

Dimensional Stability, Fire Performance and Decay Resistance in Wood Impregnated with Alkylalkoxysilanes

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Abstract—The wood, very heterogeneous and complex material, changes its volume by water absorption or desorption causing swelling or shrinkage and also it can be degraded both by action of microorganisms and fire; the above-mentioned is a great inconvenient for most commercial uses.

In this research, wood specimens of *Pinus radiata* were previously pretreated in a Soxhlet extractor for 2 hours with a solution of sodium hydroxide (activation of the cellulose) and then impregnated with alkylalkoxysilanes hydrolyzed and condensed "in situ" by the sol-gel process. Silanes selected were triethoxysilane, methyltriethoxysilane, *n*-propyltriethoxysilane, *n*-butyltriethoxysilane and *n*-octyltriethoxysilane.

Impregnation process was carried out under controlled operating conditions to achieve similar weight gains of the chemical modifier. The pH was adjusted to alkaline value for controlling kinetic of hydrolysis and condensation reactions.

Results indicated that dimensional stability increased with the increase of the length of the hydrocarbon chain of the alkoxydes, which would be based essentially on their enhanced hydrophobicity but without discarding the partial occupation of the pores by polymerized siloxanes and the interaction of alkoxydes with cell wall components.

In addition, wood specimens impregnated with mentioned alkylalkoxysilanes also showed an excellent fire performance and decay resistance.

Index Terms—wood, impregnation, alkylalkoxysilane, dimensional stability, fire performance, decay resistance.

I. INTRODUCTION

The wood used industrially, due to their intrinsic characteristics, is a very heterogeneous and complex material; it has many properties that make it attractive for using in construction. However, it is vulnerable to many causes of destruction (moisture, biological attack, fire, etc.).

Wood contains 50 to 60% cellulose; its amorphous regions are hygroscopic. The decrease in water absorption is directly related to protection of the substrate; a high coefficient of absorption allows the solubilization of high amounts of aggressive contaminants from the environment, the proliferation of microorganisms and their degrading metabolic products, sensitive modifications in pH values and finally the leaching of solubilized compounds. In addition, high water absorption leads to low dimensional stability and then, its destruction.

The volumetric shrinkage and swelling, due to daily fluctuations and/or seasonal of temperature and humidity, generally varies between 8 and 22%; this takes place as a

result of axial variation (between 0.2 and 0.6%), the radial (between 1.5 and 7.0%, i.e. about 10 times the longitudinal) and tangential (between 4.5 and 15.0%, i.e. approximately 20 times the axial). The quoted volume change of wood is inconvenient for most commercial uses; therefore, it is important give it dimensional stability.

Other frequent cause of destruction of medium- and low-density wood is that it shows reduced resistance to fire penetration due to their insufficient ability to form a char insulating layer and to maintain their mechanical properties during a conflagration. Therefore, the wood requires a fireproof treatment [1]-[3].

One of the most used pretreatments is thermal modification of wood. This method is knowingly beneficial since it improves dimensional stability, hydrophobicity and decay resistance of the wood [4]-[8].

Beyond the scientific and technological advances reached in thermal treatments, the chemical modification of wood is also a very used method [9]-[18]. Commercially available chemicals used to modify the wood usually include anhydrides, isocyanates, chlorides, lactones, nitriles, etc. [19]-[23].

The chemical modification is based on the well-known reaction between hydroxyl groups of cellulose, hemicellulose and lignin with different reagents, which should be selected according to the desired properties (decay resistance, dimensional stability, fire resistance, etc.).

In this study, researches were developed to establish the properties of chemically modified wood by impregnation with alkylalkoxysilanes with different length of hydrocarbon chain, hydrolyzed and condensed "in situ" by the sol-gel process, in order to allow fundamentally greater dimensional stability (low water absorption) as well as satisfactory fire control and adequate decay resistance.

II. MATERIALS AND METHODS

The experiment included (i) preparation of wood specimens; (ii) choice and characterization of wood modifying reagents; (iii) selection of sol-gel process conditions, and finally (iv) selection of impregnation conditions.

Preparation of wood specimens. *Pinus radiata* was selected since it is a porous wood (oven-dry density, 0.606 g.cm⁻³) and moderately penetrable. Wood specimens, free of

defects, were prepared for each test with the proper size. It is noteworthy that the hydroxyl groups of the lignin have high reactivity to chemical agents while in the case of those present in the cellulose, the accessibility (reactivity) is low. The above bases the previous activation of the cellulose; for this purpose, the specimens were pretreated in a Soxhlet extractor for 2 hours with a solution of sodium hydroxide (pH 8.5) and then for about 5 minutes with distilled water to remove the alkali remaining on surface; in this process generally is observed a partial removal of hemicellulose and lignin. Subsequently, the specimens were exposed in a chamber under controlled temperature and humidity conditions (20 ± 2 °C and $60 \pm 5\%$ RH) until reaching the equilibrium moisture according to the guidelines of ASTM D 4933.

Choice and characterization of wood modifying reagents. Alkylalkoxysilanes were selected as wood reactive modifiers. They were triethoxysilane (A.I, chemical formula, $C_6H_{16}O_3Si$; molecular weight, 164.3; aspect, colorless clear liquid; density, 0.875 g.cm^{-3}); methyltriethoxysilane (A.II, chemical formula $C_7H_{18}O_3Si$, molecular weight 178.3; aspect, colorless clear liquid; density, 0.895 g.cm^{-3}); n-propyltriethoxysilane (A.III, chemical formula $C_9H_{22}O_3Si$, molecular weight 206.4; aspect, colorless or yellowish clear liquid; density, 0.892 g.cm^{-3}); n-butyltriethoxysilane (A.IV, chemical formula $C_{10}H_{24}O_3Si$, molecular weight 220.4; aspect, colorless clear liquid; density, 0.890 g.cm^{-3}) and n-octyltriethoxysilane (A.V, chemical formula $C_{14}H_{32}O_3Si$, molecular weight 276.5; aspect, colorless clear liquid; density, 0.880 g.cm^{-3}). It is worth mentioning that the selected alkoxides exhibit low toxicity and are not polluting to the environment.

In the present experiment, 4/1 solvent mixture (1/1 toluene-ethyl glycol acetate v/v ratio) / alkoxide molar ratio was used. The pH was adjusted to alkaline value for controlling kinetic of hydrolysis and condensation reactions; for this purpose, ammonium hydroxide (conc.) was used until reaching pH 8.2 ± 0.1 .

Selection of sol-gel process conditions. It involves the hydrolysis and condensation reactions of metal-organic precursors. In this process, the pH of the solution is an important variable for the influence exerting on the polymerization kinetic. To prepare high-density gels, it is not recommended a high kinetic of hydrolysis and condensation reactions since many $\equiv Si-OH$ and/or $\equiv Si-OR$ groups may remain trapped (difficult condensation due to steric hindrance). In this experiment and taking into account the above, it was considered convenient to select an alkaline medium.

The hydrolysis and condensation reactions lead to the formation of aggregates (clusters), which are then linked to form a single large aggregate called gel. After gelation, the system continues producing nanostructural and chemical changes (aging, which involves the expulsion of the liquid phase contained in the wood pores, i.e. water and alcohol). At this stage, the polymerization reactions continue increasing the links $\equiv Si-O-Si \equiv$, attaining the hardening of the gel

(xerogel).

Simultaneously to the aforementioned reactions, the wood chemical modification also occurs. Many researchers have studied chemical modifications that involve the reaction of hydroxyl groups [24]-[29]. Bonds $\equiv Si-O-C \equiv$ would arise from hydrolysis of alkoxides and the subsequent condensation of $\equiv Si-OH$ with the $-OH$ of the wood [30].

In this experiment, solid wood specimens were exposed under controlled laboratory conditions for allowing the gelation and the aging (natural drying).

Selection of impregnation conditions. This process was carried out at $45-50$ °C in an autoclave equipped with vacuum pump and compressor, under controlled operating conditions. In all cases, the 3/1 impregnant solution/wood v/v ratio was selected to ensure that the wood specimens were completely submerged during the entire process. Then, the autoclave was charged with the wood specimens and it was applied a vacuum of 200 mm Hg for 10 minutes to release air and water vapor from the cells to facilitate the penetration of chemical modifier.

Later, the corresponding alkoxide solution was added without decreasing the vacuum level. The operating conditions were adjusted to achieve similar weight gains of the chemical modifier: the pressure was gradually increased from 1.5 to 6.5 kg.cm^{-2} to facilitate the penetration; this stage lasted from 15 to 60 minutes. The next one was the application of a slight vacuum (about 50 mm Hg for 10 minutes) to remove the excess alkoxide on the wood specimen's surface.

Finally, the wood specimens were removed after reaching atmospheric pressure; later, they were exposed into a chamber under controlled temperature and humidity conditions (20 ± 2 °C and $60 \pm 5\%$ RH) for three weeks for allowing the gelation and aging.

Average weight gain for all selected samples was $10.05 \pm 0.43\%$ w/w; for each specimen, weight gain was determined by using the equation $WG = [(W_m - W_o) / W_o] \times 100$, where W_o and W_m are the weight of the wood specimens pretreated in the Soxhlet and the weight of those chemically modified in the autoclave, respectively (all of which were previously dried in an oven at 100 ± 3 °C up to constant weight).

In addition, the penetration (depth reached by the impregnating solution solids) was qualitatively determined by visual and microscopic observations on cuts of wood specimens; this was practically complete (the whole of the specimen thickness) in all cases.

III. LABORATORY TESTS

The following laboratory tests were carried out in triplicate:

A. Inorganic polymers characteristics

To understand some aspects of inorganic polymers, X-ray studies were carried out on alkoxides hydrolyzed and condensed outside of wood pores to know some of their

characteristics. In addition, thermal expansion coefficients and densities were measured; thermo-gravimetric analyses (TGA) were also carried out.

Finally, several wood specimens were observed by scanning electron microscopy (SEM) to visualize the structure change experienced by specimens impregnated with alkoxides after curing inside the wood pores. For micrographs, cuts in three directions were previously carried out and then a polishing with thick wool cloth was made; finally, surface of specimens was coated with gold.

B. Dimensional stability

Test specimens, free of defects, were prepared with size of 20 x 20 x 20 mm. The degree of dimensional stability was determined by estimating the Volumetric Swelling Coefficient S and the Anti-Swell Efficiency ASE.

The saturation water was evaluated by using the ASTM D 4442. The specimens were immersed in distilled water at 20±2 °C up to constant weight; then, the specimens were removed, the excess water was drained and the volume of specimens was determined by the mercury displacement method. Finally, the specimens were dried in oven at 100±3°C and the volumes were again quantified by the aforementioned method.

Finally, the Volumetric Swelling Coefficient was calculated by using the equation $S, \% = 100 (V_2 - V_1) / V_1$, where V_2 and V_1 are the volumes of saturated and oven dried specimens, respectively.

Concerning Anti-Swell Efficiency, it was calculated by using the expression $ASE, \% = 100 (S_s - S_m) / S_s$, where S_s and S_m are the average expansion coefficients of the unmodified and modified specimens, respectively.

Finally, the immersion process was repeated at 20±2 °C in distilled water for 72 hours in order to determine the leachability of the cured impregnant through the S and ASE values in a second cycle.

C. Determination of performance against fire

Two-Foot Tunnel (ASTM D 3806). Test specimens, free of defects, were prepared with size of 6 x 100 x 610 mm. The Flame Spread Index FSI was computed by using the equation $FSI = (L_s - L_o) / (L_b - L_o)$, where L_s is average of the three highest flame-advances on experimental panels, L_o is average of the three highest flame-advances on asbestos-cement board and L_b is average of the three highest flame-advances on Reference. It is worth mentioning that the value L_o is the flame-advance produced by the reflection of flame of Bunsen burner on asbestos-cement board during testing in Two Foot Tunnel; in the experiment, L_o was 50 mm.

In addition, the Panel Consumption PC was also carried out. PC represents directly the weight loss during the test and indirectly the resistance to fire penetration.

Finally, the Smoke Density SD was measured (device includes a chimney, a light source and a photocell in the opposite point of ignition); the direct reading in percent (0.0-100.0) of light transmission received in the photocell was recorded (an opaque card was used for calibrating the zero

value of scale). The maximum values were registered during the test.

Oxygen Index (ASTM D 2863). This test determines the minimum oxygen concentration in a nitrogen/oxygen mixture that supports material combustion under equilibrium conditions as candle-like burning. The determination of OI index was carried out with a flow rate of 3.2 cm·s⁻¹ by using specimens, free of defects, prepared with size of 150 x 10 x 10 mm.

D. Decay resistance

After finishing de Cycle II, impregnated specimens of *Pinus radiata* (20 x 20 x 20 mm size) were exposed for 12 weeks under controlled conditions (25±5 °C and 60-70% RH) to *Polyporus meliae* (brown rot) and *Coriolus versicolor* (white rot), following the general guidelines of ASTM D 2017.

Then, the specimens were placed in an oven at 100±3 °C up to constant weight. Weight loss was determined for each specimen by using the following equation $WL, \% = [(W_o - W_f) / W_o] \times 100$, where W_o and W_f are the weight of the dried specimens without and with exposure to fungi, respectively.

IV. RESULTS AND DISCUSSIONS

A. Properties of inorganic polymers

Studies applying X-ray show an interatomic distance between Si and O about 1.62 Å and that each oxygen is linked to two silicon atoms.

Values of inorganic polymer unidirectional thermal expansion indicate, at first temperature intervals studied, an almost lineal increase whereas a faster rise is noted at higher temperatures. Furthermore, the volumetric coefficients, in total correspondence with those of lineal dilatation, show a reduced expansion even at temperatures between 25 and 800 °C (approximately those registered in fire): the values oscillated in a small range of 1.704 to 1.673%. This would promote the dimensional stability of treated wood, and consequently its mechanical resistance during conflagration.

On the other hand, density values at 20 °C oscillated between 2.112 and 1.939 g·cm⁻³; the analysis of inorganic polymer density indicates that the impregnation would increase the density of treated wood according to the retention degree.

It is important to point out that preliminary thermo-gravimetric analyses (TGA) indicated that these inorganic polymers cured at laboratory conditions are extremely stable at high temperatures: the loss by volatilization showed very reduced values at 800 °C (inferior to 0.1% w/w).

Figure 1 clearly displays the difference of hollow spaces between wood specimen taken as Reference and that impregnated after curing (A.5). In addition, in EDX determinations before immersion, the axial duct and rays were observed covered by calcium and carbon associated with organic and inorganic compounds; however, after immersion, large proportion of these two elements was removed.

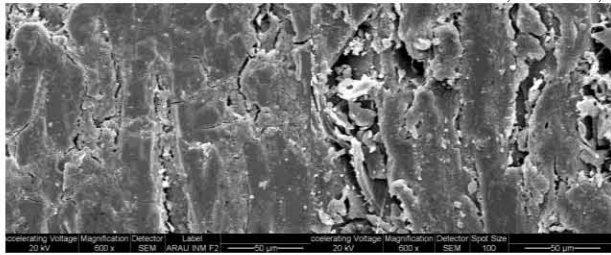


Fig 1. SEM micrographs of wood specimens: Reference, left and impregnated after curing (A.5), right

B. Dimensional stability of modified wood

In the first stage, the values of S and ASE were calculated for both cycles of immersion in distilled water.

The average results of S and the standard deviations are listed in Table 1. The values for unmodified specimens were similar for the first and second cycles of immersion; it would be based on that extractives were removed in a previous stage and in the high insolubility of the cured alkoxide.

After finishing the modifications of the specimens with alkoxides, it is observed that values of S decreased significantly as the length of hydrocarbon chain increased, which would be attributable to the rising hydrophobicity. Accordingly, the alkoxide A.V (n-octyltriethoxysilane) displayed the lowest S value (e.g. cycle I, 2.54±0.16%) whereas the alkoxide A.I (triethoxysilane) the highest one (e.g. cycle I, 7.29±0.59%).

In addition, the very small volumetric expansion due to water absorption up to saturation point of fibers in respect of the reference specimen could be attributable to the partial occupation of pores by the polymerized siloxanes and to the interaction of reactive alkoxides with cell wall components.

With regard to ASE efficiency, the results indicate that in chemically modified wood, the reduction of volumetric expansion due to water absorption until equilibrium moisture is significant; therefore, for the most hydrophobic siloxane (A.V), the volumetric expansion decreased approximately 75% with respect to the untreated sample whereas for the siloxane without hydrocarbon chain (A.I), the reduction was around 29%. In the latter case, this reduction would not be essentially by hydrophobic action but by the above-mentioned occupation of the pores and the reactivity of the alkoxide.

Alkoxide	Dimensional stability			
	S, %		ASE, %	
	Cycle I	Cycle II	Cycle I	Cycle II
A.I	5.02±0.42	5.00±0.43	50.44	50.88
A.II	4.63±0.48	4.51±0.52	54.29	55.70
A.III	3.99±0.21	4.04±0.28	60.61	60.31

A.IV	3.67±0.17	3.71±0.22	63.77	63.56
A.V	2.54±0.16	2.48±0.13	74.92	75.64
Reference	10.13±0.73	10.18±0.79	-----	-----

Table 1. Dimensional stability

C. Determination of performance against fire

Two-Foot Tunnel. It is not observed a marked influence on fireproof efficiency of the length of hydrocarbon chain corresponding to the selected alkoxides as chemical modifiers. Consequently, the quoted improved performance against fire in between would be attributable just to the partial occupation of pores by the polymerized siloxanes and to the interaction of reactive alkoxides with cell wall components.

Whole of treated wood specimens showed an enhanced performance in flame spread (low FSI values, between 0.14 to 0.18) with regard to the Reference (FSI = 1.00, which implies a flame advance along the whole of the panel length). For example, some wood specimens showed a significant decrease of the FSI reaching a 0.14 value (that is about 78 mm beyond the flame advance registered on the panel of asbestos-cement whose average value was 50 mm), Figure 2.

Values of PC corroborated the conclusions reached when analyzing the FSI; thus, values oscillated between 2.55 to 2.62% while the Reference reached a value of 8.55%.

Regarding smoke density in the Two-Foot Tunnel, results displayed a reduced amount for the whole of treated wood specimens (light transmission ranged between 68.3 to 71.2% during the entire test) while the Reference showed higher smoke quantity (in some moments of test, light transmission was only 5%).

The excellent results obtained in the trials conducted to establish the performance against fire action could be based on that the inorganic polymers would act as a layer that partially insulates the wood from the heat source (barrier action), separating the flammable materials (i.e. lignocellulose) because they promote the interfacial contact between organic and inorganic phases.



Fig 2. Flame Spread in Two-Foot Tunnel

Oxygen Index. Experimental results, corresponding to all alkoxides used as wood modifier and the weight gain reached in autoclave, showed a self-extinguishing capability since their oxygen index was higher than that corresponding to the experimental accepted limit for this type of chamber, OI 28%. All OI values for treated wood specimens ranged between 48

and 52% while for Reference it was 16% (sample easily combustible); significantly lower than the supply of oxygen available in the air.

D. Decay resistance

Table 2 displays a significant reduction in weight loss of the modified specimens in relation to the unmodified one (Reference) after 12 weeks of exposure to *Polyporus meliae* and *Coriolus versicolor*. Therefore, the specimen A.V displayed a weight loss of 0.22% and the control specimen of 38.22% for the brown rot (respectively 0.60% and 33.65% for the white rot).

The improved resistance to fungal exposure would be based on the wood chemical modification produced by the reactions inside the pores: the protection of cellulose would be caused by steric hindrance of $\equiv\text{Si-O-Cellulose}$, which prevents the formation of enzyme-substrate complex [31].

Moreover, the results also would be based on the enhanced hydrophobicity of the treated wood (that is, high dimensional stability, which corresponds with values of S and ASE obtained in experiments). The low water absorption, which limits the growth of the spores, is generated by both the decreasing of the amount of polar hydroxyl groups of unmodified wood due to condensation reactions with low polarity alkoxides and the partial occupation of pores with polysiloxanes formed by sol-gel process.

Specimen	Weight loss, % w/w	
	<i>Polyporus meliae</i>	<i>Coriolus versicolor</i>
A.I	2.38±0.21	8.22±0.66
A.II	2.09±0.14	5.56±0.42
A.III	1.37±0.08	4.34±0.37
A.IV	0.99±0.05	3.12±0.28
A.V	0.22±0.01	0.60±0.03
Reference	38.22±2.23	33.65±2.41

Table 2. Weight loss of the modified and unmodified woods by fungal action

V. CONCLUSION

- The cured alkoxides have very low water solubility, which justifies the similar values of S and ASE for both immersion cycles. The very small releasing of polyalkoxides during two cycles of immersion was verified determining impregnant material retention and penetration values; although the retention diminished as maximum 1% in all test specimens, the depth distribution observed by microscopy indicated a profile of retention practically homogeneous on the surface like in the specimen core. In summary, in all cases the polymerization degree was enough to keep the whole of impregnant into the specimens after immersion.

- According to visual and microscopic observations during

burning of treated specimens, flame retardant mechanism would imply the following stages: (i) the polysiloxane phase would isolate the underlying material retarding its degradation kinetics, (ii) the highly-stable and chemically-formed hybrid interface between wood and polysiloxanes would also contribute in fireproofing performance (average dissociation enthalpies ΔH° of $\equiv\text{Si-O-}$ and $-\text{O-C}\equiv$ are respectively 460 and 357 $\text{kJ}\cdot\text{mol}^{-1}$) and, finally (iii) the organic material would form the known retardant residue (char) before that the interface and polysiloxanes are exposed again.

- The improved decay resistance would be based on the wood chemical modification produced by the alkoxides cured inside the pores since, as well-known, the modification by reaction of only a hydroxyl group of glycoside ring leads to the protection of the cellulose from enzymatic attack. Because the alkoxides used have the same reactivity (three reactive ethoxy groups generating by hydrolysis silanol groups, which are responsible of subsequent condensation reactions) and the same retention level in impregnation, the different performance against fungal action would be based on the different length of the hydrocarbon chain (hydrophobicity) of the alkylalkoxides.

- Finally, the authors consider necessary to evaluate the influence of the length of hydrocarbon chain of alkylalkoxysilanes on other wood properties by applying the wide variety of standardized available methods, which provides comparative results according to test variables. In addition, despite the progress made, it is interesting to continue the studies involving the chemical modification of any type and specie of wood through the reaction of the hydroxyl groups by using modern environmentally friendly materials and easy impregnation and curing inside wood pores like alkylalkoxysilanes.

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