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(54) **A PROCESS OF WOOD MINERALIZATION USING ACETOACETATE SOLUTIONS TO IMPROVE THE ESSENTIAL PROPERTIES OF WOOD**

VERFAHREN ZUR HOLZMINERALISIERUNG UNTER VERWENDUNG VON ACETOACETATLÖSUNGEN ZUR VERBESSERUNG DER WESENTLICHEN EIGENSCHAFTEN VON HOLZ

PROCÉDÉ DE MINÉRALISATION DU BOIS FAISANT APPEL À DES SOLUTIONS D'ACÉTOACÉTATE POUR AMÉLIORER LES PROPRIÉTÉS ESSENTIELLES DU BOIS

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Description

Field of the invention

[0001] The invention presented relates to the field of wood modification, specifically to the mineralization of wood i.e. the incorporation of $CaCO_3$, $MgCO_3$, $SrCO_3$ into the structure of the wood, and methods for such mineralization.

Background of the invention

[0002] The combustibility and flammability of wood is a threatening problem which represents a major challenge in the use of wood and wood products in load-bearing structures, as non-load-bearing cladding material, in furniture, and for other uses. Several approaches have been proposed to reduce the flammability of wood i.e. to improve its reaction to fire. These include the addition of flame-retardants (FRs), chemical modification using conventional FRs, the development of wood-inorganic composites, and the application of FR coatings. Compounds used as FR may be nitrogen, phosphorus, boric acid and borax compounds, inorganic salts such as borates, stannates and silicates, and aluminum and magnesium based minerals. The main disadvantage of using some of these compounds is that they release toxic and carcinogenic compounds (i.e. halogenated FRs) when they burn, or they produce smoke and carbon monoxide (i.e. phosphorus-based inhibitors). Their use is therefore strictly controlled, regulated by law, and increasingly restricted. In contrast, mineral fillers, such as calcium carbonate ($CaCO_3$), are not controversial in terms of their environmental impact and are therefore considered "green" flame retardants.

[0003] Some processes for incorporating $CaCO_3$ into the structure of wood (i.e. wood mineralization) in order to reduce its flammability, increase hydrophobicity, and improve mechanical properties, are already known. One such wood mineralization process is the *in-situ* formation of $CaCO_3$, achieved by immersing the wood in an aqueous $CaCl_2$ solution for 1 hour, then in an aqueous NaOH solution for 1 hour, and finally in supercritical CO_2 in a high pressure vessel for 1 hour. The result of the process is reduced flammability of the wood (*C. Tsioptsias, C. Panayiotou, Thermal stability and hydrophobicity enhancement of wood through impregnation with aqueous solutions and supercritical carbon dioxide:* Journal of Materials Science, 2011, vol. 46 (16), pp. 5406-5411*).* Another procedure involves the double diffusion method. In this method, the wood is immersed in a solution of Na_2CO_3 for 24 hours and then for a further 24 hours in a solution of $CaCl_2$ with added methanol and dodecanoic acid. Finally, the wood is washed with distilled water and ethanol. Mineralized wood prepared using this method is hydrophobic and leads to improved mechanical properties (C. Wang, C. Liu, J. Li, Preparation of Hydrophobic CaCO3 - Wood Composite In Situ: Advanced Materials Research, 113-116, 2010, pp. 1712-1715*).* A common challenge in the methods described above is incorporating the $CaCO_3$ deep into the structure of the wood, as $CaCO_3$ is negligibly soluble in water. Incorporating $CaCO_3$ deep into the cellular structure of wood is possible through in-situ alkaline hydrolysis of dimethyl carbonate, which serves as a source of "liquid" CO_2 (V. Merk, M. Chanana, T. Keplinger, S, Gaan, I. Burgert, Hybrid wood materials with improved fire retardance by bio-inspired mineralization at the nano- and submicron level, Green Chemistry, 17 (3) 2015, pp. 1423-1428 *in* I. Burger, M. Chanana, V. Merk, US Pat. 0043497 A1, 2017*).* Following this process, mineralized wood shows a relatively high increase in mass (up to 20%), improved durability and mechanical properties (e.g. hardness), and increased resistance to fire, with a reduced water uptake. A review of the literature shows that the most efficient wood mineralization process with an improved resistance to fire was performed by Merk et al. (V. Merk, M. Chanana, S. Gaan, I. Burgert, Mineralization of wood by calcium carbonate insertion for improved flame retardancy, Holzforschung, 70 (9) 2016, pp. 867-876*)* through the in-situ formation of $CaCO_3$, predominantly within the wood lumina and to a lesser extent in the adjacent cell walls. In this case mineralization was achieved by vacuum impregnation of wood, using an aqueous solution of $NaHCO_3$ and alcoholic $CaCl_2$. The impregnation process can take varying lengths of time (a shorter reaction cycle lasts 2 hours, a longer one 24 hours), and consists of one or more (of up to 4) cycles. As the cycle length, or the number of reaction cycles increases, so does the mass of $CaCO_3$ introduced and consequently the total mass of the wood increases. Using 24-hour cycles, for example, the mass of a piece of spruce was shown to increase by 20% after one cycle and by approximately 35% following 3 cycles (I. Burger, M. Chanana, V. Merk, U.S. Pat. 0043497 A1, 2017).

[0004] The main disadvantage of the above-mentioned methods of wood mineralization is the formation of by-products (i.e. NaCl), which can affect the appearance of wood and can also corrode metal elements (e.g. binders), which are often embedded in wood and wooden products. In the case of the process of alkaline hydrolysis of dimethyl carbonate, in addition to NaCl, toxic methanol is formed. Furthermore, the procedure is time consuming, as it takes place in two stages, with one cycle lasting several hours (up to 24 hours), and there is a need to use repeated cycles (up to 4 times). Finally, the wood needs to be washed several times to remove the by-product, i.e. NaCl.

[0005] Relevant prior art can for example be found in documents JP6368939 and JPS63159008.

Technical problem

[0006] Technical problem solved by the proposed invention is mineralization of wood or wood composites with carbonates in a simpler and more efficient way, in order to improve the essential properties of wood and wood composites, i.e. resistance to fire, durability and mechanical properties. The definition of wood and wood composites includes wood of any moisture content, for example freshly-cut wood, wood at the fiber saturation point, air-dried, or absolutely dry wood, wood of any tree species, and wood subjected to any type of fiber pre-treatment, such as thermally-modified wood or wood previously exposed to ultrasound, used wood or wood composites. Through the process of mineralization, i.e. the transformation of organic matter to inorganic, the wood improves its resistance to fire, resistance to fungi, mechanical properties, durability and other properties. In this document, the term 'reference wood' will be used to represent any wood that has not been treated or modified, and will be used for comparison with the modified wood (that which has been mineralized or thermally modified or treated in some other way). In the document, the term 'thermally modified wood' is used to describe wood prepared by the commercial Silvapro® process (G. Rep, F. Pohleven in S. Kosmerl, Wood modification - A promising method for wood preservation, Proceedings of the 6th European Conference on Wood Modification, University of Ljubljana, Slovenia, str. 11-17, 2012*).* In the process of thermal modification, spruce and beech were heated to 220 ° C, then the wood was conditioned for 4 weeks under laboratory conditions (T = 20 ° C; RH = 65%).

[0007] Wood mineralization takes place in two phases - namely, in the first phase, the wood is impregnated with an impregnating solution, an aqueous solution of acetoacetates, with one of the known impregnation methods (the most commonly used impregnation method involves exposing wood to an impregnating solution in an environment with varying vacuum and overpressure) so that the impregnating solution penetrates deep into the structure of the wood. The process of changing vacuum and overpressure generally results in the best impregnation properties (i.e. a more homogeneous distribution, deeper penetration, and greater absorption of the impregnating solution into the wood; H. Yorur, K. Kayahan, Improving impregnation and penetration properties of refractory woods through cryogenic treatment, BioResources. 13 (1) 2018, pp. 1829-1842*).* This process is followed by an after-treatment step, where the impregnating solution is transformed to carbonate. The advantage of the mineralization process proposed, over and above the methods used to date as described above, is that carbonate(s) are formed only when the impregnating solution penetrates deep into the structure of wood or wood composites by means of a known impregnation method.

Description of the solution to the technical problem

[0008] The invention will be described below, and is also presented in the following figures:

Figure 1 shows the penetration depth of the impregnating solution in the spruce, both in the direction of the fibers and perpendicular to the fibers
Figure 2 shows SEM images of $MgCO_3$ (a, b) and $CaCO_3$ (c, d) mineralized spruce
Figure 3 shows microtomographic images of $MgCO_3$ (a, b) and $CaCO_3$ (c, d) mineralized beech, either transversely (a, c) or longitudinally (b, d)
Figure 4 shows diffractograms of reference spruce samples (a), $CaCO_3$ mineralized spruce (b), reference beech (c) and $CaCO_3$ mineralized beech (d)
Figure 5 shows the heat release rate (HRR) of reference spruce and $MgCO_3$ mineralized spruce
Figure 6 shows the heat release rate (HRR) of reference spruce, thermally modified spruce, $MgCO_3$ mineralized spruce and spruce which has been thermally modified and then mineralized with $MgCO_3$
Figure 7 shows the heat release rate (HRR) of reference beech and beech mineralized either once or twice with $MgCO_3$
Figure 8 shows the heat release rate (HRR) of reference beech, and beech mineralized with $MgCO_3$, $CaCO_3$ and $SrCO_3$
Figure 9 shows the heat release rate (HRR) of reference beech, beech mineralized with $CaCO_3$, beech mineralized with $MgCO_3$, and beech mineralized with a mixture of $CaCO_3$ and $MgCO_3$ in a 50 : 50 weight ratio
Figure 10 shows the heat release rate (HRR) of the reference beech, beech mineralized with $SrCO_3$ or $MgCO_3$, and beech mineralized with a mixture of $SrCO_3$ and $MgCO_3$ in a 50 : 50 weight ratio
Figure 11 shows the heat release rate (HRR) of reference beech, thermally modified beech, beech mineralized with $CaCO_3$, and thermally modified beech mineralized with $CaCO_3$
Figure 12 shows the smoke growth rate index (SMOGRA) of reference beech and beech mineralized with $CaCO_3$
Figure 13 shows the contact angle for the reference spruce (a) and spruce samples mineralized with $CaCO_3$ (b) and $MgCO_3$ (c)
Figure 14 shows loss of mass from decomposition as a result of the presence of three different fungi *Gloeophyllum trabeum* (GT), *Poria Monticola* (PM) and *Trametes versicolor* (TV) in the reference samples (R), $CaCO_3$ mineralized

samples (Ca), thermally modified samples (T) and thermally modified $CaCO_3$ mineralized (TCa) samples for both spruce and beech

Figure 15 shows the Brinell hardness of the reference (R), $CaCO_3$ mineralized (Ca), thermally modified (T), and thermally modified $CaCO_3$ mineralized (TCa) spruce samples

[0009] The wood mineralization process according to the invention comprises the following phases:

- an impregnation phase, wherein the wood is with the use of vacuum and/or overpressure impregnated with an impregnating agent, which is a solution of at least one metal beta carboxylate or a mixture of different metal beta carboxylates in a solvent, wherein the concentration of metal beta carboxylate or a mixture of different metal beta carboxylates in the solvent is up to 30% by weight and whereby the impregnating agent penetrates deep into the structure of the wood;
- an after-treatment phase of the impregnated wood, whereby by regulating the temperature, humidity and exposure time of the impregnated wood to these conditions or by exposing the impregnated wood to ultrasound the metal beta-carboxylate is converted into carbonate(s).

[0010] The metal beta-carboxylate is a metal acetoacetate selected from calcium acetoacetate $Ca(OAcAc)_2$, magnesium acetoacetate $Mg(OAcAc)_2$ orstrontium acetoacetate $Sr(OAcAc)_2$, or mixtures thereof in any weight ratio.

[0011] The solvent is water, and the metal acetoacetate solution is selected from aqueous solutions of calcium acetoacetate $Ca(OAcAc)_2$, magnesium acetoacetate $Mg(OAcAc)_2$ or strontium acetoacetate $Sr(OAcAc)_2$ or mixtures thereof in any weight ratio. The process of impregnation using vacuum and/or overpressure involves impregnation of the wood using either the "full-" or "empty-" cell process. In the process of the "full" cell method, or the so-called "Bethell process", the wood is placed in an impregnation chamber and exposed to a vacuum below 100 mbar for a period of 30 to 60 minutes to remove air from the wood and impregnation chamber. The impregnating solution is then poured into the chamber while maintaining a constant vacuum. This is followed by exposure to a overpressure of above 10 bar, causing the impregnation solution to penetrate deep into the structure of the wood. Preferably, the wood is exposed to an overpressure above 10 bar for at least 180 minutes. Optionally, the excess impregnation solution is drained out using an additional vacuum below 100 mbar for at least 5 minutes (Emission Factor Documentation for AP-42 Section 10.8, Wood Preserving, Final Report, MRI project No. 4945, 1999, https://www3.epa.gov/ttn/chief/ap42/ch10/bg-docs/b10s08.pdf). When using the "empty" cell method the most commonly used processes are "Rueping" and "Lowry". In the "Rueping process", the wood is first placed in an impregnation chamber and exposed to a pressure between 172 and 690 kPa for a period of a few minutes to 1 hour, then an impregnating solution is poured into the chamber at a maintained pressure in order to increase the pressure in the chamber and thus allow the solution to penetrate deep into the wood. The procedure continues until a sufficient amount of solution is absorbed. This is followed by removal of the impregnating solution, and, optionally, exposure of the samples to a vacuum. In the "Lowry process", an impregnating solution is poured into the chamber without maintaining the vacuum or overpressure. This is followed by exposure to overpressure until a sufficient amount of the solution has been absorbed into the wood. The final stage involves removal of the solution and optional exposure of the samples to a vacuum.

[0012] In all the impregnation processes, the wood is exposed to vacuum and/or overpressure until a sufficient amount of solution penetrates into the wood. The exposure time depends on the type and quality of the wood or wood composites. Preferably, the wood should be exposed to an overpressure above 10 bar for at least 180 minutes. Optionally, the wood can then be exposed to an additional vacuum below 100 mbar for at least 5 minutes in order to remove any excess solution.

[0013] Preferably, the exposure to the additional vacuum takes place at a vacuum between 50 and 60 mbar, for a period between 20 and 30 minutes.

[0014] Optionally, a modified "full" cell process can be used, where the wood is placed in an impregnation chamber filled with an impregnating solution, then first exposed to a vacuum below 100 mbar for between 30 and 60 min. The wood is then exposed to an overpressure above 10 bar until a sufficient amount of solution penetrates into the structure of the wood.

[0015] The impregnation phase may consist of one step or multiple steps. In a one-step process, as the impregnating agent the solution of a single metal acetoacetate, (for example only $Ca(OAcAc)_2$ or only $Mg(OAcAc)_2$), or a solution of a mixture of different metal acetoacetates in any weight ratio (for example a mixture of $Mg(OAcAc)_2$ and $Ca(OAcAc)_2$ in a weight ratio of 50 : 50) may be used.

[0016] When the impregnation phase consists of multiple steps (a two-step or a multi-step impregnation), as the impregnating agent in each individual step either a solution of a single metal acetoacetate or a solution of a mixture of different metal acetoacetates in any weight ratio may be used, wherein the individual steps may follow each other in any order.

[0017] In one embodiment, for example in all steps, that is in each individual step, the wood or wood composites may be impregnated with the same metal acetoacetate(s) solution in each step, e.g. using a solution of either $Ca(OAcAc)_2$,

$Mg(OAcAc)_2$ or $Sr(OAcAc)_2$, or alternatively using a solution containing a mixture of $Ca(OAcAc)_2$ and $Mg(OAcAc)_2$ in a 50:50 weight ratio. In another embodiment in each individual step, however, the wood or wood composites may be impregnated with different solutions in each step (containing different metal acetoacetates and/ or various mixtures thereof in any weight ratio). In the first step, for example, the wood or wood composite may be impregnated with a $Mg(OAcAc)_2$ solution, followed by a second impregnation with a $Ca(OAcAc)_2$ solution; or, for example, in the first step, the wood or wood composite may be impregnated with a solution of $Mg(OAcAc)_2$, in the second step a solution containing $Mg(OAcAc)_2$ and $Ca(OAcAc)_2$ mixed in a weight ratio of 50:50 may be used; or, for example, in the first step the wood or wood composite may be impregnated with a solution containing a mixture of $Mg(OAcAc)_2$ and $Ca(OAcAc)_2$ in a weight ratio of 50:50, followed by a second step using a solution containing $Mg(OAcAc)_2$ and $Sr(OAcAc)_2$ mixed in a weight ratio of 50 : 50. The use of other concentrations, the use of aqueous or non-aqueous solutions of different metal acetoacetates in varying concentrations, or mixtures thereof in arbitrary ratios, and sequential impregnation with solutions or mixtures of individual metal acetoacetates (in any ratio), is therefore also possible.

[0018] Preferably, the impregnation phase is one-step and follows a modified "full" cell process, where the wood is placed in an impregnation vessel filled with an impregnating agent which is a 20% by weight aqueous solution of the metal acetoacetate(s). This is followed by 30 minutes exposure to a vacuum between 50 and 60 mbar, and 180 minutes at an overpressure between 10 and 12 bar. Optionally, a vacuum between 50 and 60 mbar is applied for another 20 to 30 minutes to remove any excess impregnation solution from the wood's structure.

[0019] The effectiveness of wood impregnation, i.e. the depth of penetration of the impregnating agent into the wood, and the amount of absorbed impregnating agent (degree of uptake), can be adjusted by the impregnation method, i.e. by choosing the impregnation process selected, most commonly by changing the values of overpressure and vacuum inside the chamber and the time of exposure of wood to these conditions. Another way to increase the efficiency of impregnation is to pre-treat the wood with ultrasound, preferably at a frequency of 28 kHz to 40 kHz and an intensity of 300 W, at a temperature between 40 °C and 100 °C for at least 30 minutes. This increases the diffusion of water, breaks microfibers on the cell walls, ruptures the membranes, and reduces the content of extractives, amongst other things (Z. He, Z. Zhao, F. Yang, S. Yi, Effect of ultrasound pretreatment on wood prior to vacuum drying, Maderas, Ciencia y tecnologia, 16 (4) 2014, 395-402*)*. A third way to increase the efficiency of impregnation is to add surfactants to the impregnating agents, which allow the impregnating agent to penetrate deeper into the wood structure.

[0020] Optionally, the impregnation phase may be followed by an intermediate phase, which is a drying phase of the impregnated wood, in which the impregnated wood is dried at room temperature for at least 1 day, preferably for 3 days, at room temperature, before entering the after-treatment phase.

[0021] The impregnation phase is followed by the after-treatment phase, in which the impregnating agent s converted to carbonate(s).

[0022] In the after-treatment phase, the acetoacetate in the impregnated wood is converted to the corresponding carbonate depending on the metal acetoacetate solution selected in the impregnation phase, i.e. $CaCO_3$, $MgCO_3$, $SrCO_3$

[0023] There are several possibilities for after-treatment, what they all have in common is to ensure the conversion of acetoacetates into carbonates. This is achieved by regulating the temperature, the relative humidity, and the time the impregnated wood is exposed to these conditions, or by using ultrasound at an elevated temperature. It is desirable to expose the impregnated wood to higher temperatures and relative humidity, preferably between 40 °C and 100 °C and at a relative humidity of at least 35%, as this accelerates the conversion of acetoacetate(s) to carbonate(s). The conversion does take place at lower temperatures and humidity levels, but the time required becomes significantly extended. Impregnated wood can also be exposed to higher temperatures (T> 100 ° C) and lower relative humidity (RH <35%) for a suitable length of time. The conversion of acetoacetate(s) to carbonate(s) can also be accelerated through exposure to ultrasound, preferably at a frequency of 28 kHz - 40 kHz and an intensity of 300 W for at least 60 min, at an elevated temperature of between 40 °C and 100 °C.

[0024] The after-treatment phase can also take place under variable conditions, by dividing the entire phase into time intervals and defining a temperature and relative humidity for each interval. Time intervals can be the same length or different lengths.

[0025] In one embodiment, conditions may be alternated using intervals of the same length, namely: 1st step 8 h at 80 ° C and 90% RH, 2nd step 8 h at 80 ° C and 40% RH, 3rd step 8 h at 80 ° C and 90% RH, 4th step 8 h at 80 ° C and 40% RH, 5th step 8 h at 80 ° C and 90% RH, 6th step 8 h at 80 ° C and 40% RH , and the 7th stage 8 h at 80 ° C and 90% RH.

[0026] In a preferred embodiment, the after-treatment phase is carried out by placing the dry impregnated wood in a chamber where it is exposed to elevated temperatures of T = 80 ° C, with relative humidity of 40% and 90% being exchanged at equal time intervals.

[0027] In the presence of water or moisture in the air, the acetoacetate ion decomposes into a carbonate ion, carbon dioxide (CO_2), and acetone (CH_3COCH_3). The acetone and CO_2 evaporate, leaving solid carbonate. The conversion of metal acetoacetate to carbonate is shown in the following formula:

$$2\ CH_3COCH_2COO^- + H_2O \rightarrow CO_3^{2-} + CO_2 + 2\ CH_3COCH_3$$

[0028] $Ca(OAcAc)_2$, $Mg(OAcAc)_2$ and $Sr(OAcAc)_2$ decompose into their corresponding carbonate, according to the following formulas:

$$Ca(OAcAc)_2 + H_2O - CaCO_3 + CO_2 + 2\ CH_3COCH_3$$

$$Mg(OAcAc)_2 + H_2O - MgCO_3 + CO_2 + 2\ CH_3COCH_3$$

$$Sr(OAcAc)_2 + H_2O - SrCO_3 + CO_2 + 2\ CH_3COCH_3$$

[0029] It is desirable to keep the mineralized wood at room temperature for at least another week before it is suitable for use, or to briefly expose it to vacuum conditions (for a couple of hours up to one day), or higher temperatures i.e. up to 60 °C.

[0030] The amount of impregnation solution introduced (wet uptake), and thus the amount of carbonate formed in the structure of the wood, depends on the type, geometry, humidity and pre-treatment of the wood composite the impregnation process selected and any potential additives in the impregnating solution. Larger amounts of carbonates can be introduced by adjusting the conditions (for example by increasing the vacuum and overpressure values) and by prolonging the impregnation time, by increasing the concentration of acetoacetate(s) in the impregnation solution(s), or by repeating the impregnation process (two or more times) using either the same or a different solution (for example by using a solution of $Ca(OAcAc)_2$ followed by a solution of $Mg(OAcAc)_2$), or even with a mixture of different impregnating solutions (for example an aqueous solution of $Ca(OAcAc)_2$ and $Mg(OAcAc)_2$ mixed in a 50:50 weight ratio).

[0031] The incorporation of carbonates (e.g. $CaCO_3$, $MgCO_3$, $SrCO_3$) into the structure of the wood reduces the flammability of wood, wood composites or wooden products, because decomposition of carbonates at higher temperatures is an endothermic process, which, together with the release of CO_2 and/or H_2O, cools flammable gases in the event of a fire. The carbonate(s) thermally decompose(s) into CO_2 and metal oxide. The thermal decomposition of $CaCO_3$, $MgCO_3$ and $SrCO_3$ is shown in the formulas below. $MgCO_3$ can thermally decompose into MgO, CO_2 and H_2O, as the conversion of $Mg(OAcAc)_2$ to $MgCO_3$ can result in the hydrated crystalline modification(s) of $MgCO_3$ (e.g. nesquehonite, which has the chemical formula $MgCO_3 \cdot 3H_2O$).

$$MgCO_3 \xrightarrow{\sim 400°C} MgO + CO_2$$

$$CaCO_3 \xrightarrow{\sim 700°C} CaO + CO_2$$

$$SrCO_3 \xrightarrow{\sim 900°C} SrO + CO_2$$

Examples

Example 1: Preparation of aqueous acetoacetate solutions

[0032] To make the impregnating solutions (aqueous solutions of $Ca(OAcAc)_2$, $Mg(OAcAc)_2$ and $Sr(OAcAc)_2$ 200 g of either $CaCO_3$, $MgCO_3$ or$SrCO_3$ were added to a beaker. 1000 g of water was added, and the mixture was stirred with a magnetic stirrer for approximately 10 minutes. Varying quantities of 1,3-acetonedicarboxylic acid were then gradually added in small quantities: 615 g (for the preparation of $Ca(OAcAc)_2$), 713.9 g (for the preparation of $Mg(OAcAc)_2$), 407.45 g (for the preparation of $Sr(OAcAc)_2$). In the preparation of aqueous solutions of $Ca(OAcAc)_2$, $Mg(OAcAc)_2$ and $Sr(OAcAc)_2$ the beaker was then placed in a 33 °C water bath for 16 hours. Once synthesis was complete, the solution was filtered and diluted to a concentration of 20% by weight.

Example 2: The impregnation phase in wood and wood composites

[0033] The impregnation phase was carried out using a one-step impregnation process, by directly placing the wood samples in a 20% by weight $Ca(OAcAc)_2$, $Mg(OAcAc)_2$ or $Sr(OAcAc)_2$ solution, prepared according to the procedure described in Example 1. The samples were then exposed to a 50-60 mbar vacuum for 30 minutes, followed by 3 hours at 8-10 bar and subsequently another 20-30 min at a vacuum of 50-60 mbar.

[0034] The penetration in the grain direction was prevented by coating based on epoxy resin.

Example 3: After-treatment phase of wood and wood composites

[0035] In the after-treatment phase, the impregnated wood samples (prepared according to Example 2) were first dried at room temperature for at least 3 days, then exposed to an elevated temperature and relative humidity for the following amounts of time: 1st step 8 h at 80 °C and 90% RH, 2nd step 8 h at 80 °C and 40% RH, 3rd step 8 h at 80 °C and 90% RH, 4th step 8 h at 80 °C and 40% RH, 5th step 8 h at 80 °C and 90% RH, 6th step 8 h at 80 °C and 40% RH, 7th step 8 h at 80 °C and 90% RH.

[0036] The mineralized wood was then aged at room temperature for one week.

Example 4: Determining the degree of impregnation

[0037] Samples of spruce and beech wood were prepared as described in examples 1 to 3. With a single impregnation of $Mg(OAcAc)_2$ solution we were able to introduce 110 wt.% $Mg(OAcAc)_2$ into spruce, meaning 9.2 wt.% of the resulting $MgCO_3$ (dry intake) was absorbed into the structure of the wood. In the same wood, using a single impregnation of $Ca(OAcAc)_2$ solution, we were able to introduce 137 wt.% $Ca(OAcAc)_2$, meaning 12.1 wt.% of the $CaCO_3$ formed in the wood's structure. In beech samples, 84% by weight of $Mg(OAcAc)_2$ was introduced with a single impregnation (meaning 6.9% by weight of the $MgCO_3$ formed), compared to 86% by weight of $Ca(OAcAc)_2$, (meaning 5.6% by weight of the $CaCO_3$ formed).

[0038] The results are presented in Table 1.

Table 1: Mass of spruce or beech samples before impregnation, mass of samples after impregnation, calculated proportions re wet uptake of impregnating solutions (aqueous solutions of $Mg(OAcAc)_2$ and $Ca(OAcAc)_2$), and share of the dry uptake (proportion of $MgCO_3$ / $CaCO_3$) by weight in mineralized spruce and beech samples.

	Sample mass (g) (mean ± s.d)	Samples mass after impregnation (g) (mean ± s.d)	Average wet intake (%) (mean ± s.d)	Average dry intake (%) (mean ± s.d)
Spruce mineralized by $MgCO_3$	84.6 ± 2.3	174.0 ± 28.4	110.0 ± 27.6	9.2 ± 2.5
Spruce mineralized by $CaCO_3$	94.1 ± 1.3	216.7 ± 12.6	136.9 ± 16.3	12.1 ± 1.3
Beech mineralized by $MgCO_3$ beech	143.7 ± 1.4	256.9 ± 3.2	83.8 ± 3.1	5.6 ± 0.6
Beech mineralized by $CaCO_3$	139.4 ± 1.7	252.1 ± 8.4	85.9 ± 2.9	6.9 ± 0.3

Example 5: Determining the penetration depth of the impregnating agent

[0039] The penetration depth of the impregnating solution was checked in both the fiber direction and perpendicular to the fibers by impregnating a 140 mm (l) × 100 mm (w) × 10 mm (h) mm wood sample with an aqueous solution of Ca $(OAcAc)_2$, according to Examples 1 and 2. Following this, the samples were dried at room temperature for 2 days, after which the impregnated samples were cut through the middle both transversely and longitudinally, as shown in Figure 1. An indicator i.e. 10% aqueous sodium nitroprusside solution ($Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$; Sigma Aldrich) was then applied to each cross-section, by placing the cut side of the sample onto a napkin impregnated with the indicator. The red colour, which identifies the presence of acetoacetates, develops in about 30 minutes. As shown in Figure 1, the impregnating solution evenly penetrates into the spruce to a depth of at least 5 mm in the direction perpendicular to the fibers and at least 7 cm in the direction of the fibers. In this particular case, the entire depth of the sample was impregnated.

Example 6:_Determination of carbonate distribution throughout the structure of the wood

[0040] Following the mineralization of spruce or beech with either $MgCO_3$ or $CaCO_3$ (as described in examples 1 to 3), the distribution of carbonate through the structure of the wood was determined. Scanning electron microscopy (SEM) and microtomography (μCT) images show that, in spruce wood, $MgCO_3$ (Fig. 2a, b) and $CaCO_3$ (Fig. 2c, d) precipitate along the entire length of the tracheid. The locations of $MgCO_3$ or $CaCO_3$ are marked with arrows in Figures 2 and 3. In beech wood, however, $MgCO_3$ is primarily formed in the trachea (Fig. 3a, b), while $CaCO_3$ mainly precipitates in the tracheids and parenchymal cells (Fig. 3c, d). In both types of wood used (spruce and beech), $MgCO_3$ formed in an

elongated shape (Figure 2b, Figure 3b), while $CaCO_3$ was spherical (Figure 2d, Figure 3d), occurring in varying sizes up to 100 μm in diameter.

Example 7: Determination of the crystal carbonate structure within the wood

[0041] Figure 4 shows the diffractograms of reference spruce (a), $CaCO_3$ mineralized spruce (b), reference beech (c), and $CaCO_3$ mineralized beech (d), each prepared as described in Examples 1 to 3. The patterns of spruce mineralized with $CaCO_3$ correspond to vaterite crystal modification. The diffractograms on the right (Figure 4b and d) are marked with dots where the patterns do not overlap with those of the reference spruce or beech but instead are characteristic for vaterite CaCO3 crystal modification (marked with V).

Example 8: Determining the effect of wood mineralization on improving the wood response to fire

[0042] Reaction to fire was determined using a cone calorimeter according to ISO 5660-1:2015, for all of the following samples in both beech and spruce, each prepared as described in examples 1 to 3: (a) reference, (b) mineralized with $MgCO_3$ or $CaCO_3$ or $SrCO_3$, (c) thermally modified then mineralized with $MgCO_3$ or $CaCO_3$, (d) twice mineralized with $MgCO_3$ (beech only), and (e) mineralized with a mixture of either $MgCO_3$ and $SrCO_3$ or $MgCO_3$ and $CaCO_3$, each in a 50 : 50 mass ratio. Specimens of dimensions 100 mm (l) × 100 mm (w) × 10 mm (h) were exposed to a heat flux of 50 kW/m^2. The results are shown in Table 2; average values and standard deviations of ignition time, total heat release in the first 600 seconds of the test (THR_{600s}), and smoke growth rate index (FIGRA) are listed for all specimens. Figures 5 and 6 show two examples of heat release rate (HRR) in the specimens made of spruce, while Figures 7 to 11 show examples of beech wood. An example of the smoke growth rate index (SMOGRA) in a specimen from beech wood is shown in Figure 12.

[0043] In both spruce and beech the fire characteristics measured (ignition time, THR_{600s} and FIGRA) are significantly better in the mineralized samples compared to either the reference (R) or thermally modified (T) samples. The average time to ignition in the reference spruce was 20.8 s, which increased considerably following mineralization with $MgCO_3$, $CaCO_3$ or $SrCO_3$, to values of 31.8 s, 29.2 s and 23.2 s respectively. Total heat release, THR_{600s}, slightly decreased after mineralization with $MgCO_3$ (from 21.0 MJ to 19.1 MJ), but did not change significantly after mineralization with either $CaCO_3$ or $SrCO_3$. A considerable decrease in the average FIGRA value was observed following the mineralization of spruce (falling from 372.6 Ws^{-1} to 223.0 Ws^{-1}, 255.7 Ws^{-1} and 349.4 Ws^{-1} for $MgCO_3$, $CaCO_3$ and $SrCO_3$ respectively). The positive effect of carbonates as flame retardants in the burning of wood can be explained by the endothermic nature of their thermal decomposition: since $MgCO_3$ thermally decomposes at approximately 400°C, $CaCO_3$ at around 700 °C, and $SrCO_3$ at around 900 °C, $MgCO_3$ is expected to be the most effective flame retardant. We have also verified the effectiveness of the mineralization of spruce, utilising various mixtures of carbonates, with regard to its reaction to fire. In comparison to spruce mineralized with $MgCO_3$, the mineralization of spruce with $MgCO_3$ and $CaCO_3$ in a 50 : 50 mass ratio (indicated in Table 2 by Ca:Mg) slightly increases ignition time, to 34.6 s, while FIGRA decreases considerably, to 187.2 Ws^{-1}, and THR_{600s} remains the same. No considerable improvement in fire characteristics was noticed following mineralization with a mixture of $MgCO_3$ and $SrCO_3$; all values remain similar to those of spruce mineralized with $MgCO_3$.

[0044] The effect of mineralization on the fire properties of beech exhibited a similar trend, yet with an even greater improvement. In comparison to the reference sample, the ignition time increased following mineralization with $MgCO_3$ from 29.8 s (R) to 46.2 s ($MgCO_3$), THR_{600s} decreased from 43.5 MJ (R) to 31.3 MJ ($MgCO_3$), and FIGRA decreased from 530.3 Ws^{-1} (R) to 203.9 Ws^{-1} ($MgCO_3$). In the case of beech, we evaluated the effect of double mineralization with $MgCO_3$ and found that fire behaviour was improved even further (indicated in Table 2 by $MgCO_3$-2x): ignition time increased to 54.8 s, while THR_{600s} and FIGRA decreased further to 25.7 MJ and 167.2 W s^{-1}, respectively.

[0045] It is known that thermal modification increases resistance to fungi but impairs the reaction to fire (N. Yilor, S.N. Kartal, Heat Modification of Wood: Chemical Properties and Resistance to Mold and Decay Fungi, Forest Products Journal, 60 (4) 2010, 357-361 in H. Sivrikaya, A. Can, T. de Troya, M. Conde, Comparative Biological Resistance of Differently Thermal Modified Wood Species Against Decay Fungi, Reticulitermes grassei and Hylotrupes bajulus, Ciencia y tecnologia, 17 (3) 2015, 559-570*).* We examined the fire properties of thermally modified beech and spruce and the influence of mineralization with $MgCO_3$ or $CaCO_3$ on the improvement of its reaction to fire. In both spruce and beech, thermally modified samples (marked T in Table 2 - upper part) exhibited poorer fire properties than the reference samples (marked R in Table 2). Thermally modified spruce has an ignition time of 20.0 s, THR_{600s} of 30.4 MJ and FIGRA of 488.6 Ws^{-1}. Following mineralization with $MgCO_3$ (marked T- $MgCO_3$ in Table 2), the ignition time increased to 32.4 s, while the THR_{600s} and FIGRA decreased to 15.6MJ and 191.5 Ws^{-1} respectively. These values are even better than those of spruce which had only been mineralized and not previously thermally modified (marked $MgCO_3$ in Table 2). Furthermore, fire properties improve following the mineralization of previously thermally modified spruce with $CaCO_3$ (marked T-$CaCO_3$ in Table 2), but to a slightly lesser extent. It can be seen in the heat release rate curves of the spruce samples (Figures 5 and 6) that the time to ignition delays (the peak of the curve for mineralized spruce moves to the right compared

to the curve for the reference spruce), and that the heat release rate of the mineralized wood samples also delays and decreases compared to the reference spruce. Similar to the findings for the spruce, mineralization significantly improves the fire properties of beech which has been previously thermally modified. It can be seen in the lower part of Table 2 that the thermally modified beech (mark T) has an ignition time of 26.5 s, THR_{600s} of 46.0 MJ and FIGRA of 662.9 Ws^{-1}.

[0046] After mineralization with $MgCO_3$ (marked T-$MgCO_3$) the ignition time increases to 45.3 s, THR_{600s} decreases to 24.2 MJ and FIGRA decreases to 173.6 Ws^{-1}. Similar values were observed after mineralization with $CaCO_3$ (marked T-$CaCO_3$). This synergistic effect of mineralization alongside thermal modification is also observed in beech - the fire properties of wood are best when these two modification methods are combined. It can be seen from the curves of heat release rate in beech samples (Figures 7 to 11) that the ignition time is delayed in mineralized samples (the top of the curve shifts to the right in the mineralized beech relative to the curve of the reference beech). Similarly, the heat release rate of the mineralized samples is also delayed and decreased in comparison to the reference samples. In Figure 12 it can be seen that the smoke growth rate index (SMOGRA) for the sample mineralized with $MgCO_3$ is significantly decreased and shifted to the right in comparison to the reference sample.

Table 2: Ignition time, total heat release, THR_{600s} and fire growth rate index (FIGRA) for the various spruce and beech samples: reference (R); thermally modified (T); mineralized with $MgCO_3$ ($MgCO_3$), $CaCO_3$ ($CaCO_3$), or $SrCO_3$ ($SrCO_3$); thermally modified and mineralized with $MgCO_3$ (T-$MgCO_3$) or $CaCO_3$ (T-$CaCO_3$); twice mineralised with $MgCO_3$ ($MgCO_3$ - 2x-beech only); mineralized with mixtures of $MgCO_3$ and $SrCO_3$ (Mg:Sr) or $MgCO_3$ and $CaCO_3$ (Ca:Mg) (results are presented as the average value and standard deviation of five measurements).

		Ignition time / s	THR_{600} / MJ	FIGRA / Ws^{-1}
spruce	R	20.8 ± 2.6	21.0 ± 0.4	372.6 ± 50.3
	T	20.0 ± 1.0	30.4 ± 0.4	488.6 ± 52.0
	$MgCO_3$	31.8 ± 4.5	19.1 ± 1.5	223.0 ± 35.7
	T-$MgCO_3$	32.4 ± 5.9	15.6 ± 0.8	191.5 ± 40.3
	$CaCO_3$	29.2 ± 1.3	21.6 ± 0.5	255.7 ± 14.3
	T-$CaCO_3$	30.0 ± 4.6	20.8 ± 2.0	225.1 ± 43.6
	$SrCO_3$	23.2 ± 3.2	23.5 ± 4.4	349.4 ±57.8
	Ca:Mg	34.6 ± 4.8	19.4 ± 1.4	187.2 ± 27.7
	Mg:Sr	31.8 ± 5.8	21.5 ± 4.8	246.1 ± 93.8
beech	R	29.8 ± 3.8	43.5 ± 2.7	530.3 ± 51.0
	T	26.5 ± 0.7	46.0 ± 1.0	662.9 ± 0.6
	$MgCO_3$	46.2 ± 3.8	31.3 ± 1.9	203.9 ± 20.7
	$MgCO_3$ - 2x	54.8 ± 8.3	25.7 ± 5.0	167.2 ± 20.8
	T-$MgCO_3$	45.2 ± 3.8	24.2 ± 3.4	173.6 ± 10.0
	$CaCO_3$	46.8 ±6.2	31.8 ± 2.1	217.2 ± 9.4
	T-$CaCO_3$	46.3 ± 4.0	25.5 ± 2.3	198.6 ± 20.2
	$SrCO_3$	40.2 ± 7.8	36.7 ± 4.8	266.5 ± 30.5
	Ca:Mg	44.6 ± 9.3	30.3 ± 4.8	224.8 ± 30.0
	Mg:Sr	45.8 ± 4.4	33.0 ± 2.1	222.3 ± 19.6

Example 9: Contact angle and pH value measurements for spruce wood

[0047] Using spruce mineralized with $MgCO_3$ or $CaCO_3$ (according to procedures 1 to 3), we used a Drop Shape Instrument FTA 1000 to measure the contact angle, forming a 2.5 μl ± 0.2 μl size drop and dropping it to the surface (Figure 13). The contact angle was measured immediately after the drop contacted the surface. From the results, calculated as an average of 10 measurements, we determined that the contact angle increases from 43 ° for the reference spruce, to 90 ° for spruce mineralized with $MgCO_3$, and 142 ° for spruce mineralized with $CaCO_3$ (Table 3, Figure 13). With increased hydrophobicity water absorption is reduced, thus increasing dimensional stability and reducing the risk

of wooddecay (i.e wood durability is increased).

[0048] The pH values of wood samples mineralized with $MgCO_3$, $CaCO_3$ or $SrCO_3$, and thermally modified wood samples additionally mineralized with $MgCO_3$, $CaCO_3$ or $SrCO_3$ (prepared as described in examples 1 to 3) were measured by applying 3 ml of water on wood surface. The pH was then measured using a pH meter (Basic Titrino) with a flat electrode, and the average of five measurements calculated for the results. The unmodified spruce had a pH value of 5.5, compared to 6.8 for the thermally modified spruce (Table 4). Following mineralization with $MgCO_3$ the pH value increased to 9.4, after mineralization with $CaCO_3$ to 8.2 and after mineralization with $SrCO_3$ to 7.9. The results show that the pH values of samples which had been both thermally modified and mineralized spruce samples did not change significantly compared to those which had only undergone the mineralization process. A similar trend is observed in the beech. A slightly acidic environment is optimal for fungal growth and wood decay (pH values from 4.5 to 5; *M. Humar, B. Lesar ,D. Krzišnikm, Tehnična in estetska življenjska doba lesa. Acta Silvae et Ligni (121) 2020, 33*-48), as higher pH values can inhibit wood decay from fungal growth (*N. Little, T. Schultz in D. Nicholas, Effect of different soils and pH amendments on brown-rot decay activity in a soil block test, Holzforschung 64 (5) 2010, str. 667-671).* The high pH values of mineralized wood and thermally modified wood which is then mineralized can therefore increase its durability.

Table 3: Contact angles of reference spruce (R), and spruce samples mineralized with MgCOs and $CaCO_3$. Results given are the average of 10 measurements.

	R	$MgCO_3$	$CaCO_3$
Contact angle / °	43 ± 8	90 ± 6	142 ± 5

Table 4: pH values of the various spruce and beech samples; reference (R), thermally modified (T), mineralized with $MgCO_3$ ($MgCO_3$), thermally modified and mineralized with $MgCO_3$ (T-$MgCO_3$), mineralized with $CaCO_3$ ($CaCO_3$), thermally modified and mineralized with $CaCO_3$ (T-$CaCO_3$), mineralized with $SrCO_3$ ($SrCO_3$), and thermally modified and mineralized with $SrCO_3$(T-$SrCO_3$). Results given are the average of 5 measurements.

	pH value							
	R	T	$MgCO_3$	T-$MgCO_3$	$CaCO_3$	T-$CaCO_3$	$SrCO_3$	T-$SrCO_3$
Spruce	5.5 ± 0.3	6.8 ± 0.9	9.4 ± 0.1	9.2 ± 0.2	8.2 ± 0.2	7.9 ± 0.2	7.9 ± 0.1	7.8 ± 0.1
Beech	5.4 ± 0.5	5.2 ± 0.4	9.4 ± 0.3	9.1 ± 0.2	8.1 ± 0.3	7.9 ± 0.1	8.0 ± 0.1	7.7 ± 0.1

Example 10: Durability against decay fungi

[0049] In accordance with standard EN 113:1996, resistance to decay fungi was determined in reference spruce and beech samples, and previously thermally modified spruce and beech samples mineralized with $CaCO_3$ according to procedures 1 to 3. For each wood species (spruce and beech), we prepared three different sample sets sized 50 mm (l) × 25 mm (w) × 15 mm (h), three times (in order to expose each set to three different types of wood decay fungi). The first set of samples consisted of 5 parallels of reference wood (spruce or beech) and 5 parallels of thermally modified wood, the second set contained 5 parallels of reference wood and 5 parallels of wood mineralized with $CaCO_3$, and the third set 5 parallels of reference wood and 5 parallels of wood which had been both thermally modified and mineralized with $CaCO_3$. Before exposure to the fungi, the samples were dried to an absolutely dry state and weighed. Prior to exposure to the fungi, the samples were conditioned under laboratory conditions for two weeks. Samples were exposed to 3 different wood decay fungi: *Gloeophyllum trabeum* (GT), *Poria monticola* (PM) and *Trametes versicolor* (TV). After 16 weeks of exposure, samples were absolutely dried and weighed again and mass loss, attributed to the fungal decay of the wood, was determined.The highest mass loss determined (approximately 40 %) was seen in the reference beech and spruce samples exposed to the GT fungus (Figure 14a). It can be seen that mineralization with $CaCO_3$ inhibits the decomposition of wood with GT. Mass loss in the mineralized samples was approximately 20 % for beech and 35% for spruce. As expected, a much lower mass loss was seen in the thermally modified samples, totalling approximately 8 % in beech and 14 % in spruce. It is known that thermal modification increases resistance to wood decay fungi (N. Yilor, S.N. Kartal, Heat Modification of Wood: Chemical Properties and Resistance to Mold and Decay Fungi, Forest Products Journal, 60 (4) 2010, 357-361*).* Hemicellulose, which is an excellent food for microorganisms, is decomposed during the process of thermal modification. Mineralization of wood that has been previously thermally modified further increases its resistance to GT fungus. The smallest mass losses were determined in samples which had been first thermally

modified and then mineralized with CaCOs; approximately 5% in beech and 10% in spruce. The resistance of wood samples to PM and TV fungi exhibited a similar trend to that of those with GT. The highest mass loss was exhibited in the reference samples of spruce and beech, while samples which had been thermally modified, mineralized, or both, showed a significantly better resistance to the PM and TV fungi (Figure 14b-c).

Example 11: Determining the resistance to indentation (Brinell hardness)

[0050] The influence of mineralization on the hardness of spruce was determined in reference samples as well as in samples which had been thermally modified and then mineralized with $CaCO_3$ according to methods 1 to 3. Resistance to indentation (Brinell hardness) was determined. The preparation of samples and all measurements were performed in accordance with European standard EN 1534: 2020. A hardened steel ball, 10 mm $\pm$ 0.01 mm in diameter, was pressed into the surface of the wood, in the radial direction, with a force of 1 kN, as prescribed by the standard. The ball was pushed in wood and then up to three minutes the diameter of the indentation was measured with respect to the wood fibers in the longitudinal and transverse directions using a magnifying glass equipped with a scale accurate to 0.1 mm. The hardness (HB) was then calculated using these measurements, as specified in the standard. The results of the reference, thermally modified, $CaCO_3$ mineralized and thermally modified plus $CaCO_3$ mineralized spruce samples are given in Figure 17 (HB values are stated as an average of 10 measurements). Results show that mineralization increases the hardness of spruce wood from 13 N/mm^2 in the reference samples to 17 N/mm^2 in the mineralized spruce. Thermally modified spruce had a similar hardness to the reference sample (13 N/mm^2), while the sample which had been both thermally modified and mineralized had a slightly higher hardness (15 N/mm^2). We found that mineralization with $CaCO_3$ increased the hardness of both the reference and thermally modified spruce wood.

Claims

1. A process of wood mineralization comprising the following phases:

   - an impregnation phase, wherein the wood is with the use of vacuum and/or overpressure impregnated with an impregnating agent, which is an aqueous solution of at least one metal beta-keto carboxylate or a mixture of different metal beta-carboxylates, wherein the concentration of metal beta-carboxylate or a mixture of different metal beta-carboxylates in the aqueous solution is up to 30% by weight, wherein the metal beta-carboxylate is a metal acetoacetate selected from calcium acetoacetate $Ca(OAcAc)_2$, magnesium acetoacetate $Mg(OAcAc)_2$ or strontium acetoacetate $Sr(OAcAc)_2$ or mixtures thereof in any weight ratio, and whereby the impregnating agent penetrates deep into the structure of the wood;
   - an after-treatment phase of the impregnated wood, whereby by regulating the temperature, humidity and exposure time of the impregnated wood to these conditions or by exposing the impregnated wood to ultrasound the metal acetoacetate(s) is converted into carbonate(s), whereby fire properties, resistance to decaying fungi and/or mechanical properties of wood are improved.

2. The process of wood mineralization according to claim 1, wherein the impregnation process using vacuum and / or overpressure comprises the impregnation of wood using either the "full" or "empty" cell process, wherein the wood is exposed to an overpressure of 10 bar for at least 180 minutes.

3. The process of wood mineralization according to the preceding claims, wherein the impregnation phase is a one-step or a multi-step, wherein as the impregnating agent in each individual step either the solution of a single metal acetoacetate or the solution of a mixture of different metal acetoacetates is used, and wherein the individual steps follow each other in any order.

4. The process of wood mineralization according to the preceding claims, wherein the impregnation phase is followed by an additional exposure of wood to a vacuum below 100 mbar for a period of at least 5 minutes for removal of the excess impregnation solution.

5. The process of wood mineralization according to the preceding claims, wherein the impregnation phase is one-step, where the wood is placed in an impregnation vessel filled with an impregnating agent which is a 20% by weight aqueous solution of the metal acetoacetate(s), followed by 30 minutes exposure to a vacuum between 50-60 mbar, and then 180 minutes exposure to an overpressure between 10-12 bar, followed by another 20 to 30 minutes exposure to a vacuum between 50-60 mbar for removal of the excess impregnation solution.

6. The process of wood mineralization according to the preceding claims, wherein the impregnation phase is followed by an intermediate phase which is a drying phase of the impregnated wood, in which the impregnated wood is dried at room temperature for at least 1 day, preferably 3 days.

7. The process of wood mineralization according to the preceding claims, wherein in the after-treatment phase the impregnated wood is exposed to a temperature between 40 °C and 100 °C and a relative humidity of at least 35%.

8. The process of wood mineralization according to the preceding claims, wherein the after-treatment phase is carried out under constant conditions, whereby the impregnated wood is exposed to the same conditions, that is the same temperature and the same relative humidity, throughout the after-treatment phase.

9. The process of wood mineralization according to the preceding claims, wherein the after-treatment phase is carried out under variable conditions, whereby the duration of the after-treatment phase is divided into time intervals, and each time interval having a defined temperature and relative humidity, and the time intervals are of the same length or of different length.

10. The process of wood mineralization according to the preceding claims, wherein in the after-treatment phase the impregnated dry wood is placed in a chamber where it is exposed to elevated temperature of T = 80 °C, and wherein the relative humidity of 40% and 90% is exchanged at equal time intervals.

11. The process of wood mineralization according to the preceding claims, wherein in the after-treatment phase the impregnated wood is exposed to ultrasound at a frequency of 28 kHz - 40 kHz and an intensity of 300 W for at least 60 min, at a temperature between 40 °C and 100 °C.

Patentansprüche

1. Verfahren zur Holzmineralisierung, das die folgenden Phasen umfasst:

   - eine Imprägnationsphase, wobei das Holz unter Anwendung von Vakuum und/oder Überdruck mit einem Imprägnierungsmittel imprägniert wird, das eine wässrige Lösung von mindestens einem Metall-beta-Ketocarboxylat oder einer Mischung verschiedener Metall-beta-Carboxylate ist, wobei die Konzentration von Metall-beta-Carboxylat oder einer Mischung verschiedener Metall-beta-Carboxylate in der wässrigen Lösung bis zu 30 Gew.-% beträgt, wobei das Metall-beta-Carboxylat ein Metall-Acetoacetat ist, ausgewählt aus Calciumacetoacetat $Ca(OAcAc)_2$, Magnesiumacetoacetat $Mg(OAcAc)_2$ oder Strontiumacetoacetat $Sr(OAcAc)_2$ oder Mischungen davon in jedem Gewichtsverhältnis, und wobei das Imprägniermittel tief in die Struktur des Holzes eindringt;
   - eine Nachbehandlungsphase des imprägnierten Holzes, bei der durch die Regulierung der Temperatur, der Feuchtigkeit und der Einwirkzeit auf das imprägnierte Holz oder durch die Einwirkung von Ultraschall auf das imprägnierte Holz das/die Metallacetoacetat(e) in Carbonat(e) umgewandelt wird/werden, wobei die Brandeigenschaften, die Widerstandsfähigkeit gegen holzzerstörende Pilze und/oder die mechanischen Eigenschaften des Holzes verbessert werden.

2. Verfahren zur Holzmineralisierung nach Anspruch 1, wobei das Imprägnierverfahren unter Anwendung von Vakuum und/oder Überdruck die Imprägnierung von Holz entweder nach dem "Voll"- oder "Leer"-Zellenverfahren umfasst, wobei das Holz mindestens 180 Minuten lang einem Überdruck von 10 bar ausgesetzt wird.

3. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, wobei die Imprägnationsphase ein- oder mehrstufig ist, wobei als Imprägniermittel in jeder einzelnen Stufe entweder die Lösung eines einzelnen Metallacetoacetats oder die Lösung einer Mischung verschiedener Metallacetoacetate verwendet wird und wobei die einzelnen Stufen in beliebiger Reihenfolge aufeinander folgen.

4. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, bei dem das Holz nach der Imprägnationsphase zusätzlich mindestens 5 Minuten lang einem Vakuum unter 100 mbar ausgesetzt wird, um die überschüssige Imprägnierlösung zu entfernen.

5. Verfahren zur Holzmineralisierung nach den vorhergehenden Ansprüchen, bei dem die Imprägnationsphase einstufig ist, wobei das Holz in ein Imprägniergefäß gegeben wird, das mit einem Imprägniermittel gefüllt ist, das eine

20 gewichtsprozentige wässrige Lösung des/der Metallacetoacetate(s) ist, gefolgt von 30 Minuten Einwirkung eines Vakuums zwischen 50-60 mbar, und dann 180 Minuten Einwirkung eines Überdrucks zwischen 10-12 bar, gefolgt von weiteren 20 bis 30 Minuten Einwirkung eines Vakuums zwischen 50-60 mbar zur Entfernung der überschüssigen Imprägnierlösung.

6. Verfahren zur Holzmineralisierung nach den vorhergehenden Ansprüchen, wobei sich an die Imprägnationsphase eine Zwischenphase anschließt, die eine Trocknungsphase des imprägnierten Holzes ist, in der das imprägnierte Holz mindestens 1 Tag, vorzugsweise 3 Tage, bei Raumtemperatur getrocknet wird.

7. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, wobei das imprägnierte Holz in der Nachbehandlungsphase einer Temperatur zwischen 40 °C und 100 °C und einer relativen Luftfeuchtigkeit von mindestens 35 % ausgesetzt wird.

8. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, wobei die Nachbehandlungsphase unter konstanten Bedingungen durchgeführt wird, wobei das imprägnierte Holz während der gesamten Nachbehandlungsphase gleichbleibenden Bedingungen, d. h. der gleichen Temperatur und der gleichen relativen Luftfeuchtigkeit, ausgesetzt ist.

9. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, wobei die Nachbehandlungsphase unter variablen Bedingungen durchgeführt wird, wobei die Dauer der Nachbehandlungsphase in Zeitintervalle unterteilt ist und jeder Zeitintervall eine definierte Temperatur und relative Feuchtigkeit aufweist und die Zeitintervalle gleich oder unterschiedlich lang sind.

10. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, wobei das imprägnierte trockene Holz in der Nachbehandlungsphase in eine Kammer verbracht wird, in der es einer erhöhten Temperatur von T = 80 °C ausgesetzt wird, und wobei sich die relative Feuchtigkeit von 40 % und 90 % in gleichen Zeitintervallen abwechselt.

11. Verfahren zur Holzmineralisierung nach einem der vorhergehenden Ansprüche, wobei das imprägnierte Holz in der Nachbehandlungsphase mindestens 60 Minuten lang bei einer Temperatur zwischen 40 °C und 100 °C mit einer Frequenz von 28 kHz - 40 kHz und einer Intensität von 300 W beschallt wird.

Revendications

1. Procédé de minéralisation du bois comprenant les phases suivantes :

   - une phase d'imprégnation, dans laquelle le bois est imprégné d'un agent d'imprégnation par utilisation de vide et/ou de surpression, qui est une solution aqueuse d'au moins un bêta-céto carboxylate métallique ou d'un mélange de différents bêta-carboxylates métalliques, la concentration de bêta-carboxylate métallique ou d'un mélange de différents bêta-carboxylates métalliques dans la solution aqueuse représentant jusqu'à 30 % en poids, le bêta-carboxylate métallique étant un acétoacétate métallique choisi parmi l'acétoacétate de calcium $Ca(OAcAc)_2$, l'acétoacétate de magnésium $Mg(OAcAc)_2$ ou l'acétoacétate de strontium $Sr(OAcAc)_2$ ou des mélanges de ceux-ci dans n'importe quel rapport pondéral, et l'agent d'imprégnation pénétrant profondément dans la structure du bois ;
   - une phase de post-traitement du bois imprégné, ce par quoi, par régulation de la température, de l'humidité et du temps d'exposition du bois imprégné à ces conditions ou par exposition du bois imprégné à des ultrasons, le ou les acétoacétate(s) métallique(s) est/sont converti(s) en carbonate(s), ce par quoi des propriétés de résistance au feu, de résistance à la dégradation des champignons et/ou des propriétés mécaniques du bois sont améliorées.

2. Procédé de minéralisation du bois selon la revendication 1, dans lequel le procédé d'imprégnation utilisant le vide et/ou la surpression comprend l'imprégnation du bois selon le procédé de la cellule « pleine » ou « vide », dans lequel le bois est exposé à une surpression de 10 bars pendant au moins 180 minutes.

3. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel la phase d'imprégnation se déroule en une ou plusieurs étapes, dans lequel on utilise comme agent d'imprégnation dans chaque étape individuelle soit la solution d'un seul acétoacétate métallique, soit la solution d'un mélange de différents acétoacétates

métalliques, et dans lequel les étapes individuelles se succèdent dans un ordre quelconque.

4. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel la phase d'imprégnation est suivie d'une exposition supplémentaire du bois à un vide inférieur à 100 mbar pendant une période d'au moins 5 minutes pour éliminer l'excès de solution d'imprégnation.

5. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel la phase d'imprégnation se fait en une seule étape, le bois étant placé dans une cuve d'imprégnation remplie d'un agent d'imprégnation qui est une solution aqueuse à 20 % en poids d'acétoacétate(s) métallique(s), suivie d'une exposition de 30 minutes à un vide compris entre 50 et 60 mbar, puis d'une exposition de 180 minutes à une surpression comprise entre 10 et 12 bar, suivie d'une autre exposition de 20 à 30 minutes à un vide compris entre 50 et 60 mbar pour l'élimination de l'excès de solution d'imprégnation.

6. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel la phase d'imprégnation est suivie d'une phase intermédiaire qui est une phase de séchage du bois imprégné, dans laquelle le bois imprégné est séché à température ambiante pendant au moins 1 jour, de préférence 3 jours.

7. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel, au cours de la phase de post-traitement, le bois imprégné est exposé à une température comprise entre 40 °C et 100 °C et à une humidité relative d'au moins 35 %.

8. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel la phase de post-traitement est effectuée dans des conditions constantes, le bois imprégné étant exposé aux mêmes conditions, c'est-à-dire à la même température et à la même humidité relative, tout au long de la phase de post-traitement.

9. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel la phase de post-traitement est effectuée dans des conditions variables, la durée de la phase de post-traitement étant divisée en intervalles de temps, chaque intervalle de temps ayant une température et une humidité relative définies, et les intervalles de temps étant de même durée ou de durée différente.

10. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel, dans la phase de post-traitement, le bois sec imprégné est placé dans une chambre où il est exposé à une température élevée de T = 80 °C, et où l'humidité relative de 40 % et 90 % est échangée à intervalles de temps égaux.

11. Procédé de minéralisation du bois selon les revendications précédentes, dans lequel, dans la phase de post-traitement, le bois imprégné est exposé à des ultrasons à une fréquence de 28 kHz - 40 kHz et à une intensité de 300 W pendant au moins 60 min, à une température comprise entre 40 °C et 100 °C.

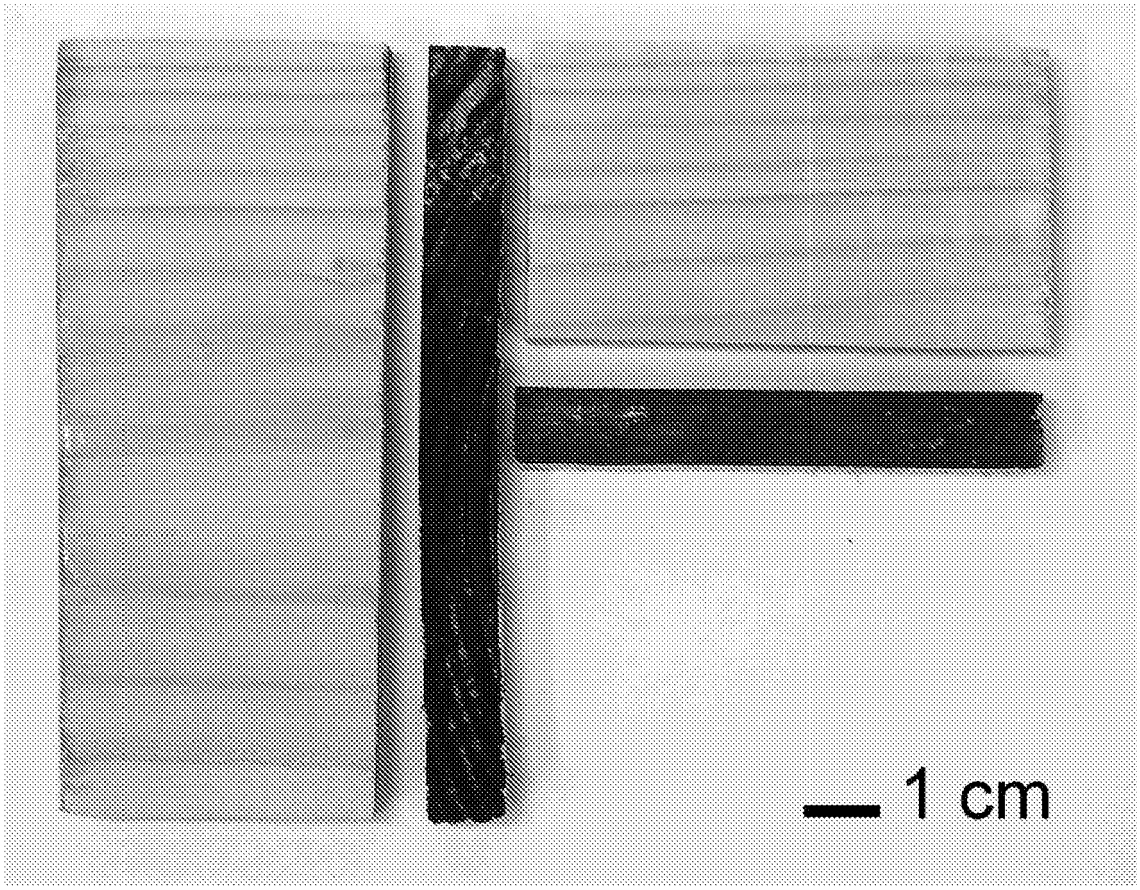


Figure 1

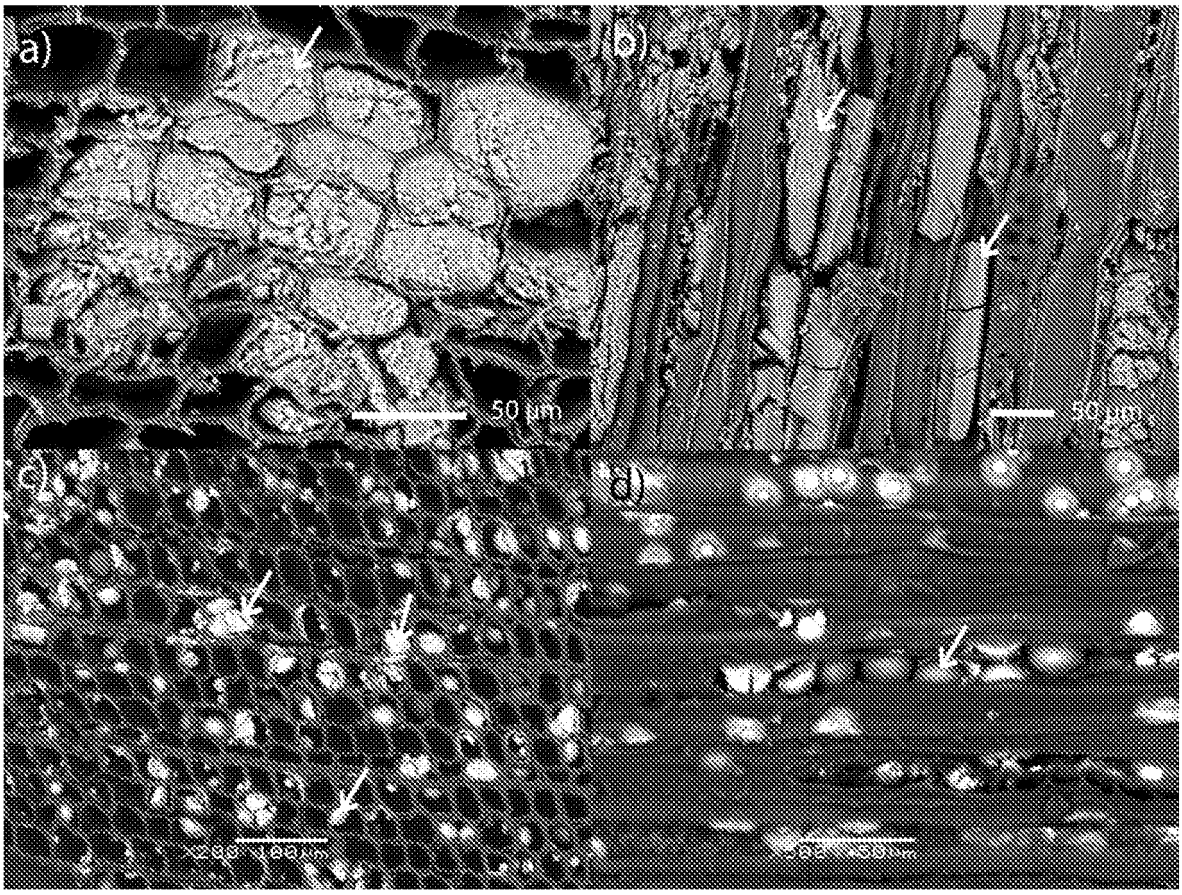
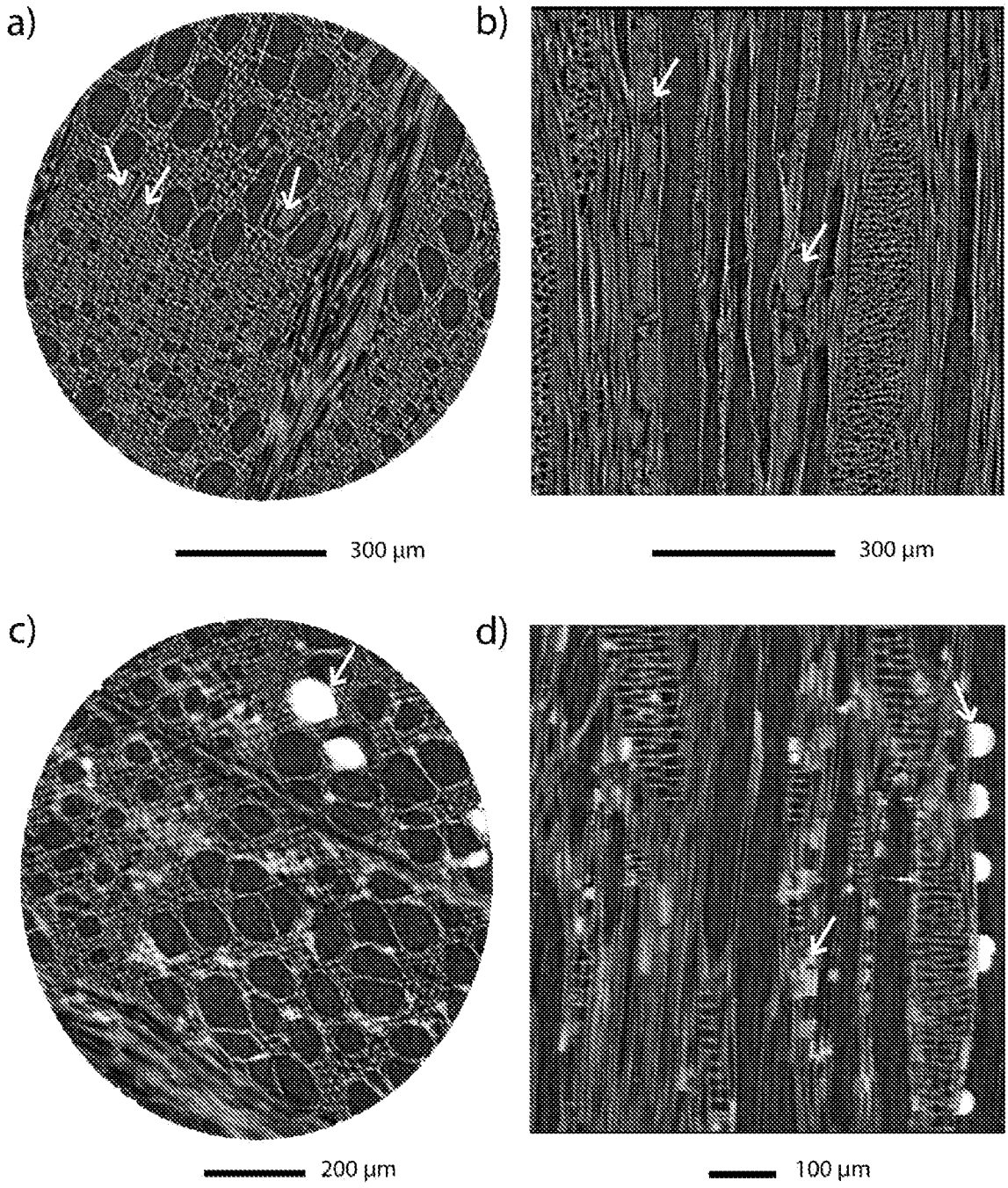


Figure 2



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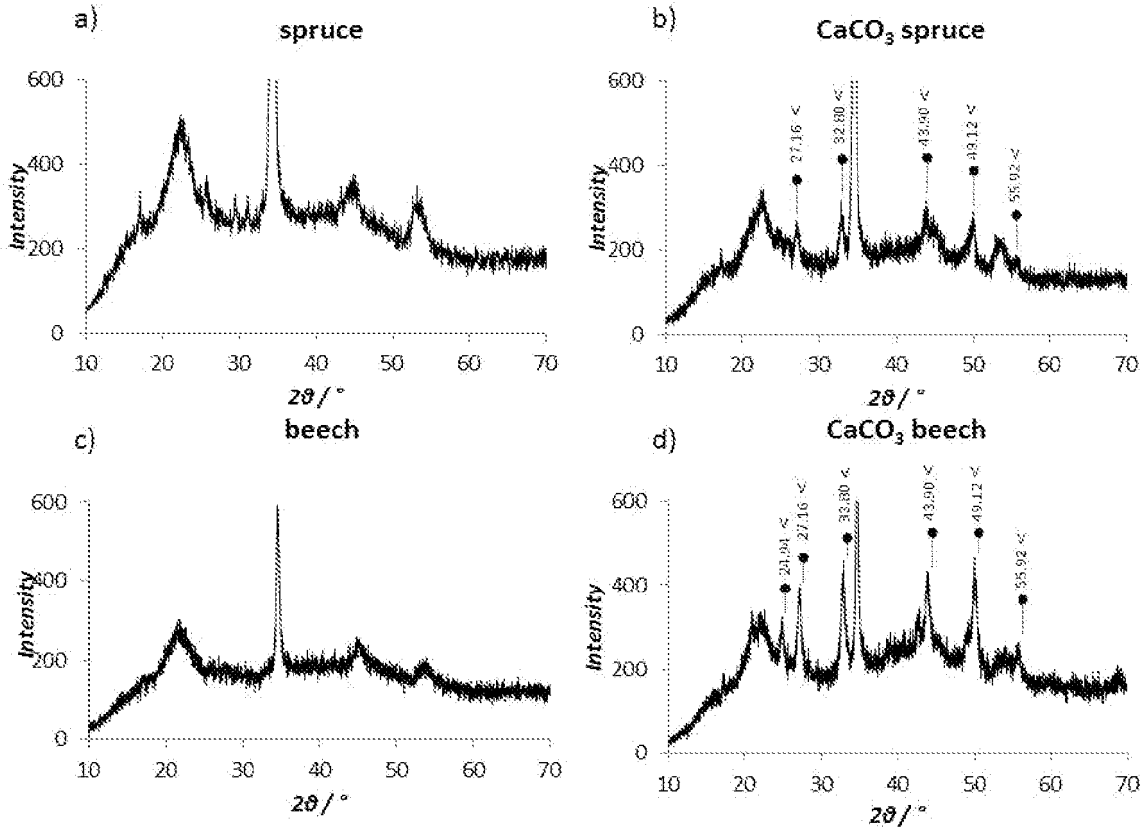

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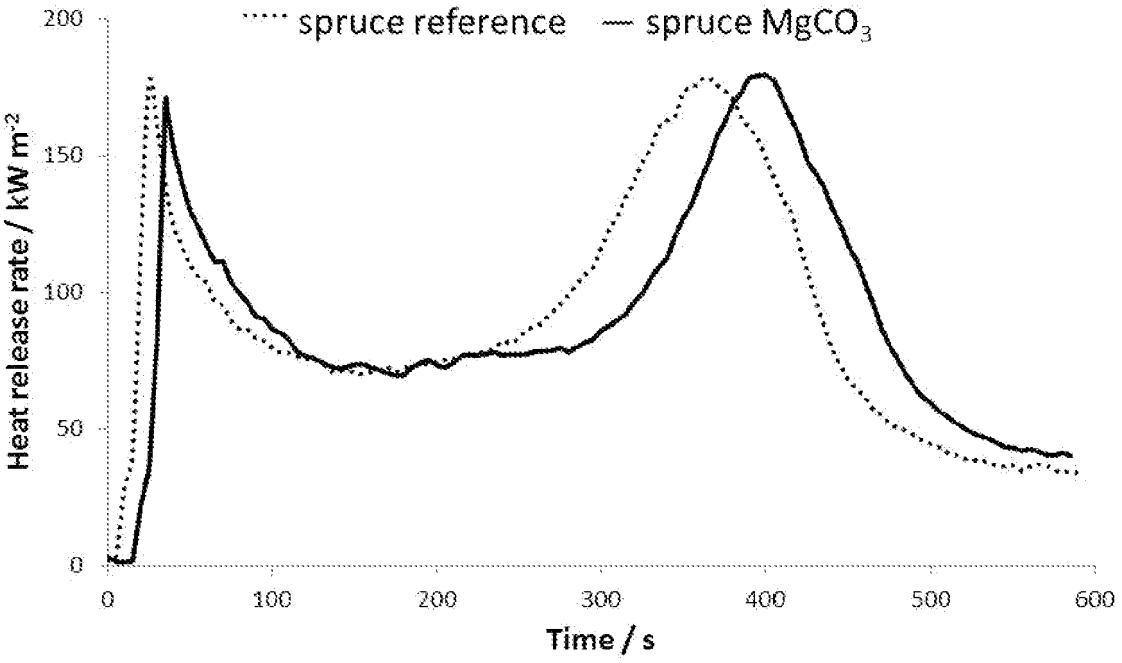

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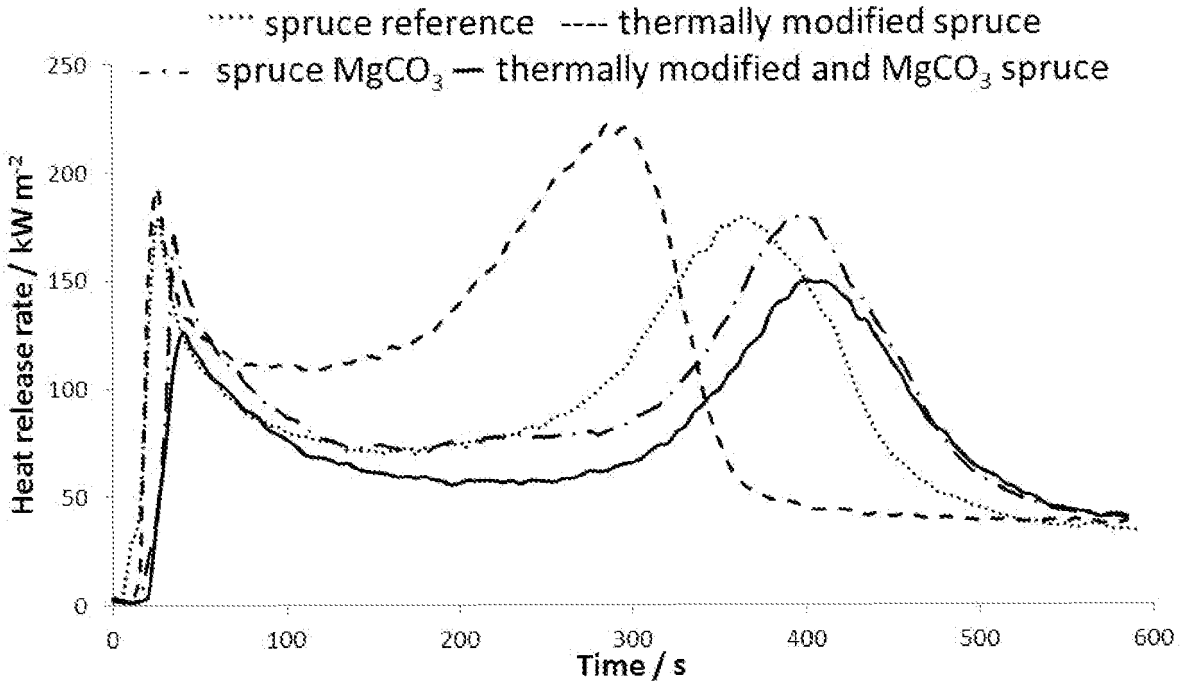

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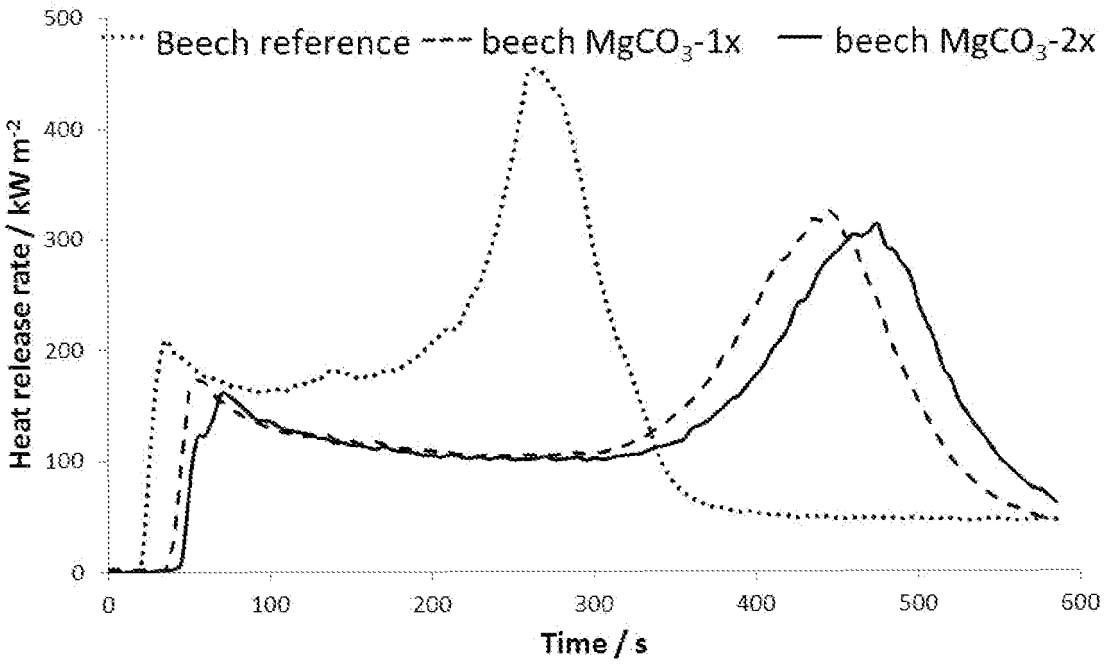

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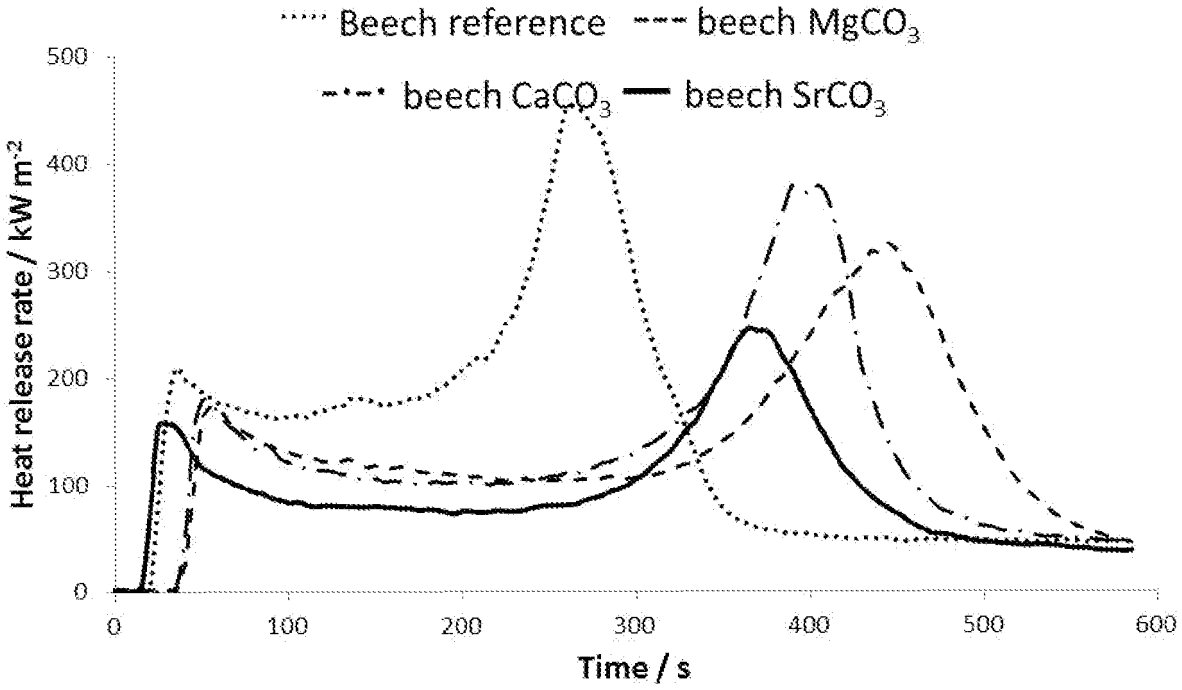

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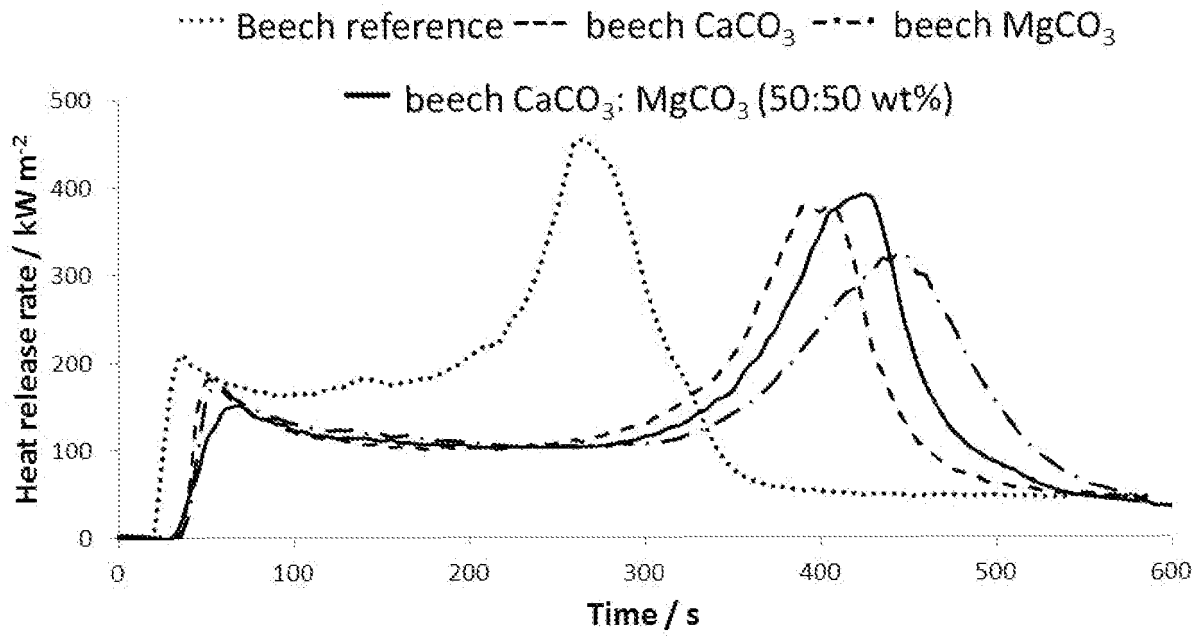

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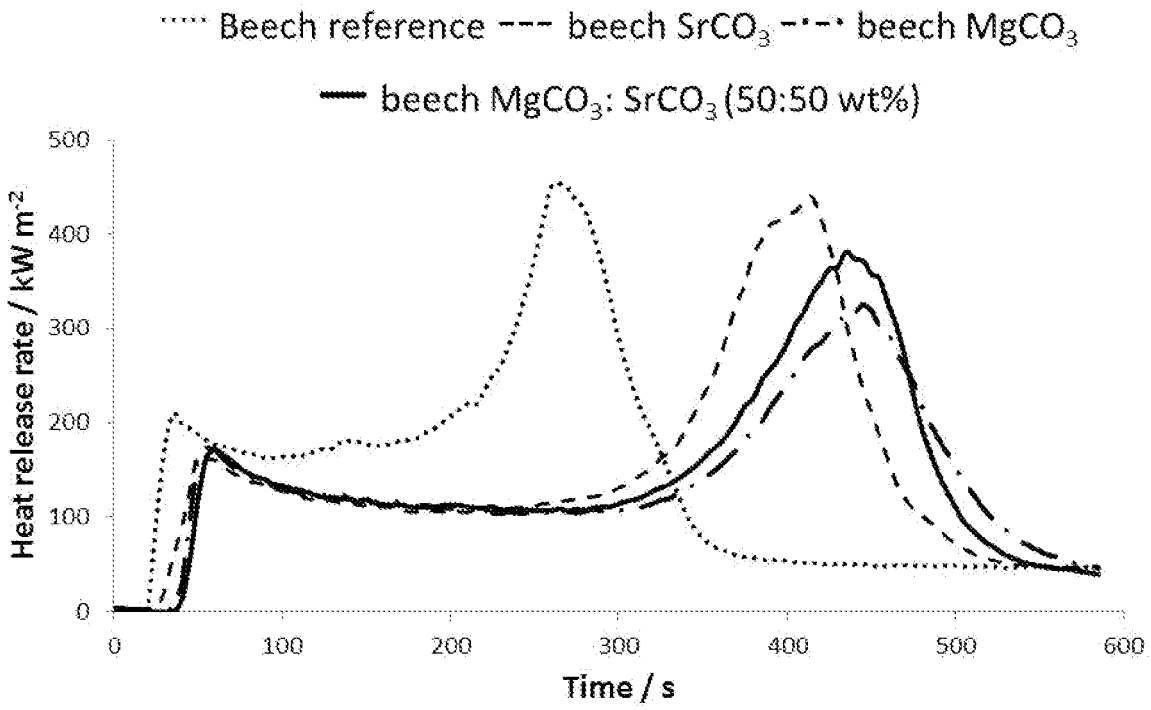

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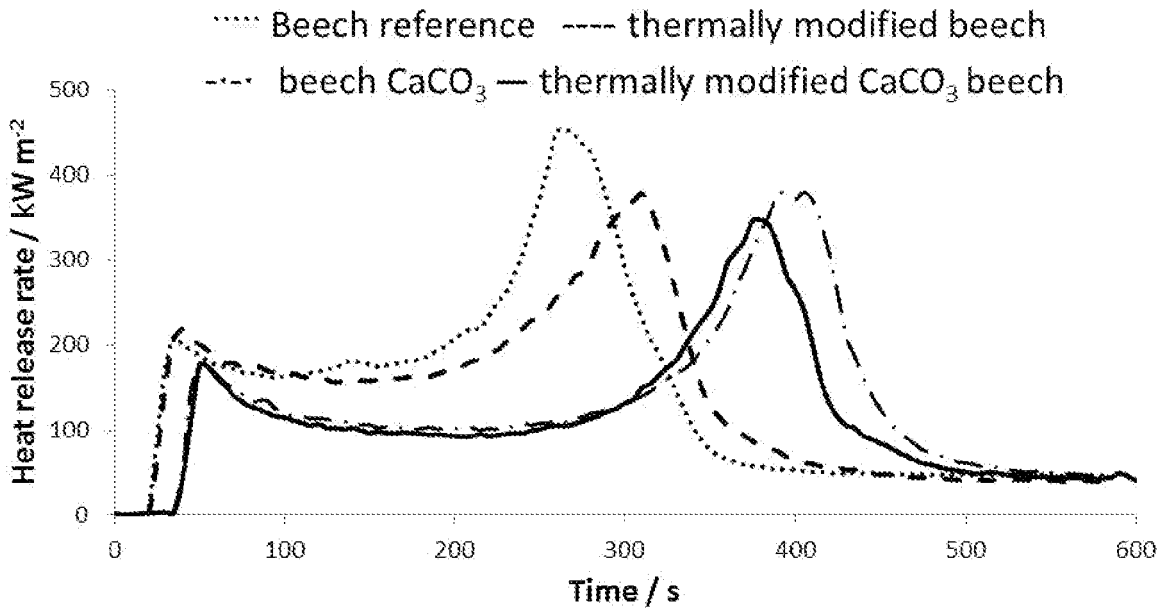

Figure 11

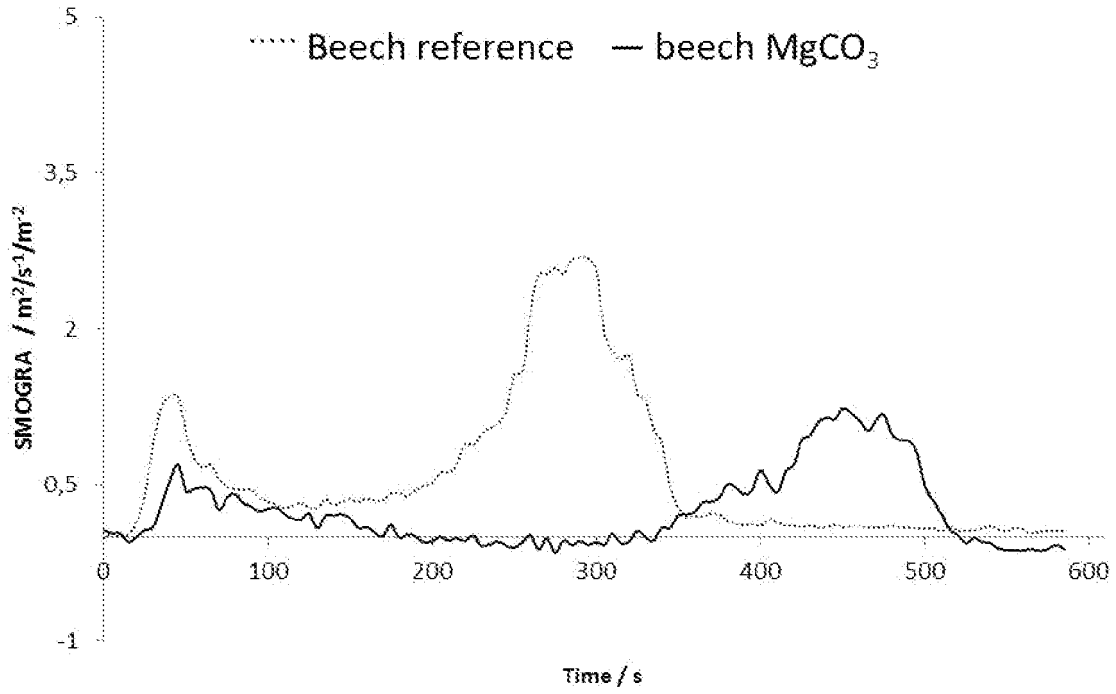

Figure 12

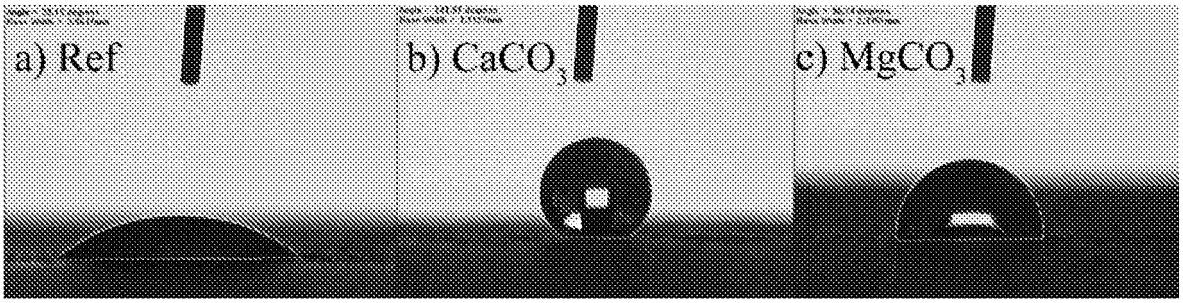

Figure 13

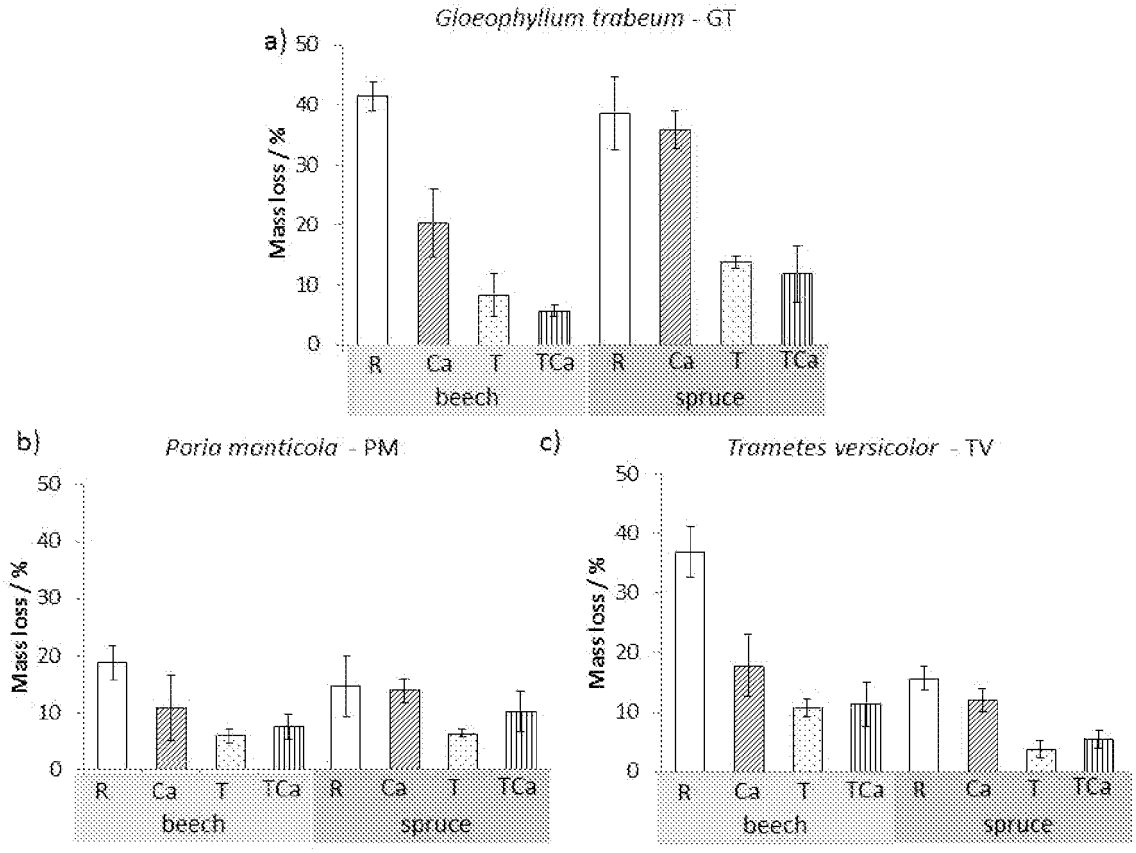

Figure 14

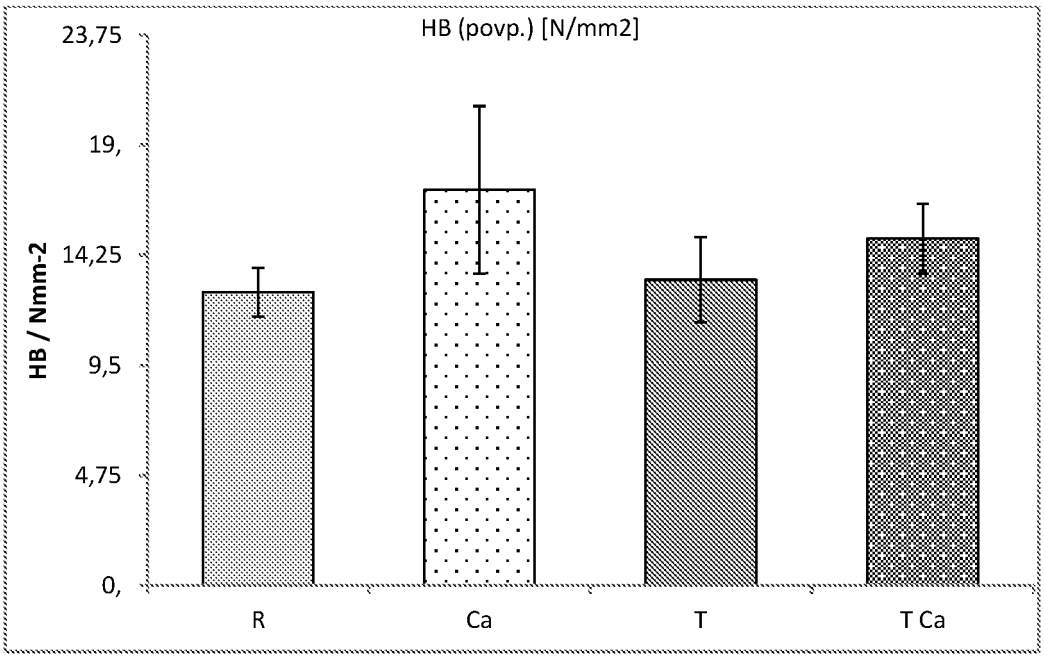

Figure 15

REFERENCES CITED IN THE DESCRIPTION

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