IMPREGNANT FORMULATION TO THE PRESERVATION, PROTECTION AND CONSOLIDATION OF WOOD HERITAGE ASSETS

Paula V. ALFIERI[1*], Rosana LOFEUDO[1], Guadalupe CANOSA[2,3]

[1] LEMIT (Laboratorio de Entrenamiento Multidisciplinario para la Investigación Tecnológica),
Calle 52 e/ 121 y 122, (1900) La Plata, Argentina
[2] CIDEPINT (Centro de Investigación y Desarrollo en Tecnología de Pinturas),
Calle 52 e/ 121 y 122, (1900) La Plata, Argentina
[3] UTN-FRLP (Universidad Tecnológica Nacional, Facultad Regional La Plata),
Calle 60 y 124, (1900) La Plata, Argentina

Abstract

The protection of cultural heritage is an integral part of the world's material wealth. The cultural heritage, movable and immovable, together with the natural environment, represents values that contribute to the education and social culture of the community. It also has a significant economic impact because, it represents the basic prerequisite for a tourism industry. Therefore, the modern developing based on non-polluting technological products for the protection of patrimonial is needed. Also, it is necessary to build a bridge between the basic knowledge generated as a product of scientific research and applied science. The knowing of what kind of deterioration occurs and how it impacts the physical-mechanical properties of the materials are important issues and, that must be considered so that the constructions made can be adequately conserved and/or consolidated. Wood was treated with an innovate formulation based on silanes (methyltriethoxysilane, MTES and n-octyltryethoxysilane, OTES) to achieve the protection and the consolidation of the heritage assets. The performance of treatment about dimensional stability, fire and biodeterioration/biodegradation resistance was investigated. It was concluded that the treatment resulted effective as a protective and consolidate lasur system based on silanes by surface treatment for wood heritage assets.

Keywords: Heritage; Old wood, Consolidation, Treatment for preservation; Restoration; Protection

Introduction

Wood is a traditional building material and its deterioration and biodegradation are important critical factors for its durability. Wood structures are usually degraded by wood decay fungi and they generate mainly loss of dimensional and structural stability [1-3].

A wood biodegradation and biodeterioration effect depends on abiotic factors such as moisture and temperature, but also on the fungal decay which alter the chemical and physical properties of wood [4]. Some fungi species may be facilitated, inhibited or neutralised by the actions of other species [5].

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* Corresponding author: paulaalfieri@gmail.com

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In this regard, it is attempting to applied biology and chemistry knowledges as tools to evaluate the key factors that affect the heritage asset and, were capable to find the most appropriate technological solutions. This will respond to the wide variety of issues involved in the proper protection of raw materials considering the requirements necessary to solve the problem of heritage preservation: efficiency, economy and environment-friendly characteristics.

Wood is very susceptible to the action of biotic and abiotic agents due to by its chemical technique: it can be mentioned as the three main ones, wood-decay fungi, humidity and fire.

The intensity of the biological alterations occurs in function of the available organic components and of the environmental conditions; the adsorption and desorption of water causes the wood to lose its physical-mechanical properties such as the dimensional stability; and finally, the irreversible human and economic diseases produce by the fire. These are same causes of the research and development of the products to protect wood against abiotic and biotic agents.

Thus, the necessary requirements to solve the problem of wood preservation are: (i) to know in depth the chemical composition, structure and properties of the material to be protected, (ii) to deepen the study of agent protection mechanisms and finally, (iii) correctly selecting protective materials [6-10].

Many protective treatments for low density wood are applied by impregnation to give water-repellent and to control pathologies that usually have this substrate (lack of dimensional stability, wet spots, microorganism growth, efflorescence, etc.) [12-14].

An efficient impregnant must substantially reduce water absorption of the substrate, present an adequate penetration and show an excellent resistance to environmental exposure [11-13]

The organic polymers often specified as impregnants (acrylic, polyurethane, epoxy, etc.) usually block the pores decreasing the coefficient of capillary water absorption and the water vapor permeability; the latter limits the drying kinetics [15, 16]

The study of other impregnants led to the use of water-soluble alkali silicates as reactive treatments; nevertheless, silicification reaction to form inorganic polymers involves a slight acidification by solubilization of carbon dioxide from the air: the secondary formation of alkali carbonates makes that impregnation with silicates is disused today because their tendency to form white spots [17-21]

Currently, consolidates and repellents based on organosilicon compounds are used in construction (e.g. brick, concrete, plaster, etc.), but they are not widely studied in wood treatments.

The silanes most commonly used show hydrocarbon chains (linked by covalent bonds to the silicon) that may or may not be functionalized (e.g. with amino groups); to avoid yellowing generated by aromatic structures exposed to sunlight the chains must be aliphatic. These hydrocarbon chains should have a length those facilities the kinetic of hydrolysis reaction during the sol-gel process (it improves with shorter chains) and gives hydrophobicity (it increases with chain length) [22-25].

Wood was treated with an innovate formulation based on silanes (methyltriethoxysilane, MTES and n-octyltryethoxysilane, OTES) to achieve the protection and the consolidation of the heritage assets. The performance of treatment about dimensional stability, fire and biodeterioration resistance was investigated.

Materials and Methods

The experiment included: (i) selection of wood specimens; (ii) choice of silanes; (iii) formulation design; (iv) substrate preparation and protective system application and finally, (v) laboratory tests.

Selection of wood specimens. Wood deteriorated was acquired of different wood heritage construction of La Plata, Buenos Aires City. All samples were records acquired from pieces of material degraded and detached from the structure. To characterise the degradation caused by biotic and wood abiotic agents found on wood samples, direct observation and stereoscopic magnifier were used. To establish the cellular degradation of wood and its fungal colonisation, scanning electron microscopy (SEM) images were analysed. The fungal attack was measured by area occupied by mycelium and basidiomata, (digital photography software analysis, ImageJ).

Choice of siloxanes. Since the monomers derived from silicon with low molecular weight show a high reactivity with the hydroxyl groups of cellulose present in wood cell wall, the following alkylalkoxysilanes were selected: methyltriethoxysilane (MTES; chemical formula, $C_7H_{18}O_3Si$; M_{Wt} = 178.3; aspect, colorless liquid; density = 0.895g·cm^{-3}), n-octyltriethoxysilane (OTES; chemical formula, $C_{14}H_{32}O_3Si$; M_{Wt} = 276.5; aspect, colorless liquid; density = 0.880g·cm^{-3}) and mixtures of both in 50/50% volume ratio.

Formulation design. Silanes are soluble in many alcohols, so the solutions were prepared with ethanol/water 70/30%, at 7.5% for both silanes. Then, the solutions were diluted at 50% with an organic clarified solvent (linen oil)/turpentine (30/70%v/v).

Substrate preparation and protective system application. The traditional methods of cleaning and surface preparation were used, generating a soft abrasion and tow. The formulation was applied in three successive times with a brush, treating as if the solutions were a lasur. The drying time between each application was 24h. Later, the wood specimens were exposed to a chamber under controlled temperature and humidity conditions (20±2°C and 60±5%RH) for three weeks for allowing the gelation and aging.

Laboratory tests

Decay resistance. Treat specimens (20×20×20mm size) were exposed for 12 weeks under controlled conditions (25±5°C and 60-70%RH) to Phenillus chaquensis (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

$$WL, \% = [(Wo - Wf)/Wo] \times 100 \qquad (1)$$

where: Wo and Wf are the weight of the dried specimens without and with exposure to fungi, respectively.

Dimensional stability. The dimensional stability was determined by measuring the water absorption (WA), swelling (VS) and water repellent (WRE) values using the water immersion method of Rowell and Ellis, 1978 [26], by the application of drying-water-soaking cycles. The specimens were exposed to a series of eight cycles, each of which includes the following procedure: oven drying at 103°C until weight is constant, then the specimens are placed in a vessel with water for 24 hours at (25°C), here the volume change (change of radial

and tangential length, measured with gauge) and mass of the weighing samples in the precision scale are measured here. It is dried again, and mass and volume are measured again. According to the authors of the test, it is considered that 8 cycles are enough to obtain the dimensional stability of the wood tested.

S coefficient was calculated by using the equation:

$$S = 100(V_2-V_1)/V_1 \, (\%), \qquad (2)$$

where: V_2 and V_1 are respectively the volumes of saturated and oven-dried specimens.

ASE efficiency, it was calculated by using the expression:

$$ASE = 100(Ss-Sm)/Ss \, (\%), \qquad (3)$$

where: Ss and Sm are the average coefficients S of unmodified and modified samples, respectively.

Fire resistance

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 $3.2 cm \cdot s^{-1}$ by using specimens, free of defects, prepared with size of $150 \times 10 \times 0mm$.

Intermittent test. The Flame Spread Index FSI was computed by using the equation:

$$FSI = (Ls - Lo)/(Lb - Lo), \qquad (4)$$

where: Ls is average of the three highest flame-advances on experimental panels, Lo is average of the three highest flame-advances on asbestos-cement board and Lb is average of the three highest flame-advances on Reference. It is worth mentioning that the value Lo 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, Lo was 50mm. 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. The maximum values were registered during the test.

Results and discussion

In first instance, visual observation allowed to observe the good performance of all the treatments as a protective and consolidating system. All treated wood presented the reversion of deterioration rehydration and crack sealant before the application; acting as a biocide too (Fig. 1).

Anti-swelling effectiveness. As known, the wood cell wall is mainly composed of polymers with hydroxyl and other oxygen-containing groups, which attract moisture through hydrogen bonding. As water is added to the cell wall, wood volume increases nearly proportionally to the volume of water added. Swelling increases until the cell wall is saturated: this point is called fiber saturation point. This process is reversible, and wood shrinks as it loses moisture below the fiber saturation point. Furthermore, wood also stocks water outside of a fiber, which does not contribute to swelling; this is called free water and it is found in the empty cell structures and/or interstitial spaces.

The effectiveness of a treatment to reach water-repellent can be defined as its ability to reduce or prevent the swelling/shrinking of wood resulting from absorption/desorption of water

therefore, the water repellent in immersion condition were studied through the coefficients above-mentioned (Fig. 2).
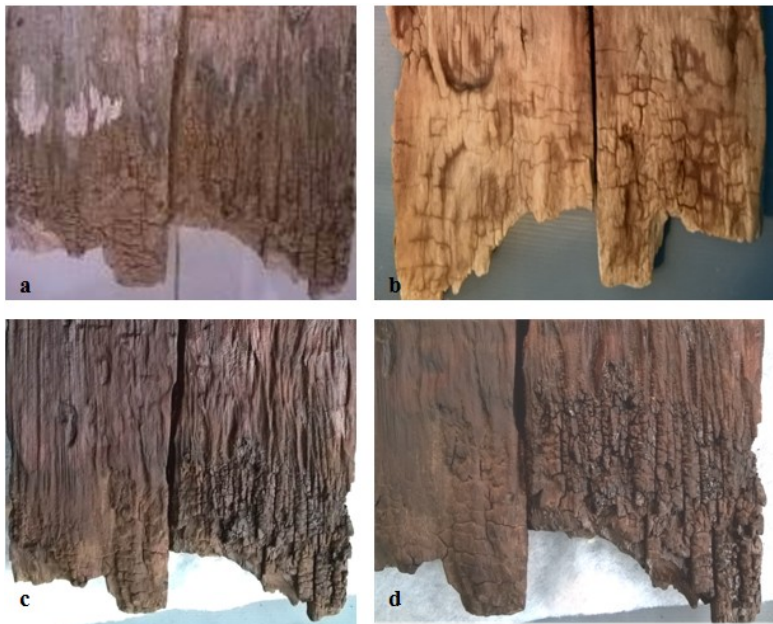

Fig. 1. Deteriorated wood after y before treatment: a. deteriorated wood, b. wood after cleaner, c. wood treated just after it was applied, d. wood after treatment curing
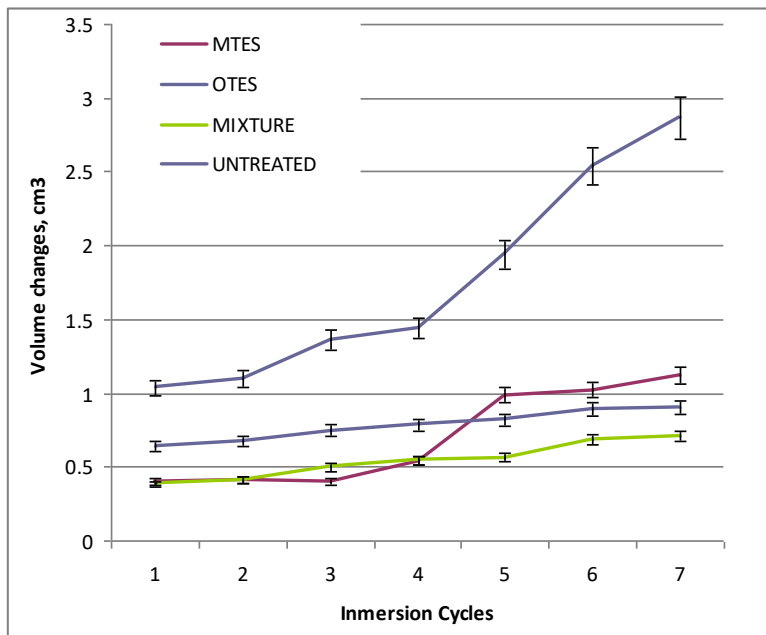

Fig. 2. Volume changes of wood treated with MTES, OTES and mixture

In the cases of wood only modified with MTES, the results indicate that a dense and compact coating would be formed in the pore improving the performance with respect to untreated wood due to its chemical modification. Nevertheless, it is not enough to prevent the inlet of water in liquid state because polymerized MTES does not present high water-repellent.

On the other hand, wood treated with only OTES also would form a hydrophobic coating and discontinuous by steric hindrance; this would support the better anti-swelling effectiveness compared to untreated wood and even with those treated with MTES.

With respect to alkoxides mixture 50/50 volume ratio ASE values were the highest, which would be base in the reduced and acceptable swelling. It would be attributable to the compact coating formed on wood due to on the high packing density (the reduced steric hindrance between the methyl and octyl groups of reactive alkoxides) and the optimal hydrophobicity of the organosilicon polymers that coat the wood

For the most hydrophobic organosilicic polymer, the volumetric expansion decreased between 66 and 67%, whereas for that polymer with the shortest hydrocarbon chain, the reduction was between 30 and 32%. Respect to ASE, for the impregnants based only on MTES and OTES lead to lower ASE values than those in untreated wood (Fig. 3) or MTES/OTES mixtures, the results indicate that the reduction of the volumetric expansion due to water absorption up to the equilibrium point is significant.
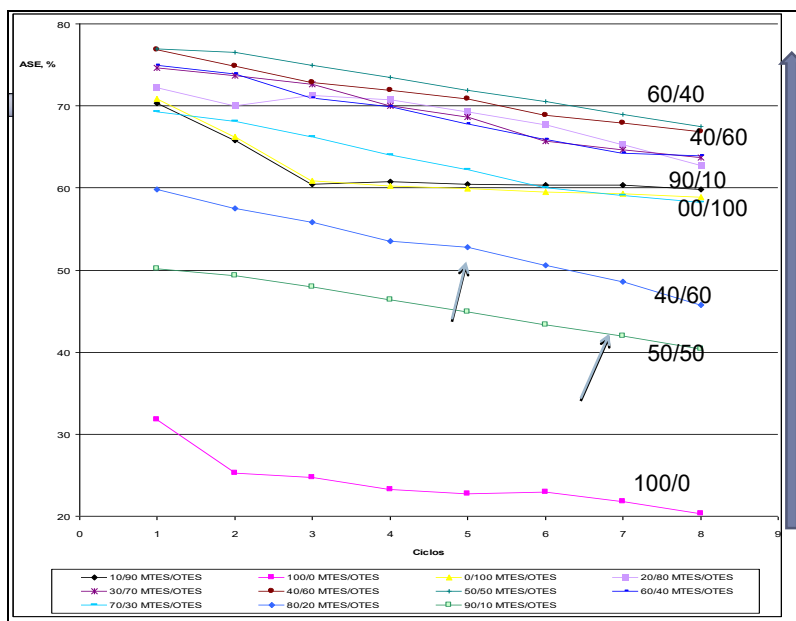

Fig. 3. ASE%: With the increase of OTES (blue arrow) the anti-swelling behavior improves (higher ASE)

The chemical change produced at the interface is due to sol gel process: the hydrolysis and condensation reactions lead to particle associations, which then are linked to form a single 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, alcohol and carrier solvent). At this stage, the polymerization reactions continue increasing the links $\equiv$Si-O-Si$\equiv$, up to attain the hardening of the gel (xerogel film). Simultaneously with the reactions, the wood chemical modification also occurs. Many researchers have studied chemical modifications that involve the reaction of hydroxyl groups: bonds $\equiv$Si-O-C$\equiv$ would arise from

hydrolysis of alkoxides and the subsequent condensation of ≡Si-OH with the -OH of the wood [27-34].

The above mentioned was observed by FT-IR, (Fig. 4): Wood panels, cut with a microtome provided with a biplane blade (angle sharpened, 30º) and dried at 100-105ºC, were analyzed by Fourier Transform-Infrared Spectroscopy (FT-IR) for determining the chemical modifications after finishing the described treatments. The spectra were obtained by using a Perkin Elmer (model Spectrum One; method of Attenuated Total Reflectance, single rebound); the equipment consists of a zinc selenium viewer and a diamond crystal as an interface between the sample and infrared radiation.
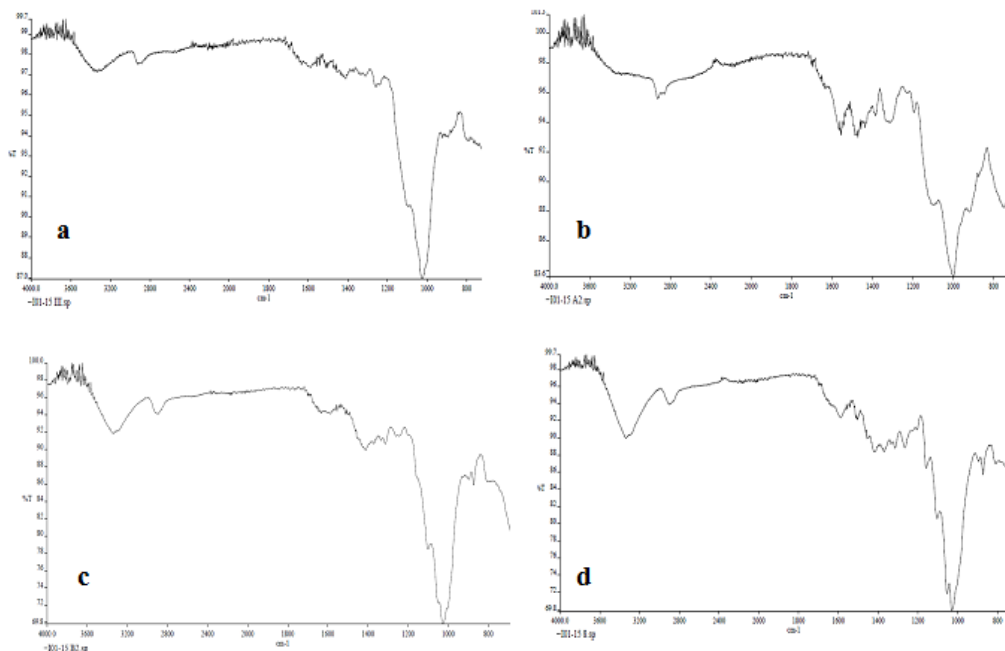

Fig. 4. FT-IR spectra: a. untreated wood; b. wood treated with MTES;
c. wood treated with OTES; d. wood treated with MTES/OTES 50/50

FT-IR spectra of wood before (Fig. 4a) and after treatments (Fig. 4b-d). It was observed the characteristic vibrations of the aliphatic bonds C–H and the asymmetric and symmetric vibrations of the groups –CH$_3$ and -CH$_2$ (between 600 and 1000cm^{-1}) as well as the typical band of –OH group around 3400cm^{-1} belonging to organic compounds such as cellulose, hemicellulose and lignin [25].

Furthermore, for spectra of treated woods, an initial analysis indicates that the spectra are markedly different, which indicates that chemical changes were generated during polymerization.

The above figures display bands around 1050cm^{-1}, which could be assigned to -Si–O–Si- of the inorganic polymer formed by the hydrolysis and condensation reactions. They also allow the observation of bonds around 1120cm^{-1}, which could be attributable to -Si–O–C- formed from the hydrolysis of alkoxides and subsequent condensation of silanol groups with the –OH groups of the wood. The last ones are not good defined [24]. With respect to signal to the 3400cm^{-1} (typical of the –OH groups), it is worth mentioning that Following with the analysis of peak at 3400cm^{-1}, it is observed a significant decrease of this signal in all wood treated,

which is attributable to the reaction of –OH groups of wood with the hydrolyzed alkoxides; it corroborates the indicated chemical modification of wood components [35, 36]

Determination of performance against fire

It is not observed a marked influence on fireproof efficiency of the length of hydrocarbon chain corresponding to the selected alkoxides. Consequently, the quoted improved performance against fire in between would be attributable to the interaction of reactive alkoxides with cell wall components.

Intermittent test. Whole of treated wood specimens showed an enhanced performance in flame spread (low FSI values, between 0.14 to 0.18) about 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 78mm beyond the flame advance registered on the panel of asbestos-cement whose average value was 50mm).

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%. The 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.

Oxygen Index. It defined as self-extinguishing capability since samples oxygen index results were 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.

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^{o} of $\equiv$Si-O and -O-C$\equiv$ are respectively 460 and 357kJ·mol^{-1}) and, finally (iii) the organic material would form the known retardant residue (char) before that the interface and polysiloxanes are exposed again.

Decay resistance

The results of decay resistance were present in Figure 5. It was observed in all treated sample it was observed significant reduction in weight loss of the modified specimens in relation to the unmodified one (Reference) after 12 weeks of exposure to *Trametes versicolor* (brown rot) and *Perenniporiella neofulva* (white rot). Therefore, the specimen displayed average weight loss of 1.8±0.4% and the control specimen of 38.22±0.2% for the brown rot and 2.2±0.3% and 33.65±0.2%, respectively for the white rot.

The improved resistance to fungal exposure would be based on the wood chemical modification produced: the protection of cellulose would be caused by steric hindrance of $\equiv$Si-O-Cellulose, which prevents the formation of enzyme-substrate complex [37-39]. 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) which generated an inhospitable environment for fungal development.
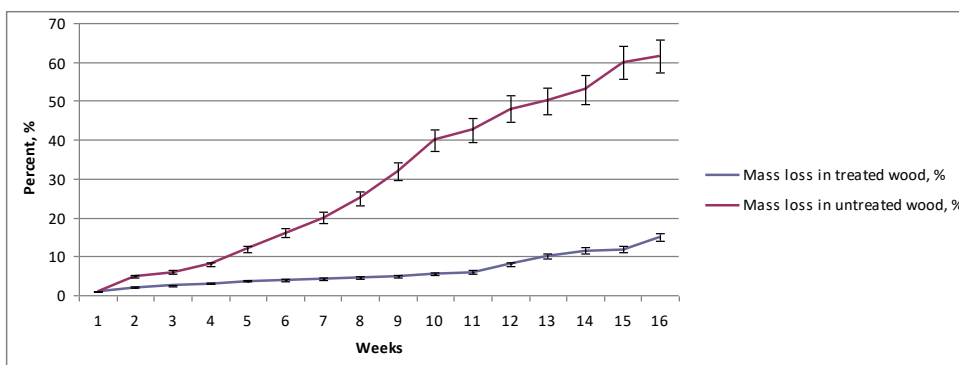
Fig. 5. Decay resistance. Weight loss during week of cultivation

Conclusions

The impregnants interact with cell wall components during the reactions of hydrolysis and condensation (sol-gel), forming a non-occlusive coatings on wood are supported in the following items: (i) during impregnation, the solvent mixture carries the water-repellent substances (alkoxysilanes) until deposit them on the surface of the wood where the polymerization by the sol-gel process takes place; (ii) then, this solvent mixture, together with water and alcohol generated, is evaporated during the xerogel film formation (curing and aging); (iii) the coating formation occurs in some areas surrounding to other uncoated ones, i.e. that the coating is formed on a cluster of cells enclosing an untreated core. The would base the total wood protection employing only low levels of impregnant.

The greatest water-repellent (highest ASE) was observed in those treatments that formed a continuous and highly hydrophobic interface.

Organosilicon impregnants give important characteristics to the protective system: the cited non-occlusive coating keeps unaltered the water vapor permeability allowed the natural water absorption and desorption of wood.

The system proposed was an effective restoration, protection and conservation technique for heritage asset and it can also be applied in similar cases (it has already been implemented in other heritage and non-heritage assets, with excellent results in terms of improving dimensional stability). This is relevant since this treatment exceeds the traditional methods of restoration since it does not use toxic solvents, does not form an internal polymer structure, shorter curing time, among others.

Acknowledgements

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