to Hosseinpourpia *et al.* 2019). GL: glycerol pretreatment; VHT: vacuum-heat treatment; GL-VHT: glycerol-vacuum-heat treatment

polymer in the glassy state (Hosseinpourpia *et al.* 2016). Slight reduction in the sorption hysteresis of vacuum-heat treated sample as compared with untreated control can be due to a reduction in hydroxyl group content of the cell wall as a result of the degradation of cell wall polysaccharides. Considerably lower sorption hysteresis of combined treated samples in comparison with sole treatment and untreated control might be related to the reduction of cell wall stiffness. As indicated in Table 3, the MOE value was strongly decreased by the combined treatments. Therefore, this resulted in increasing the flexibility of wood cell wall at different RH changes during adsorption and desorption runs, and reduction of sorption hysteresis, subsequently.

Conclusions

Pretreatment of Scots pine with propanetriol (common name is glycerol) and followed by vacuum-heat treatments increased the Δ*w* values. Fixation of glycerol in wood matrices, as indicated by Δ*w* after leaching, were significantly increased when the wood samples were subjected to the higher temperatures. The glycerol pretreatment induced cell wall bulking (Δ*v*), while its effect on wood swelling is more pronounced after vacuum-heat treatments. The vacuum-heat-treated samples showed the lowest colour changes as compared to the other treatments. The sole vacuum-heat treated samples exhibited comparable bending properties to the untreated controls. While, the combined treatments significantly reduced the bending properties. The moisture content of the samples was strongly increased by glycerol pretreatment. The vacuum-heat-treated samples demonstrated the lowest EMC values in whole RH range during adsorption and desorption runs. The inferior EMC values obtained in combined treated samples as compared with the control ones, particularly at the RHs ranges below 70%. The sorption hysteresis of the samples decreased considerably by glycerol pretreatment. The results indicated that the flexibility of wood cell wall considerably increased by glycerol pretreatment, which might be due to delivering of additional hydroxyl groups into the matrix.

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Disclosure statement

No potential conflict of interest was reported by the author(s)

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