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Combining mineralisation and thermal modification to improve the fungal durability of selected wood species

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ABSTRACT

The development of non-biocidal and environmentally friendly systems to protect wood against biological decay has become a high priority in recent years. In the present study the impact of an innovative modification procedure, combining two environmentally friendly modification methods: thermal modification and mineralisation, using an aqueous solution of calcium acetoacetate as a precursor, on the fungal durability of wood was evaluated. European beechwood (*Fagus sylvatica*) and Norway sprucewood (*Picea abies*) were selected as model wood species. Wood samples were treated using either a single or combination of both methods and exposed to four different fungi: *Gloeophyllum trabeum*, *Rhodonia placenta*, *Trametes versicolor* and *Pleurotus ostreatus*. The effect of the different modifications on moisture content, dynamic vapour sorption, contact angle and pH value was also evaluated. Overall, the highest durability against *Rhodonia placenta*, *Trametes versicolor* and *Pleurotus ostreatus* was achieved through thermal modification in both wood species, while the combination of mineralisation and thermal modification has a synergistic effect against degradation by *Gloeophyllum trabeum*. In the case of beechwood the mass loss decreased from 41% for native to 6% for combined modified samples. We proved that the effectiveness of different treatment against fungal decay of wood were in strong dependence of their moisture content, dynamic vapour sorption, contact angle and pH values. The role of fungi on the morphology of the wood and on crystal structure of formed carbonate was investigated using SEM-EDS analysis.

1. Introduction

Wood is a natural, organic and renewable material which has been used in many applications for thousands of years (Dunningham and Sargent, 2015). It has sufficient strength, flexibility, machinability and is broadly available at low cost. However, wood as a biological material is hygroscopic and it is prone to dimensional changes, as well as biotic and abiotic degradation (Ditommaso et al., 2020).

Wood with moisture content (MC) above a certain threshold is prone to fungal degradation (Thybring, 2017; Kržišnik et al., 2020). This threshold has been recognised to be significantly lower than the fibre saturation (FS) of untreated wood (Meyer and Brischke, 2015; Kržišnik et al., 2020). In some cases, depending on the type of fungi and wood species, studies have shown that fungal decay is possible even if this threshold is not reached, if a water source is available nearby (Meyer et al., 2016). This is especially true for thermally modified (TM) wood (Humar et al., 2020a), which could be due to the ability of fungi to transport water into the wood from an external source (Meyer et al., 2016; Thybring, 2017). On average, FS is about 30% in most European wood species, but this differs among species (Meyer and Brischke, 2015) and is affected by different treatments of the wood (i.e. thermal modification, chemical modification, etc.) (Hill, 2006). Limiting the moisture content of wood can extend the service life of wood and wood-based materials (Thybring et al., 2018; Ringman et al., 2019). It is therefore of great importance to keep the MC of wood below the threshold necessary for fungal degradation.

Most European wood species have low natural durability (Humar et al., 2020a); protection, therefore, is indispensable (Eckhard et al.,

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2005; Dunningham and Sargent, 2015). Protection techniques include the use of biocides, water repellents and coatings, and protection by design, amongst other methods (He et al., 2020; Humar et al., 2020a). Biocides pose a potential health hazard to humans and the environment (Eckhard et al., 2005; He et al., 2020). Due to toxicity and harmful effects, most of the classical biocidal systems have therefore been banned or removed from the market following the introduction of the Biocidal Product Regulation (EU Regulation No.: 528/2012). Currently, there is a growing attention on more environmentally friendly biocidal protection (Šimůnková et al., 2021). Non-biocidal (environmentally friendly) methods therefore need to be developed for wood that is used outdoor in order to keep up with an environmental requirements (Guo et al., 2018; He et al., 2020) and social demand (Lahtela and Kärki, 2016).

One environmentally friendly modification process to improve the fungal durability of wood is thermal modification at temperatures between 180 °C and 260 °C in anoxic conditions (Hill, 2006). The key advantages of thermal modification are reduced hygroscopicity (Tjeerdsma et al., 1998; Hill et al., 2012), improved dimensional stability (Olek et al., 2013; Sandberg and Kutnar, 2016) and biological durability (Rapp, 2001; Rep and Pohleven, 2001), while the disadvantages are loss of strength (Srinivas and Pandey, 2012) and increased brittleness (Lahtela and Kärki, 2016; Sandberg et al., 2017). TM wood is also more acidic than untreated wood due to the formation of acetic (Chu et al., 2019) and formic acids (Boonstra et al., 2007) during treatment at elevated temperature, which can alter the fungal decay process (Miklečić and Jirouš-Rajković, 2016). Furthermore wood darkens according to the temperature of modification (Repič, 2018; Humar et al., 2020b).

Another, less known type of environmentally friendly wood modification is mineralisation, which fundamentally reduces the flammability of wood (Merk et al., 2015; Merk et al., 2016). The main challenge in mineralisation is to embed the minerals deep into the structure of the wood, as mineral particles can aggregate and prevent sufficient penetration (Matsunaga et al., 2009). An improvement of flame-retardancy (Tsioptsias and Panayiotou, 2011; Yang et al., 2020), mechanical properties (Jia et al., 2012; Huang et al., 2018) and hydrophobicity of wood (Wang et al., 2010; Jia et al., 2012) and a reduction in liquid water uptake (Merk et al., 2014) have been reported following mineralisation.

In previous publications we have proposed the use of an aqueous calcium acetoacetate solution, $Ca(OAcAc)_2$, as a precursor for the in-situ formation of $CaCO_3$ (Pondelak et al., 2019; Pondelak et al., 2021). The single-step wood mineralisation process involves vacuum-pressure impregnation with $Ca(OAcAc)_2$, which converts into $CaCO_3$ inside the wood structure up to 1 cm deep when dried at elevated temperatures and relative humidity (Pondelak et al., 2021).

The effect of mineralisation on the equilibrium moisture content (EMC) of wood has been studied to a lesser extent. Moya et al. (2020) showed that the moisture content and liquid water absorption of hardwood samples mineralised with $CaCO_3$ are higher in comparison to untreated samples, but data regarding the water performance of mineralised wood is scarce; existing research has been performed only on a small number of species (Moya et al., 2020). Wood mineralised with hygroscopic inorganic materials may have a higher moisture content (Tsioptsias and Panayiotou, 2011; Merk et al., 2015). Tsioptsias and Panayiotou (2011) therefore suggested the use of a hydrophobic coating in order to limit the hygroscopic effect.

It has been reported that a slightly acidic environment (pH 4–6) is optimal for fungal growth and consequently leads to the fastest degradation of wood (Maurice et al., 2011; Humar et al., 2020a). Little et al. (2010) reported that soil acidity is beneficial for the fungal decay of wood, and showed that increasing the soil pH value decreases degradation in a "soil block test". Since $CaCO_3$ is of an alkaline nature (pH 9) (Martín-Martínez, 2002), the mineralisation of wood could inhibit fungal degradation through the pH-dependent mechanism. Moreover, we hypothesised that a combination of thermal modification and $CaCO_3$ mineralisation could synergise against wood-destroying fungi. The former decreases MC, while the latter increases the pH value.

This paper evaluates the impact of an innovative modification technique, combining two environmentally friendly modification methods ($CaCO_3$ mineralisation and thermal modification) on the fungal durability of wood in two representative species. The moisture performance of the treated wood (moisture content (MC), dynamic vapour sorption (DVS), and contact angle (CA)) and the pH value of the wood was also evaluated. To our knowledge, this is the first study investigating the fungal durability of wood mineralised with $CaCO_3$. By combining the two methods used in this research, we aimed to produce a sustainable wooden material with enhanced durability and fire performance, which at the same time is environmentally friendly, safe to use, and non-hazardous at the end of its use. It should be considered that some other modification treatment might result in better durability against wood decay fungi but exhibits considerably poorer fire performance.

2. Materials and methods

2.1. Materials

Two common European wood species were used for this study: European beech (*Fagus sylvatica* L.), which is the most common deciduous species, and Norway spruce (*Picea abies* K.), which is the most common coniferous species in Slovenia and central Europe (Brus, 2012). Both these species of wood have low natural durability.

Three different wood modification procedures were performed: (a) wood mineralisation, (b) thermal modification and (c) a combination of the two - thermal modification followed by the mineralisation process.

The samples were prepared as described in EN 113–1:2021. Small wooden blocks (50 mm × 25 mm × 15 mm) were cut from each of the materials studied (Table 1) and conditioned at T = 20 °C and RH = 65%. Samples of the same size were used for all experiments.

In the case of dynamic vapour sorption analysis (DVS), five samples were ground to fractions smaller than 1 mm using a Retsch SM 2000 mill (Retsch GmbH, Haan, Germany) and a perforation sieve with 1 mm perforations (Conidur®). The ground samples were conditioned in a desiccator at 20 °C and 1 ± 1% RH. A RH as low as this was achieved by blowing dried compressed air through the desiccator. Compressed air was passed through an adsorption dryer PDAD (Festo, DE) equipped with a PDAD-SP-12000 (Festo, DE) desiccant cartridges and complies with air purity class at the output up to 2:1:2 in accordance with ISO 8573–1:2010 at a pressure dew point of −70 °C.

Prior to the pH measurement, samples were sanded with 240 grit sandpaper (20 strokes). Any remaining dust was then wiped from the surface with a dry cloth and the samples were dried in laboratory conditions (T = 20 °C; RH = 65%) at least one week.

2.1.1. Thermal modification

Thermal modification (TM) was conducted using the Silvapro® procedure (Rep and Pohleven, 2001; Rep et al., 2012), that is commercially used by Silvaprodukt (Slovenija). The wood was modified at 220 °C, with mass losses (Δm) of 11%–15% and 6%–8% determined for European beechwood (beechwood) and Norway sprucewood

Table 1
List of materials studied, their abbreviations and descriptions.

Abbreviation	Description
B	Native beechwood
B Ca	Beechwood mineralised with $CaCO_3$
BT	Thermally modified beechwood
BT Ca	Thermally modified beechwood mineralised with $CaCO_3$
S	Native sprucewood
S Ca	Sprucewood mineralised with $CaCO_3$
ST	Thermally modified sprucewood
ST Ca	Thermally modified sprucewood mineralised with $CaCO_3$

(sprucewood), respectively. The entire modification process, including cooling, took 24 h. Following modification the wood was conditioned at a temperature of 20 °C and relative humidity of 65% for three weeks.

2.1.2. Mineralisation

Mineralisation was performed according to the procedure proposed by Pondelak et al. (2019) In summary, wood was impregnated with an aqueous solution of calcium acetoacetate ($Ca(OAcAc)_2$) under vacuum (30 min at 60 kPa ab) and pressure (3 h at 1 MPa ab). In the final step any excess solution was removed by placing the samples in a vacuum for 20 min. Calcium acetoacetate was prepared from $CaCO_3$, water and 1,3 acetondikarboxylic acid, synthesis is described in detail by Škrlep et al. (2014). Impregnated samples were left to dry for three days in laboratory conditions (T = 20 °C; RH = 65%). Following the impregnation process the acetoacetate was converted to $CaCO_3$ by heating the samples for 80 h at 80 °C, with relative humidity cycled between 40% and 80%. During this treatment, calcium acetoacetate reacts with water and $CaCO_3$ is precipitated. Acetone and CO_2 are produced as by products which are removed/evaporated from the wood during the drying phase by conditioning the samples for three weeks under laboratory conditions (T = 20 °C; RH = 65%). $CaCO_3$ uptake into the wood was 12% ± 4% for both the sprucewood and the beechwood samples. A list of the materials, with abbreviations and their descriptions, is presented in Table 1.

2.2. Methods

2.2.1. Equilibrium moisture content

A total of 5 samples of each material were selected to determine equilibrium moisture content (EMC) according to the EN 13183–1:2002. Samples were dried at 103 °C ± 2 °C for 48 h in order to determine their oven dry weight. Oven dry samples were then exposed in a climatic chamber (Kambič, Slovenia) to laboratory conditions (T = 20 °C; RH = 65%). Samples were conditioned in the given climate until a constant mass was reached (i.e. until the difference in mass between two successive weightings separated by an interval of 2 h is less than 0.1%). Laboratory scale (Precisa gravimetrics EP320, CH) used in this research has a resolution of 0.1 mg and the mass of the samples ranged from 6.8 g to 16 g.

Samples were then weighed, and their EMC was calculated as required by the standard. Glass et al. (2018) determined in their experiments that the errors in the EMC from the widely used 0.002%/min stop criterion are found to be as large as 1.2% MC, and the average error for 20 test cases is 0.5% MC, so we decided to round the EMC values to the nearest integer. Additionally, the effect of the weight of the $CaCO_3$ was determined. Mass of the incorporated $CaCO_3$ was deducted from the mass of the mineralised samples as described by Akitsu et al. (1993) and Thybring (2017).

2.2.2. Dynamic water vapour sorption

Water vapour sorption analysis of the treated and native (i.e. reference, non-treated, untreated) samples was performed using a gravimetric dynamic sorption analyser (DVS Intrinsic, Surface Measurement Systems Ltd., London, UK). Samples were ground and conditioned prior to analysis, as described in the materials section (2.1.). A small amount (≤400 mg) of the ground sample was used. Measurement was performed at a constant temperature of 25 °C ± 0.2 °C. A total of two sorption and desorption cycles were measured from 0% RH to 95% RH and vice versa.

The programme for DVS had steps every 5% RH. The given RH was maintained until the weight change of the sample was less than 0.002%/min for at least 10 min. Data was recorded every 20 s throughout the measurement. DVS analysis was mainly used for comparison of the hygroscopic properties of the various materilas, thus the mass of the $CaCO_3$ was not deducted from the mass of the wood. In addition, it should be noted, that $CaCO_3$ is not inert material thus the deduction is hard to be accurate through the whole hygroscopic range.

2.2.3. Contact angle

The sessile drop method was used to determine contact angles, using an FTA 1000 (FTA, USA) automated drop shape analyser and FTA32 software as proposed by Petrič and Oven (2015). Samples were conditioned under laboratory conditions (T = 20 °C, RH = 65%), sanded, cleaned and dried before measurement. A 4 μL droplet was applied to the surface and the contact angle was measured 1 s, 5 s and 10 s after the droplet detached from the needle. The contact angle was determined on the semi-radial surface (with the angle of the growth rings approximately 45° to the surface of the sample) and in the axial direction according to the sample. A total of 5 measurements were made for each material each on separate samples. Measurements were all performed at laboratory conditions (T = 20 °C, RH = 65%).

2.2.4. pH value determination

The pH value of the wood was determined by hot water extraction method using a Titrino probe with a flat electrode as described by Humar et al. (2001). Five wooden blocks (50 mm × 25 mm × 15 mm) conditioned in laboratory conditions (T = 20 °C, RH = 65%) were ground to fractions smaller than 1 mm as for DVS analysis described already in section 2.1. 5 g of ground samples were added to 50 mL of boiling de-ionized water. Covered mixture was stirred for 5 min. After 30 min of standing at room conditions, the mixture was filtered and rapidly cooled to the room temperature and the pH of the extract was measured at laboratory conditions to an accuracy of two decimal places. The measurement ended when the pH value remained constant for 30 s, the duration of the measurement was approximately 5 min. Three parallel measurements were conducted (standard deviations of pH values for all samples were up to 0.1).

2.2.5. Fungal decay test

The fungal decay test was performed according to the European standard EN 113–1:2021. Four different fungi were used in order to determine the efficiency of mineralisation against both white rot and brown rot fungi. The two species representing white rot were *Trametes versicolor* (*T. versicolor*) and *Pleurotus ostreatus* (*P. ostreatus*), while brown rot was represented by *Gloeophyllum trabeum* (*G. trabeum*) and *Rhodonia placenta* (*R. placenta*). The fungi originated from the fungal collection of the Biotechnical Faculty, University of Ljubljana, which is available to research institutions on demand. Information regarding the origin of the fungal isolates and details about their identification are available in the respective catalogue (Raspor et al., 1995). *G. trabeum* was selected because it is one of the most common fungi that degrade softwoods and it is considered to be sensitive to various biocides. *R. placenta*, on the other hand, was selected as a fungal strain tolerant to several commercial biocidal solutions. The last two white-rot fungi *P. ostreatus* and *T. versicolor* were used as two standard test fungi.

Potato dextrose agar (PDA) (Difco, USA) was prepared and poured into sterilised glass jars. The samples and growth media filled jars were then sterilised in an autoclave at a temperature of 121 °C and pressure of 150 kPa for 20 min. From this point on, everything was done in a sterile environment using sterile equipment. Plastic mesh (HDPE) was placed over the PDA in the jars in order to prevent direct contact between the samples and the growth media. Samples were oven dried (103 °C, 48 h), weighed and conditioned under laboratory conditions (T = 20 °C, RH = 65%) for three weeks prior to the experiment. Each jar contained a control sample and a treated sample and was covered with a pierced lid with an opening clogged with cotton wool to enable air exchange and prevent contamination. Five replicates were prepared for each type of material and fungi. A total of 240 samples in 120 jars were exposed in incubation chamber (T = 25 °C; RH = 85%) for 16 weeks. Following the incubation period, mycelium was carefully removed from the surface of the samples, then samples were weighed for quality control and oven dried at 103 ± 2 °C for 48 h. The samples were then weighed, and Δm was calculated according to the following equation (Akitsu et al., 1993).

$$\Delta m\ [\%] = \frac{m_0\ [g]\ -\ m_1\ [g]}{m_0\ [g]} \times 100\% \quad (1)$$

Where m_0 is the oven dry mass of the sample prior to fungal exposure and m_1 is the oven dry mass of the sample following it. Additionally, the effect of the weight of the $CaCO_3$ was determined and considered. Mass of the incorporated $CaCO_3$ was deducted from the mass of the mineralised samples both before and after exposure as described by Akitsu et al. (1993) and Thybring (2017).

2.2.6. Scanning electron microscopy (SEM)

Samples were investigated using a scanning electron microscope (Jeol JSM-IT 500 LV, Japan). The specimens, of approximately (10 × 10 × 10) mm^3, were cut from bigger samples, vacuum impregnated by epoxy resin and polished with diamond suspation 0.25 μm. Oven dried specimens were placed on carbon tape with no additional coating on the surface prior examination. The images were carried out in the low vacuum mode; a working distance of 10 mm, an accelerated voltage of 10 kV, and a backscattered electron detector in shadow mode (BED-S) were used.

2.2.7. X-ray powder diffraction (XRD)

Crystal modifications of the $CaCO_3$ were identified using a D4 Endeavor, Brucker AXS with Cu Kα radiation (λ = 0.154 nm) and a Sol-X detector. Measurements were performed in a 2 theta range of 10–70° with a scanning step of 0.02° and 6 s counting time per step.

3. Results and discussion

3.1. Equilibrium moisture content and dynamic vapour sorption

The equilibrium moisture content (EMC) of wood greatly affects its durability when it is exposed to wood-destroying fungi (Meyer and Brischke, 2015). We determined the EMC of all the materials used in this study under different climatic conditions. The gravimetrically determined EMC of the samples exposed under laboratory conditions (T = 20 °C; RH = 65%) are presented in Fig. 1a (left columns). Additionally, the weight of $CaCO_3$ in the wood was determined and considered. Mass of the incorporated $CaCO_3$ was deducted from the mass of the mineralised samples. Two EMC values were calculated for each sample, initial (presented in the columns on the left in Fig. 1a) and corrected EMC values (presented in the columns on the right in Fig. 1a). There are slight differences between the corrected and the initial results in the case of mineralised samples, but trend is generally the same.

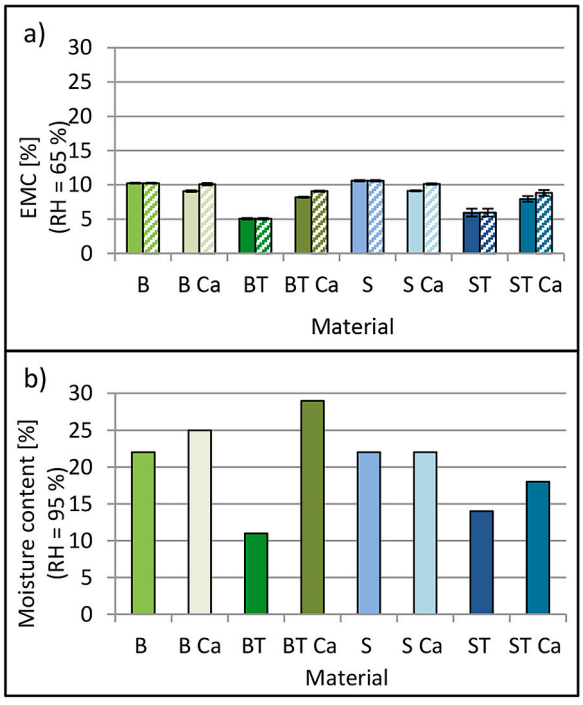

Fig. 1. EMC of the samples (a) conditioned at 20 °C and 65% RH and (b) derived from DVS analysis, 25 °C and 95% RH.

Of the samples exposed under laboratory conditions native sprucewood (S) had the highest MC (11%), while the thermally modified beechwood (BT) had the lowest MC (5%). In general, it can be seen that mineralised wood has approximately the same MC compared to native wood (Fig. 1a). The MC of wood treated with both procedures is higher than the TM wood but lower than the native and mineralised wood.

95% RH (T = 20 °C) was the maximal relative humidity applied within our research. Higher RH is hard to control. The EMC of wood was derived from dynamic vapour sorption (DVS) analysis, and the results are presented in Fig. 1b. Since differences between corrected and non-corrected values are negligible in the previous case (Fig. 1a) correction was not applied for these results. Furthermore, it should be noted that the DVS analysis was performed primarily for the purpose of comparing materials within this study.

DVS showed that mineralised beechwood (B Ca) had a slightly higher EMC than the native sample (B) (25% compared to 22%). A similar trend but with a far more significant difference can be observed for the beechwood treated with both procedures (BT Ca) compared to BT. Amongst all the materials tested the TM beechwood had the lowest EMC, which can be explained by the relatively high temperature of the TM procedure. It is known that, when carried out at the same temperature, TM has a more profound effect on hardwood species compared to softwood species (Hill, 2006). In our case, TM was performed under the same conditions for all samples, resulting in the strongest effect on beechwood. In general, in humid climates, the EMC of the mineralised samples was higher or approximately the same than in the non-mineralised samples. The presence of $CaCO_3$ increases the mass of wood but is not as hygroscopic as wood, as seen from DVS analysis. However, it should be considered that $CaCO_3$ could result in additional condensation sited within the crystals at higher RH.

It is also evident that the trend observed under high RH conditions is not consistent with the trend obtained at 65% RH. It should be considered that moisture performance has a significant influence on the durability of the wood. Recent models assessing the performance of wood in above-ground outdoor applications according to the dose-response principle have demonstrated that wood with improved sorption properties performs better than native wood in outdoor conditions (Meyer-Veltrup et al., 2017). EMC is not, however, the only parameter that influences water performance. Capillary water uptake also has a considerable effect.

A different trend was obtained under laboratory conditions and at specimens conditioned at 95% RH. The increased EMC of the mineralised samples compared to the non-mineralised samples is more evident in the atmosphere with 95% RH than under laboratory conditions. This can be explained by the sorption behaviour of the wood mineralised with $CaCO_3$ and the incorporated $CaCO_3$ (Supplementary material: Fig. S1 – Fig. S9). It should be considered that the sorption properties of $CaCO_3$ (Supplementary material: Fig. S9) differ from the sorption curve of wood (Supplementary material: Fig. S1 – Fig. S8). At high levels of humidity, i.e. above 70%, adsorption is enhanced by tiny surface pores (mesopores with pore diameters of 2 nm–50 nm). These attract water molecules on more than one side through capillary condensation. This leads to hysteresis at this level of humidity, caused by the reluctant release of the adsorbed water (Mangel, 2000). Different processes need to be considered with respect to the interaction of water vapour with the sample, namely the physical interactions through weak forces such as van der Waals or hydrogen bonding, and chemical interactions between water and the sample (Mangel, 2000). It is also worth mentioning that the differing behavior of the various mineralised species could be

attributed to their inherent properties.

3.2. Contact angle

Contact angles of water on wood surfaces are generally considered the most important indicator of the wettability. As water is a significant factor contributing to wood ageing, various ways of hydrophobisation of wood surfaces were reported (Petrič and Oven, 2015). This information is important for assessing the performance of wood in outdoor environments, as well as for surface coating and the application of adhesives on modified wood. Fig. 2 shows the contact angle (CA) of water determined on the surface of beechwood (a) and sprucewood (b) treated as described above. However, we are aware that water performance can not be determined by single method. Therefore multiple water performance tests were carried out.

CA was measured 1 s, 5 s and 10 s after the droplet was deposited on the surface. CA is highest at the beginning and then gradually decreases, which is due to the good wettability of the sample and, to a certain extent, absorption of the water droplet into the sample itself. We found the similar trend of CA comparing differently modified samples for both wood species after 1 s, 5 s and 10 s, therefore only results after 1 s are discussed.

After 1 s, the highest CA was seen for the mineralised samples in both types of wood species. In beechwood the highest CA measured was on the mineralised samples (B Ca = 120.1° ± 13.5°) and the samples treated with both procedures (BT Ca = 119.2° ± 9.9°). The contact angles determined on the TM and native samples of beechwood were noticeably lower than on the mineralised samples (BT = 78.3° ± 8.2° and B = 89.4° ± 15.9°). A high CA and the hydrophobic nature of wood mineralised with $CaCO_3$ compared to native wood, were also reported by Wang et al. (2010). The high CA values in mineralised wood could be explained by its surface morphology. Submicron particles of $CaCO_3$ on the surface of the wood probably affects the contact angle by reducing the free energy of the surface (Zheng et al., 2004; Wang and Dai, 2016).

A similar trend was observed in the sprucewood samples, where the highest CA was measured on the samples treated with both procedures (ST Ca = 123.9° ± 6.8°), followed by the mineralised sprucewood (S Ca = 122.3° ± 14.9°). In our study TM samples exhibited a slightly lower CA than native ones, which is in line with the observations of Kržišnik et al. (2020), who reported that CA after 1 s was 123° on native sprucewood and 115° on TM sprucewood. The authors suggested that the poor water performance of the TM samples was due to changes in the wood (increased porosity or destruction of the wood cells) resulting from the thermal treatment. Contrary, Miklečić and Jirouš-Rajković (2016) determined that the CA is higher on TM beechwood than on native beechwood.

The lower CA determined in our study in comparison to that of Kržišnik et al. (2020) can be explained by the dependence of the sorption properties of TM wood on cyclic changes in RH (Hill, 2006; Majka et al., 2016). In our study the samples were thermally modified several months before the experiments and were exposed to fluctuations in moisture and temperature, which led to a decrease in the contact angle. A reduction in the contact angle of thermally modified wood due to natural weathering was also reported by Žlahtič-Zupanc et al. (2018).

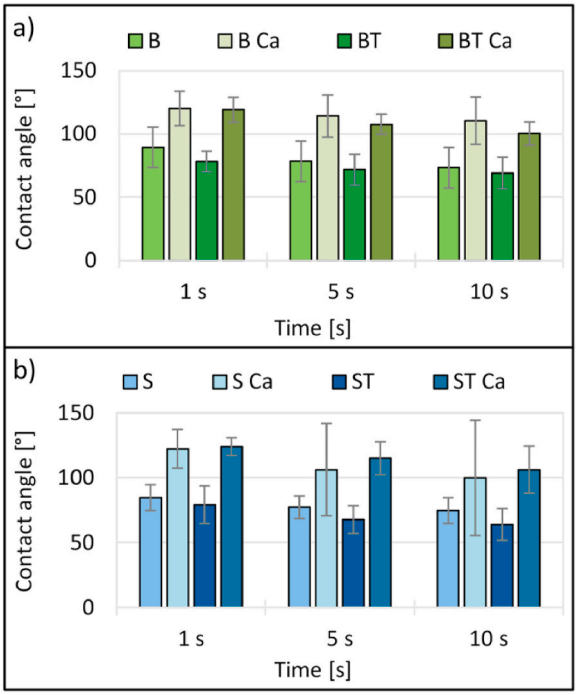

Fig. 2. Contact angle on the surfaces of the (a) beechwood and (b) sprucewood.

3.3. pH of wood

The pH value of wood affects the curing of some adhesives as well as fungal growth (Maurice et al., 2011). The pH values of the materials used are shown in Fig. 3. All the mineralised samples were alkaline (pH 7.5–7.9), while the native and TM samples were acidic (pH 4.6–5.4). The latter pH range is optimal for fungal growth (Maurice et al., 2011; Humar et al., 2020a), while the alkaline values of the mineralised beechwood and sprucewood could decrease the fungal activity and affect the mechanisms of degradation (Martín-Martínez, 2002). It can be seen from the results that the TM wood is more acidic than native samples. These findings are in line with the literature as the TM wood should have lower pH value than native sample due to the formation of acetic and formic acids during thermal modification (Boonstra et al., 2007; Miklečić and Jirouš-Rajković, 2016).

3.4. Fungal decay test

To check the fungal durability of the wood modified in different ways, after the fungal decay test the mass change (Δm) or mass loss was determined gravimetrically. Fig. 4 shows the Δm values for the various beechwood and sprucewood samples (native, mineralised, thermally modified and treated with both processes) degraded by *Gloeophyllum trabeum* (*G. trabeum*) (brown-rot fungi; Fig. 4a), *Rhodonia placenta* (*R. placenta*) (brown-rot fungi; Fig. 4b), *Trametes versicolor* (*T. versicolor*) (white-rot fungi; Fig. 4c) and *Pleurotus ostreatus* (*P. ostreatus*) (white-rot fungi; Fig. 4d). Samples of the sprucewood and beechwood before and after exposure to fungi can be seen in the Supporting material (Figs. S10 and S11).

Additionally, the weight of $CaCO_3$ in the wood was determined and considered. Two mass loss values were calculated for each sample (Akitsu et al., 1993): mass loss determined according to the EN 113–1: 2021, presented in the columns on the left in Fig. 4a–d, and corrected

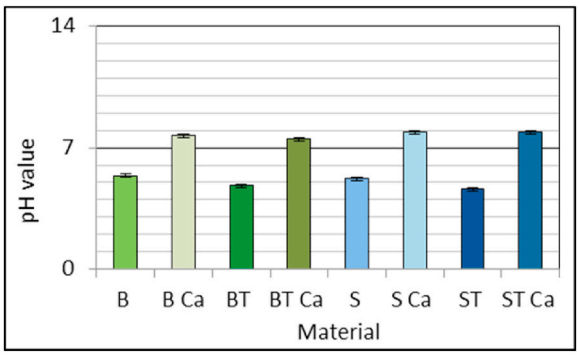

Fig. 3. pH values of the materials used in this research.

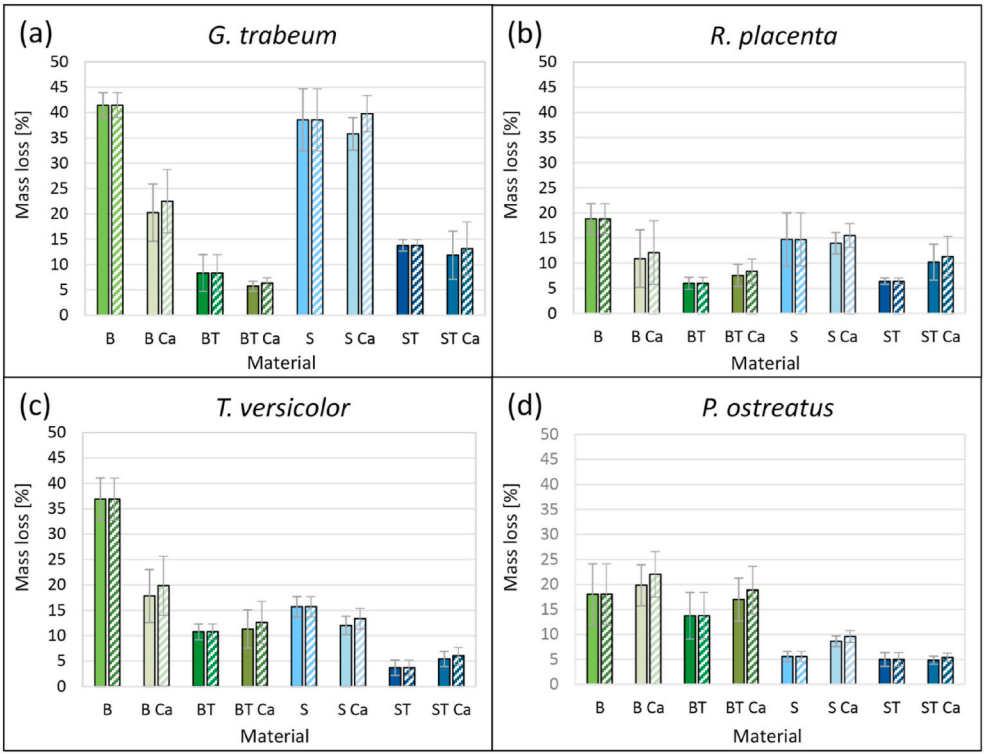

Fig. 4. Mass loss (Δ*m*) of the reference, mineralised, thermally modified and thermally modified and mineralised beechwood and sprucewood samples exposed to (a) *G. trabeum*, (b) *R. placenta*, (c) *T. versicolor* and (d) *P. ostreatus*; columns on the left present Δ*m* determined according to the EN113-1:2021, while columns on the right correspond to the corrected Δ*m* described by Akitsu et al. (1993) and Thybring (2017).

mass loss values, as described by Akitsu et al. (1993) and Thybring (2017), presented in the columns on the right in Fig. 4a–d. By comparing the standard results with the corrected values it can be seen that the trend is generally the same. Differences in the results of the two calculations are negligible and lie in the range of the standard deviations.

At the end of the 16-week decay test, the highest Δ*m* in the reference beechwood samples (41.5%) occurred following exposure to the brown rot fungi (*G. trabeum*). The Δ*m* in the native sprucewood exposed to the same fungi was 38.6%. This proves that the fungi were vital and that the material was susceptible to fungal decay.

Compared to the other test fungi, the samples exposed to *G. trabeum* had the highest Δ*m*. The Δ*m* in the mineralised beechwood was significantly lower than the Δ*m* in the non-mineralised samples, while in the case of sprucewood the mineralisation had a negligible effect on Δ*m*; it can therefore be concluded that mineralisation with $CaCO_3$ improves durability to *G. trabeum* in the case of beechwood, while the effect od mineralisation is negligible for sprucewood. The lowest Δ*m* was measured in the beechwood samples treated with both procedures (approximately 6%).

A similar but less pronounced trend is observed for the samples exposed to *R. placenta*. The Δ*m* of the reference samples was 18.8% and 14.7% for beechwood and sprucewood, respectively, while the TM samples had the lowest Δ*m* (6.0% and 6.4%, respectively). The virulence of *R. placenta* was on the limit, but median loss exceeded 20%, as required by the respective standard. The respective fungus was considered in the research, as sometimes, this fungus degrades treated wood to higher extent than the untreated reference (Humar and Thaler, 2017). Fungal degradation of the mineralised samples is slower or equal than that of the untreated wood. Samples treated with both procedures had a greater Δ*m* (approximately 8% and 11% for the beechwood and sprucewood, respectively) than the samples that had only been thermally modified. This can be explained by the higher EMC in the samples that had been treated with both procedures compared to the TM samples.

While *T. versicolor* is a white-rot fungi. It is therefore not surprising that the highest Δ*m* (36.9%) was determined in the reference beechwood samples, compared to only 15.7% in the reference sprucewood samples. The lowest Δ*m* were observed in the TM beechwood samples (10.8%) and the TM sprucewood (3.7%). Mineralisation affects beechwood the most, as their Δ*m* is approximately half the value of that of the non-treated samples. In both species of wood, the Δ*m* in the samples treated with both procedures was slightly larger than that of the samples which had only been thermally modified.

In the case of *P. ostreatus*, the Δ*m* was similar for the reference beechwood, the mineralised beechwood and the beechwood treated with both procedures (values range from 17% to 20%). As the mass loss of the treated wood was even higher than the mass loss of the untreated wood, this confirms the virulence of the fungi. In comparison, the TM beechwood was found to be the most resistant (Δ*m* = 13.7%). A similar trend can be observed in the sprucewood samples. It can be clearly seen (Fig. 4d) that *P. ostreatus* prefers beechwood over sprucewood, which is not surprising given that it is a white-rot fungi.

According to CEN/TS 15083–1:2005, residual mass loss can be used to classify durability based on the mean percentage mass loss. This classification clearly proves the synergistic effect of mineralisation and thermal modification of the wood. Namely, native sprucewood and beechwood can be classified as the wood species most susceptible to decay (durability class 5; DC5). This is in agreement with data from the literature and the EN 350:2017. Mineralisation slightly improved the durability of beechwood (DC4), but had no effect on the durability of sprucewood. This is probably related to the lower retention of the aqueous calcium acetoacetate solution following impregnation in the sprucewood samples. Thermal modification results in improved durability. The durability class of the thermally modified sprucewood and beechwood was 3 (moderately durable wood), while the durability class of the beechwood and sprucewood both mineralised and thermally modified was 2 (durable wood).

These results are in accordance with the EMC of the samples. The activity of *P. ostreatus* (PLO) is promoted by the higher moisture content

of the mineralised samples, while the low EMC of the TM samples inhibits decay.

In general, the native beechwood samples were degraded most by *G. trabeum, R. placenta and T. versicolor*. The mineralised samples had a lower Δ*m* than the native samples, except with *P. ostreatus*, where the mineralised beechwood samples had the highest Δ*m*. Of the beechwood samples, Δ*m* was lowest in the *T. versicolor* samples following exposure to *R. placenta, T. versicolor* and *P. ostreatus*. The same trend can be observed in the TM sprucewood samples. Following exposure to *G. trabeum* the lowest Δ*m* occurred in the samples treated with both procedures, in both the beechwood and the sprucewood.

The Δ*m* results, which indicate the effectiveness of different treatment against fungal decay, were consistent with the results of moisture content and pH values described above. TM wood inhibits fungal decay due to its low EMC; when thermally modified, the reduction in EMC is evident. When TM is combined with mineralisation, the wood has a higher EMC than in TM wood but it is still lower than in native wood. A similar trend can be observed for the Δ*m* results for the majority of fungi in decay test. Mineralisation has a pronounced effect on the pH values of the samples (native and TM samples had pH values of between 4.6 and 5.4, while mineralised samples had pH values from 7.5 to 7.9). In our case, the pH value of the mineralised wood influenced the fungal decay. The alkaline nature of the samples inhibited fungal decay, in line with the fact that a slightly acidic environment is optimal for fungal degradation (Maurice et al., 2011; Humar et al., 2020a).

The combination of the two procedures used in this study has a synergistic effect against degradation by *G. trabeum*. This effect was less pronounced in the other fungi.

3.5. SEM and XRD analysis following exposure to fungi

SEM analysis was conducted on each of the eight samples degraded by *G. trabeum* in order to investigate the role of fungi on the morphology of the wood samples modified in various ways. We selected *G. trabeum* as a case study because the largest differences in Δ*m* between the non-mineralised and mineralised samples were found after exposure to this fungus. SEM images of the surface and cross-section of the mineralised wood before and after exposure to this fungus are shown in Fig. 5. The morphology of the carbonates incorporated into the structure of the wood after the decay test differs from that prior to exposure (Fig. 5a and c show the SEM images of the mineralised sprucewood before the exposure, while Fig. 5b and d shows the same sample after exposure to the *G. trabeum* fungi). It can be seen that spherical $CaCO_3$ particles (Fig. 5c), characteristic of vaterite, transformed into cubic crystals (Fig. 5d), which are characteristic of calcium oxalate hydrate. This crystal phase transformation was confirmed by XRD analysis (Supplementary material - Fig. S12). The reflections of the mineralised sprucewood are characteristic of the vaterite $CaCO_3$ phase, while the reflections of the mineralised sprucewood following exposure to *G. trabeum* are found to belong to calcium oxalate hydrate (Supplementary material - Fig. S12). It is known that wood decay fungi are able to produce oxalic acid and precipitate calcium oxalate (Connolly et al., 1999).

4. Conclusions

We have proposed and investigated an innovative non-biocidal procedure for the modification of wood to increase its fungal durability. This procedure comprises two environmentally friendly methods: thermal modification and mineralisation using an aqueous calcium acetoacetate solution as a precursor. European beechwood and Norway sprucewood were selected as the model wood species. In both types of wood the highest durability to *Rhodonia placenta*, *Trametes versicolor* and *Pleurotus ostreatus* was achieved through thermal modification, while in the case of *Gloeophyllum trabeum* the newly proposed combination of mineralisation and thermal modification offered the most effective durability, proving their synergistic effect. We have shown that moisture content, dynamic vapour sorption, contact angle and pH value all have a

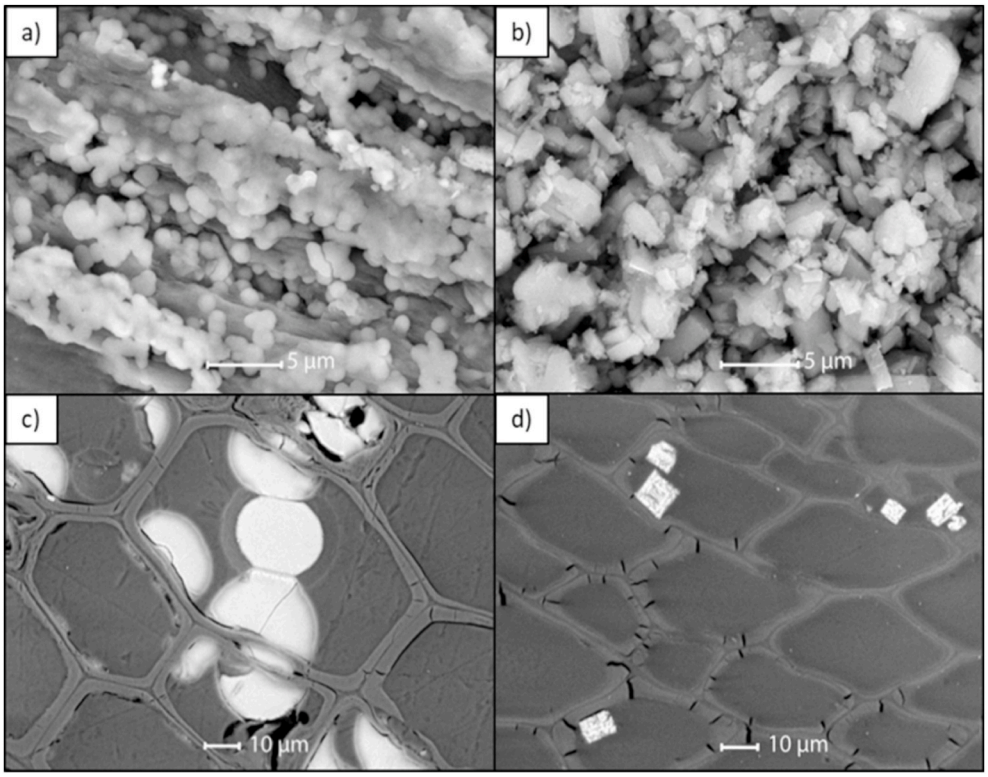

Fig. 5. SEM images of the surface of the mineralised sprucewood (a) before and (b) after exposure to fungi; cross-section of the mineralised sprucewood (c) before and (d) after exposure to fungi.

strong influence on fungal decay. In the thermally modified wood samples, the excellent fungal durability is probably due to the fact that the moisture content is below the fibre saturation. As the moisture content of both the mineralised and reference wood samples is above the fibre saturation, the wood should be subject to fungal decay. It was found that the slightly alkaline environment (pH 7.5–7.9) of both the mineralised wood species is probably one of the key parameters for slowing down fungal activity compared to the more acidic environment (pH 4.6–5.4) of the native and thermally modified wood. Through SEM-EDS analysis of the mineralised samples we confirmed the crystal phase transformation from vaterite to calcium oxalate hydrate during exposure to *G. trabeum*.

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CRediT authorship contribution statement

Rožle Repič: Conceptualization, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Andreja Pondelak:** Conceptualization, Validation, Investigation, Writing – review & editing, Supervision. **Davor Kržišnik:** Validation, Formal analysis, Investigation, Writing – review & editing. **Miha Humar:** Methodology, Validation, Data curation, Writing – review & editing, Visualization, Supervision, Funding acquisition. **Andrijana Sever Škapin:** Conceptualization, Validation, Resources, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. We confirm that the manuscript has been read and approved by all named authors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2022.131530.

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