NANO/SILANE IMPREGNATION SYSTEM FOR WOOD PROTECTION FROM BIOTIC AND ABIOTIC FACTORS

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Abstract

Wood is very susceptible to the action of biotic and abiotic agents: it can be mentioned as the three main ones, wood-decay fungi, humidity and fire Currently, there is a growing interest in the protection of wood and wood products to extend it life in service, using environmentally friendly preservatives. The aim of this paper was the study of nano/silane impregnation system for Wood protection from biotic and abiotic factors. The biotic agents studied have been wood decay fungi and the abiotic agents have been moisture and fire. In conclusion, this paper has shown that all the treatments have presented an excellent protective performance against biotic and abiotic agents. In important to mentioned that a synergistic effect can be observed when generating the silane/nanoparticle mixtures, resulting in protective systems with excellent efficiency for all the degrading agents. Moreover, it presents an easy application (immersion), which represents not only a watertight protective system, but also a set of systems that may be used and managed according to the availability of the active components, the available costs, and, most importantly, without having to modify the form of application.

Keywords: Silane; Nanometals; Wood; Protection; Biotic and abiotic agents

Introduction

Wood is very susceptible to the action of biotic and abiotic agents: 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 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.

Nowadays, there is a growing interest in extending the service life of wood and wood products by means of using environmentally friendly preservatives, with low or no toxicity indexes and also, with a minimum environmental impact [1]. Greater importance takes when it comes to the consolidation of heritage wood.

Organosilicon compounds comply with most of the above-mentioned requirements. It is due to they are currently used as consolidates and repellents on many materials. They are characterized by high thermal stability and chemical resistance to external factor [2-4]. Due to their bifunctional structure and to their specific reactivity, they have also been used for the preservation and conservation of wood and wood-based products [3-7]. They contain readily

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hydrolysable alkoxy groups, as well as an organic functional group which makes them possible the modified chemically the material.

The polymerization of alkoxysilanes, called the sol-gel process, takes place through a series of consecutive hydrolysis and condensation reactions [8, 9]. The hydrolyzed alkoxy groups can react to other silane molecules by means of establishing Si-O-Si bonds in the condensation process. Simultaneously, they can also interact with hydroxyl groups present on wood polymers generation a wood chemical modification [6-11]. This technique is useful for example for enhance and stabilize the weakened cell walls of degraded waterlogged wood [12, 13].

The interaction of nanoparticles with microorganisms and its uses is an expanding field of research. Recently, there has been a growing interest in silver formulations as a means of wood preservatives. In a preliminary study, ionic salts have been examined in order to test their effect on decay fungi and termites [12-14]. Example of nanoparticles used is the nanocopper, particularly due to their effectiveness as a biocide and relatively low mammalian toxicity; Cu, Zn, and Ag to increase the resistance of wood against fungi and termites and, in addition, Ti-oxides which bring against UV radiation, scratch and abrasion, fire properties and less protective activity against algal growth and colonization by mold fungi [15, 16].

As mentioned, wood preservation treatment is esencial to increase the service life of wood by imparting it with bactericidal, fungicidal and insecticidal properties, thus, the objective of this paper was the study of nano/silane impregnation system for Wood protection from biotic and abiotic factors.

Experimental part

Materials

The wood that has been used in this case is a *Pinus ponderosa Dougl. ex C. Lawson*. The percentage of late wood in the cuts used has been between 25% and 30%. The wood samples have been dried before impregnation at 105ºC.

The systems which have been studied have been: Silanes, Silanes/Silanes, Nanoparticles and Silanes/Nanoparticles (Table 1).

Table 1. Impregnating formulations

Id.	Agent	Method	Solute/ Solvent	Concentration
The silane-based impregnating formulations used				
APTES	3-Aminopropyltrietoxisilane			
MPTMS	3-(Mercaptopropil) trimethoxysilane		80mL of	
MTES	Methyltriethoxysilane	Silanol	ethanol +	15 **v/v %**
OTES	n-octyltriethoxysilane		4mL of	
MTES/OTES	Methyltriethoxysilane		NH$_4$OH	
	n- octyltriethoxysilane			

Id.	Agent	Solvent	Concentration	
The impregnating formulations based on nanoparticles used				
Si	nanoSiO$_2$	100mL of		
Ag	nanoAg	ethanol/water		
Zn	nanoZn	(90/10 % v/v)	1%	m/v %
Cu	nanoCuO	+ 5mL of NH$_4$OH		

Id.	Agent	Solvent	Concentration
The impregnating formulations based on silanes/nanoparticles			
MTES/Si	Methyltriethoxysilane/nanoSiO$_2$		
MTES/Ag	Methyltriethoxysilane/nanoAg		Silane/nano = 0.3
MTES/Zn	Methyltriethoxysilane/nanoZn	80/20 % v/v	
MTES/Cu	Methyltriethoxysilane/nanoCuO	ethanol/	
OTES/Si	n-octyltriethoxysilane/nanoSiO$_2$	ammonium	Silane/nano = 0.5
OTES/Ag	n-octyltriethoxysilane/nanoAg	hydroxide	Silane/nano = 0.8
OTES/Zn	n-octyltriethoxysilane/nanoZn		
OTES/Cu	n-octyltriethoxysilane/nanoCuO		

Modifier or protective agents involve silanes and nanoparticles. The basis for the choice of these compounds has been mainly determined by their inorganic character and their ability to chemically react to the substrate. On the other hand, for nanoparticles the choice has been based on the particle size (which allows it to penetrate better into the substrate), and its high surface area (which gives greater probability of interaction).

The silanes have been selected by their hydrocarbon chain being: Methyltriethoxysilane (95% Sigma-Aldrich) and n-octitriethoxysilane (98% Xiameter, Dow Corning). On the other hand, 3-mercaptopropyltimetoxysilane (95% Sigma-Aldrich), 3-aminopropyltriethoxysilane (99% Sigma-Aldrich) have been used as sol-gel control (Table 1a)

Moreover, the selected nanoparticles have been a) nanosilica oxide (or nanosilica or Sigma Aldrich 200nm mesopores), b) nanosilver (NanoArg-NanoTek S.A. nanoparticle ≤50nm, 30-35 p/v % in triethylene glycol monoetilether), c) nanocopper (NanoKupro-NanoTek S. A. in powder 100nm), and d) nanozinc oxide (NanoOxZn-NanoTek S.A. in powder 100nm), Table 1b. Stock solutions have been made at a pH close to 7 (pH = 6.8±0.2).

Methods

The specimens for water absorption and biodeterioration resistance tests have been 20x20x20mm, as well as non-standardized specimen sizes (300x20x20mm), to see if this has had any effect on fungal development. On the other hand, the specimens used for fire tests have been 200x100x3mm, and each treatment has been carried out twice. All the specimens have been obtained from rods with 3-6 growth rings per centimeter, free of defects and without any visible resin or fungal growth. All the specimens have been stored until reaching a moisture content of 15±3%. After the impregnant treatment has taken place, all specimens have been parked again for 3 weeks at room temperature and humidity (20±2ºC and 65±5% RH).

Hydrolysis is the one that regulates the process, by means of using a minimum rate, so that the silanes do not react outside wood. In addition, a low r has been used to ensure that there is branching, and thus forming a film and not a particulate aggregate. Therefore, pH changes have been managed with the addition of NH_4OH at the time of application.

As for the sol-gel process, the aim has been to form a silanol. With this procedure, the ethoxysilanes are hydrolyzed to silanols, and the silane is diluted with alkaline ethanol: the addition of 3mL of NH_4OH (imitating the Stöber method [21]) and agitated for duration of 15-20min [11].

The application of the protective systems has been achieved through immersion: samples have been washed with ethanol for a period of 10 minutes, and later dried at 60ºC for 6 hours to surface prepared. Then, they have been immersed in solutions for 20 minutes and again dried at 103ºC for an hour. This procedure has been repeated 3 times in order to achieve as much impregnation as possible.

The controls used have been in wood previously exposed to each of the formulations and applications conditions, but without the active materials.

The treated and untreated material has been characterized by scanning electron microscopy, SEM-EDAX in order to locate the impregnation (silanes and/or nanoparticles) in the material. The chemical reactions produced between the wood and the different preservative agents will be evaluated through FT-IR in a comparative way. The FT-IR spectra have been carried out at CIDEPINT, at room temperature, with a wavelength reading range between 4000 and 600cm^{-1} and with a resolution of 4cm^{-1}. These spectra have been made by reflectance using the U-ATR (attenuated total reflectance) accessory, which allows the sample to be irradiated directly, without previous preparation. The sample size used has been 200x200x200mm.

The biotic agents studied have been wood decay fungi and the abiotic agents have been moisture and fire.

- Biodeterioration: Wood samples have been exposed to three species of fungi representing each of the rots under laboratory conditions, following the general guidelines of ASTM D 2017

(Soft rot, *Chaetomium globosum*; White rot, *Phenillus chaquensis* and, Brown rot, *Trametes versicolor*).

The evaluation of the performance has been determined gravimetrically by weight loss and by micro and macro scale observation of the state of the substrate. The inoculations have been carried out in containers with sterilized sand as a support surface for the wooden specimens, and using it as a water retention means to provide humidity to the system. The addition of water has consisted in 12.5mL of distilled water twice a week. Then, the panels have been kept out from the culture bottles, the micelles have been removed and finally, they have been placed in an oven at $100\pm3°C$ until constant weight. The weight loss has been determined through the following equation:

$$\text{Weight loss, } \% = [(P_o - P_f) / P_o] \times 100$$

where: P_o and P_f are respectively the weights of both dry samples without exposure and with exposure to fungi.

Dimensional stability has been determined by measuring the values of water absorption (WA), swelling (VS) and anti-swelling efficiency (ASE) by means of using the water immersion method of the Rowell and Ellis (1978) test [22], through the application of water-soak cycles. Once these data have been obtained, the above-mentioned coefficients have been calculated using the following equations:

$$WA = 100 \times \left(\frac{M_2 - M_1}{M_1} \right) \quad (1)$$

where: WA is the water absorption (%), M_1 is the weight of dry woods and M_2 is the weight of saturated woods.

$$VS = 100 \times \left(\frac{V_2 - V_1}{V_1} \right) \quad (2)$$

where: VS is the volumetric swelling (%), V_1 volume of dry woods and V_2 is the volume of saturated woods.

$$ASE = 100 \ \text{x} \ \frac{S_2 - S_1}{S_2} \quad (3)$$

where: ASE is the antiswelling efficiency %, S_1 and S_2 are the volumes of untreated and treated samples, respectively.

For the fire study, the Oxygen Index (OI) determination test has been carried out, according to ASTM D 2863, which determines the minimum concentration of oxygen in a mixture with nitrogen that can maintain the combustion of a material in equilibrium conditions, such as the combustion of a candle. That is to say, that the oxygen index is the minimum concentration of oxygen, expressed as a percentage in volume, in a mixture of oxygen and nitrogen that achieves the combustion of a material at room temperature and under the conditions of this method:

$$n, \% = (100 \text{ X } O_2) / (O_2 + N_2)$$

where: O_2 is the volumetric flow of oxygen ($cm^3 \cdot s^{-1}$) and N2 is the volumetric flow of nitrogen ($cm^3 \cdot s^{-1}$).
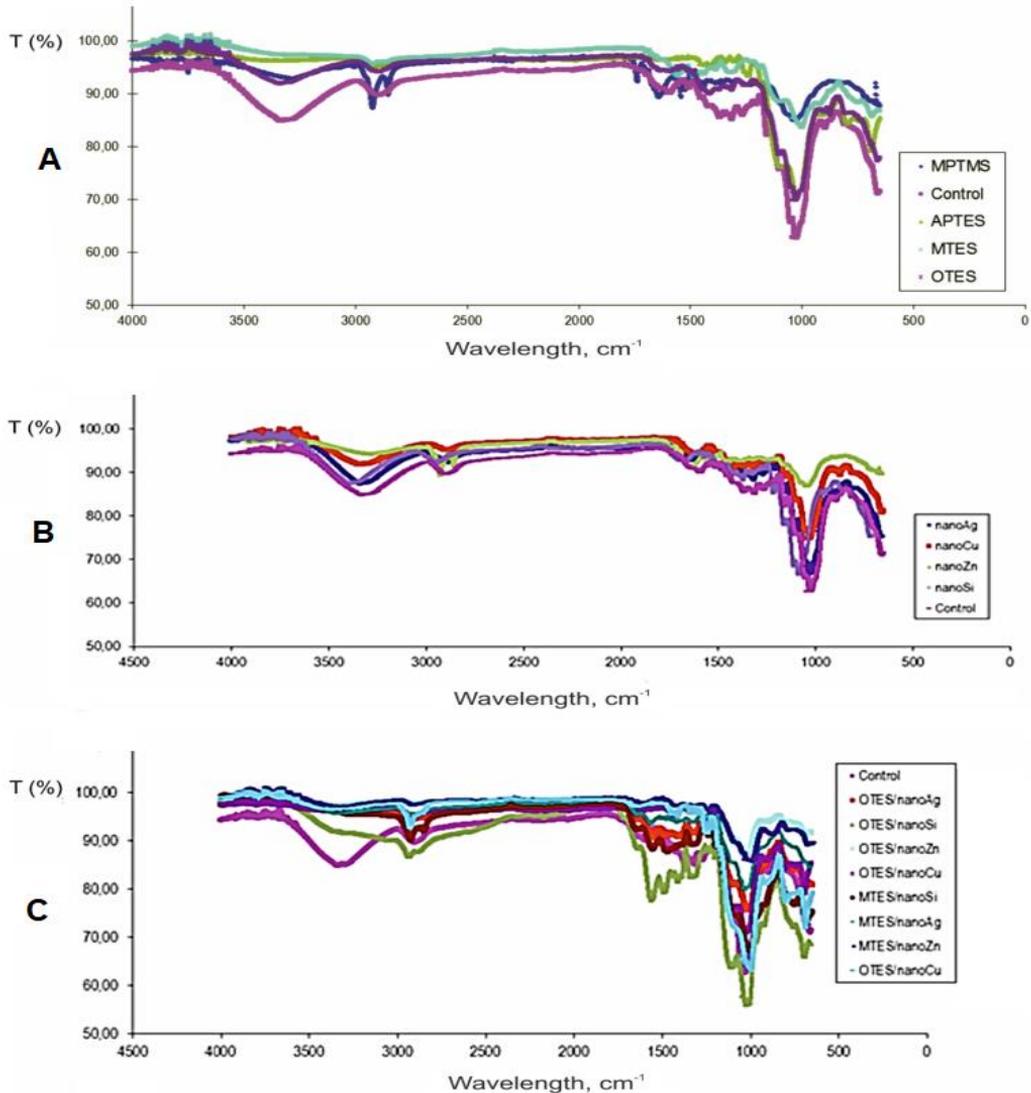
Results and discussion

FT-IR

Firstly, the characteristic bands of the untreated wood have been identified, and those belonging to each of the components have been considered (spectra provided by the commercial characterization).

The characteristic bands of the -OH of the wood cell wall are: at 3400cm^{-1} of strong absorption and a band of lesser absorption at 2950cm^{-1} which represents the O-H bond stretch, another at 1650cm^{-1} which represents the -OH deformation band. Finally, a wide band has been observed in the interval of 1000-1200cm^{-1} due to the O-H bending of primary and secondary hydroxyl groups of cellulose, as it may be seen in figure 1 [23].

Figure 1A shows the spectra of the woods which have been previously treated with the silanes. The typical bands of cellulose and silane bonds have been detectable, although they overlap to a large extent. The bands due to the silanes have been: 800cm^{-1} (symmetrical stretch Si-O-Si), 1070cm^{-1} (asymmetrical stretch Si-O-Si), 1270cm^{-1} (symmetrical stretch Si-CH$_3$), 1108cm^{-1} (stretch Si-O-R, R = ethoxy group) [24].

Fig. 1. Graphs for FTIR Spectra: A. Wood treated with silane-based impregnators;
B. Wood treated with nanoparticles-based impregnators;
C. Wood treated with impregnating agents based on silane/nano mixture

Regarding OTES, it may be observed that there has not been a considerable decrease in the intensity of the -OH stretching band, but it differs in the bending and deformation bands of the -OH. This has been an expected result, since they have been the largest molecular silanes due to their substitutes. So, a steric hindrance may be causing hydrogen bridges to form to stabilize, but not to complete the sol-gel process to a great extent.

When the substitution has not been high enough to remove the hydroxyl groups, the bands always remain present: all the -OH bands remained intact in terms of shape and intensity.

In the case of nanoparticles, in figure 1B, the spectra have shown themselves to be very similar to each other, repeating the fact that the bending, stretching or deformation of the -OH of the cellulose has been modified, though not all at the same time. In particular, it has been observed that, for silver and silicon dioxide nanoparticles, they have not modified the bands of cellulose, as the copper oxide and zinc oxide nanoparticles have been. In addition, it has been observed that, in all cases, there have occurred variations in the peaks found in the area of 1200 and 800cm^{-1} with respect to the control. The first variations would correspond to water molecules adsorbed by the nanoparticles in the dispersion that they drag into the interior of the wood, whereas for the second band, it should be noted that the nanoparticles vibrate around the areas of 600-900cm^{-1}, so it is probably an indicator of their presence [25].

On the other hand, the higher intensity of one of the two characteristic peaks of the cellulose may also indicate a higher amount of -OH available, which would show a stronger reactivity of the system. This could then translate into the presence of an electron density destabilizing the polymer structure of the cellulose which would allow any highly charged nanoparticles in this group to be immobilized (principle of drug immobilization). This phenomenon could be an explanation of the spectra of the samples previously impregnated with Ag and SiO$_2$ nanoparticles [26].

The peaks at 3400 and 1500cm^{-1} in the spectrum of all samples have been attributed to the stretching vibrations of the hydroxyl groups, which have been mainly chemical bonds interacting with the silanes, such as the ones mentioned mentioned above [26, 27], and that may be seen in figure 1.

The peaks at 1400 and 1112cm^{-1} in both samples have been attributed to the bending vibration of the bonds and the asymmetric stretching vibration of the Si- O- Si bonds [28]. The new spectrum emerging at 600cm^{-1} has been attributed to the vibration of the Si-O-Si bond. The peak at 2900cm^{-1} corresponds to the asymmetric stretching and vibration of -CH$_3$ [17]. The emergence of -CH$_3$ has been caused by the hydrolysis and polymerization of the wood and silanes, which have shown that the mixture of silanes/nanoparticles produced the most efficient chemical modification, as can be seen in figure 1C.

On the other hand, the peak of the C-C groups at 1664cm^{-1}, as previously reported, has not been observed in the spectrum of any of the wood types. This may indicate the breakdown of the -C-C bonds, demonstrating full hydrolysis and condensation with the components of the wood [17].

SEM-EDAX

SEM has been carried out on the samples in order to observe the structure of the cell walls of the wood, and, at the same time, the samples impregnated with nanoparticles have been analysed with the EDAX module. This technique has been carried out mainly to reliably corroborate the presence of these, due to the scarce, or null information obtained from the FT-IR spectra in this particular case.

Figure 2 shows SEM images of the nanoparticle-impregnated samples. The images have shown a clear agglomerate of nanoparticles uniformly dispersed in the wood fibres, which has been attributed to the presence of nanoparticles. Due to the fact that the presence of nanoparticles could not be detected with FTIR, a semi-quantitative chemical analysis has been carried out using the EDAX probe, as it may be seen in figure 2. As observed in the spectra, the particle corresponds to the nanoparticles.
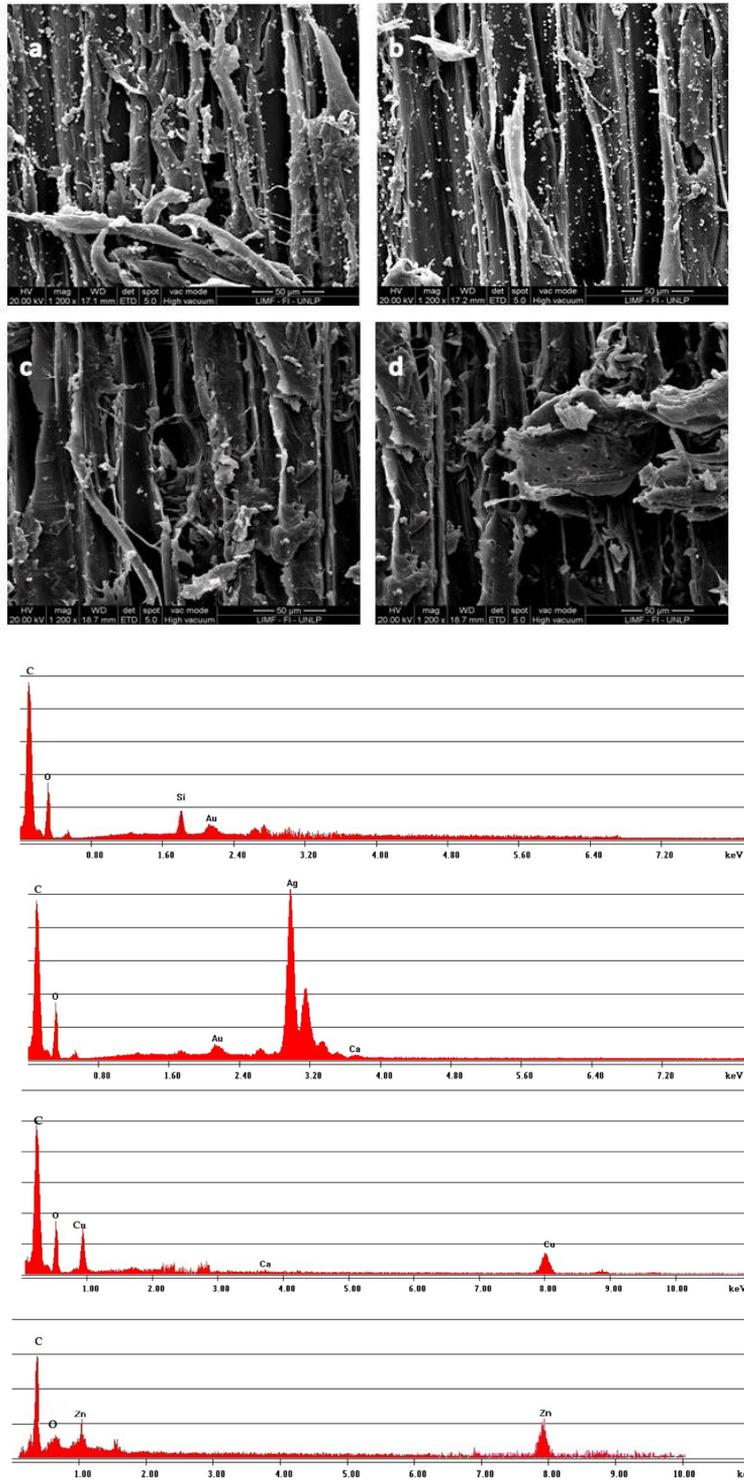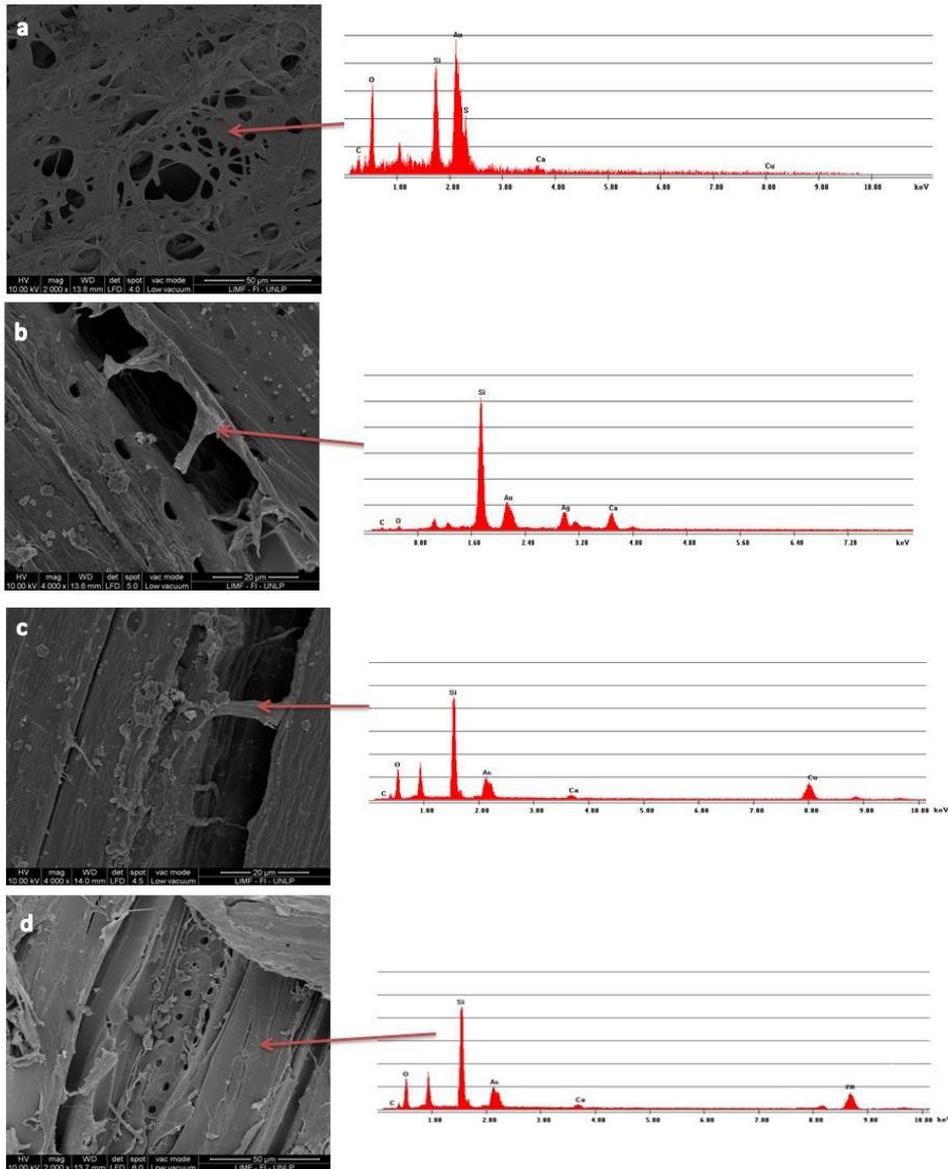
Fig. 2. Scanning electron microscopy (SEM) with EDAX module of samples
impregnated with nanoparticles: a. Si; b. Ag; c. Cu, d. Zn

Finally, figure 3 has presented the SEM images of the impregnation with silanes/nanoparticles and their respective EDAX analysis. In all cases (Fig. 3a-c), except in the use of nanozinc (Fig. 3d), a microstructure formation between the cell walls of the tracheids has been observed.

Fig. 3. SEM-EDAX of impregnants based on Silanes and nanoparticles (wood impregnated with MTES):
a. nanoSi; b. nanoAg; c. nanoCu; d. nanoZn

As it has been mentioned before, it may be observed the chemical presence of all the components dealing with the composite system. Therefore, it should be mentioned that all the treatments and application of the method proposed have generated wood chemical modification.

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Water-repellency and dimensional stability

It may be observed that all treatments have the capacity to reduce the water absorption rate and to improve dimensional stability (Figs. 4-7).

For the silanes (Fig. 4), the highest volume change is 1.0±0.2% and is obtained with the MTES treatment and a lowest of 0.72±0.15% with the MTES and OTES mixture. With regards to the water absorption rate, it may be observed that both OTES and their mixture with MTES have the same performance in terms of dimensional stability, but substantially improved water-repellency, for which reason a synergistic effect between both compounds may be attributed. In the case of MTES alone, the absorption rate has been high from the fourth immersion cycle, stabilizing only in the fifth cycle, and then continued to increase in volume.

The aforementioned proves that the hydro-repellence in the mixture has been given by OTES, as expected, due to its long hydrocarbon chain as a substitute and the dimensional stability that has been achieved with the presence of both. These results indicate that the wood modified only with MTES would form a dense and compact coating on the cell wall, as it has been observed on the SEM images.

However, it would not sufficiently prevent the entrance of water in a liquid state, because it has not presented high hydro-repellence. This is why with the mixing with OTES the performance has been improved, since a compact coating may be obtained, but with more hydrophobicity given by the presence of OTES. On the other hand, wood that has been treated only with OTES may also form a reactive coating, but with hydrophobic characteristics and discontinuous due to steric hindrance.

For this reason, its behavior has improved when it has been mixed, since a dimensional stability has been achieved due to a greater surface area of the cell walls and water-repellence in virtue of the presence of the hydrocarbon chain of OTES [10, 19, 29-31]. On the other hand, it can be affirmed that the formulations with MTES alone have been hydro-repellent, but not dimensional stabilizers, adjusting more to a type II protective system.
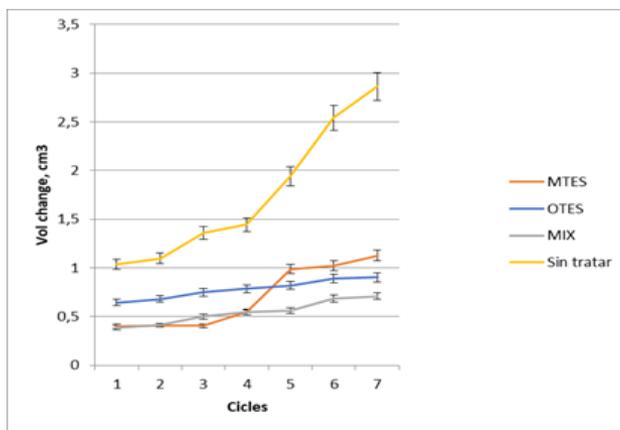

Fig. 4. Water-repellent efficiency of silane-based impregnators

The performance of the nanoparticles has been shown in figure 5. They have resulted better as a water-repellent treatment in comparison to silanes, since a maximum volume change of 0.8% and a minimum of 0.5±0.11% with regard to the almost 3% of untreated wood which has been obtained. Within this group, it may be observed that the silica nanodioxide and copper nano-oxide have given them greater dimensional stability, having a minimum water absorption rate

(there have been almost no changes in the slope of the curves, or at least, very progressive changes throughout the cycles).
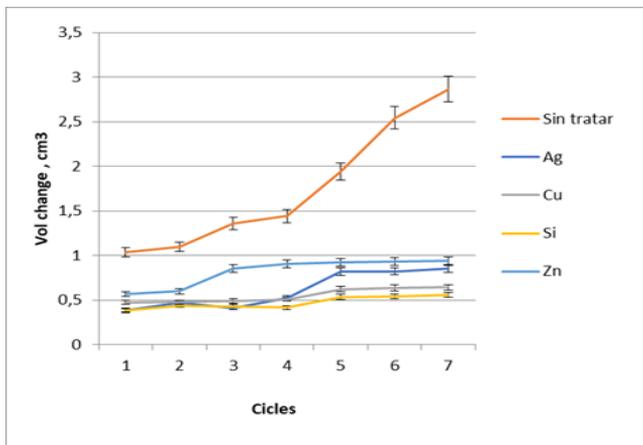

Fig. 5. Water-repellent efficiency of impregnators based on nanoparticles

The same has not been obtained in the case of the nano-silica and zinc nano-oxide, in which it has been observed that the first one has a high absorption rate in the first cycles and then enters a plateau, while the second one presents the maximum rate of water absorption between the fourth and fifth cycle, being this a better water-repellent performance.

Possibly, this performance could be due to what has been observed in the SEM (Fig. 2) in which a uniform distribution of nanoparticles can be seen along the fibres, which would imply a change in the capillarity of the wood: the nanoparticles obstruct the -OHs of the cellulose responsible for absorbing water by forming hydrogen bridges. Therefore, water molecules may not be adsorbed, attributing this to water-repellency and dimensional stability. This last one is because of the absence of volume increase. As regards silanes, the difference in performance has been produced because water-repellency has consisted in capillary occlusion due to polymer formation: now the hydrophilicity has resulted from the composite that has been formed and not from the wood per se. Furthermore, the dimensional stability, in the case of the silanes, has also been given by the polymeric structure that limits their natural expansion, given the intra- and inter-molecular structures observed in the SEM images. This difference in the proposed mechanism can explain why nanoparticles tend to be more efficient than silanes are [32-35].

Finally, the performance of the mixture of silanes and nanoparticles has been studied, as it may be seen in figure 6. This has been done under the hypothesis that there could be some synergistic effect between these two components which have been useful to protect the wood from the abiotic agent under analysis.
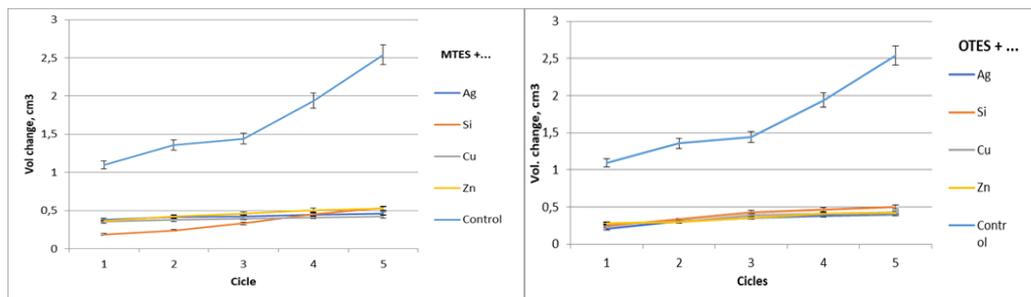

Fig. 6. Water-repellent efficiency of impregnators based on the mixture of silanes and nanoparticles: a. MTES and b. OTES

It may be observed that the hypothesis has been fulfilled since, regardless of the mixture, the system's performance has been the same: for both silanes and for all the nanoparticles under study, the highest volume change obtained has been 0.48±0.12% and the water absorption rate has been lower, with respect to each of the individual treatments, as it may be seen in figure 7. In this case, the combination of both technologies may generate such changes that they would behave separately from the chemical origin of each of the individual compounds. This would indicate that there is an efficient change in the chemical and physical capillarity in which water absorption has been almost zero [36, 37].

It can, therefore, be concluded that a mixture of silanes and nanoparticles are the best treatments for water-repellency, acting as dimensional stabilisers and reducing the rate of water absorption in the same proportion, something that is not commonly achieved.
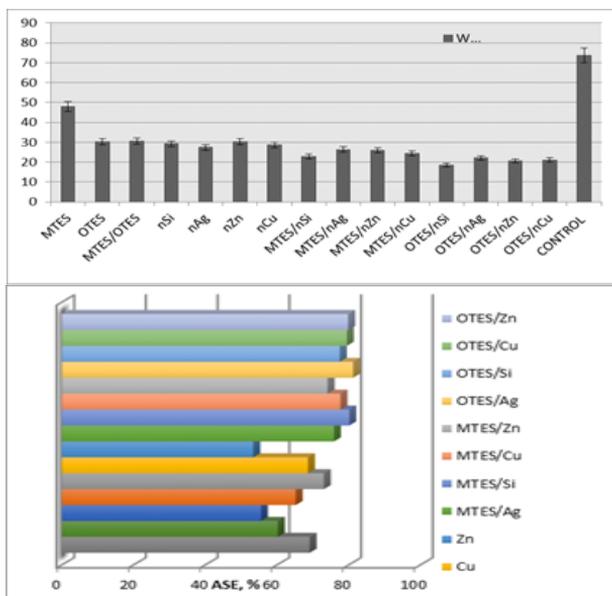

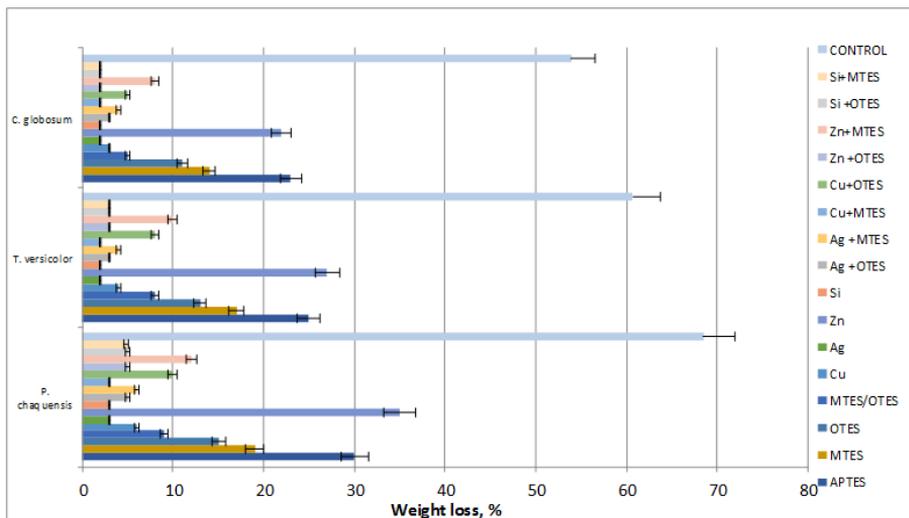**Fig. 7.** Anti-swelling-efficiency coefficient (ASE%) and water absorption (WA%)

Biodeterioration

The results of this study have been shown in figure 8, in which there can be observed that the percentage of weight loss of each treatment at 16 weeks of exposure of each of the species represents the three most important types of rot.

It may be observed that, in all cases, treatments have reduced the loss of mass in all the test tubes, regardless of the species exposed. Therefore, it is possible to state that all treatments have the ability to protect the wood from fungal degradation, without taking into consideration the type of rot it produces. This last concept leads us to think that the chemical modification effectively takes place in the different layers of the cell wall, since the variety of rot is basically given by the polymer that the fungi attacks [38-40].

Among the species, it may be seen that through analyzing the differential weight loss of the controls according to the species which have been exposed, we can determine that the most aggressive is *P. Chaquensis* (white rot degrades lignin), followed by *T. versicolor* (brown or cubic rot degrades cellulose) and finally *C. globosum* (soft rot, degradation of medium laminae). This order is consistent with the identified type of rot that these produce.
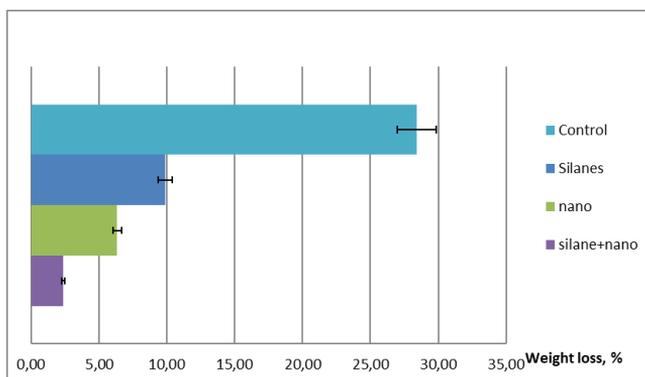
From a global analysis determined by the type of impregnation implemented, it may be possible to discriminate which group has obtained the best performance in resistance to biological degradation, as it may be seen in figure 8.

Fig. 8. Percentage of weight loss of each treatment at 16 weeks of exposure of each
of the species that represent the three most important types of rot.

The graph shows the average obtained from the loss of mass after 16 weeks of exposure
to the active ingredient variables of the formulations. For this purpose, the weight losses of the
three rots have been averaged for each formulation variable. This analysis allowed to discriminate
that the best performance in terms of fungal resistance has been given through the mixture of
silanes/nanoparticles, followed by the nanoparticles, and finally by the silanes.

In figure 9, it can be observed that the formulations followed the same performance
pattern, without taking into consideration the type of rot: the least mass loss occurred with the
mixture of silanes/nanoparticles (with losses of 3.13±2.34%; 2.45±2.23% and 1.58±0.96% for *P.
chaquensis, T. versicolor* and *C. Globosum*, respectively), followed by formulations based on
nanoparticles (with losses of 8.65±1.73%; 5.81±3.2% and 4.65±0.49 % for *P. chaquensis, T.
versicolor* and *C. Globosum*, respectively), followed by silanes (with losses of 12.10±6.17%;
9.98±3.42% and 7.55±0.,96% for *P. chaquensis, T. versicolor* and *C. globosum* respectively).

Fig. 9. Percentage of weight loss of each treatment after 16 weeks
of exposure of the treatments without discriminating by type of rot

With regards to the differential growth, it has been observed that within the treatments
there may be differences in terms of the type of protection: all the formulations that have
presented nanoparticles, as an active component, have shown a fungicidal performance, while

those formulations based on silanes or alkoxysilanes have presented a fungistatic performance, as it may be seen in figure 10.

Fig. 10. Morphological development and differential growth of fungal species compared to different treatments based on controls (untreated wood)

From this analysis, it can be determined that, in general, the best performance has been given by formulations with nanoparticles (alone or mixed with silanes), followed by the mixture of silanes, as it can be seen in the overall analysis, and in accordance with their fungicidal or fungistatic performance.

In this case, the performance of the treatments against biotic agents has demonstrated a synergistic effect, as well as in the hydro-repellence: when the silanes and the nanoparticles have been combined in the formulation, they perform with a higher number, than the sum of each one individually. This suggests that the chemical modification of the wood would be giving the resistance to degradation and not the presence of the compounds. This means that the protection in this case has been achieved by the change in the chemical and physical structure of the wood,

preventing the fungus from using it as a source of carbon: the structural and chemical change of the wood polymers prevent the enzymatic hydrolysis, because their batteries may not "recognize" them as enzymatic substrates (in the keylock model, the enzyme-substrate complex is very specific, so any change prevents their function), not allowing their development [40].

There have been differences between fungistatic and fungicidal behaviour: in fungistatic cases the hyphae may penetrate the substrate in a limited way, but they may achieve it, so that the organism can begin its development by means of non-enzymatic oxidations, obtaining rapid energy from available carbon sources that are necessary to generate the specific enzymatic battery. This process allows the organism to develop to its fullest capacity, and that is when exponential biomass growth takes place. Once the enzymes have been generated and released, they cannot reach the organic polymers, because they encounter the composites formed, the fungus then enters a dormant phase and the growth observed stops, as it may be seen in figure 10.

On the other hand, in the case of the fungicides, these have not allowed the micellar development due to the impediment of the penetration of the fungal hyphae to the substrate, which prevents the organism from generating the absorption of nutrients and water and consequently not allowing the fungus to develop directly and, in turn, die. As it has been previously mentioned, this occurs in the presence of nanoparticles, either alone or mixed with silanes. In the case of the mixture, it has been observed that this formed more branched polymers that covered a larger surface area. Therefore, this would cover all possible penetration spaces.

In the case of the nanoparticles, it has been observed that there has not been any polymer formation, or microarrangements of the relevant wood polymers, but that there has been an orderly arrangement of these along the cell wall, in the different layers of the cell wall. This allows to infer that hypha would generate the grooves between the walls (lamellae), or in the cell walls (depending on the type of rot), but it would meet the nanoparticles, which would prevent the recognition of the substrate (chemically different environment), and so penetration would be unfeasible [38-40]. It may be concluded that for fungicides there would be two mechanisms at work: non-recognition of the substrate by chemical modification and steric hindrance. The combination of these two mechanisms plus steric hindrance in the mixtures may, then, explain the synergistic effect achieved with the silane/nano mixture.

It should be noted that some of the formulations escape the classification just given, such as it is the case of the nanozinc. This may be due to the fact that zinc is an enzymatic co-factor, which is why it has become a well-known compound in biological organisms. Since the concentrations used are low, they can metabolize them without any inconvenience, and there is also bibliographic data showing their gradual leaching over time [41, 42]. Probably, in this case, the performance is given by the reduction of water absorption that it generates, as it has been analyzed above.

Another case to highlight has been the behavior of silica nanodioxide and nanosilver, which behave the same, or better than the silane/nano mixture, as it has been predicted above. In this case, it would be an active contact polymer: As it has been observed, nanoparticles are deposited in the different layers of the cell wall due to their high energy and natural surface charge thanks to their electronic composition, plus the one they have taken when they have been formulated. This energy decreases when interacting with the components of the wood, but there is a "back-up" of remaining charge that, when it comes into contact with biological membranes, would have the capacity to destabilize them by electronic change of their surface [43, 44], disintegrating it, or failing that, and not allowing the fungal hyphae to continue proliferating. This would then prevent the absorption of nutrients and fungal development [45-48].

Fire resistance

Table 2 shows the values obtained for the oxygen index. The importance of determining the OI, not only lies in measuring the ease of combustion of the substrates to compare results, but an OI greater than 28 allows the substrate to be classified as non-combustible in atmospheric conditions. It should be mentioned that this method is not representative of the real performance

of a material in contact with fire, but it is one of the preferred methods in the development of fire-retardant treatments, because it allows obtaining reproducible numerical values.

In table 2, it may be noticed that all the treatments have been fireproof with respect to the control, due to the fact that the consumption of oxygen necessary for the sample to enter into combustion has been much greater than that available in the atmosphere, so it could be said that they all present a fireproof behaviour.

Table 2. Results of Oxygen Index. All samples are fireproof

Treatment	OI,%
CONTROL	18
Zn	25
Cu	27
Ag	29
Si	29
OTES	33
MTES	36
OTES/Zn	37
MTES/Si	38
MTES/Ag	40
OTES/Cu	40
MTES/Cu	43
OTES/Ag	44
MTES/OTES	45
MTES/Zn	45
OTES/Si	45

In this case, a clear synergistic effect has been observed when both technologies (silanes/nanos) have been combined with respect to each other individually: it has been known that silanes and siloxanes are good fireproof treatments due to their inorganic nature, which contributes to the formation of natural char with a greater inorganic contribution, generating an insulating layer of better quality.

In addition, since it has been polymerised inside the wood, the organic/inorganic composite has had a higher ignition point than the organic one (untreated wood), so the activation energy necessary for combustion to start is greater and removing this side of the fire triangle [10, 49, 50].

As for the nanoparticles, it has been observed that they behave basically like untreated wood, this is due to the fact that very low concentrations have been used, so that they can bring changes to the system by themselves.

In the case of silane/nano-composite systems, the synergistic effect could be explained by the following mechanism: the chemical modification generates an organic/inorganic hybrid substrate that causes the ignition point to be modified, the surface area begins to heat up, starting to increase the temperature of the system and with it the energy available for the activation of the combustion, the first layer of the substrate begins to burn generating a carbonaceous layer as in any wood that acts as an insulator, but with the addition of inorganic polymers and nanoparticles, this causes heat dissipation and lowers the energy of the system, this results in not enough activation energy for the combustion reaction to occur and, therefore, there is no oxygen demand in the system.

The heat then penetrates into the deeper adjacent layer in which the inorganic components can melt, or soften again slowing down the heat conduction, while the organic ones may be degraded into smaller products contributing to the formation of more carbonaceous residue ("char"). The heat continues to penetrate and reaches an even deeper layer, also causing its degradation and forming products that can be transferred to the combustion zone through the carbonaceous residue: the system forms a carbonaceous material with a high inorganic content that accumulates at the interfaces during combustion, isolates the underlying material and
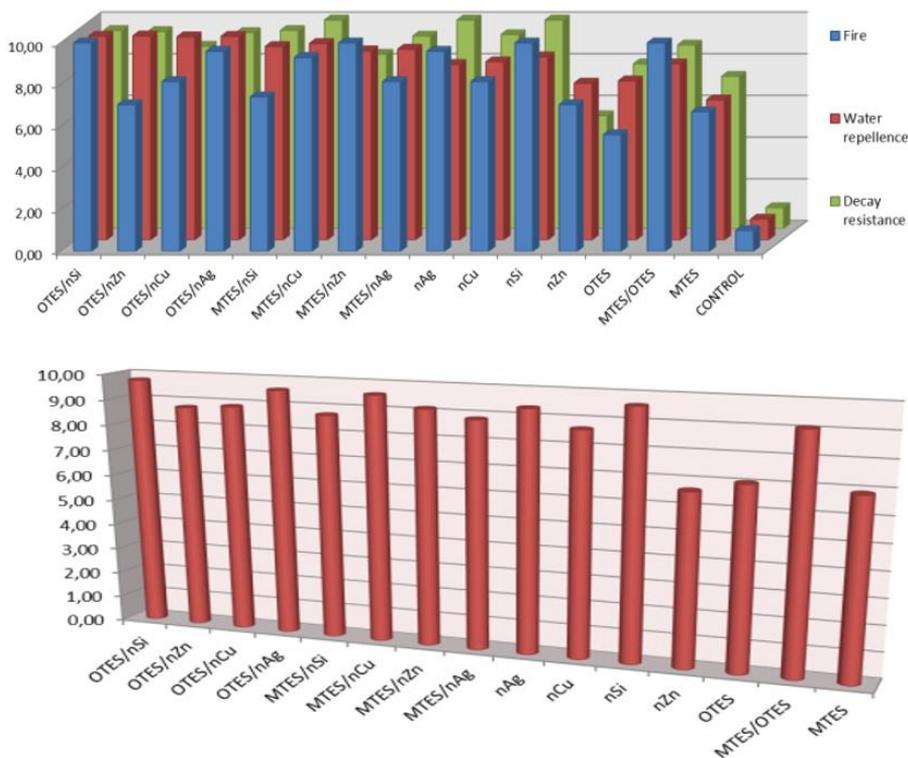
decreases the loss of mass from the decomposition products, thus giving it a self-extinguishing character.

The high resistance of inorganics has been due to their high molecular stability against the energy delivered by fire [51, 52].

Global analysis of results

For the global analysis of results, an average of the performance of each treatment against the different degrading agents exposed has been made and a score has been given: 10 being the best performance, and 1 the worst. Afterwards, from these defined extremes, the intermediate values have been weighted. With this, it is possible to discriminate, in a general way, the behavior of the treatments against biotic and abiotic agents, as it may be seen in figure 11.

The synergistic effect can be observed when generating the silane/nanoparticle mixtures, resulting in protective systems with excellent efficiency for all the degrading agents. In order to corroborate this hypothesis, a multiple linear regression has been made, posing as hypothesis that when confronting the results of the individual components, nano/silanes should give a regression very near to the linear one, since, if the improvement of the results is given by the sum of the individual components, the performance should not be very far in the mixtures. The results of the systems gave a R= -0.14766 and a p >0.76 which indicates that there has not been a linear regression between these results. Therefore, checks that in the mixture they have been behaving as an independent system, and not as the sum of both independent, demonstrating the mentioned synergy.

Fig. 11. Global analysis of the results. Above discriminated by
degrading agent and below the general performance of
each treatment against biotic and abiotic agents

The two best have been the OTES/nanosilica mixture with a score of 9.75, followed by the nanosilica with 9.6 points, followed by the silane/nanosilica mixtures which ranged from 9.6-9 points (the highest being the OTES/Ag mixture and the lowest being the MTES/nanosilica series), followed by the nanoparticles with 8.5 points, followed by the silane mixture, with a score of 8-7, then the silanes alone obtaining around 7-6 points.

It should be noted that the behavior of silica nanoparticles escapes the pattern observed, since they have given the same performance as the mixture with silanes-nanos when it is alone, but it has not generated a synergistic effect when it is in conjunction with silanes. This may lead us to infer that its protective efficiency may be given by the amount of charge and surface energy of this nanoparticle, so that, once it is in contact with the silanes, this energy may decrease by polymerization and this will make it less efficient.

Conclusions

It is concluded then, that there is a synergistic effect when silane/nano technologies have been used, which allows to generate protective systems of high performance.

This synergistic effect allows working with low concentrations of active ingredients which generates that these systems are low cost and friendly with the environment, since they are free of volatile organic solvents

Another peculiarity observed has been the importance of substitutes in the silanes: it may be seen that, in hydro-repellence, all the systems with OTES have performed better than any other silane with shorter hydrocarbon chains. This has allowed to infer that it is important to know, characterize and study each of the components of a formulation separately, in order to be able to exploit all their potentials. This management means that it is not necessary to use high concentrations of active principles, but rather to be able to find synergetic relationships that give protective capacities at low costs.

Finally, it has been observed that the best performances of resistance to biodeterioration have been given with the presence of nanoparticles, which allows us to infer that the composite formed by nano-wood, nano-silane-wood, are bioactive.

Therefore, this paper has shown that all the treatments have presented an excellent protective performance against biotic and abiotic agents. Moreover, it presents an easy application (immersion), which represents not only a watertight protective system, but also a set of systems that may be used and managed according to the availability of the active components, the available costs, and, most importantly, without having to modify the form of application.

Acknowledgments

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