SUPPORTING INFORMATION

Improvement of flame retardancy of wood using an eco-friendly mineralization process

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Experimental section

Mineralization of beech. The European beech wood used in this work was *Fagus sylvatica* from Slovenia. Beech wood, without visual defects was cut into specimens of size (140×100×10) mm^3 (for SEM, µCT, XRD, FT-IR spectroscopy, TG/DTA and cone calorimetry) and (500x50x25) mm^3 (for moisture content). The penetration in the grain direction was prevented by coating based on epoxy resin. Before impregnation specimens were stored in climate chamber (23 °C ± 2 °C and 50% RH ± 5%) until the constant mass was achieved. Specimens were vacuum/pressure impregnated in four steps process with 20 wt.% water solution of calcium acetoacetate – $Ca(OAcAc)_2$ (corresponding to 8.3 wt.% of theoretically formed $CaCO_3$), where solution was poured directly on the beech specimens. The synthesis of calcium acetoacetate is fully described elsewhere [1]. In the 1st step, the specimens were exposed 30 minutes to 50-60 mbar vacuum, then pressure was reduced to normal. In the 2nd step specimens were exposed to a pressure of 8-10 bars for 3 hour. In 3rd step specimens were 30 minutes exposed to vacuum (50-60 mbar) in order to remove excess of the impregnation solution. In 4th step the impregnated beech wood were dried 3 days at room temperature and then placed into a chamber with constant elevated temperature (80 °C) and relative humidity fluctuations (40% and 90%). Drying process lasted 56 hours: 7 cycles, where the program of cycle was 4 hours at 80 °C and 90% RH and 4 hours at 80 °C and 40% RH. Elevated temperature accelerates the conversion of $Ca(OAcAc)_2$ to $CaCO_3$, where fluctuations in humidity was used to obtain vaterite modification [2]. It was found[2] that the stable vaterite was formed only when exposed to the highest RH. Exposing $Ca(OAcAc)_2$ to lower RH lead to much more soluble amorphous $CaCO_3$ formation [2,3]. For this reason, the vaterite crystal modification was targeted. Before the characterization mineralized beech specimens were maintained for at least 7 days at room temperature; the epoxy resin was cut out and specimens with appropriate dimensions were prepared as described in each method below.

Penetration depth (indicator method). The penetration depth of $Ca(OAcAc)_2$ was determined by applying indicator sodium nitroprusside, $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ (5% water solution; Sigma Aldrich) on the cross section of impregnated beech specimens, the size of (140×100×10) mm^3(before testing specimens were dried for three days at RT). In parallel, the indicator was also applied on native (i.e. reference, non-treated) beech. In the period of few minutes the red colour appeared resulting from the reaction of acetoacetate with nitroprusside [4]. Additional information are available in paper by Ropret et al. [4].

Scanning electron microscopy (SEM). The morphology of mineralized beech and the size of formed $CaCO_3$ particles were investigated using SEM (JEOL JSM-IT500LV, Japan) with EDS analyser (Oxford Instruments) and FE-SEM (Zeiss ULTRA plus) equipped with an energy-dispersive spectrometer (EDXS, Oxford Instruments). Mineralized beech specimens, of approximately (10 x 10 x 10) mm^3, were cut from bigger pieces, vacuum impregnated by epoxy resin and polished to granulation 6000 grit. Oven dried specimens were placed on double sided carbon tape with no additional coating prior examination. SEM images were performed in a low-vacuum mode; 10 kV electron acceleration, a working distance of 10 mm and a Backscattered electron detector were used. For FE-SEM EDS analysis an InLens detector was used with 20 kV electron acceleration. The samples were placed on double sided carbon tape and additionally Pt-coated prior to examination using Gatan, PECS, Model 682. The thickness of Pt coating was 3 nm.

X-ray micro-computed tomographic imaging (µCT). Distribution, the shape and size of incorporated $CaCO_3$ particles inside beech were examined by Xradia µCT-400" tomograph (XRadia, Concord, California, USA). By using a 20X magnification optical objective, a working voltage of 40 kV, energy of 125 µA and a spatial resolution of 0.88 µm, 3D images were obtained. Specimen with a length of approximately 40 mm and diameter of approximately 2 mm, was cut at the edge of larger piece. The regions of interest (ROI) were selected in the centre of rounded sample. The projection data for each tomographic scan consisted of 1600 projection images, which were taken from different view-points with exposure times of 30 s per projection. These images were reconstructed into 3D tomographic volumes using Avizo Fire 3D-image analysis software. The segmentation procedure and quantification for the particle size determination was performed by using Avizo Fire 3D-image analysis software.

X-ray powder diffraction (XRD). Identification of crystal modification of formed $CaCO_3$ were performed on specimens with dimensions (10x10x3) mm^3, by using D4 Endeavor, Bruker AXS with Cu Kα radiation (λ = 0.154 nm) and Sol-X detector. The 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.

Fourier Transform Infrared (FTIR) spectroscopy. The formed $CaCO_3$ phases was analysed using FT-IR spectroscopy. FT-IR spectra were recorded with Pelkin Elmer Spectrum 100 FT-IR spectrophotometer in the region 4000-375 cm^{-1}, with a spectral resolution of 4 cm^{-1} and 16 scans. Spectra were acquired in ATR mode by placing small amount of bulk sample directly on the ATR crystal.

Thermogravimetric analysis (TG). Measurements were performed using a Netzsch STA 409 instrument (Germany) from room temperature up to 1000°C, at a heating rate of 10°C/min. Samples with an initial mass of approximatelly 100 mg were placed in Al_2O_3 crucibles. During the measurements, the furnace was purged by means of a synthetic air flow at a rate of 20 mL/min. Weight loss from 25°C to 1000 °C were determined using the Netzsch Proteus Thermal Analysis software (version 5.2.0). Results of weight loss are the average of 5 measurements per each wood sample. Each specimen was conditioned before the measurements at 23 °C ± 2 °C and 50% RH ± 5%.

Cone Calorimeter Test (cone calorimetry). The reaction to fire performance parameters of native and mineralized beech samples were measured with cone calorimeter (Fire Testing Technologies, UK). The two simulated parameters total heat release in the first 600 s of the test (THR_{600s}) and fire growth index (FIGRA) were calculated using ConeTools developed at SP Swedish National Testing and Research Institute.[5] Specimens were cut into the size (100x100x10) mm^3. The experiments were based on ISO 5660-1 with the incident heat flux of 50 kW/m^2. Cone data are the average values of measurements of 5 parallels. In order to evaluate potential change of fire characteristics, in particular reaction to fire caused by mineralization of wood, SBI parameters were simulated with ConeTools software and compared with the parameters of non-treated wood.

Moisture content (MC). Native and mineralized beech specimens were oven-dried at 103 °C ± 2 °C to constant mass (absolute dry) and stored in climate chamber (23 °C ± 2 °C and 50% RH ± 5%) until the constant mass is achieved (equilibrium moisture content)MC are determined gravimetrically as the difference between the masses of absolute dry sample and sample with equilibrium moisture content. Results are the average of 2 specimens.

Scanning electron microscopy

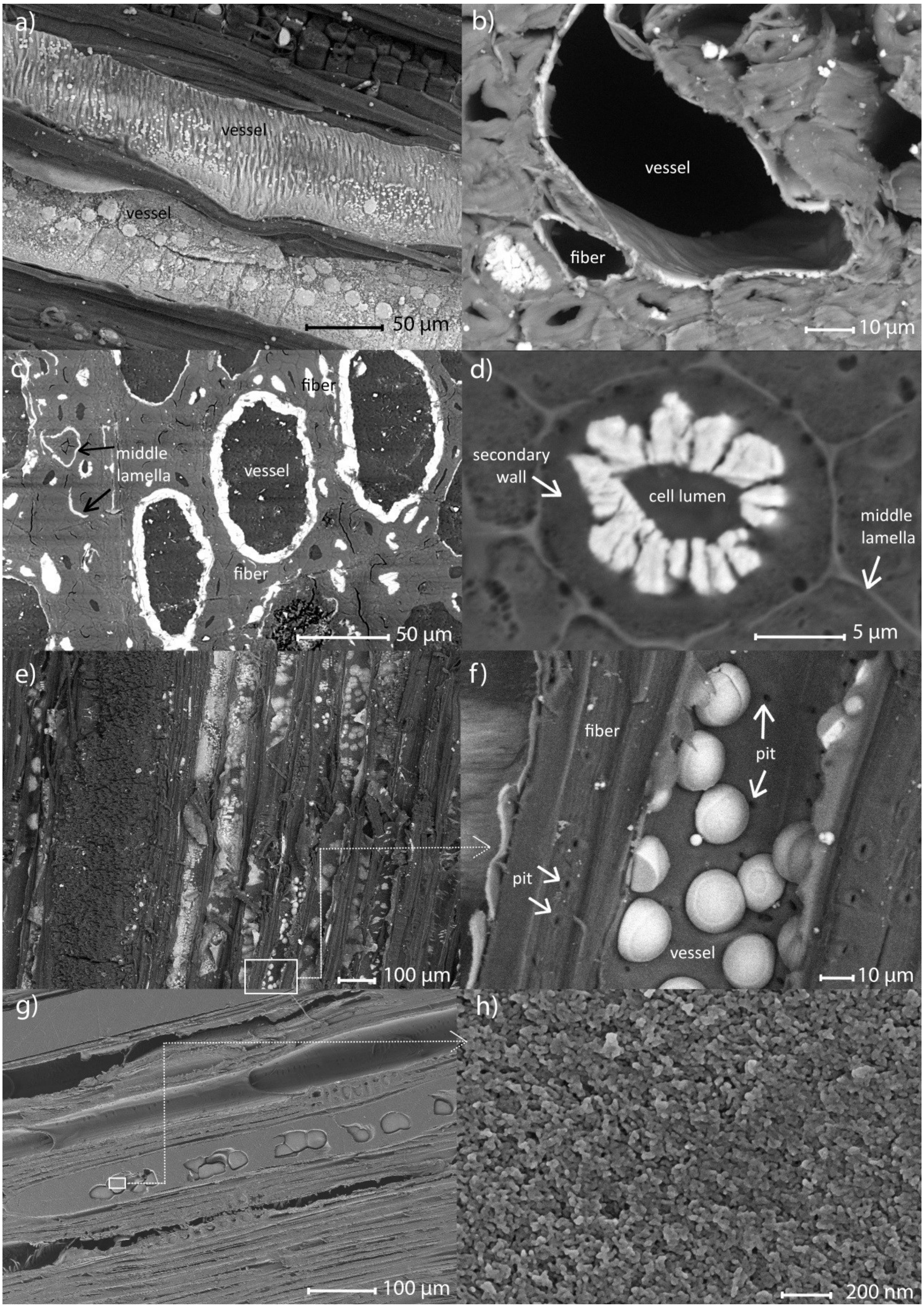

Fig. S1: SEM images of mineralized beech: in longitudinal (a, e, f, g, h) and radial (b, c, d) direction. $CaCO_3$ is distributed around the vessels in the form of spheres (a, b, c) e, f) with radius between 3 µm and 20 µm, inside and around fibres (b, c, d); in the middle lamella (c) and in the pits (f). The image (h) shows the vaterite nanoparticles with the size between 13 nm to 30 nm.

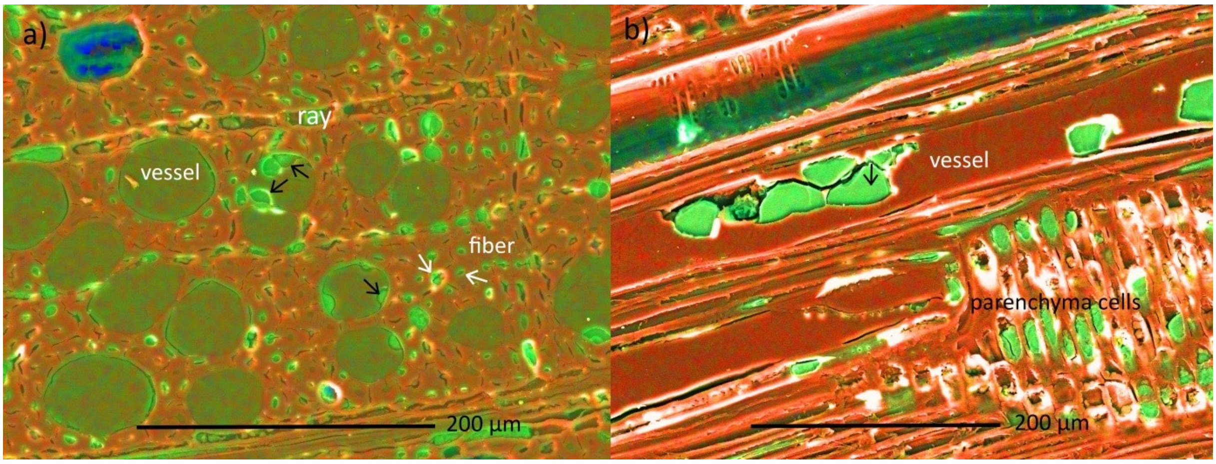

Fig. S2: EDS analysis of mineralized beech: a) in longitudinal and b) radial direction where green areas represent calcium reach areas.

Discussion about bonding of impregnation substances with wood components

Pectin is found in: a) the membranes in the boarded pits between wood cells, b) the middle lamella and c) high concentration in the parenchyma cell walls[6], where adsorption of Ca^{2+} could interact with the negatively charged surfaces of wood components[7]. On the other hand, hydrogen bonding can be established between $(OAcAc)^-$ and hydroxyl rich groups, on the lumen surface of the S3 layer, rich in hemicelluloses and cellulose [5].

Cone calorimetry

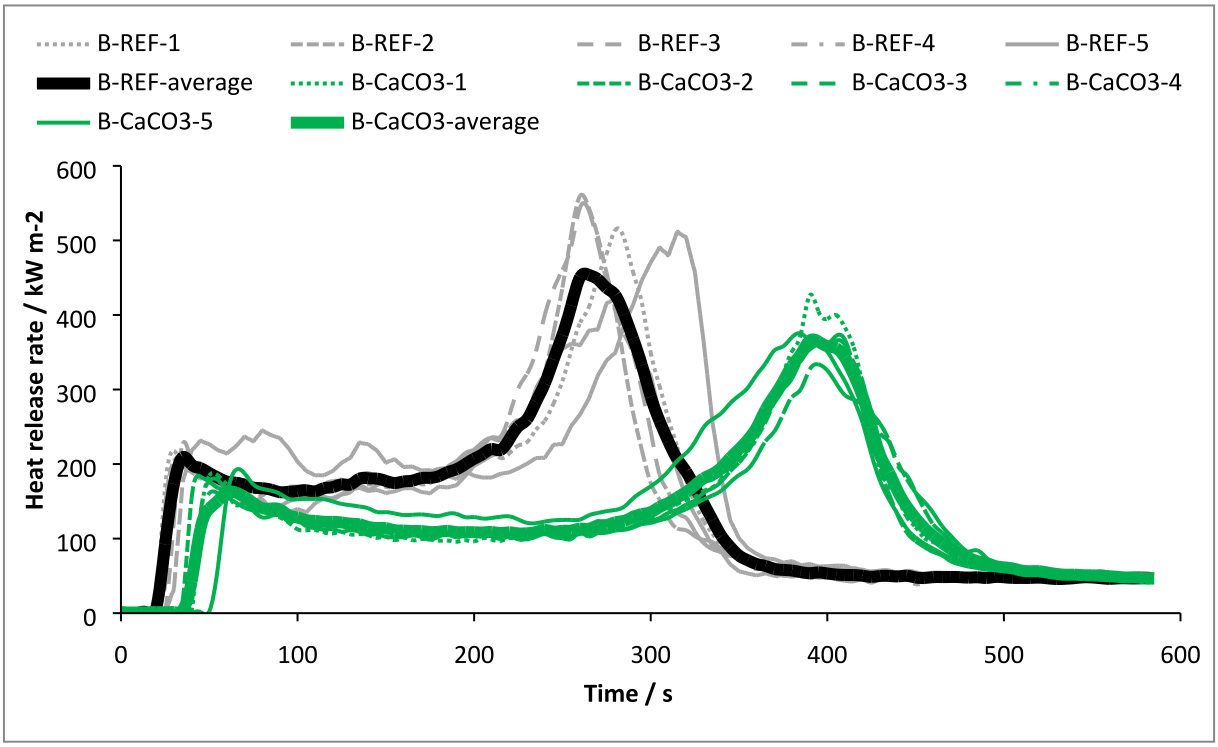

Fig. S3: Raw data of heat release profiles of a native beech (black curves) and beech mineralized by $CaCO_3$ (green curves) for all five specimens.

Thermogravimetric analysis

Table S1: The moisture content (MC) of the native and mineralized beech determined gravimetrically (marked with ^{a}) and the mass of inserted $CaCO_3$, determined by means of TG-DTA (marked with ^{b}). The raw TG data using for calculation of the weight loss of the native and mineralized beech by program Netzsch Proteus Thermal Analysis software are shown in Fig. S4.

	Native beech	**$CaCO_3$ beech**	**Difference (%)**
MC (%)^a	7.8 ± 0.1	9.3 ± 0.9	+2
$\Delta m_{25\text{-}1000\ °C}$ (%) ^{b}	99.0 ± 0.9	94.9 ± 0.7	-4
m_{CaCO3} (%) ^{b}	/	7.4 ± 1.3	/

The mass of $CaCO_3$ inside wood was calculated from the difference in total weight losses ($\Delta m_{25\text{-}1000\ °C}$) between native and mineralized beech, according the reaction of thermal decomposition of $CaCO_3$ (1). CaO is formed when mineralized wood is heated to 1000 °C. The equation (1) indicates that one mole of CaO is generated for each mole of $CaCO_3$ that decomposes. Using equation (2), formed $CaCO_3$ can be calculated.

$$CaCO_3(s) \longrightarrow CaO\ (s) + CO_2(g) \tag{1}$$

$$m_{CaCO3} = \frac{M_{CaCO3} * m_{CaO}}{m_{CaO}} \tag{2}$$

Please note that calculations of the amount of inserted $CaCO_3$ were simplified by taking into account that the amount of ash in mineralized beech is the same as in the native beech, which is about 1%. Similar amount of ash (0.92%) was obtained by heating the beech wood in the research paper by Boukaous et.at[8].

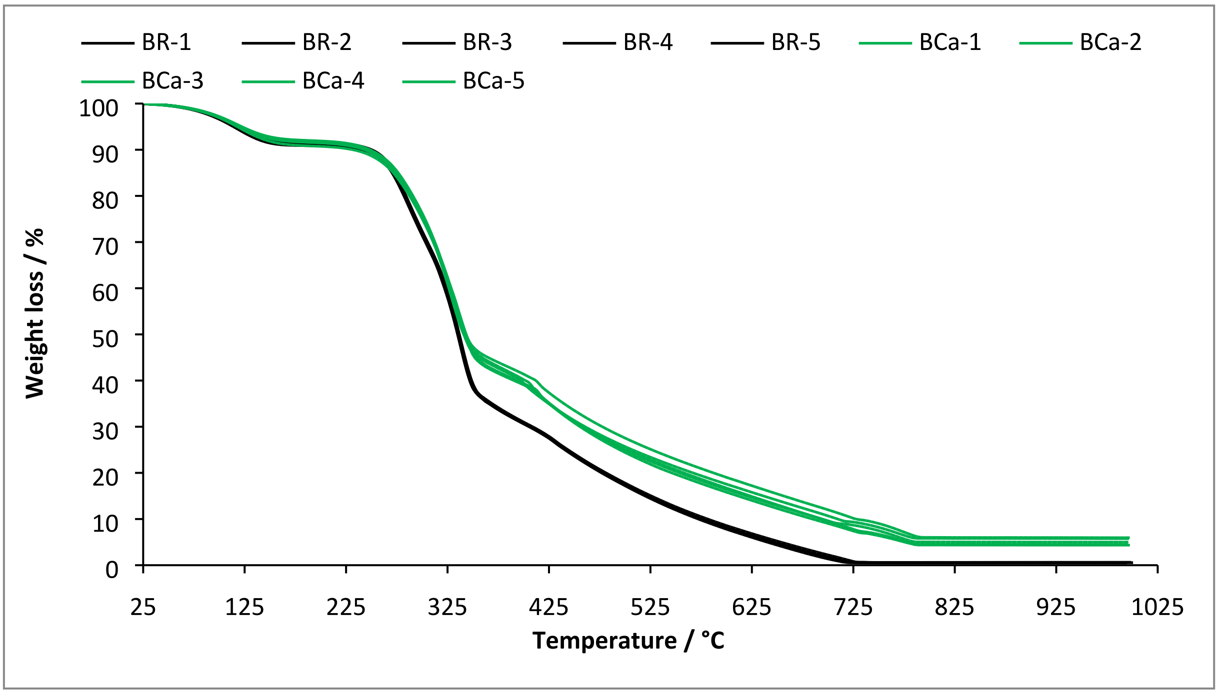

Fig. S4: Mass loss (%) of native beech (black curves) and beech mineralized by $CaCO_3$ (green curves) determined by TG analysis.

References

1 L. Škrlep, A. Pondelak, A. Sever Škapin, EU Pat., 3004028, 2014.

2 A. Pondelak, F. Rosi, C. Maurich, C. Miliani, S. Škapin, A. Sever-Škapin, *Appl.Surf. Sci.,* 2020, 506, 144768.

3 I. C. Mayorga, J. M. Astilleros, L. Fernandez-Diaz, *Minerals,* 2019, **9**, 178.

4 P. Ropret, L. Legan, K. Retko, T. Špec, A. Pondelak, L. Škrlep and A. Sever Škapin, *J. Cult. Herit.,* 2016, **23**, 158-156

5 Björn Sundström, Doctoral dissertation, Lund Institute of Technology, 2007.

6 R. Rowell, R. Pettersen, J. Han, J. Rowell, M. Tshabalala, *Cell wall chemistry: Handbook of wood chemistry and wood composites*, CRC Press, Boca Raton; Florida, 2005, pp. 35-74.

7 V. Merk, M. Chanana, T. Keplinger, S. Gaan and I. Burgert, *Green Chem.,* 2015, **17**, 1423-1428.

8 N. Boukaous, L. Abdelouahed, M. Chikhi, Ab. H. Meniai, C.Mohabeer and T. Bechara, *Energies*, 2018, **11**, 2146.