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PERFORMANCE OF WOOD IMPREGNATED WITH ALKOXYSILANES

Canosa, Guadalupe[1,2]*; Alfieri, Paula[2]; Caprari, Juan[1]; Giudice, Carlos[1]

1: Universidad Tecnológica Nacional (UTN)
e-mail: guadalupecanosa@yahoo.com.ar

2: Centro de Investigación y Desarrollo en Tecnología de Pinturas (CIDEPINT)

KEYWORDS: Wood, alkoxysilane, decay resistance, dimensional stability, fire.

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.

Solid wood specimens of *Araucaria angustifolia* were impregnated with alkoxysilanes hydrolyzed and condensed "in situ" by the sol-gel process. Alkoxysilanes selected were aminopropyl methyldiethoxysilane and aminopropyl triethoxysilane; it was also used the aminopropyl methyldiethoxysilane/aminopropil triethoxysilane mixture in 50/50 w/w ratio. The pH was adjusted to alkaline value for controlling kinetic of hydrolysis and condensation reactions.

Impregnation process was carried out at 45–50 ºC in an autoclave, controlling the operating conditions for achieving different weight gains. Unmodified and modified wood specimens were exposed to brown rot (*Polyporus meliae*) and white rot (*Coriolus versicolor*) under laboratory conditions.

The results indicate that the improved resistance to fungal exposure would be based on the wood chemical modification (the protection of cellulose caused by steric hindrance of ≡Si-O-Cellulose preventing the formation of enzyme-substrate complex). Moreover, the results also would be based on the enhanced dimensional stability of the treated wood; the quoted high dimensional stability, which limits the growth of the spores, is supported in the hydrophobicity generated by both the decreasing of the amount of polar hydroxyl groups and the partial occupation of pores with polysiloxanes.

Fire laboratory tests were carried out in Two-Foot Tunnel (flame spread index, panel consumption and smoke density) and in TGA detector (mass loss).

The performance can be explained according the reactivity of the alkoxides; the results indicate that as weight gain increase the performance of impregnants against fire also does.

1. INTRODUCTION

The civil and industrial use of wood requires pretreatment and maintenance for controlling its biodeterioration and fire attack.

High-density woods display excellent performance against fire action since they maintain their mechanical properties longer time than steel and concrete structures [1-3]. Nevertheless, medium- and low-density woods and their subproducts (plywoods, agglomerates, laminates) are more widely used in the construction for a lot of technical and economical reasons (e.g. fast growing). These woods, without any fireproof treatment, show 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 [4,5].

One of the most used pretreatments is thermal modification of wood [6-8] but the chemical modification of wood is also a very used method [9,11]. Many authors have studied the chemical modification of wood [12-14]; other authors have developed efficient flame-retardant treatments for woods applied by impregnation or as surface coating [15-17].

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, investigations were developed to establish the properties of chemically modified wood by impregnation with alkoxysilanes hydrolyzed and condensed "in situ" by the sol-gel process, in order to permit the preservation against microorganism attack and fire resistance.
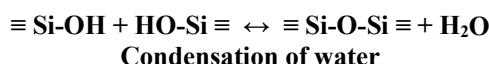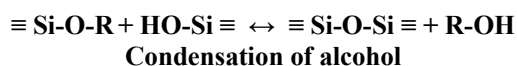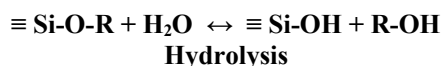
2.   MATERIALS AND METHODS

2.1   Cellulose activation

The hydroxyl groups of the lignin have high reactivity to chemical agents while in the case of those present in the cellulose, the reactivity depends substantially on whether its structure is crystalline or amorphous. This bases the previous activation of the cellulose. Although various methods have been developed (i.e. enzymes, controlled microorganisms, etc.), the use of alkaline solutions of sodium hydroxide is still widely used. For this reason, this activation method was selected in this experiment.

2.2   Sol-gel process

It involves the hydrolysis and condensation reactions of metalorganic precursors. In the case of silicon, the above reactions are as follows:

$$\equiv Si\text{-}O\text{-}R + H_2O \ \leftrightarrow \ \equiv Si\text{-}OH + R\text{-}OH$$
Hydrolysis

$$\equiv Si\text{-}O\text{-}R + HO\text{-}Si \equiv \ \leftrightarrow \ \equiv Si\text{-}O\text{-}Si \equiv + R\text{-}OH$$
Condensation of alcohol

$$\equiv Si\text{-}OH + HO\text{-}Si \equiv \ \leftrightarrow \ \equiv Si\text{-}O\text{-}Si \equiv + H_2O$$
Condensation of water

Simultaneously, the wood chemical modification also occurs [18-22]. The bonds $\equiv Si\text{-}O\text{-}C\equiv$ would arise from hydrolysis of alkoxides and the subsequent condensation of $\equiv Si\text{-}OH$ with the -OH of the wood according to reaction:

$$\equiv Si\text{-}OH + HO\text{-}Cellulose \ \leftrightarrow \ \equiv Si\text{-}O\text{-}Cellulose + H2O$$
Condensation of water
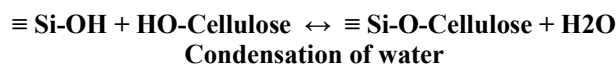
During the evolution of the reactions of hydrolysis and condensation and even after their completion, the system contraction takes place because of the expulsion of the liquid phase contained in the wood pores (water and alcohol).

2.3   Preparation of specimens of Araucaria angustifolia for tests

Specimens of *Araucaria angustifolia*, free of defects, were prepared with the proper size for each test. In a first stage, the specimens were pretreated for 2 h with a solution of sodium hydroxide (pH 8.5)

and then for about 5 min with distilled water to remove the alkali remaining on surface. 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.

2.4 Selection of wood modifying reagents and operating conditions of impregnation

Wood modifying reagents. Alkoxysilanes were selected as wood reactive modifiers. They were aminopropyl methyldiethoxysilane ($C_8H_{21}NO_2Si$) and the aminopropyl triethoxysilane ($C_9H_{23}NO_3Si$); in the research, it was also used the aminopropyl methyldiethoxysilane/aminopropyl triethoxysilane mixture in 50/50 ratio w/w. Ethanol was used as solvent in 4/1 ethanol/alkoxide molar ratio.

Conditions of impregnation. It was carried out at 45-50 °C in an autoclave, under controlled operating conditions. In all cases, the 3/1 impregnant solution/wood v/v ratio was selected. It was applied a vacuum of 200 mmHg for 10 min to release air and water vapor from the cells to facilitate the penetration of chemical modifier. The operating conditions were adjusted to achieve different 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 120 min. Then it was applcited a slight vacuum (about 50 mmHg for 10 min) to remove the excess alkoxide on the wood specimen surfaces. Finally, the wood specimens were removed and 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.

Weight percent gain was determined by using the equation WPG = $[(Wm-Wo)/Wo]\times100$, where Wo and Wm are the weight of the wood specimens pretreated and the weight of those chemically modified in the autoclave, respectively (previously dried in an oven at 100 ± 3 °C up to constant weight).

2.5 Laboratory tests

Dimensional stability. Was determined by estimating the Volumetric Swelling Coefficient S and the Anti-Swell Efficiency ASE [18,20]. The saturation water was evaluated 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 volume was again quantified by the aforementioned method. Finally, the Volumetric Swelling Coefficient was calculated by using the equation S,%=$100(V2-V1)/V1$ where V2 and V1 are the volumes of saturated and oven dried specimens, respectively. The Anti-Swell Efficiency was calculated by using the expression ASE,%=$100(Ss-Sm)/Ss$, where Ss and Sm 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 h in order to determine the leachability of the cured impregnant through the S and ASE values in a second cycle.

Decay resistance. All the specimens of *Araucaria angustifolia* were exposed, under laboratory conditions, to *Polyporus meliae* (brown rot) and *Coriolus versicolor* (white rot), following the general guidelines of ASTM D 2017. The specimens were maintained for 12 weeks under controlled conditions (25 ± 5 °C and 60-70% RH)and then were placed in an oven at 100 ± 3 °C up to constant weight. Weight loss was determined by using the equation: WL,% = $[(Wo-Wf)/Wo]\times100$, where Wo and Wf are the weight of the dried specimens without and with exposure to fungi, respectively.

Evaluation of thermal behavior. Wood panel with prior cellulose activation (control panel) and those treated by impregnation with alkoxides after gel formation and aging "in situ" were tested in a Shimadzu TGA-50 H detector (wood amount, about 5 mg; heating rate, 10 °C/min in static air atmosphere) for performing the thermogravimetric analysis (TGA).

Determination of performance against fire. In this study, the tests were carried out in a Two-Foot Tunnel (Atlas Electronic Devices Company, Model TFT, Serial Nº 1000, USA), under guidelines of ASTM D 3806 Standard. The Flame Spread Index FSI was computed by using the equation: FSI = (Ls - Lo)/(Lb - Lo), where Ls is average of the three highest flame-advances on experimental panels, Lo is average of the three highest flame-advances on cement board and Lb is average of the three highest flame-advances on control panel. 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.

To interpret the influence of main effects, results were statistically treated according to the following factorial design: 3 alkoxides (A, B and C) x 6 weight gains (I, II, III, IV, V and VI), which are 18 panels manufactured in duplicate. The variance was calculated and then the Fisher F test was run. The considered variables showed an important influence on performance against fire [23].

For the statistical analysis of the flammability tests as a whole, in a first stage the values of FSI, PC and SD were turned into a scale with values from 0 to 10, which were assigned to 1.00 and 0.00 for FSI; to 8.55% and 0.00% for PC and to 5.0 and 100.0% for SD, respectively (1.00 for FSI, 8.55% for PC and 5.0% for SD correspond to control panel). The value 10 interprets the best behavior in each test; intermediate values were proportionally considered.

3. RESULTS AND DISCUSSIONS

Table 1 displays specimen identification and the weight gain after alkoxide gelation and subsequent drying of wood specimens.

Table 1: Weight percent gain and standard deviation of modified wood specimens

Alkoxide	WPG	Specimen
A, aminopropyl methyldiethoxysilane	2.28 (0.38)	A.I
	6.03 (0.29)	A.II
	9.89 (0.43)	A.III
	12.98 (0.68)	A.IV
	16.21 (0.99)	A.V
	19.42 (1.01)	A.VI
B, aminopropyl triethoxysilane	2.61 (0.28)	B.I
	6.45 (0.33)	B.II
	10.05 (0.43)	B.III
	13.63 (0.55)	B.IV
	16.62 (0.39)	B.V
	18.75 (0.66)	B.VI
C, aminopropyl methyldiethoxysilane / aminopropyl triethoxysilane (50/50 w/w)	2.80 (0.24)	C.I
	6.61 (0.36)	C.II
	10.33 (0.46)	C.III
	13.42 (0.68)	C.IV
	16.78 (0.55)	C.V
	20.02 (0.78)	C.VI
D, control	0.00	D

3.1 Dimensional stability of modified wood

The average results of S and the standard deviations are listed in Table 2. 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. It is observed that values of S decreased significantly as the modification degree increased (weight gain of alkoxides hydrolyzed and condensed inside the wood pores).

For comparison, Table 2 includes the average values for specimens modified with each alkoxide for both cycles of immersion in distilled water. It is concluded that there was less volumetric expansion in those treated with the alkoxide B, then with C and finally with A, for all weight gains considered. The different reactivity of the alkoxides and therefore the dissimilar modification degree of the wood components would base the results obtained. Furthermore, the similar values in both immersion cycles indicate the high insolubility of the cured alkoxide.

Table 2: Dimensional stability and weight loss of modified wood specimens

Specimen	Dimensional stability				Weight loss, %	
	S, %		ASE, %		*Polyporus meliae*	*Coriolus versicolor*
	1st cycle	2nd cycle	1st cycle	2nd cycle		
A.I	7.09 (0.98)	7.03 (1.00)	36.86	37.29	15.88 (1.11)	24.68 (1.48)
A.II	5.99 (0.92)	6.00 (0.93)	46.66	46.48	2.65 (0.21)	13.25 (0.93)
A.III	5.06 (0.42)	5.07 (0.43)	54.94	54.77	1.71 (0.12)	6.85 (0.48)
A.IV	4.49 (0.39)	4.47 (0.40)	60.02	60.12	0.69 (0.05)	3.66 (0.29)
A.V	3.91 (0.15)	3.87 (0.19)	65.18	65.48	0.34 (0.01)	1.63 (0.09)
A.VI	3.39 (0.15)	3.37 (0.11)	69.81	69.94	0.28 (0.01)	0.78 (0.03)
Average value	4.99	4.97	55.58	55.68	3.59	8.48
B.I	5.74 (0.98)	5.87 (0.91)	48.89	47.64	12.70 (1.01)	19.68 (1.47)
B.II	4.73 (0.48)	4.61 (0.52)	57.88	58.88	2.12 (0.17)	10.73 (0.75)
B.III	4.03 (0.28)	4.14 (0.31)	64.11	63.07	1.37 (0.08)	5.34 (0.37)
B.IV	3.58 (0.18)	3.48 (0.21)	68.12	68.96	0.55 (0.03)	3.03 (0.21)
B.V	3.13 (0.13)	3.08 (0.15)	72.13	72.52	0.27 (0.01)	1.30 (0.09)
B.VI	2.74 (0.16)	2.78 (0.13)	75.60	75.20	0.22 (0.01)	0.60 (0.03)
Average value	3.99	3.99	64.46	64.38	2.87	6.78
C.I	6.38 (0.99)	6.26 (0.93)	43.19	44.16	14.22 (0.99)	22.31 (1.56)
C.II	5.45 (0.69)	5.39 (0.60)	51.47	51.92	2.43 (0.17)	12.32 (0.86)
C.III	4.55 (0.45)	4.56 (0.40)	59.48	59.32	1.49 (0.10)	6.03 (0.42)
C.IV	3.95 (0.28)	3.98 (0.36)	64.83	64.50	0.62 (0.04)	3.26 (0.23)
C.V	3.52 (0.21)	3.48 (0.14)	68.66	68.96	0.31 (0.02)	1.48 (0.10)
C.VI	3.05 (0.18)	3.03 (0.21)	72.84	72.97	0.24 (0.01)	0.69 (0.05)
Average value	4.48	4.45	60.08	60.30	3.22	7.68
D	11.23 (1.13)	11.21 (1.19)	-----	-----	43.28 (3.03)	31.63 (2.21)

The very small volumetric expansion due to water absorption up to saturation point of fibers, which indicates a high hydrophobicity of the wood after modification (low content of the equilibrium moisture), could be attributed to the partial occupation of pores by siloxanes and fundamentally to the interaction of reactive alkoxides with cell wall components.

With regard to ASE (Table 2), the average values denote a significant dependence on the modification degree; they increased as weight gain increased. Values of ASE for the modified wood corroborated values of S.

3.2 Decay resistance

Table 2 displays a significant reduction in weight loss of the modified specimens in relation to the unmodified ones after 12 weeks of exposure to *Polyporus meliae* and *Coriolus versicolor*. For all weight gains recorded in the chemical modification of wood, the lowest weight loss was registered with specimens modified with alkoxide B, then with the C and finally with the A; in all cases, greater

weight gain led to a better performance. The average values for each modifier corroborate the above mentioned.

The results indicate that the improved resistance to fungal exposure would be based on the wood chemical modification (the protection of cellulose caused by steric hindrance of ≡Si-O-Cellulose preventing the formation of enzyme-substrate complex). Moreover, the results also would be based on the enhanced dimensional stability of the treated wood (reduced Volumetric Coefficient Swelling S and elevated Anti-Swell Efficiency ASE). The quoted high dimensional stability, which limits the growth of the spores, is supported in the hydrophobicity generated by both the decreasing of the amount of polar hydroxyl groups of unmodified wood due to condensation reactions with low polarity alkoxides used in the treatment of impregnation and the partial occupation of pores with polysiloxanes formed by sol-gel process.

3.3 Evaluation of thermal behavior

Figure 1 displays the performance of the thermal degradation of the original wood previously treated with sodium hydroxide solution. In this figure, it is noted that the panels exhibited a rapid mass loss in the 250-450 °C range. At 500 °C, the mass loss was approximately 95%, indicating that the sample burnt almost completely.

For the minimum weight gain of the three impregnants, it is not observed a substantial difference in the initial temperature of decomposition for treated samples in comparison with control panel: values for wood modified with the reactive impregnants A, B and C showed respectively an initial temperature of decomposition of 250, 260 and, finally 255 °C, Figure 2.

In all cases, TGA analysis indicates that as weight gain increased the performance for the three impregnants improved, Figure 3. Thus, for the highest weight gain, it was verified a substantial increase in the initial temperature of decomposition and a significant decrease in mass loss.
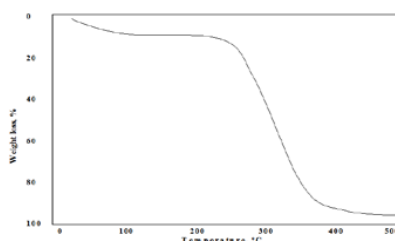

Figure 1: Thermal degradation of wood pretreated with sodium hydroxide solution (control)
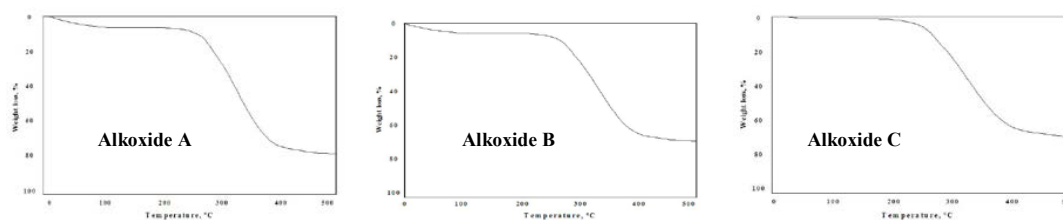

Figure 2: Thermal performance of wood modified with alkoxides A, B and C for the lowest weight gain

Figure 3 also displays that the range of fast thermal decomposition was significantly lower in all samples treated with the highest weight gain than control. The above-mentioned results support the conclusion that the best performance was observed in woods treated with alkoxide B, followed by the modified ones with mixture C and finally by those with alkoxide A. The different reactivity of the alkoxides could explicate the performance in thermal analysis. Thus, for example, the alkoxide B

would present the highest reactivity since in its molecular structure has three ethoxide groups, which hydrolyzing for giving silanol groups participating in condensation reactions; on the other hand, the alkoxide A has only two hydrolyzable ethoxy groups while alkoxide C would be in an intermediate position. In addition, the rising thermal stability of treated samples with weight gain would be also based on the major amount of polysiloxanes introduced in the wood pores (e.g. 20% in the case of samples with the highest weight gain).
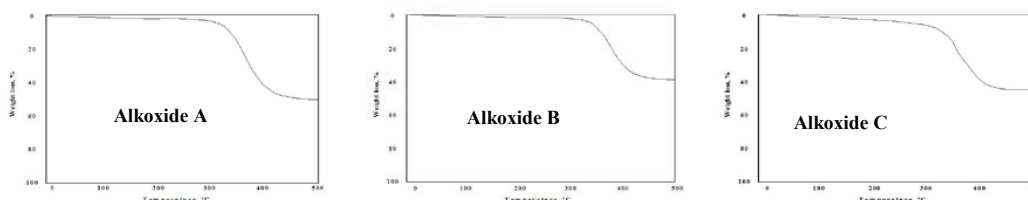

Figure 3: Thermal performance of wood modified with alkoxides A, B and C for the highest weight gain

3.4 Determination of performance against fire

Results of flammability tests are included in Table 3. A global analysis indicates an improved performance of all treated panels compared with control one as well as a marked influence on fireproof efficiency of the alkoxides selected as chemical modifiers and of the weight gains produced by impregnation in the wood pores. With the aim of determining the performance of the studied variables, the average of main effects was calculated (all of them on a scale ranging from 0 to 10), Table 4; the best performance corresponds to the highest average value. In summary, samples impregnated with alkoxide B (in the two highest levels of weight gain) showed the best average performance in flammability tests carried out.

Table 3: Results of flame-retardant tests

	Sample	FSI	PC, %	SD, %
A	I	0.71	5.60	38.0
	II	0.52	4.43	51.0
	III	0.38	3.59	62.5
	IV	0.27	2.62	70.5
	V	0.19	2.32	76.0
	VI	0.18	2.29	75.5
B	I	0.72	5.52	39.0
	II	0.43	4.01	57.0
	III	0.26	3.05	68.0
	IV	0.18	2.47	74.0
	V	0.13	1.95	79.0
	VI	0.12	1.92	79.5
C	I	0.73	5.54	39.0
	II	0.47	4.19	53.5
	III	0.31	3.29	64.5
	IV	0.22	2.50	72.5
	V	0.17	2.08	77.5
	VI	0.15	2.06	78.0
Control panel		1.00	8.55	5.0

Table 4. Average values of main effects

Sample	Weight gain	Average
A.I	3.3	
A.II	4.8	
A.III	5.7	6.0
A.IV	7.0	
A.V	7.6	
A.VI	7.6	
B.I	3.3	
B.II	5.5	
B.III	6.8	6.6
B.IV	7.5	
B.V	8.1	
B.VI	8.1	
C.I	3.3	
C.II	5.2	
C.III	6.4	6.3
C.IV	7.3	
C.V	7.8	
C.VI	7.9	
Control	0.0	0.0
Weight gain level		Average
I		3.3
II		5.2
III		6.3
IV		7.3
V		7.8
VI		7.9

4.   CONCLUSIONS

- Polysiloxanes synthesized inside the wood pores by the solegel process, by using aminopropyl methyldiethoxysilane, aminopropyl triethoxysilane and aminopropyl methyldiethoxysilane/ aminopropyl triethoxysilane mixture in 50/50 ratio w/w as precursors, proved to be efficient for controlling the decay resistance and improving the dimensional stability of Araucaria angustifolia.
- For all chemical treatments, the decay resistance and dimensional stability increased significantly with the modification degree (weight gain of alkoxides hydrolyzed and condensed inside the wood pores); technical and economic studies should define the most appropriate level for each condition of use of the modified wood.
- For all impregnants, results of fire tests improved significantly with the weight gain of alkoxides hydrolyzed and condensed inside the wood pores; technical and economic studies should define the most appropriate level for each condition of use of the modified wood.

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