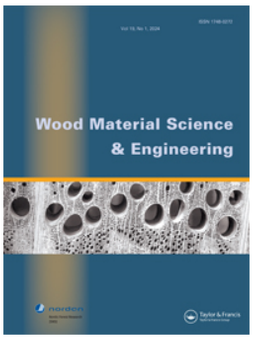

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ORIGINAL ARTICLE

Environmentally friendly protection of European beech against fire and fungal decay using a combination of thermal modification and mineralisation

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ABSTRACT

The demand for construction timber is continuously increasing, due to its favourable characteristics. However, the adequate protection of wood is key to its successful use, as it is flammable and susceptible to biodegradation. Given that thermal modification enhances the durability of wood, and mineralisation with $CaCO_3$ considerably improves its fire properties, it is worth considering the combined effects of the two methods.

European beech (*Fagus sylvatica*) was selected to determine the effects of a) thermal modification, b) mineralisation through the *in-situ* formation of $CaCO_3$, and c) a combination of the two procedures, on resistance to decay fungi, reaction to fire and the mechanical properties of the wood. Microscopic analysis and comparisons of the samples before and after exposure to fungi were also conducted.

Mineralised wood generally had a slightly alkaline pH value and higher equilibrium moisture content, while thermal modification lowered the equilibrium moisture content. The present study demonstrated the combined effect of thermal modification and mineralisation: the best response to fire as well as resistance to fungi was achieved when the two treatments were combined. Results from the Brinell hardness and three-point bending tests indicate that both modification procedures can slightly impair the mechanical properties of the wood.

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Wood; protection; durability; mechanical properties

Introduction

Throughout history, wood has been considered to be one of the most important materials, and has been used for a wide variety of applications (Dunningham and Sargent 2015, Eder 2021). The main disadvantages of wood are its poor dimensional stability, flammability and susceptibility to biodegradation (Sandberg *et al*. 2017, Humar *et al*. 2020). Durability is especially important for outdoor applications. When the inherent natural durability of wood is insufficient, it needs to be protected to prolong its service life. The more intensive use of wood in recent decades, primarily for construction purposes, has increased the need for its protection (Dunningham and Sargent 2015). It is predicted that there will be an even greater shortage of wood over the coming decades (Odppes *et al*. 2021). Due to environmental awareness, in most countries a ban has been imposed on most conventional active ingredients used in the production of wood preservatives, and this, combined with a lack of supply of naturally durable wood species, has shifted development towards so-called green methods of wood protection (Singh and Singh 2012, Dunningham and Sargent 2015). One of the most important and environmentally acceptable methods is thermal modification (TM), which involves heating wood in conditions of reduced oxygen concentration to temperatures between 160°C and 240°C (Hill 2006, Zelinka *et al*. 2022). This method omits the need for potentially hazardous chemicals (Poncsak *et al*. 2009). An improvement in the inherent durability to fungal decay is only one of several positive changes achieved by thermal modification (Humar *et al*. 2020), but unfortunately the fire performance of wood is also compromised (Čekovska *et al*. 2017). Wood-based materials are known to have poor fire resistance, making them a fire safety hazard and presenting a limiting factor for the broader utilisation of wood in construction (Huang *et al*. 2018, Ali *et al*. 2019). Conventionally, fire-retardants have been used to address this problem. They are beneficial in the early stages of fire development and are crucial for the safe evacuation of a burning building (Yona *et al*. 2021). On the other hand, there are many drawbacks of fire-retardant treatments, which can cause environmental and health issues (Merk *et al*. 2015, Guo *et al*. 2019) as well as increase the hygroscopicity, impair the dimensional stability, impair adhesion, increase the roughness, and reduce the mechanical properties of wood, amongst other things, as well as cause corrosion of fasteners (Taghiyari 2012). Many effective commercial fire-retardants are based on phosphate or borate salts to reduce flame spread. The mechanism of acid dehydration, however, which effectively reduces flame spread, can

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also lead to a loss of strength in treated wood (Lebow and Winandy 1999, Ozyhar *et al*. 2021). Improving the fire properties of wood is challenging, because it is difficult to meet the ever-evolving fire safety standards while minimising the impact on the environment and human health (Ozyhar *et al*. 2021). Over time, several methods have been developed to improve the reaction of wood to fire. One such method is mineralisation with inorganic materials such as carbonates, which can be considered an environmentally acceptable alternative to conventional fire-retardant treatments (Merk *et al*. 2016). Various carbonate mineralisation processes have been proposed, primarily differing in the way in which minerals are introduced into the structure of the wood (Pondelak *et al*. 2021b). Many authors have demonstrated an improved reaction to fire in wood mineralised with $CaCO_3$ (Merk *et al*. 2015, Merk *et al*. 2016, Huang *et al*. 2018, Moja *et al*. 2020 and Pondelak *et al*. 2021b). A similar improvement has also been observed in composites made from pine flakes mineralised with $CaCO_3$ (Tao *et al*. 2019). Due to this positive effect on the fire properties, the mineralisation of wood with carbonates improves its reliability for use in buildings without compromising its intrinsic properties, meaning that wood modified in this way has excellent potential for use in buildings (Merk *et al*. 2015) and even outdoor applications (Pondelak *et al*. 2021b). But on the other hand, the influence of mineralisation on mechanical properties of wood has not yet been fully investigated, therefore its use in construction purposes might be hindered. Additionally, $CaCO_3$ acts as an adsorbent and can neutralise hazardous acidic combustion emissions (i.e. hydrochloric acid) during burning (Ozyhar *et al*. 2021).

The synergistic effect of thermal modification and mineralisation on the resistance of wood to fungal decay was confirmed in a study by Repič *et al*. (2022), but the effects on its fire properties were not determined. The aim of the present study was to comprehensively investigate the combined or even synergistic effects of these two environmentally acceptable methods (mineralisation and thermal modification) on the relevant properties of wood i.e. flammability, susceptibility to biodegradation and mechanical properties. The possibility of improving the durability and fire properties of wood by combining these two methods was investigated, furthermore mechanical properties and visual appearance of the wood following each modification were considered as well.

Materials

European beech wood (*Fagus sylvatica*) was selected as the model wood species because it is the most widespread wood species in Slovenia (Brus 2012) and the most common hardwood in Europe (Gryc *et al*. 2008, Beqo *et al*. 2015). We prepared various samples (described in detail for each method) of thermally modified (BT) and mineralised (B Ca) beech wood, as well as samples treated using both procedures (BT Ca). The samples treated with both protection methods were first thermally modified and then mineralised. In parallel, we also tested untreated beech wood (B) as a reference. All samples were made from wood of the same origin, such that variability was kept to a minimum.

The wood was thermally modified at 220°C, according to the commercial Silvapro® process (Rep and Pohleven 2002, Rep *et al*. 2012). The entire modification process, including cooling, lasted approximately 24 h. The mass loss after modification was between 11% and 15%, indicating the severity of the modification. Following modification, the wood was conditioned for three weeks under standard laboratory conditions ($T = 20$°C; $RH = 65\%$) before further processing.

Mineralisation was carried out according to the procedure proposed by Pondelak *et al*. (2021b), where the wood is impregnated with a solution of calcium acetoacetate, which is then converted to calcium carbonate during post-treatment (Pondelak *et al*. 2021a, 2021b). During post-treatment, wood was exposed to high relative humidity (RH ? 80%) at a temperature of 80°C. The synthesis of the calcium acetoacetate solution is described in detail by Škrlep *et al*. (2014, Example 2). Following mineralisation, the wood was conditioned under standard laboratory conditions ($T = 20$°C; $RH = 65\%$) for three weeks. The retention of carbonates was 12 wt. % ± 4 wt. %.

Methods

From the data obtained regarding mass (m) and volume (V), the density of the oven dry samples (ρ_0) according to the method by Kollman (1951) was calculated. Next, the water performance of the wood was investigated using various methods. In addition to the moisture content of the samples, the data for which was taken from Repič *et al*. (2022), the fibre saturation (FS) was determined by calculating the ratio of volume swelling (α_v) to dry density (ρ_0), according to Eq. (1), and correcting for the density of adsorbed water (Gorišek, 2009):

$$FS = \frac{\alpha_v}{\rho_0} \times \rho_{vv} \tag{1}$$

Where the density of adsorbed water (ρ_{vv}) is higher than the density of free water and is 1130 kg/m^3 as stated by Gorišek (2009).

Five samples of each material, 50 mm × 25 mm × 15 mm in size, were placed upright in a rig such that only the cross-sectional surfaces of the samples were submerged, to a depth of approximately 0.5 mm below the water surface. Capillary uptake of liquid water by the cross-sectional surface was measured after 200 s of exposure. The samples were weighed and the amount of water absorbed per unit area was determined. The average and standard deviation of the 5 measurements were then calculated. Similarly, five samples of each material, 50 mm × 25 mm × 15 mm in size, were then immersed in water and the water uptake was determined after 1 and 24 h. The liquid water uptake results are presented as the average and standard deviation of 5 parallels given in grams, assuming that the area of all the samples was approximately equal. Volumetric shrinkage (β_v) was calculated as the percentage change in volume from the fresh (V_{vl}) to the oven dry state (V_0). To determine the dimensions of the samples in the completely wet state, the samples were pressure impregnated with water at the end of the water uptake experiments. The volumetric shrinkage of each sample was determined according to Eq. (2) by Gorišek (2009) and presented as the average and standard deviation of the 5 measurements:

$$\beta_v = \frac{V_{vl} - V_0}{V_{vl}} \tag{2}$$

The anti-shrinking efficiency (*ASE*) was also determined based on the volumetric shrinkages (βv) calculated. *ASE* was determined for all the treated samples with respect to the untreated reference sample, according to Eq. (3) by Gennari *et al*. (2021):

$$ASE = \frac{\beta_{ref} - \beta_{tre}}{\beta_{ref}} \quad (3)$$

where β_{ref} is the volumetric shrinkage of the untreated reference sample, and β_{tre} is the volumetric shrinkage of the treated sample.

In addition to the hot water extract pH data taken from Repič *et al*. (2022), surface pH value was determined using a Titrino titrator (Metrohm, Switzerland), as described by Ammann *et al*. (2016). Five samples, 100 mm × 100 mm × 10 mm in size, were conditioned for three weeks under laboratory conditions (T = 20°C, RH = 65%), sanded, wiped with a damp cloth and dried before measurement. First, 1 mL of deionised water was applied to the surface, then the probe was brought into contact with the surface. The measurement ended when the pH value remained constant for 30 s. The pH value was measured to an accuracy of two decimal places. The total duration of the measurement was approximately 3 min. No change in the amount of water applied to the surface of the sample was observed during this time. The results given are the average of a total of 10 measurements taken on 5 different samples of the same material. Measurements were performed in a room subject to laboratory conditions (T = 20°C, RH = 65%). Both the pH value of the hot water extract and the pH value of the surface are reported in this work.

Resistance to wood decay fungi was determined according to the standard (CEN 2020a). The procedure is described in detail by Repič *et al*. (2022). Briefly, two different wood decay fungi were used: white rot, represented by *Trametes versicolour* (TV) (ZIM L057), and brown rot, represented by *Gloeophyllum trabeum* (GT) (ZIM L017). The fungi were obtained from the fungal collection of the Biotechnical Faculty, University of Ljubljana, which is available to research institutions on demand. Detailed information regarding the origin and identification of the fungal isolates are available in the respective catalogue (Raspor *et al*. 1995). Potato dextrose agar (DIFCO, USA) was used as the culture medium, which was poured into glass jars. The sterile samples were then placed in the jars and subjected to fungal decomposition for 16 weeks. After 16 weeks the samples were cleaned, dried to a dehydrated state, and weighed, then the amount of weight loss was determined. 5 samples of each material were exposed to each of the fungi.

Microscopic analysis was conducted with a scanning electron microscope (Joel IT 500 LV, Japan). The working distance and accelerating voltage were 10 mm and 10 kV, respectively. Micrographs were captured at 200× magnification. The samples for SEM analysis originated from the resistance to wood decay fungi experiment. Exposed and unexposed samples were cut to a length of 10 mm, vacuum impregnated with a commercial epoxy resin, Crystalres (Samson Kamnik, Slovenija), and polished with a diamond suspension, MicroPolish (Buehler, USA) (0.3 µm), using a Beta vector grinder-polisher (Buehler, USA). The samples were placed on a carbon tape and observed in low vacuum mode.

The fire properties of the samples were determined using a cone calorimeter (FTT, UK) according to the standard (ISO 2018). Samples with dimensions of 100 mm × 100 mm × 10 mm were conditioned under laboratory conditions prior to the test, wrapped in aluminium foil and exposed to uniform radiation of 50 kW/m^2. The fire properties were determined in five samples of each material. Each measurement lasted 600 s. Using ConeTools software (RISE, Sweden), the data measured were used to simulate measurements according to the standard (CEN 2020b) (single burning item - SBI) to determine values for two key criteria in the classification of reaction to fire according to the standard (CEN 2019); namely, the total heat release in the first 600 s of the test (THR_{600s}) and the fire growth rate index (*FIGRA*). The time of ignition for the samples was also measured.

Two different experiments were performed to evaluate the mechanical properties of the samples. The hardness and bending properties of all samples were determined according to the standards (CEN 2020c and ISO 2014). The samples were conditioned for three weeks under laboratory conditions (T = 20°C, RH = 65%) before conducting the mechanical tests.

Brinell hardness was measured using a Zwick Z100 testing machine (Zwick Roell AG, Germany). A polished, hardened steel ball with a diameter of 10 mm was used as the indenter. A force of 1000 N was reached after approximately 15 s. This 1000 N force was maintained for another 25 s, then the indenter was removed. Three minutes after the indenter was withdrawn, residual indentation measurements were made, such that two diameters were obtained for each indentation (across the grain (d_1) and along the grain (d_2)). The average indentation diameter (d) was then calculated from d_1 and d_2. Brinell hardness was calculated according to Eq. (4) as prescribed by the standard (CEN 2020c):

$$HB = \frac{2F}{\pi D\left[D - \sqrt{D^2 - d^2}\right]} \quad (4)$$

Where F is the applied force (1000 N), D is the diameter of the indenter (10 mm) and d is the average indentation diameter.

The hardness was measured on samples of 100 mm × 100 mm × 10 mm in size. Ten measurements were made for each material tested, and the average results are reported along with standard deviations.

Bending strength was determined using a Zwick Z100 testing machine (Zwick Roell AG, Germany), with 10 replicates tested for each material. The dimensions of the samples were 360 mm × 20 mm × 20 mm, and the distance between supports was 280 mm. The samples were oriented half-radially (the inclination of the growth rings on the cross-section was approximately 45°). The radius of the loading head was 40 mm. The test was conducted at a speed of 10 mm/min, with test duration of approximately 3 min for all samples. The modulus of elasticity, modulus of rupture and strain at break were reported as an average of 10 measurements per material and calculated using the software testXpert III (Zwick Roell AG, Germany).

Results and discussion

Water performance of wood

The moisture content (MC) of wood plays an important role on its service life, as it is one of the main factors influencing fungal decay (Thybring *et al*. 2018). The moisture performance of wood cannot be assessed by a single test, therefore several tests were performed (Meyer-Veltrup *et al*. 2017). In addition to the moisture content of the wood exposed to laboratory conditions ($T = 20°C$; $RH = 65\%$), as obtained in a study by Repič *et al*. (2022), the capillary water uptake over 200 s and the water uptake over 24 h (in the submersion test) were also determined, and the fibre saturation, volumetric shrinkage and anti-shrinking efficiency were calculated from these measurements (Table 1).

The moisture content of wood was determined after conditioning at $RH = 65\%$. The lowest *MC* was observed in thermally modified beech (BT), while the reference beech (B) had the highest equilibrium moisture content (Table 1). Under the conditions given, the mineralised beech (B Ca) and beech with the combined treatment (thermally modified and mineralised) (BT Ca) had a moisture content lower than the reference beech, but higher than that of the TM beech. This is in line with data from the literature, confirming that thermal modification improves the sorption properties of wood (Esteves and Pereira 2009).

The effect of thermal modification on fibre saturation (FS) is evident; BT reaches FS at approx. 19% MC, compared to at approx. 33% MC in the reference sample. The effect of mineralisation on FS is not as pronounced. B Ca and BT Ca reached FS at approx. 30% MC, which is comparable to in the reference sample. The FS in BT Ca sample was about 10% higher than in the BT sample (approx. 19%). This is very positive, as the introduction of crystals did not affect the sorption properties of the wood in this regard.

Table 1 shows that liquid water capillary uptake in the axial direction was most notable in BT Ca, followed by B and B Ca. The lowest capillary uptake was observed in the BT sample and was about one third of that of the BT Ca sample. A similar result was obtained for water uptake, which was determined by the 1 and 24 h submersion tests. In general, mineralisation increased water uptake in the submersion test, while thermal modification had the opposite effect (Table 1). An increased water uptake in submersion tests following mineralisation with $CaCO_3$ was also reported by Moya *et al*. (2020), while crystals in the wood were previously seen to have a similar effect on sorption properties in wood treated with NaCl and H_3BO_3 (Lesar *et al*. 2011). In mineralised thermally modified wood, the thermal modification somehow neutralises the effect of mineralisation. This is one of the benefits of combining mineralisation with thermal modification.

It is known that European beech wood is subject to considerable dimensional changes (Grych *et al*. 2008). Volumetric shrinkage from a water-saturated state to the oven dry state was found to be highest in B Ca (approx. 17%), followed by B (Table 1). The values of volumetric shrinkage are comparable to those for European beech wood published by Skaravelis and Mantanis (2013) (15.2–15.6%). BT samples show the lowest shrinkage of approx. 9%, while BT Ca samples show a shrinkage the B and BT sample. The shrinking of wood is related to its MC, and the good performance of the BT sample can be attributed to its favourable sorption properties (Sandberg *et al*. 2017). On the other hand, the increased shrinkage of the mineralised sample (B Ca) can be attributed to its higher moisture content, relatively high density, and low porosity. The anti-shrinkage efficiency (ASE) was calculated for all treated samples in relation to the reference (Table 1). Mineralisation has a negative effect on ASE, as the shrinkage of the B Ca sample was 13% higher than that of the reference. The highest ASE is achieved through thermal modification (38%), while a combination of the two methods led to an ASE of 9%. A similar (40–60%) reduction in volumetric swelling in different wood species as a result of thermal modification was also reported by Militz and Altgen (2014) and Gennari *et al*. (2021).

pH value

In general, wood is slightly acidic, and in the case of thermal modification, the pH may decrease slightly, which may also affect fungal degradation (Boonstra *et al*. 2007). With the process of mineralisation, the pH value of the wood increases significantly. This information is important when considering the protection of wood against fungal decay, as fungi require a slightly acidic environment for decay to occur (Maurice *et al*. 2011). The results of the pH value measurements on the surface of the samples are presented in Table 2. Mineralised

Table 1. Physical properties of samples. Data on moisture content and pH value of hot water extract were taken from Repič *et al*. (2022).

Sample	Abbreviation Description	B Reference	B Ca Mineralised	BT Thermally modified	BT Ca Thermally modified and mineralised
Water performance	Moisture content (%) (T = 20°C; RH = 65%)	10.2 ± 0.1	10.1 ± 0.2	5.1 ± 0.1	9.1 ± 0.1
	Fibre saturation (%)	33.3 ± 1.7	32.8 ± 1.8	19.3 ± 1.0	28.1 ± 0.4
	Capillary water uptake in 200 s (g/mm^2)	25.3 ± 5.3	20.0 ± 10.8	13.8 ± 3.4	39.6 ± 9.5
	Water uptake in 1 h submersion (g)	2.6 ± 0.1	3.2 ± 0.2	1.7 ± 0.2	3.0 ± 0.3
	Water uptake in 24 h submersion (g)	6.2 ± 0.3	7.1 ± 0.5	4.2 ± 0.2	6.1 ± 0.4
	Volumetric shrinkage (%)	15.0 ± 0.7	16.9 ± 0.7	9.2 ± 0.6	13.6 ± 0.4
	Anti-shrinking efficiency (ASE) (%)	0	−13	38	9
pH value	Hot water extract	5.44 ± 0.01	7.74 ± 0.02	4.76 ± 0.01	7.49 ± 0.02
	On the surface	5.37 ± 0.52	8.07 ± 0.26	5.16 ± 0.38	7.90 ± 0.09
Exposure to fungi	Mass loss GT (%)	41.5 ± 2.5	20.2 ± 5.6	8.3 ± 3.6	5.7 ± 1
	Mass loss TV (%)	36.9 ± 4.2	17.8 ± 5.2	10.8 ± 1.6	11.3 ± 3.7
Fire properties	Ignition time (s)	29.8 ± 3.8	46.8 ± 6.2	26.5 ± 0.7	46.3 ± 4.0
	THR_{600s} (MJ)	43.5 ± 2.7	31.8 ± 2.1	46.0 ± 1.0	25.5 ± 2.3
	FIGRA (Ws^{-1})	530.3 ± 51.0	217.2 ± 9.4	662.9 ± 0.6	198.6 ± 20.2

Table 2. Mechanical properties of samples.

Sample	Abbreviation / Description	B Reference	B Ca Mineralised	BT Thermally modified	BT Ca Thermally modified and mineralised
Density of oven dry samples (kg/m^3)		595.2 ± 7.4	700.0 ± 23.3	596.9 ± 26.1	633.2 ± 2.6
Porosity of oven dry samples (%)		60.3 ± 0.5	53.3 ± 1.6	60.2 ± 1.7	57.8 ± 0.2
Brinell hardness (MPa)		38.5 ± 3.1	35.5 ± 2.4	35.7 ± 7.1	36.6 ± 4.7
3-point bending	Modulus of elasticity MOE (MPa)	9510 ± 1120	7450 ± 2920	10 000 ± 825	9470 ± 512
	Modulus of rupture MOR (MPa)	141.0 ± 12.2	128.0 ± 17.0	96.6 ± 17.2	86.3 ± 31.2
	Strain at break (%)	1.7 ± 0.4	1.6 ± 0.4	0.79 ± 0.2	0.76 ± 0.3

samples have higher pH values (approx. 8) than the reference beech and TM beech (approx. 5). The increase in the pH value of mineralised wood is attributed to the incorporation of $CaCO_3$, which is basic (pH 9) (Martín-Martínez 2002).

The results obtained in this study (by measuring the pH value on the surface of the samples) show the same trend as presented in our previous study, where the pH values of the hot water extract were measured (Repič *et al*. 2022). In general, it can be seen that the standard deviation is much lower when the pH value of the hot water extract is measured. With both methods, the pH values determined for both the reference and the TM sample are also within the standard deviation of the mean. A slightly more significant difference can be seen in the mineralised samples, as the pH value of the surface is higher than that of the hot water extract. We believe this is due to the higher concentration of alkaline $CaCO_3$ at the surface of the sample. Using both methods, we have shown that the pH value at the surface can differ from the average pH value of the whole sample. We therefore believe that both measurements are important, especially when the material is subjected to surface treatment or adhesive bonding.

Resistance to wood decay fungi

A well-established method for assessing the resistance of wood to decay fungi is to determine the weight loss after 16 weeks of exposure to the specified fungi (CEN 2020a). We selected two fungi, *Gloeophyllum trabeum,* representing brown rot, and *Trametes versicolour,* representing white rot, to investigate the durability of wood samples against fungi. The percentage of mass loss of the samples is shown in Table 1, and the samples after exposure to fungi are shown and compared with the non-degraded samples (on top) in Figures 1 and 2. It should be pointed out that the appearance of samples exposed to fungi can be misleading, as deposits of calcium carbonate and some mycelium are visible on the surface of mineralised samples, but do not represent decay.

In their work Repič *et al*. (2022) established that the maximum mass loss occurred in the reference beech (B), and that the two treatments together provided a synergistic effect against fungal decay, which was particularly pronounced in the case of *Gloeophyllum trabeum* – the mass loss for B was 41.5 ± 2.5%, while after both treatments (BT Ca) it was only 5.7 ± 1.0%.

A similar trend can be observed between the moisture content of the wood and its mass loss. The improved durability

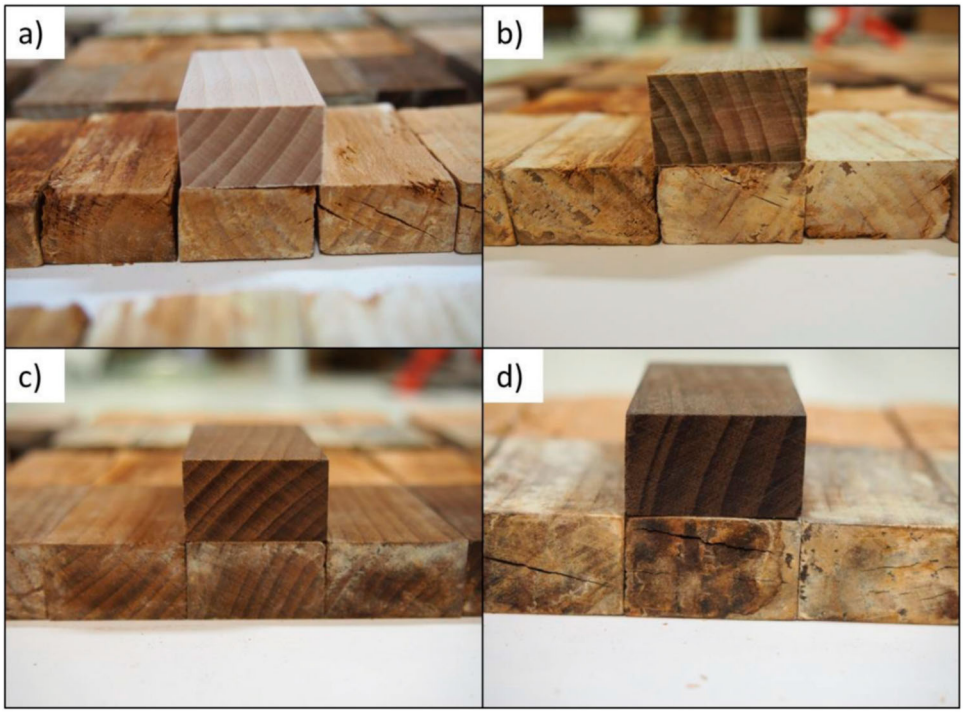

Figure 1. Samples following exposure to *Gloeophyllum trabeum* in a) the reference beech wood, b) the mineralised wood, c) the thermally modified wood, and d) the wood treated using both procedures. The unexposed sample is placed on the top of the degraded samples for comparison.

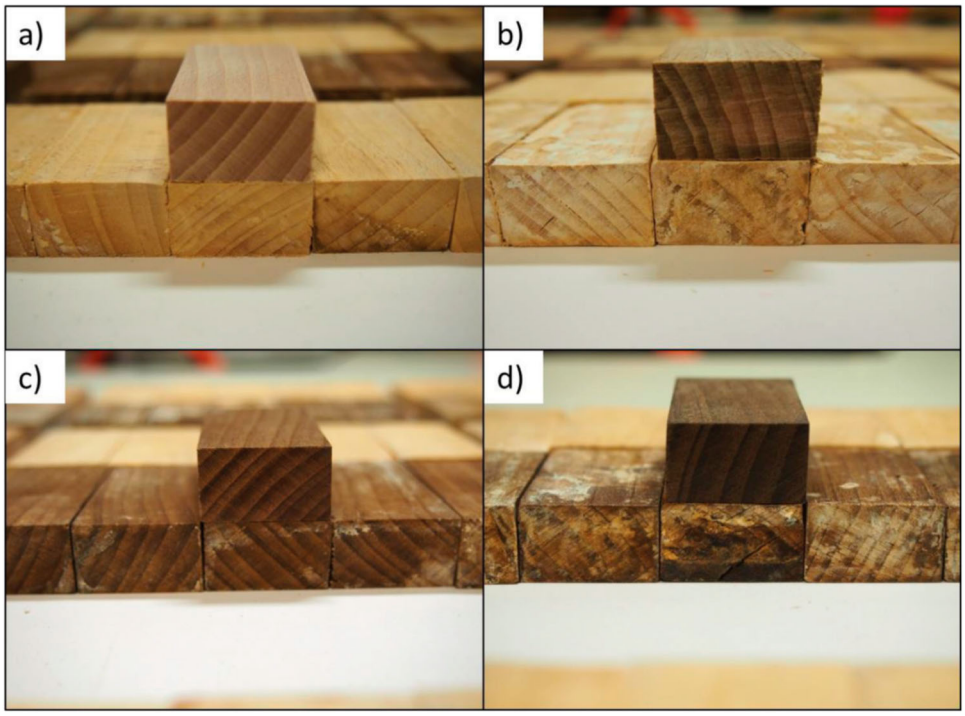

Figure 2. Samples following exposure to Trametes versicolour in a) the reference beech wood, b) the mineralised wood, c) the thermally modified wood, and d) the wood treated using both procedures. The unexposed sample is placed on the top of degraded samples for comparison.

of the mineralised samples could also be attributed to the increased pH values (on average the pH of mineralised beech was 2.5 higher than that of non-mineralised beech). The results of fungal durability were also confirmed by microscopic analysis, described in following chapter.

Microscopic analysis

SEM images of the samples before and after exposure to GT fungi are shown in Figures 3 and 4, respectively. As can be seen in all the images in Figure 3, some cracks occurred, mainly in the cell walls of the fibres and between the ray cells and the axial elements. These cracks are partly attributed to the way in which the samples were prepared, the harsh drying before SEM observation and the vacuum drying of the samples during SEM observation. The main cause of this structural damage is likely to be the surface tension forces of the water during sample drying, although the use of low vacuum settings reduces the likelihood of cracking (Turkulin *et al*. 2005, Das Murtey and Ramasamy 2016). It can be seen by comparing Figures 3 and 4 that the samples have more cracks and distortions after exposure to fungi (Figure 4), which is to be expected, as the samples are degraded. Brown rot fungi caused a thinning of the cell wall and degradation of cellulose (Schmidt 2006). Degraded wood is therefore very brittle and can easily be destroyed during sample preparation.

The epoxy resin used to prepare the samples for SEM analysis filled most of the empty vessels. It did not, however, manage to penetrate all the fibres of the reference beech wood (Figure 3a), which is not surprising given that Zelaya-Lainez *et al*. (2019) found that embedding wood with resin does not necessarily lead to the pores being completely filled. It should be remembered that beech wood belongs to the group of easily treatable wood species; impregnation of wood species such as Norway spruce would, therefore, be even more challenging. Better penetration of the resin was observed in the TM beech, where it penetrated even into the fibres (Figure 3c), which could be ascribed to the degradation of tyloses and new micro cracks in the cell wall resulting from the TM process, as reported by Awoyemi and Jones (2011). It can be concluded that TM has a positive effect on impregnability, presumably due to increased permeability (Zelinka *et al*. 2022). TM was therefore used in the study in question to increase the uptake of mineralising chemicals. This is in line with the results from Bender *et al*. (2022), who found that thermal modification can also have the side effect of increasing impregnability, due to the reduced density of TM wood. The increase in permeability resulting from TM, however, strongly depends on the type of wood species used and the process of thermal modification, predominantly with respect to the modification temperature (Bender *et al*. 2022). It can be seen in Figure 3b and d that the epoxy resin does not fill all the voids in the mineralised sample. The mineralisation could, to some extent, cause a bulking effect, hindering impregnability as the $CaCO_3$ particles become deposited around or distributed within the vessels (Figure 3b and d) (Pondelak *et al*. 2021b). By comparing Figures 3 and 4, it can also be concluded that exposure to fungi generally improved the epoxy impregnability of the samples in this study. This is consistent with the reference data, as fungi can be used to incise the wood prior to impregnation (Thaler *et al*. 2012).

Before fungal exposure, the anatomical characteristics of the reference beech are easily distinguished (vessels, fibres, and parenchyma rays) (Figure 3a). It is known that TM at high temperatures can lead to collapse, longitudinal fractures in the

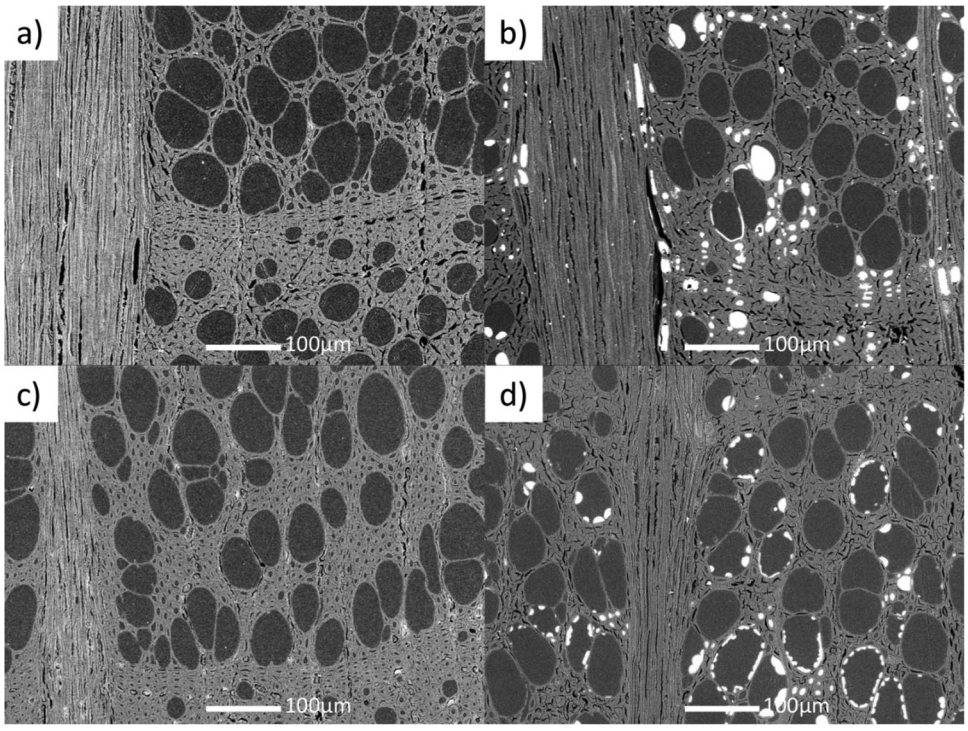

Figure 3. SEM images of the (a) reference beech, (b) mineralised beech, (c) thermally modified beech, and (d) thermally modified and mineralised beech.

vessels, deformation of the fibres, radial cracks and merging of the earlywood vessels (Welzbacher *et al*. 2011). The afore-mentioned degradation processes were not very pronounced in the present study. TM resulted in a thinning of the cell walls (Figure 3c) and opening of the pits, which allows for better impregnability (Awoyemi and Jones 2011).

After mineralisation carbonate crystals are found throughout the sample cross-sections, exactly in vessels, parenchyma rays, and also fibres (Figure 3b and d; Figure 4b and d). The calcium carbonate forms spherical vaterite crystals of varying sizes (Pondelak *et al*. 2021b), which are attached to the cell wall around the perimeter of the vessels or bulk the cross-

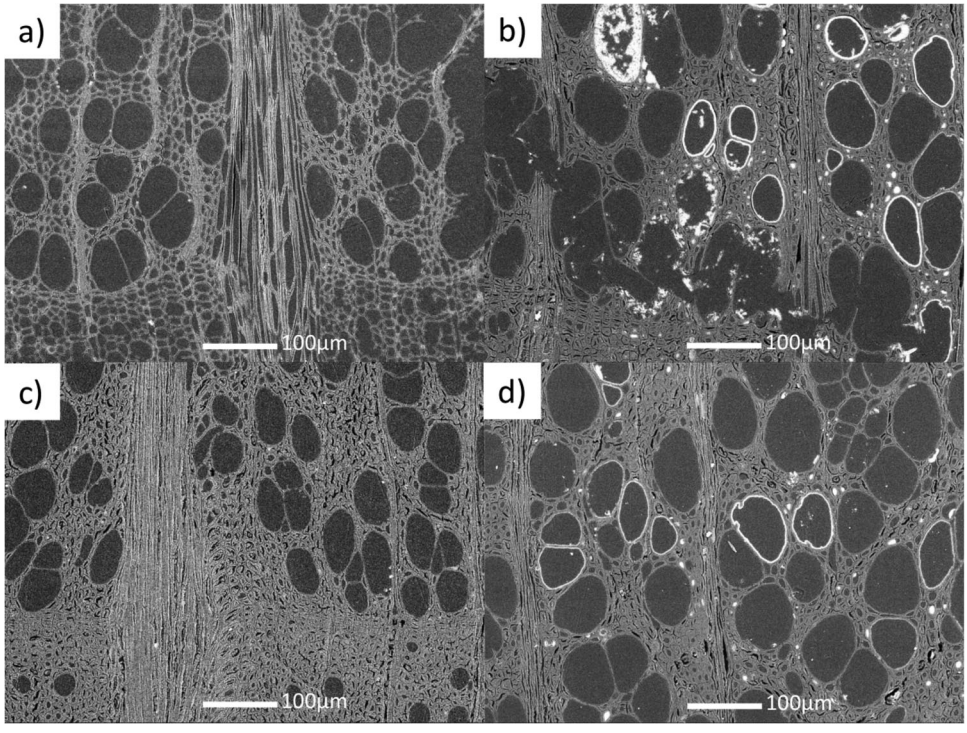

Figure 4. SEM images of samples after exposure to fungi in: (a) the reference beech, (b) the mineralised beech, (c) the thermally modified beech, and (d) the thermally modified and mineralised beech.

section of the cell (Figure 3b and d). It appears that thermal modification has a negligible effect on mineralisation, as the total amount of carbonates incorporated into the wood structure is roughly the same for both the B Ca and BT Ca samples.

Severe degradation of the reference beech sample can be observed following exposure to fungi (Figure 4a). The degradation and thinning of the cell walls can be seen in the axial elements as well as in the parenchyma rays. The most significant reduction is seen in the thickness of the fibre cell wall (Figure 4a). A similar but less pronounced degradation is observed in the TM beech samples, where a stronger deformation of the axial elements is visible (Figure 4c).

The degradation was less pronounced in the mineralised samples. The damage (crack) seen in Figure 4b is not exclusively due to fungal degradation, but was caused during sample preparation. It is clearly visible in the fibre cells that the cell wall of the mineralised sample is thicker than the reference sample, which indicates slower degradation by the fungi. It can be observed (Figure 4b) that the thin cell walls between the vessels are degraded more than the thick cell walls of the fibres. Similar degradation of the thin cell walls can also be observed in the TM sample (Figure 4c). The samples treated with both procedures resulted in the best fungal resistance of all the samples tested (Figure 4d). In these samples, no degradation can be seen in the fibres and minimal degradation can be observed in the thin cell walls of the vessels. It can be concluded that the reference sample was most degraded by fungi (Figure 4a), followed by the TM sample (Figure 4c), while the sample treated with both processes (Figure 4d) performed best, followed by the mineralised sample (Figure 4b).

The crystal structure of the calcium carbonate in the mineralised samples changed from vaterite (Figure 3b and d) to calcium oxalate hydrate (Figure 4b and d) during exposure to fungi and was also translocated. This phenomenon has been described previously by Repič *et al*. (2022) and is attributed to the fungi secreting oxalic acid and precipitating calcium oxalate (Connolly *et al*. 1999, Guggiari *et al*. 2011). This conversion of the crystal structure was not the only difference observed. Figure 4b and d shows that the cell walls of the vessels look as if they are internally lined with carbonates, although initially only spherical particles were found. After 16 weeks of exposure to fungi the characteristic vaterite crystals were nowhere to be found.

Fire properties

Figure 5 shows the heat release profiles during burning from cone calorimeter experiments on all the samples investigated. The ignition times measured and simulation results, THR_{600s} and FIGRA values obtained from the profiles in Figure 5 are further listed in Table 1. The ignition time was evaluated as the time between the beginning of an exposure to radiation and the appearance of a flame. The simulated parameter, THR_{600s}, represents the total heat released in the first 600 s of the test, while the parameter FIGRA is the fire growth rate. Both parameters are crucial for classifying a material's reaction to fire. Materials with lower THR_{600s} and FIGRA values have better fire properties and are subsequently categorised into a better reaction to fire class. A longer ignition time can also be considered as an indicator of improved fire properties.

It can be seen that B and BT burn the fastest and that BT releases more heat during burning, while mineralisation shifts the ignition time and reduces the overall amount of heat released (Figure 5, Table 1). The longest ignition times were measured in samples B Ca and BT Ca (approx. 46 s), which were almost twice as long as those for B and BT samples. Looking at the THR_{600s} values of the samples, it can also be seen that significantly less heat was released when burning the mineralised beech wood compared to the reference or thermally modified beech wood. The lowest heat release occurred in the beech wood treated with both procedures (BT Ca). The same trend can be observed for the fire growth index (FIGRA). Due to the inhibitory effect of moisture on wood burning, the poorer fire properties (shorter ignition time, higher values of THR_{600s} and FIGRA) of BT are attributed to its low equilibrium moisture content (Table 1).

Although only mineralisation was previously shown to significantly improve the fire properties of beech wood (Pondelak *et al*. 2021a, 2021b), the beech wood subjected to the combined processes of thermal modification and mineralisation (BT Ca) showed the best reaction to fire, as reflected in all three parameters studied.

The longest ignition time, the lowest heat released, and the lowest FIGRA were all found in the BT Ca wood. All parameters investigated were significantly improved compared to the reference wood; ignition time was prolonged by approximately 17 s, while THR600s was reduced by approximately 18 MJ and FIGRA by approximately 331 Ws^{-1}. Mineralisation and thermal modification therefore have a combined or even synergistic effect on improving the fire properties of beech wood. It can be concluded that, with respect to the fire properties of the wood, mineralisation is more efficient on thermally modified wood than it is on unmodified wood.

Mechanical properties

Table 2 shows the density and porosity measurements of the oven dry samples and the mechanical properties of the materials tested. As can immediately be seen from Table 2, the density of the mineralised wood is higher than that of the reference or TM wood. The densities of B and BT were approx. 595 kg/m^3, while B Ca and BT Ca have higher density. The higher or comparable density of B and BT is in part due to the variability of the wood. In addition, after TM, there is often more shrinkage as the OH groups are more tightly connected. As the dimensions decrease, the wood density often increases in beech wood (Humar *et al*. 2020). It can be concluded that the porosity of the wood is reduced by mineralisation (Table 2). The density measured in the reference samples is in accordance with data for beech wood previously published by Fengel and Wegener (1984) (490–880 kg/m^3).

One might expect that mineralisation would increase the hardness of the wood, but this effect was not particularly significant (Table 2). The highest hardness was found in the reference sample (approx. 38.5 MPa), while mineralisation and thermal modification slightly decreased the hardness of the wood to approx. 35.5 MPa, and a very similar hardness was

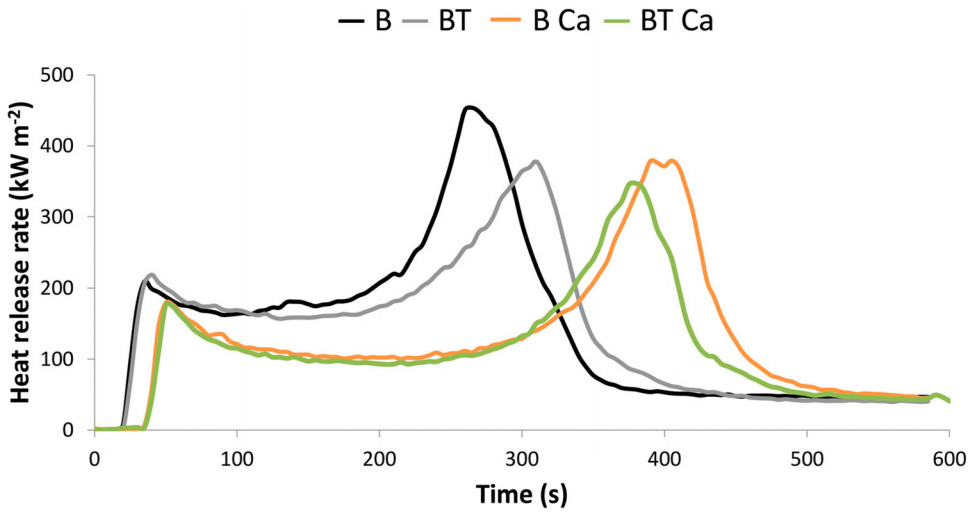

Figure 5. Heat release profiles of the reference beech (B), thermally modified beech (BT), mineralised beech (B Ca) and beech modified by both methods (BT Ca), as determined by cone calorimetry; the respective curves represent the average of five samples.

measured in the samples treated by both processes. Lower hardness values after thermal modification compared to the reference were also reported by Sedlar *et al.* (2019). It should be noted that the difference in hardness values are all within the standard deviation of the mean. The hardness of the reference sample measured in this study is slightly higher than that measured by Beqo *et al.* (2015) (27.7–33.4 MPa) and Wagenführ (2007) (34 MPa), but is within the range specified in the standard (28–41 MPa) (CEN 2020c) for reference beech wood.

The modulus of elasticity (MOE), the modulus of rupture (MOR) and the strain at break for each of the samples are also listed in Table 2. The modulus of elasticity is comparable in samples B and BT (approx. 10 000 MPa), while the mineralised samples have a slightly lower modulus of elasticity (B Ca = 7450 ± 2920 MPa and BT Ca = 9470 ± 512 MPa), but the results are all within standard deviations of the mean. The MOE values for the reference beech wood are in line with the results published by Badescu (2013). Similarly, the modulus of rupture also decreased following all types of modification. The MOR was highest in the reference (B) sample, but decreased slightly following mineralisation (B Ca). MOR also varies greatly according to the sample itself. Gašparik and Gaff (2015) reported that the MOR ranges from about 140 MPa to 175 MPa in reference beech, while Badescu (2013) found values between 77 and 115 MPa. It is evident that the thermal modification also significantly lowers the modulus of rupture, with similar results having been reported previously by Arnold (2010). We can conclude that both methods of modification influence the mechanical properties of the wood.

Conclusion

This study has demonstrated the combined effect of two discrete modification methods, thermal modification and mineralisation with soluble calcium compounds, which were combined to improve the reaction to fire and biological durability of European beech wood (*Fagus sylvatica*). Although only mineralisation significantly improves beech wood's reaction to fire, the best response to fire was achieved by combining the two processes. The best results regarding fire properties were found in wood treated by both processes. All parameters investigated were significantly improved compared to the reference wood; ignition time was considerably prolonged while total heat released and fire growth rate index were considerably reduced. A similar combined effect of the two processes was also observed with respect to the wood's fungal durability. Improving fire performance helps to increase the use of wood in buildings. Regarding findings in this study the potential use of modified wood has been suggested: as an internal floor or wall panelling or as an external building envelope or cladding, since its durability is improved as well. However, large-scale tests are definitely needed in this area to determine the behaviour of this material in a real-life application.

Furthermore, the effect of the combination of the two modification processes on the mechanical properties was also considered, which is particularly important when modified wood would be used for structural purposes. Results from the Brinell hardness and 3-point bending tests showed that both modification processes can impair the mechanical properties of the wood. There was little difference in the hardness and modulus of elasticity between the reference beech wood and that modified by both processes, while the modulus of rupture appears to be significantly reduced after all types of modification. More research is needed in the area of mechanical properties before suggested modified wood can be used for structural purposes. In particular, it would be useful to identify the reasons for the deterioration in mechanical properties of mineralised wood and their impact at a broader scale rather than just at laboratory level.

Based on the favourable fire properties, the improved resistance to decay fungi and the ecological acceptability of the two modification methods applied (mineralisation and thermal modification), it can be concluded that such wood-inorganic composites have great potential for use in a variety of non-structural applications.

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Author contributions

Conceptualisation: RR, AP, ASŠ; Data curation: RR, MH. NK, AP; Formal analysis: RR, MH, NK, DK; Funding acquisition: MH, ASŠ; Investigation: RR, AP, DK, NK; Methodology: MH, FK, DK; Project administration: ASŠ; Resources: ASŠ, MH; Supervision: ASŠ, MH; Validation: AP, DK, MH, ASŠ, FK, NK; Visualisation: RR, AP; Writing – original draft: RR; Writing – review & editing: RR, AP, DK, MH, ASŠ, FK, NK.

Disclosure statement

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