

**IMPACT OF THERMAL MODIFICATION COMBINED WITH SILICON
COMPOUNDS TREATMENT ON WOOD STRUCTURE**

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ABSTRACT

In the present study silicon containing formulations were investigated for their applicability in solid wood modification. Black pine sapwood was thermally modified at 180°C and 200°C (3, 5 and 7 hours) and afterwards, an additional chemical treatment with silicon containing systems (N-2-aminoethyl-3-aminopropyltrimethoxysilane) followed, in an attempt to invigorate hydrophobicity and durability of wood. Infrared spectroscopy (FTIR) was used to examine the formation of new bonds in the treated materials and atomic absorption spectrometry (AAS) to measure the silane concentration. The results showed a high reactivity between thermally modified wood and organosilicon compounds. The presence of bands representing vibrations of the Si–O–CH₃ group in IR spectra of modified wood and after extraction confirms the stable character of the formed bonds between the hydroxyl group of wood and the methoxy groups of organosilanes. Furthermore, reactivity between wood and AE-APTMO and alkyd resin solution was confirmed by the AAS results. Alkyd resin caused a higher concentration of silica in wood mass, which increases as the thermal treatment temperature increases. The organosilicon compounds caused a much higher resistance to water washout, revealing permanent binding of silanes to wood mass.

KEYWORDS: Alkyd resin, AAS, coatings, FTIR, organosilanes, preservation, thermal treatment, wood.

INTRODUCTION

Although wood is a valuable and versatile material, it demonstrates moisture related problems, such as dimensional instability and susceptibility to microorganisms attacks. The use of conventional wood preservatives, based on a broad spectrum of harmful biocides and heavy metals, cannot be considered acceptable nowadays, mainly because of the rising concern about human health and environmental impact (Militz et al. 1997, Hill 2006). Continual attempts are being conducted in order to find new wood preservatives that will be easily applied, ensure a long service-life to wood-based products and in parallel, to remain as safely disposable after service, as wood (Pries 2013).

Thermal modification creates a physically, chemically and mechanically different material, characterized by improved dimensional stability, increased biological resistance against fungi and microorganism attacks, slightly improved resistance to natural weathering, lower equilibrium moisture content (EMC) and density and increased wettability (Hill 2006, Awoyemi et al. 2009, Kamperidou 2019, Kamperidou and Barboutis 2021). More specifically, permanent chemical changes are induced in wood mass, involving both endothermic and exothermic reactions. This includes loss of moisture and volatile extractives, partial depolymerization of hemicelluloses and amorphous parts of cellulose, which leads to the crystallization of cellulose and the reduction of hydroxyl content within the wood cell walls (Hill 2006, Kamperidou 2021), as well as to the decrease of cellulose polymerization degree due to thermo-degradation phenomenon (Wang et al. 2018). Hemicelluloses constitute one of the most unstable polymeric wood components and produce furfuryl polymers, which are less hygroscopic, as well as methanol, acetic acid and aldehydes and various other volatile heterocyclic components (furans, γ -valerolactone, etc.) and low molecular weight extractable compounds (Diouf et al. 2011, Kamperidou et al. 2012), which tend to act as catalysts of the polysaccharide depolymerization (Tjeerdsma and Militz 2005). Furthermore, the condensation in lignin network in the form of crosslinking reactions results in the reduction of the wood hydrophilicity. As the intensity of treatment increases, lignin increases in the mass of wood, trapping some by-products of hemicelluloses decomposition and, as it becomes stronger, its phenolic groups increase as well (Tjeerdsma and Militz 2005, Gonzalez-Pena et al. 2009, Diouf et al. 2011). The breakdown of lignin macromolecule starts at temperatures above 270°C, where the gradual cleavage of C-C bonds of lignin begins (Mazela et al. 2004). As some of the volatile extracts are being lost during the process, the pH of wood decreases, due to the production of formic and acetic acid in its mass. At about 220°C, lignin begins to degrade, with the presence of phenolic compounds (vanillin, coniferaldehyde, syringyl aldehyde), where v-aryl ether linkages begin to degrade (Yildiz and Gumuskaya 2007).

Thermal treated wood, as a material of already improved hydrophobic behavior and durability could be further improved by chemical treatment of its mass, in order to strengthen the hydrophobation, dimensional stability and resistance of wood to fungal attack (Shi et al. 2007). The goal of an additional chemical modification of thermally treated wood is to change its properties and enhance its performance by altering the cell wall chemistry. Chemical modification of wood after numerous attempts tends to approach the reconciliation of durability against microorganisms enhancement, with further material properties improvement, such as

dimensional stability, moisture sorption, flammability, UV-stability, weathering performance etc. (De Vetter et al. 2006, Mai and Militz 2004).

Many types of silicon compounds have been applied for this purpose. Silanes have long been used as modification agents in a number of applications, including the attempt of rendering glass, textiles, ceramics etc. more hydrophobic and their excellent properties make them also attractive for non-mineral substrates like wood. Added to a coating formulation they are able to migrate to the substrate interface and improve bonding (Aaserud et al. 2009). Silicones impart water repellency without reducing water vapor permeability, a fact very crucial for applying them as protective agents of mineral substrates (Ghosh et al. 2009). The silanol groups of silanes can react with hydroxyl groups of cell wall polymers forming a durable covalent bond across the interface (Si–O–C), between the silicon compound and cell wall polymers. It has been proposed that these bonds are hydrolysable, but can reform, and therefore, provide a means of stress relaxation at the organic/inorganic interface. The results are improved adhesion and durability (Witucki 1992). Alkylalkoxysilanes bear at least one alkyl group which remains after the sol–gel process, because in contrast to Si–O bonds the Si–C bonds are stable against hydrolysis. It has been shown by FT-IR spectroscopy that the silanes bind to hydroxyl groups in the wood structure (Aaserud et al. 2009). Among other studies, Donath et al. (2006) used the coupling agent γ -methacryloxypropyltrimethoxysilane (TEOS) and organo functional alkoxysilanes and found satisfying incorporation into the cell wall, when conditioned wood was impregnated with alcoholic solutions of the two silanes methyltriethoxysilane and propyltriethoxysilane.

In addition to improved hygroscopic properties, the modification with silanes may have the potential to increase also biological resistance of wood against basidiomycetes and microfungi (Kartal et al. 2009, Peres et al. 2018). Durability of the treated wood towards the white rot fungus *Trametes versicolor* was increased considerably, but especially when the silane penetrated and bulked the cell wall (Donath et al. 2006). Wozniak et al. (2020) treated wood with 15% propolis extract (EEP) and two propolis-silane preparations and revealed that phenols were in lower extent leached from wood impregnated with the propolis-silane preparations, whose constituents presented permanent bonds with wood. Tetraethoxysilane and alkyltriethoxysilanes have been described to impart strong hydrophobation and moderate fungal resistance to wood (Donath et al. 2004, Mai and Militz 2004). Furthermore, it was reported that silanes ω -(methacryloxy)propylx trimethoxy silane and vinyl trimethoxy silane polymerized within the cell wall of black pine caused resistance against fungal decay (Weigenand et al. 2007, Kamperidou 2019). Pries (2013) reported that silica sols are not able to penetrate the cell wall and are solely deposited in the lumens of the cell, the treatment cannot be regarded as a real wood modification. Best water repellence was obtained with acetoxy-functional PDMS (1% proved to be sufficient for maximum water repellence). The PDMS did not penetrate the cell walls of wood sufficiently and did not cause a high and stable bulking, which is needed for dimensional stabilization. De Vetter et al. (2010) treated wood with different water-borne emulsions of silicones and found no significantly improved water repellence and no ASE for low WPG of approximately 5–6%. They concluded that only functionalized silicones may be effective enough for the treatment of wood.

Although, numerous studies have been conducted on silane modification of solid wood, there is scant research on the efficacy and influencing mechanism of silanes modification of already thermally modified wood, referring to its incorporation and chemical bonding potential.

It is the aim of this research work to evaluate the organic silicon compounds based treatment systems that so far have not been extensively tested as agents that improve wood hydrophobicity, and to examine for the first time to the best of our knowledge, the interaction between the already thermally treated wood at different conditions and organo-silicon compounds, assessing the potential utilization of these treatments combination towards the enhancement of hydrophobicity and preservation of black pine wood, as well as of similar properties species.

MATERIAL AND METHODS

Materials preparation

Black pine (*Pinus nigra* L.) sapwood was used in this research work, of Greek origin (Kalampaka region, central Greece) and naturally conditioned for 8 months. The specific species was selected in this experimental work as a species of high availability and significance for a wide applications range. Sapwood was exposed to the selected treatment methods, since it presents a higher necessity of protection against dimensional instability and biological degradation. The boards were cut parallel to grain and the dimensions of the boards intended to be exposed to thermal treatment, were 40 x 100 x 400 mm (the length was parallel to the grain). Prior treatment, the boards were conditioned in a lab chamber at $20 \pm 2^\circ\text{C}$ temperature and $60 \pm 5\%$ relative humidity till constant weight. The mean nominal equilibrium moisture content (EMC) value was found to be 11.5%. The mean density (mass/volume, measured with moisture content at the reported levels) of the pine was 0.662 g cm^{-3} .

Thermal treatment

For the thermal treatment of the boards, a laboratory heating unit (800 x 500 x 600 mm), capable of controlling the temperature within a range of $\pm 1^\circ\text{C}$ was used and it was already preheated to the final temperature when the boards were placed in the chamber. Heat treatment was performed at 180 and 200°C , for 3, 5 and 7 hours, counting 15 min more for the recovery of the temperature in the chamber in steam atmosphere.

After thermal treatment, the boards were placed into large desiccators to return gradually to ambient conditions, and conditioned at stable conditions ($60\% \pm 5\%$, $20 \pm 2^\circ\text{C}$) till constant weight once again. The equilibrium moisture content and density of all the materials were measured (Tab. 1). Thermal treatment of pine wood under the above mentioned conditions induced mass losses in the range of 10.63% - 15.25%, of which 11.44% corresponds to moisture, generated by the drying and thermo-degradation process.

Tab. 1: Mean values of equilibrium moisture content (EMC) and density of unmodified and thermally-modified pine wood after four weeks of conditioning.

Treatment	EMC (%)	Density (g·cm⁻³)
Control	11.448 (0.172)	0.662 (0.015)
180°C - 3 h	9.075 (0.622)	0.657 (0.022)
180°C - 5 h	8.875 (0.598)	0.653 (0.026)
180°C - 7 h	8.441 (0.963)	0.645 (0.021)
200°C - 3 h	8.026 (0.347)	0.600 (0.021)
200°C - 5 h	7.531 (0.826)	0.590 (0.037)
200°C - 7 h	7.049 (0.412)	0.528 (0.021)

*Standard deviation values inside the parentheses.

Chemical treatment

Wood powder representative samples (obtained from different heights, widths and lengths of the boards), were prepared from all categories of modified and unmodified black pine, using a rotating-blade “Willey” mill (Thomas Scientific, Swedesboro, USA). The samples were obtained through sieving twice to achieve the appropriate dimensions (fraction between grid apertures of 40-60 mesh).

The preparation of water-based system containing the hydrophobic agent of organosilane N-2-aminoethyl-3-aminopropyltrimethoxysilane (AE-AP TMOS) (XIAMETER OFS-6020 SILANE, San Francisco, California, USA) and alkyd resin (FTALAK S-6575; Plastbud Sp.z.o.o., Pustków, Poland) of 75% solids content, was run at deionized water solutions at room temperature at different volumetric ratios. The homogenous wood material of black pine in the form of powder was treated with silane systems (1/25 w/v) at room temperature at the simultaneous stirring with a magnetic bar stirrer for 2 hours. Wood samples were left in working solutions at room temperature for the next 2 hours, then filtered and dried in air flow at room temperature. The obtained materials were leached using continuous extraction with distilled water at a constant ratio (1/100 w/v) for 2 hours. Homogeneous samples of wood, in the amount of 5 g each, were collected from the test material just after treatment, as well as subjected to leaching.

Infrared spectroscopy

Wood powder samples were mixed with KBr (Sigma Aldrich, Darmstadt, Germany) at a 1/200 mg ratio. Each sample was ball milled for 20 sec to a very fine powder (Mikro Dismembrator, Sartorius). Then, it was placed in a standardized pellet press having a die suitable to form a pellet of 13 mm diameter, applying force of about 10 t through vacuum conditions (75 kN cm⁻² for 3 min/sample). Spectra were registered using an Infinity spectrophotometer by Mattson (Mattson ATI Genesis, Illinois, USA) with Fourier transform at a range of 500-4000 cm⁻¹ at a resolution of 2 cm⁻¹, registering 64 scans.

Flame atomic absorption spectrometry

The ground wood samples were mineralized in Mars-express CEM International semi-closed microwave mineralization system. Solutions obtained by the digestion were analyzed for silicon contents by flame atomic absorption spectrometry (FAAS) using

an AA280FS spectrometer (Agilent Technologies, Santa Clara, CA, USA). The final results were the mean values of three simultaneous measurements. Analytical curves were prepared on the basis of a series of freshly prepared standard solution with silicon concentration of 1000 mg dm^{-3} .

RESULTS AND DISCUSSION

Figs. 1 and 3 present FTIR spectra of wood treated silane with alkyd resin (AE-APT MOS) and silane (after wood treatment), while Figs. 2 and 4, those of wood treated silane with alkyd resin (AE-APT MOS) and silane, after the elution (after water leaching of treated wood).

It should be emphasized here that new band of 1730 cm^{-1} was found in all spectra of homogenous wood with tested system. They are responsible for stretching vibrations of the C=O group. The presence of this band indicates the conversion of wood treated with alkyd resin. This band is visible also on IR spectra after extraction, which indicates a permanent bond between alkyd resin and wood components.

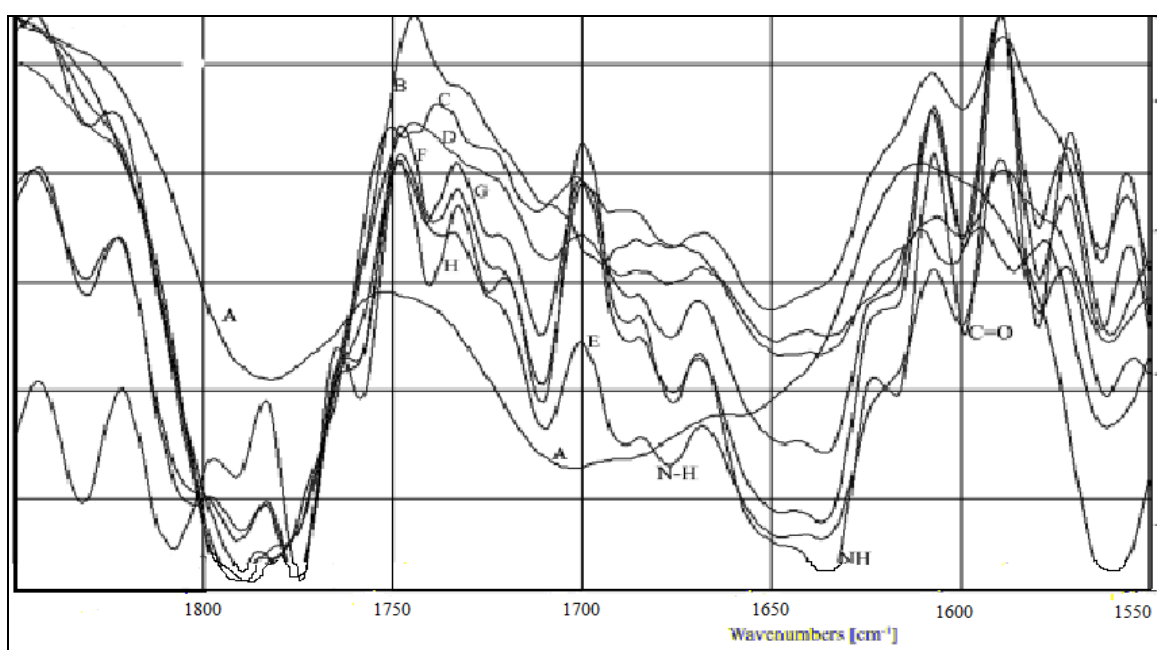


Fig. 1: IR Spectra of wood (A), wood treated with AE-APT MOS and alkyd resin (B), thermally modified wood (180°C and 3h) treated with AE-APT MOS and alkyd resin (C), 180°C and 5h (D), 180°C and 7h (E), 200°C and 3h (F), 200°C and 5h (G), 200°C and 7h (H).

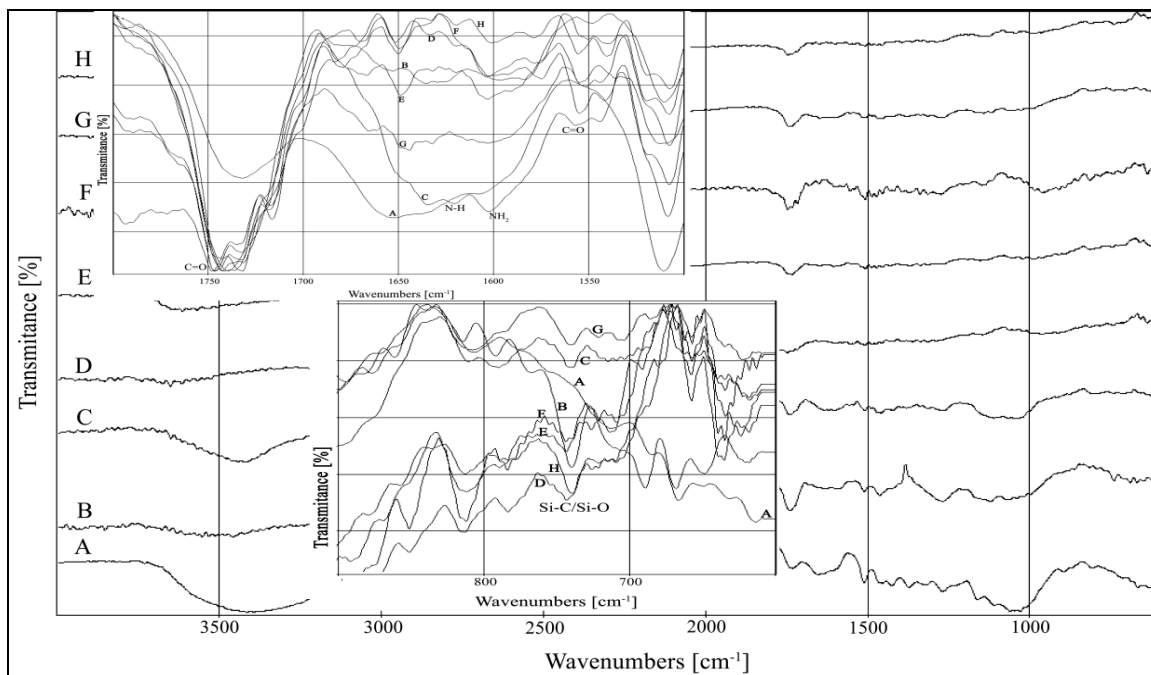


Fig. 2: IR Spectra of wood after water extraction (A), wood treated with AE-APT MOS and alkyd resin and after water extraction (B), thermally modified wood (180°C and 3h) treated with AE-APT MOS and alkyd resin and after water extraction (C), 180°C and 5h (D), 180°C and 7h (E), 200°C and 3h (F), 200°C and 5h (G), 200°C and 7h (H).

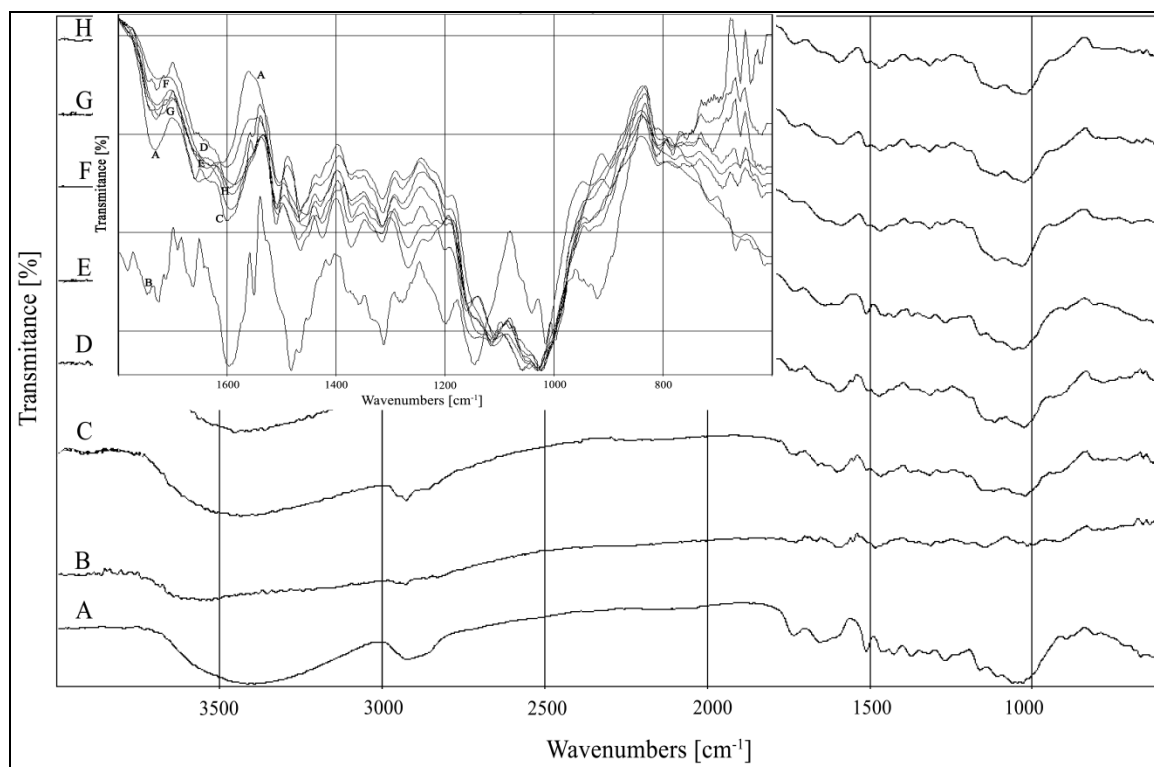


Fig. 3: IR Spectra of wood (A), wood treated with AE-APT MOS (B), thermally modified wood (180°C and 3h) treated with AE-APT MOS (C), 180°C and 5h (D), 180°C and 7h (E), 200°C and 3h (F), 200°C and 5h (G), 200°C and 7h (H).

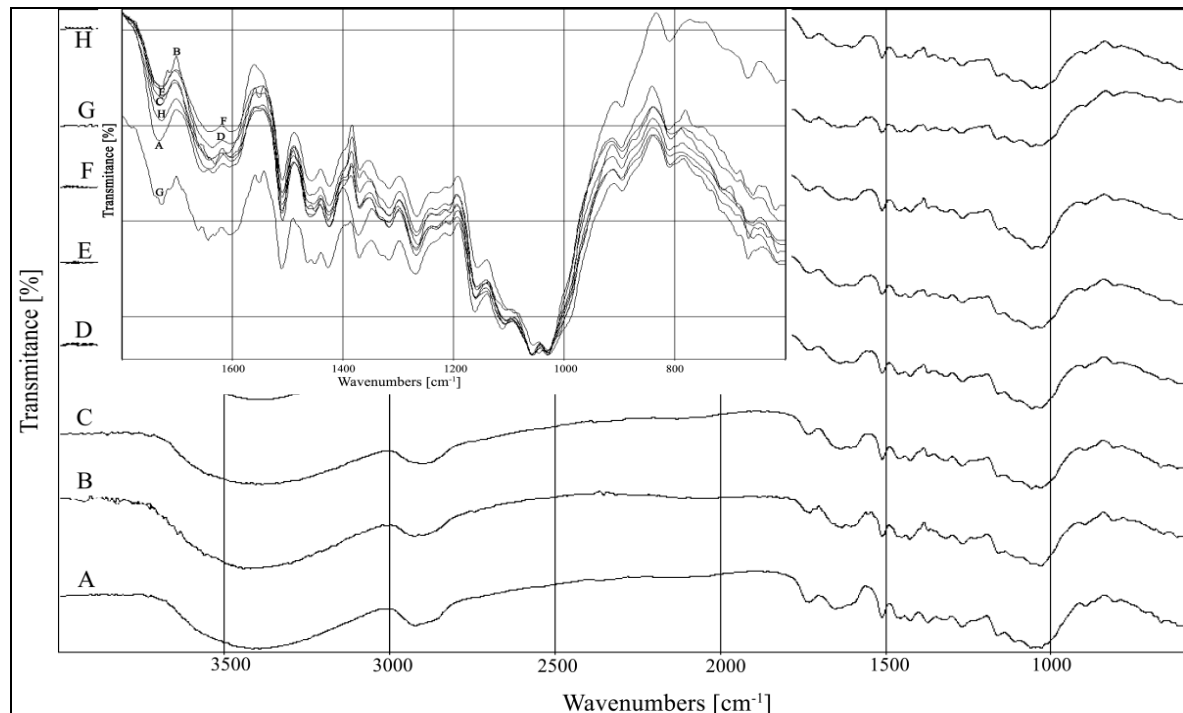


Fig. 4: IR Spectra of wood after water extraction (A), wood treated with AE-APT MOS and after water extraction (B), thermally modified wood (180°C and 3h) treated with AE-APT MOS and after water extraction (C), 180°C and 5h (D), 180°C and 7h (E), 200°C and 3h (F), 200°C and 5h (G), 200°C and 7h (H).

Following the reaction with the systems of alkyd resin/AE-APT MOS a band of 1280 cm^{-1} characteristic for Si-C and/or Si-O bonds was recorded in the wood spectra. This band is found also in wood spectra after extraction. It is characteristic for a silicon bond with carbon and oxygen atoms originating from the methoxy group present in organosilanes (Sèbe et al. 2004, Tjeerdsma and Millitz 2005, Ghosh et al. 2009). Ratajczak et al. (2018) has also detected the stable character of Si-C and Si-O bonds that has been revealed through IR spectra.

Results of AAS analysis (silicon concentration) confirm a high reactivity of wood components with tested system (Fig. 5). Thermally untreated wood contains considerable more silicon ($6380 \text{ mg}\cdot\text{kg}^{-1}$) than thermally modified wood ($4186\text{-}5066 \text{ mg}\cdot\text{kg}^{-1}$). Silicon compounds, however, are not permanently associated with the wood mass. After the aging tests, the extraction of water showed that more silicon atoms were found in thermally modified wood ($536 - 935 \text{ mg}\cdot\text{kg}^{-1}$) than the case when the wood was not thermally modified ($473 \text{ mg}\cdot\text{kg}^{-1}$). Thermal modification temperature of 200°C revealed a decrease in the amount of silicon concentration, with respect to the thermal modification at the temperature of 180°C. Using systems that included alkyd resin showed that thermally modified wood is characterized by increased silicon concentration, compared to thermally unmodified wood. The presence of the resin content significantly increases the bonding of silicon substances.

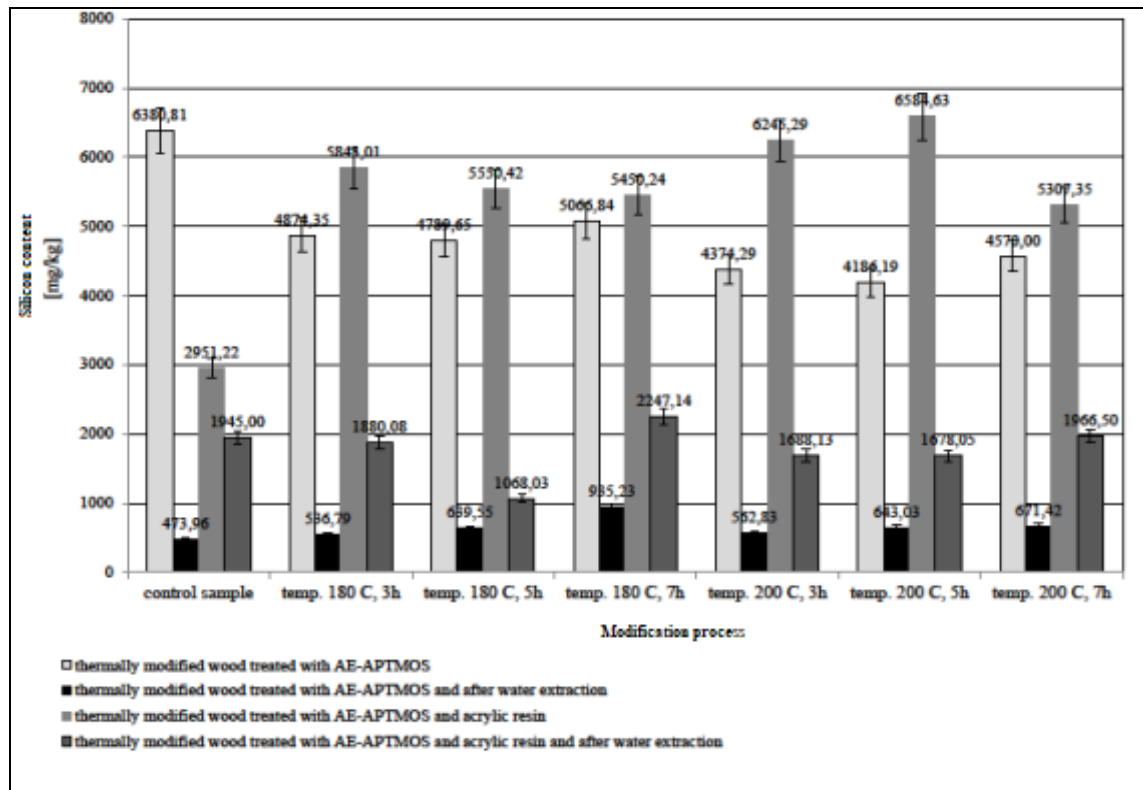


Fig. 5: AAS analysis of silicon concentrations in thermally modified wood treated with silane/alkyd resin and in thermally and chemical modified wood after extraction with water.

CONCLUSIONS

In the current work, black pine wood was initially thermally modified and then treated with AE-APTMS and alkyd resin solution aiming to fight the hygroscopic nature of wood and therefore improve some properties crucial for its further utilization. The results after extraction were analyzed by infrared spectroscopy (FTIR) and presented a high reactivity between thermally modified wood and organosilicon compounds. Moreover, the presence of bands representing vibrations of the Si–O–CH₃ group in IR spectra of modified wood and after extraction confirms the stable character of the formed bond between the hydroxyl group of wood and the methoxy groups of organosilane. Moreover, reactivity between wood and AE-APTMS and alkyd resin solution was confirmed by the AAS results. Alkyd resin causes a higher concentration of silica in wood mass (improved binding), which increases as the temperature of thermal modification of wood increases. The organosilicon compounds in systems cause a much higher and stronger resistance to water washout, a fact that proves permanent binding of silanes to wood mass.

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