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Thermal stability and hydrophobicity enhancement of wood through impregnation with aqueous solutions and supercritical carbon dioxide

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Abstract A novel process for the thermal stability and hydrophobicity enhancement of wood is proposed. The process concerns the impregnation of wood with water-soluble and water-insoluble salts. The salts are synthesized in situ in wood through aqueous solutions and supercritical carbon dioxide treatment. To protect salt-treated wood from absorbing large amounts of humidity a polymer film is formed upon the surface of wood and depending on the inherent roughness of wood, superhydrophobicity can be obtained. Characterization of the materials was performed by infrared spectroscopy, thermogravimetry, calorimetry, density, color and contact angle measurements and ignition and visual observations. The fire retardation is achieved in both glowing and smolding combustion and may be due to different mechanisms as it was concluded from the thermogravimetric analysis and ignition.

Introduction

The development of fire retarded wood, with unchanged other properties, is of great practical interest and importance. In general, wood decomposition can result from smoldering or glowing combustion. When wood is burning, a char layer is formed that acts as a protection for the rest of the material below the burning layer [1]. One major role of fire retardants (FRs) is to increase this self insulating capacity of wood. This can be done by treating wood with inorganic substances (e.g., salts) that form an increased char at temperatures lower than the major thermal decomposition temperature of wood (e.g., catalyze the dehydration of cellulose to more char and less volatiles, inhibit formation of levoglucosan, get more stable char) [1]. Other roles of FR involve the inhibition of free radicals in the flame (e.g., active oxygen atoms), the formation of coatings, thermal effects (e.g., increased thermal conductivity), and chemicals that dilute combustible gases with non-combustible ones [1–3].

Carbon dioxide is a cheap, non-toxic, non-flammable gas used in fire extinguishers. Besides this usage, it is being widely used as green solvent in its supercritical state, where its properties can be easily manipulated, in numerous applications such as materials processing, reaction medium, extractions, and other [4]. Other materials used in fire extinguishers are salts, like calcium chloride or the edible salt, sodium chloride. Such salts are highly hygroscopic and hydrophilic.

The alteration of the hydrophilic nature of a material to hydrophobic is inspired by the Lotus leafs which possess a hierarchically rough surface: alteration of the hydrophilic nature is achieved by producing a multi-scaled rough coating upon the desired substrate. Acrylic polymers, fluoro-polymers, and silicon-based polymers are used in such applications due to their generally good adhesion and their optical properties [5].

In this study, a novel process for the thermal stability and hydrophobicity enhancement of wood is proposed. The process concerns the impregnation of wood with different substances. The TGA results showed that the treated

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Dedicated to the memory of our untimely lost collaborator, Michael Bridakis.

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samples are more thermally stable than untreated wood, indicating their superior FR performance. This was confirmed by simple ignition test and visual observations.

Materials and methods

All chemicals were of at least 98% purity, purchased from Sigma-Aldrich and were used as received. PMMA (average MW = 120000) was also purchased from Sigma-Aldrich. Silane–siloxane mixture (SILRES BS 290) was purchased form Wacker. Commercial white spirit was used. A piece of Picea Abies wood (2 × 2 × 0.39 cm) was immersed in 25 mL aqueous solution of $CaCl_2$ (2 M) for 1 h and, subsequently, in 25 mL aqueous solution of NaOH (2 M) for another 1 h. Afterward, the piece of wood was placed in the high pressure cell (the high pressure apparatus is described elsewhere [4]), and exposed to supercritical CO_2 atmosphere (at 40 °C and 80 bar) for 1 h. The pressure was rapidly released, and the piece of wood was dried under vacuum. Then, it was immersed in 7% w/v PMMA solution in chloroform or in 7% silane–siloxane in white spirit for 20 min and left at room temperature for a slow solvent evaporation. The impregnation time for the silicon-based polymer-coated wood was 90 min. Finally, it was dried under vacuum. In a second sample, the procedure was the same up to the point of pressure release. The second sample, after pressure release, was immersed in distilled water several times, to remove/eliminate the water-soluble particles and, then, dried under vacuum. This second sample was not polymer coated. TGA (Shimadzu TGA-50) measurements were carried out at air atmosphere with a heating rate of 10 °C min^{-1} up to 160 °C, held for 10 min and, finally, with a heating rate of 10 °C min^{-1} up to 850 °C or up to 300 °C. Pieces, either from the surface or from the center of the sample, with typical dimensions of 1 × 1.5 × 0.8 mm were used for TGA. For the FTIR measurements (Biorad FTS-175), 16 scans with a resolution of 2 cm^{-1} were averaged. The sample preparation for FTIR was done as follows: pieces, similar to those used for the TGA, were further cut into minute particles with a sharp knife. The produced dust was mixed with KBr in mass proportion 1:150 (wood sample:KBr) and compressed into pellets. TGA measurements were conducted on at least two independent samples with reproducibility of 85–90%. The density of the samples was calculated from their mass (accuracy ± 0.1 mg) and dimensions, which were measured with a digital micrometer (accuracy ± 2 μm). For each sample, 6 or 8 color measurements (HunterLab, model mini Scan XE plus) were carried out in different parts of the sample. The PMMA-coated sample and a non-treated wood sample were set on fire in a porcelain cup. To maintain the fire, the samples were placed above paper that had been immersed in ethanol. The fire was let extinguish by itself. Afterward, the same procedure was followed using the already burnt PMMA-coated sample and a new second-untreated sample. Pictures were taken at different times (USB digital microscope, CY-800B). The same process was applied to another kind of wood, namely, beech (Fagus).

Results and discussion

Here, we propose a simple process for the preparation of fire-retarded hydrophobic wood. To accomplish this, three salts (NaCl, $CaCO_3$, and trona) are produced in situ in wood sample and, after drying, the treated wood is polymer coated. The following reactions are carried out:

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_{2(prec)} + 2NaCl \quad (1)$$

$$Ca(OH)_{2(prec)} + ScCO_2 \rightarrow CaCO_{3(prec)} + H_2O \quad (2)$$

$$3NaOH + H_2O + 2ScCO_2 \rightarrow Na_3H(CO_3)_2 \times 2H_2O \quad (3)$$

$ScCO_2$ stands for supercritical carbon dioxide and prec for precipitated. The product of reaction 3 is known as *trona*. Initially, the wood sample (spruce, Picea Abies) is immersed in an aqueous solution of calcium chloride. The impregnated wood is then removed and immersed in a sodium hydroxide solution. Immediately, calcium hydroxide (low solubility in water) is precipitated in the solution and on the surface of wood sample. Alkali hydroxides, such as calcium or sodium hydroxide, have solvating properties for some wood components [6]. Thus, their mixture can be adsorbed and absorbed by wood, and when it will meet calcium chloride, more calcium hydroxide and sodium chloride will be produced. The wood sample is placed then in a high pressure autoclave where it is impregnated with supercritical CO_2. CO_2 reacts with the absorbed calcium hydroxide giving calcium carbonate and with sodium hydroxide and water giving trona. After pressure release, the wood sample is dried, and water is removed. To protect the salt-treated wood from absorbing large amounts of humidity, it is coated by a polymer film by simply immersing the wood sample in a polymer solution and evaporating subsequently the solvent. The key advantage of this process is the application of FR not only on the surface of wood but also the deep impregnation of wood with the water-insoluble or very poorly soluble substances (that are otherwise difficult to impregnate). One can alter the FR content by simply varying the impregnation time. Different polymers were used for the coating (PMMA and silicon-based polymers).

The treated materials were dried under vacuum and then left at room atmosphere conditions for 2 days (temperature range 23–32 °C and relative humidity range 30–45%). The

PMMA-coated sample had a w/w composition of 74.3% wood, 21.2% FR, and 4.5% polymer, while the silicon-based coated sample had 64.1% wood, 33.3% FR, and 2.6% polymer. Their mass was measured at different times until it remained stable. All the treated wood samples absorbed equal or less water than the untreated ones, despite their hygroscopic content, due to their extensive hydrophobic surface character. The hydrophobicity is produced by the polymer coating, the inherent micro- and macro-roughness of wood, and the nano-roughness due to the presence of the FR particles that lead to a Cassie–Baxter surface state [5].

In Fig. 1, water droplets are presented, showing the influence of dispersed particles and the poor wetability of the surface of polymer-coated wood, treated, and untreated. The polymer-coated untreated wood has already a higher water contact angle (WCA) compared to the untreated one, but it is still hydrophilic in the case of PMMA coating. The treated wood samples (presence of FR particles) have an even higher WCA, with a hydrophobic character (WCA $> 90^{o}$) in the case of PMMA-coated wood and a superhydrophobic character (WCA $> 150°$, hysteresis angle $<10^{o}$) in the case of coated wood with silicon-based polymer. The color difference, ΔE, measured in the $L^*a^*b^*$ space, for the treated and untreated but polymer-coated wood samples, was 3.36 and 8.82 for the PMMA coated and for the silicon-based polymer coated, respectively (the coatings were transparent). It has been reported [7] that values of ΔE around 2 are close to the lower limit of eye perception. In dental applications, values of ΔE less than 3.6 are described as clinically acceptable [8]. The measurements indicate that there is a rather small color change in wood, caused by the treatment. The density of the untreated wood was 0.34 g cm^{-3}, while the density of the PMMA-treated wood was 0.44 g cm^{-3} and of the silicon-based polymer-treated wood it was 0.48 g cm^{-3}. This expected increase in wood density is also rather small.

Thermogravimetric analysis (TGA) curves of different samples are presented in Fig. 2a. First, an untreated wood and a PMMA-treated wood were examined (red and black curve, respectively, in Fig. 2a). Pieces from the surface of the samples were used. As shown, initially, the treated wood looses its mass faster than the untreated wood but, after some time, the reverse occurs. This is due to the endothermic polymer degradation, the endothermic decomposition of trona (to sodium carbonate, water, and CO_2) at 165 °C [9, 10], and, also, due to increased char produced at temperatures lower than the decomposition temperature of wood [1]. The same behavior, qualitatively, is observed for a silicon-based polymer-treated wood (gray curve in Fig. 2a). This is a good evidence that our FR suppresses the glowing combustion of wood as do the ones in the literature [1–3]. In Fig. 2b, the TGA curves for untreated wood and polymer-treated (but without salts) woods are

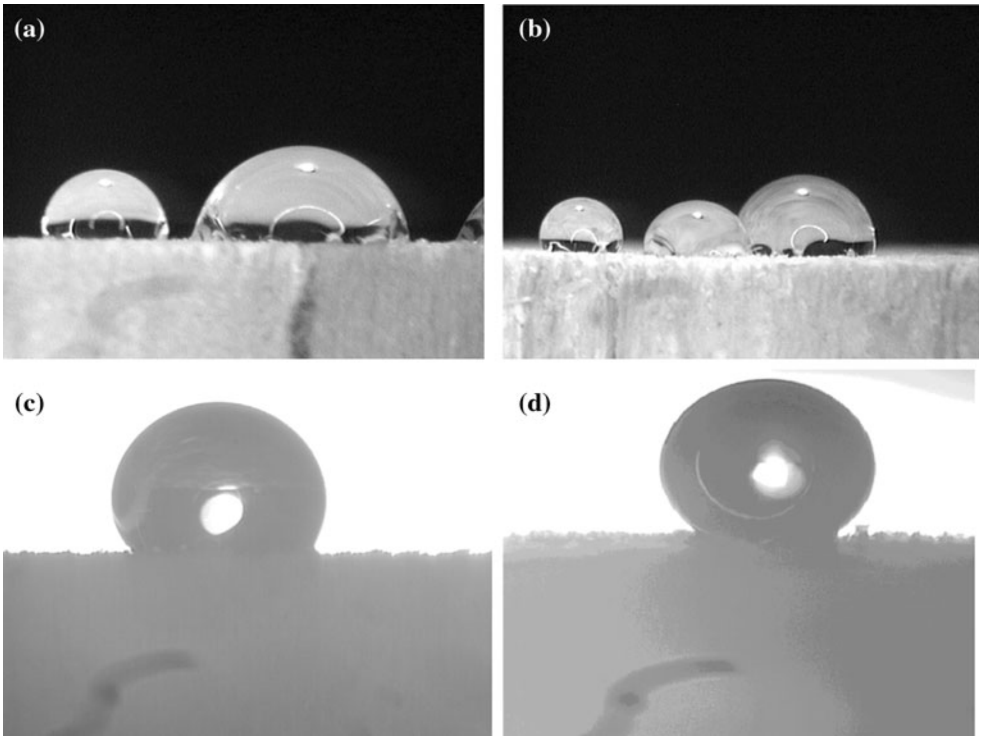

Fig. 1 Water droplets upon the surface of: **a** PMMA-coated untreated wood, **b** PMMA-coated treated wood, **c** silicon-based-coated untreated wood, and **d** silicon-based-coated treated wood

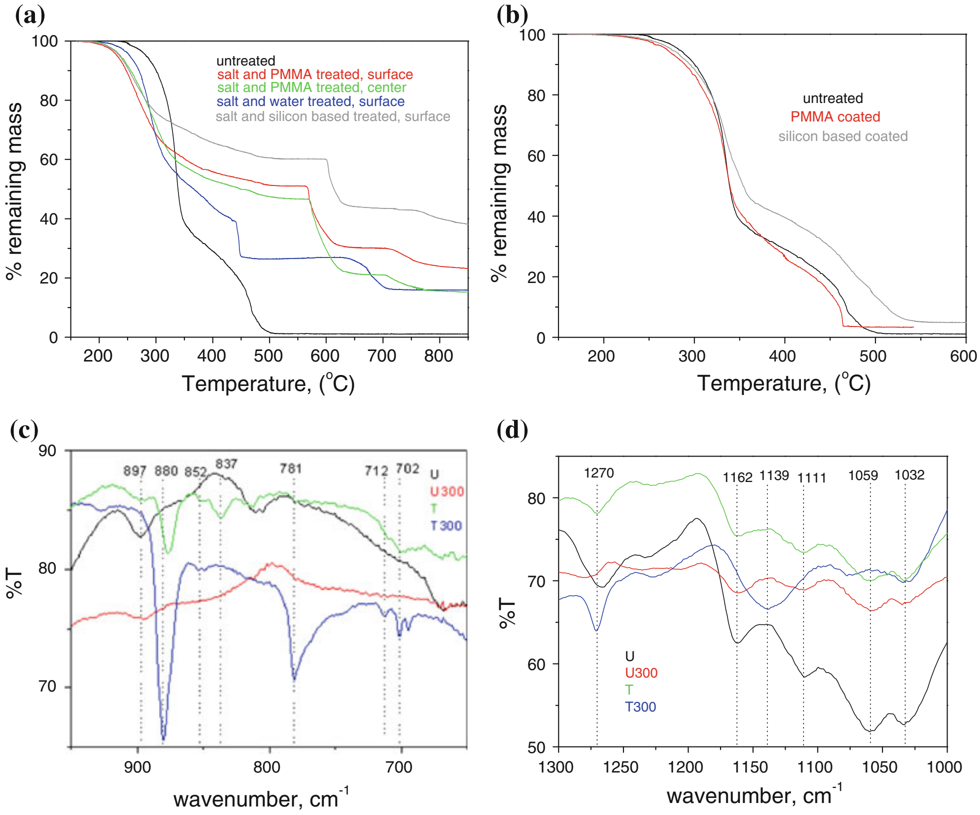

Fig. 2 **a** TGA curves of untreated and treated woods, **b** TGA curves of untreated and polymer-coated woods, and **c** and **d** FTIR spectra at different regions of untreated and silicon-based polymer-coated treated woods before and after heating to 300 °C. *U* stands for untreated wood and *T* for treated, U300 and T300 are the untreated and treated wood, respectively, that were heated to 300 °C

presented. As can be seen, the silicon-based polymer coating of wood acts also as FR, although this is a relatively small contribution. Besides the elimination of glowing combustion and in contrast to other reported FR woods [1–3], our treated FR woods exhibit a high retardation in smoldering combustion, (which is important for the mechanical integrity of wood in columns, roofs, etc.). This is obvious from the much slower mass loss at temperatures higher than 350 °C. This retardation is due to the absorbance of large amounts of heat by the impregnated materials (due to increased heat capacity and thermal conductivity) and, also, due to additional endothermal effects, namely, transformation of aragonite to calcite (two different forms of $CaCO_3$) at 387 °C [10], melting of Na_2CO_3 and NaCl above 600 °C, and decomposition of calcite to CaO and CO_2 above 850 °C with mass loss up to 23% until 800 °C [11]. A PMMA-coated and treated wood sample from the centre of the material (green curve in Fig. 2a) has qualitatively similar behavior with the sample from the external surface of the material (red curve), that is, sudden alterations in the slope of the curves occur at similar temperatures. Quantitatively, it is somewhat less stable since in the center there are less impregnating FR. However, even the centre of the treated material is much more stable than that of the untreated one. A treated wood that was washed with water to eliminate the water-soluble salts, and without polymer coating (blue curve in Fig. 2a), exhibits, qualitatively, different behavior than the fully treated woods. The initial mass loss, around 250 °C, is lower than in other untreated woods (less char). Also, mass loss is observed in them at temperatures above 600 °C, where the fully treated woods have stable mass. This mass loss can be attributed to the absence of Na_2CO_3 and NaCl (no melting and, thus, no heat absorption). The melting points of Na_2CO_3 and NaCl are 851 and 801 °C, respectively, but, since they impregnate wood, they can be considered as highly impure and a melting point depression is expected.

The above are further supported by the FTIR spectra of untreated and silicon-based polymer-coated and treated wood, before and after they are heated up to 300 °C (Fig. 2c and d). 300 °C was chosen on the basis of TGA results. At this temperature, a mass loss of 10–20% occurs for all the samples (early stage of combustion). During combustion/thermal degradation, numerous reactions take place, and there is a great number of intermediate products. The nature of the products in the early stages of combustion can provide evidence for the combustion mechanism.

Considering the salts in Fig. 2c, the bands of calcite (712 and 875 cm^{-1}), aragonite (702 cm^{-1}), and trona (852 cm^{-1}) can be seen in the spectra of treated wood (green curve) [12]. After heating to 300 °C (blue curve), the bands of aragonite and calcite are still present, the band of trona is vanished, and a new peak appears at 880 cm^{-1}.

This band is overlapping the 875 cm^{-1} band of $CaCO_3$ and is due to the formation Na_2CO_3 [12]. Regarding the polymer in Fig. 2c, the band at 837 cm^{-1} (Si–C stretching) [13] in the treated wood, after heated to 300 °C, is vanished, and a new peak appears at 781 cm^{-1} (Si–O–Si symmetric stretch) [14] associated with the formation of silicon-based non-volatile residual. Regarding wood in Fig. 2c, the band at 897 cm^{-1} (C–H stretching in cellulose) [15, 16] is present in all the samples except for the treated wood that was heated to 300 °C. In Fig. 2d, bands at 1032 and 1059 cm^{-1} associated with C–O vibrations [15, 16] are present in both heated samples, while the bands at 1111 and 1162 cm^{-1} associated again with C–O vibrations [15, 16] are present only in the heated untreated sample while a new band at 1139 cm^{-1} appears in the treated wood. In the spectra of the heated treated wood, the band at 1270 cm^{-1}, associated with Guaiacyl ring [15, 16], is present while it is vanished in the untreated sample, which indicates that lignin (the most thermally stable component of wood) [1] was degraded to some extend in the untreated wood. All these differences in the spectra of the treated and untreated heated wood indicate once again that the presence of inorganic particles causes an alteration in the decomposition mechanism.

Photographs of burning PMMA-coated treated and nontreated wood are presented in Fig. 3. The untreated wood burnt almost completely while the fire could not spread in the treated wood. In Fig. 3, the same procedure can also be seen for the already “burnt” treated wood and a second-untreated wood. The fire retardation of the treated wood is obvious.

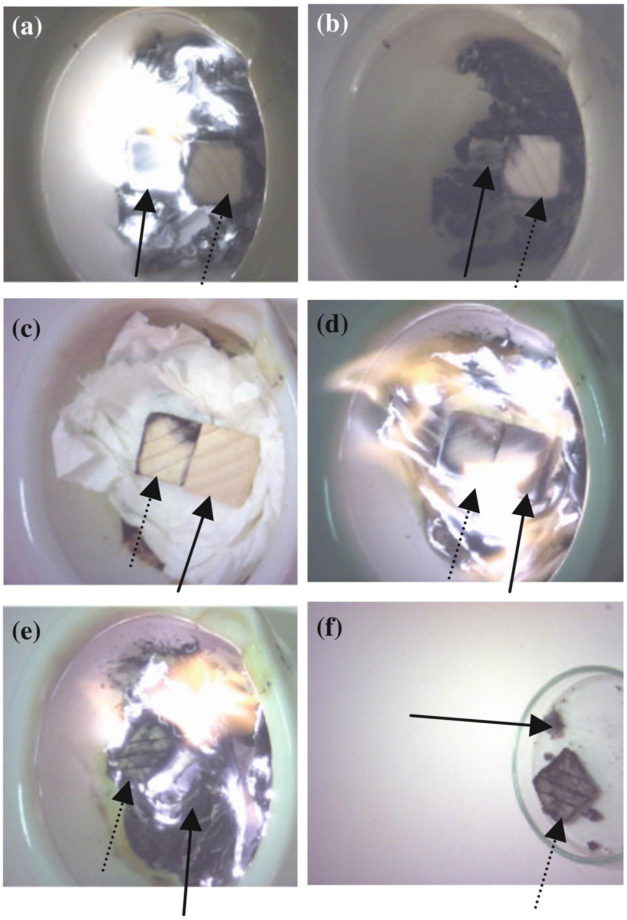

Fig. 3 One PMMA-coated treated wood and two untreated woods while burning at various times: **a** 2 min, **b** 6 min, **c** second-untreated wood 0 min, **d** second-untreated wood 1 min, **e** second-untreated wood 5 min, and **f** second untreated wood 9 min. In all the cases, the dot pointer indicates the treated wood, and the solid pointer indicates the untreated wood

Application to beech wood

The same process was applied to another kind of wood (beech). The TGA curves of silicon-based polymer-coated treated wood and untreated beech are presented in Fig. 4. The same behavior, as for spruce wood, is observed. In Fig. 5, the influence of the synthesized salt particles on the WCA of silicon-based polymer-coated wood is presented.

Beech wood did not have the same high inherent roughness as spruce wood, and only in some parts of the material superhydrophobicity was obtained. However, in any part of the sample, the WCA was greater than 140°. The density of the untreated beech wood was 0.66 g cm^{-3}, while the treated beech had a density of 0.79 g cm^{-3}. The total color change, ΔE, was 3.99. As in the case of spruce, these are rather small changes. The impregnation times in aqueous solutions and supercritical CO_2 were 1 h (for each impregnation) but, due to decreased porosity (compared to the porosity of spruce wood), the treated material had a w/w composition of 86.6% wood, 12% salts, and 1.4%

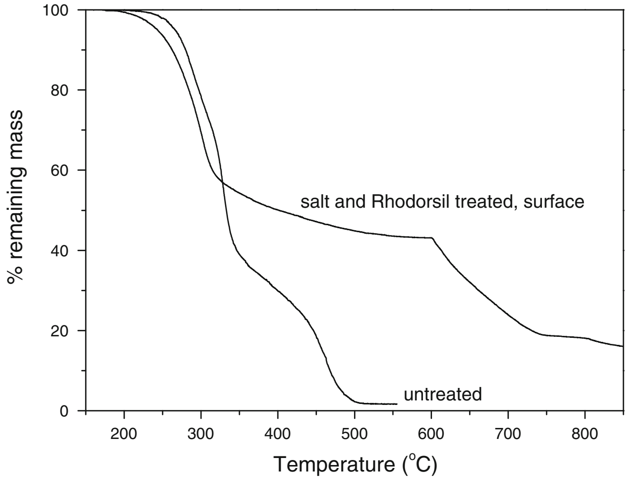

Fig. 4 TGA curves of untreated and silicon-based coated treated beech wood

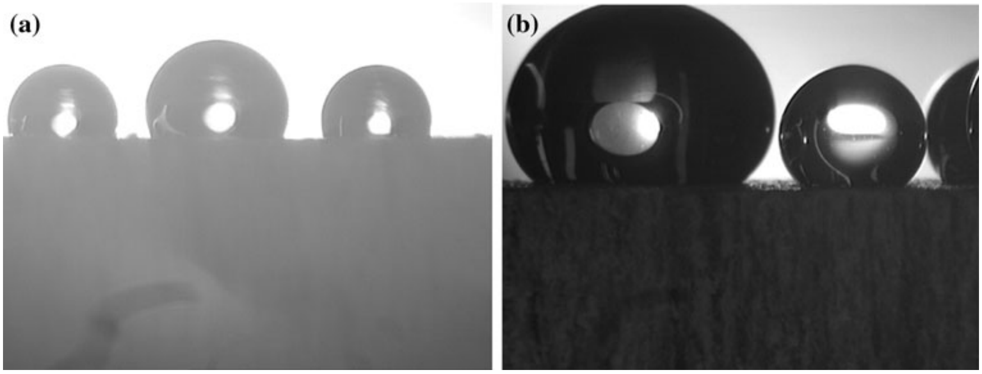

Fig. 5 Water droplets upon the surface of: a silicon-based coated untreated beech wood and b silicon-based coated treated beech wood

silicon-based polymer (less FR content compared to spruce for the same impregnation time).

FTIR spectra and DSC curves are provided as supporting information for the inorganic salts produced, as described in the experimental section, but with no connection to wood. Finally, humidity measurements of treated and untreated wood samples are provided as supporting information.

Conclusion

In summary, we proposed here a simple process for preparation of fire-retarded hydrophobic wood. The process concerns the in situ synthesis, deep in wood samples, of inorganic salts with aqueous solutions and ScCO2 and the formation of a polymer coating. By making a judicious selection of the polymer, additional retardation can be obtained. The FR result may be due to different mechanisms (increased char production, increased heat capacity and thermal conductivity, thermal effects such as melting). Other properties of wood (color and density) are not affected considerably by the treatment.

The produced materials could be used in outdoor or public building applications where high hydrophobicity and thermal stability are required. The proposed process is relatively simple and involves impregnation with liquids and drying. There is today a widespread and multifaceted use of high pressure CO_2 in an endless variety of applications, including wood impregnation, and thus the use of it should not be considered as a limiting factor of the proposed method in this study.

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