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Silicification of wood adopted for barrel production using pure silicon alkoxides in gas phase to avoid microbial colonisation

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ABSTRACT

The paper presents a new approach, covering wood with silica-based material in order to protect it from spoilage due to microbial colonisation and avoiding the loss of the natural features of the wood. Wood specimens derived from wine barrels were treated with methyltriethoxysilane in gas phase, leading to the deposition of a silica nanofilm on the surface. ^{29}Si and ^{13}C solid state Nuclear Magnetic Resonance and Scanning Electron Microscope–Energy Dispersive X-ray analysis observations showed the formation of a silica polymeric film on the wood samples, directly bonding with the wood constituents. Inductively Coupled Plasma-Mass Spectroscopy quantification of Si showed a direct correlation between the treatment time and silica deposition on the surface of the wood. The silica-coated wood counteracted colonisation by the main wine spoilage microorganisms, without altering the migration from wood to wine of 21 simple phenols measured using a HPLC-Electrochemical Coulometric Detection.

1. Introduction

Silica-based sol–gel materials are particularly useful for surface modification of traditional materials, as shown by certain examples in the fields of electronics, light interaction and protection from corrosion (Mahltig et al., 2008; Gurav et al., 2010; Sanchez et al. 2011). In the case of wood, the main methods involve dipping the materials into a gelling solution of silica precursors. Severe conditions are generally required to favour the hydrolysis of precursors and the condensation of siliceous unties with the formation of the silica layer. Panov and Nasko (2006) describe the silicification of wood with a mixture of ethyltriethoxysilane and diethyldietoxysialne, obtaining a valuable reduction in the water adsorption of wood and protecting it from fungal attack. Similar results were obtained, using other siloxanes, by Donath et al. (2010), Tshabalala et al. (2003), and Saka and Ueno (1997). In all works, a high temperature, over 80 °C, combined with high pressure (up to 12 bar) were required to allow deep impregnation of the wood by sylane, ensuring stable silicification. Therefore, these treatments are not suitable for certain applications involving wood, especially when the nature, or the use, of the objects makes it necessary to maintain the surface properties.

A valuable alternative is the direct utilisation of pure silicon alkoxides in gas phase. This solution has been found to be particularly useful, thanks to the possibility of operating in biocompatible conditions to coat viable cells, and requires the reliability of surface OH or embedded H_2O (Carturan et al., 2004; Avnir et al., 2006). This approach has the advantage of completely covering the surface of the material, independently of its weight and geometrical form (Callone et al., 2008). Moreover, the original extreme reactivity of silicon alkoxides is preserved and immediate formation of the wood–oxygen-bond can therefore be surmised. This aspect is not secondary, as the occurrence of real chemical bonds between the deposited silica layer and the wood guarantee the mechanical stability of the coating in the event of chemical, mechanical and thermal stress. An important aspect of wood protection using surface treatments regards the avoidance of biological degradation. In this case the sol–gel derived layer can provide a matrix for entrapment of biocide components, so a combination of features are obtained: the silica coating provides mechanical, thermal and fire protection and simultaneously the biocide components integrate the quality of the protection.

In this work we report on a new way of exploiting the general method for silica coating using gaseous silicon alkoxides (Carturan et al., 2006) to the treatment of wood surfaces. The paper deals with the deposition methods of organic modified silica, evaluation of the molecular structure of the inorganic matrix, possible chemical interaction with wood components using solid state NMR, study of

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the bioactivity of the samples as protection against deposition and colonisation by different microorganisms recognised as spoilage agents in the food industry.

Our attention focused on oak wood involved in the production of barrels used to make wine. *Barriques*, small wine barrels with a nominal volume of 225 L, are still produced using the traditional procedure with staves of *Quercus*, following prolonged seasoning of the wood. To produce *barriques* the staves must be flexible, so the wood is subjected to heat treatment, carried out by direct exposure to flame during the assembly of barrels. This procedure gives the *barriques* special proprieties and encourages direct effects on wine quality (Singleton, 1995). It is known that the permanence of wine inside barrels leads to a complex combination of chemical reactions, which directly involve the components of wood or, more generally, are indirectly mediated by wood, thanks to the particular environment that it helps to create inside *barriques*. Despite these precious effects on wine quality, the use of barrels leads to some problems. The porosity and inertness of wood favour the growth of a complex microbiota. New barrels are normally free from spoilage microorganisms but after few months of wine storage, growth of unwanted yeast or bacteria up to 10^3–10^4 cells for cm^2 can already be measured (Renouf et al., 2006; Oelofse et al., 2008) and the sanitization techniques currently available have generally been shown not to be very effective (Guzzon et al., 2011).

Wood silicification using pure silicon alkoxides in gas phase may represent a feasible solution. Previous results have demonstrated that the silica film obtained was uniform, with adequate mechanical and chemical stability (Callone et al., 2008). The texture resulting from the condensation of methyltriethoxysilane (MTES) unities provides narrow porosity and excludes the migration of microorganisms thought the silica film, while at the same time fully preserving chemical exchanges (Carturan et al., 2004; Callone et al., 2008). A detailed description of this new approach to wood silicification is proposed here, accompanied by chemical/physical characterisation of the material obtained. Considering that the work is still at an experimental stage, conducted in the laboratory using wood samples, all the experiments are discussed by comparing the behaviour of wood samples coated with silica gel with untreated wood samples, in order to highlight the properties caused by the presence of the silica nanofilm bonded to the wood surface.

2. Materials and methods

2.1. Materials

Methyltriethoxysilane ($CH_3Si(OEt)_3$), ethanol, and other chemicals were purchased from Sigma–Aldrich as reagent-grade products and used without further purification. All reagents and apparatus involved in the microbiological tests were sterilised at 121 °C × 15 min before use. Yeasts and acetic acid bacteria were cultured in Modified Wallenstein Broth Medium (Oxoid); lactic bacteria cells were cultured in MRS Broth (Oxoid).

2.2. Wood coating

Two types of wood samples were used in this study, according to the goal of each experiment. The first type of sample was made up of oak wood blocks (50 × 40 × 30 mm) obtained by cutting up medium toasted barrique staves (G & P Garbellotto S.p.A); these samples were used in all the experiments. The specimens were washed in water (60 °C × 15 min) and dried (30 °C × 24 h). Five sides of each sample were covered with paraffin wax (low mp 70–80 °C, Sigma–Aldrich); only one side (surface 20 cm^2) remained available for silica coating. The wood samples were hermetically sealed in the reaction chamber (Fig. 1). A second type of samples was used only for the tests on the release of phenols in wine. This samples was made up of medium toasted oak staves (dimensions 5 × 5 × 50 mm; Tonnellerie National Italia). MTES vapours were obtained by treating a MTES solution in the heating chamber at 90 °C. The vapours were transferred using a N_2 gas flux (0.5 L/min) in the reaction chamber containing the wood samples. The treatment was performed for 4 different durations (from 5 to 20 min); the temperature in the reaction chambers remained below 40 °C for the entire treatment duration. Finally, the wood samples were dried for 60 min at 25 °C.

2.3. Physical and chemical characterisation

Microscopic observation of samples was carried out using a SMZ80 stereoscope, equipped with a DSFi1 Digital Camera (Nikon). Physical characterisation of the treated wood block was performed as proposed by Donath et al. (2010), the weight of samples was determined using a Mettler Toledo PM460 balance. The modifications in the weight and volume of the samples after exposure to silica alkoxide gas were described as a weight percent gain (WPG) and bulking effect (B) (Donath et al., 2010) when,

$$\mathrm{WPG} = \frac{m_{\mathrm{treated}} - m_{\mathrm{untreated}}}{m_{\mathrm{untreated}}} \times 100\%$$

$$B = \frac{V_{\mathrm{treated}} - V_{\mathrm{untreated}}}{V_{\mathrm{untreated}}} \times 100\%$$

Micro-structural analysis was carried out using a JEOL JSM 5500 Scanning Electron Microscope (Oxford Instruments Analytical) at various magnifications at 10 kV, 20 kV for Energy Dispersive X-ray analysis (EDX).

^{29}Si and ^{13}C solid state NMR spectra were recorded with a Bruker 400 WB spectrometer with carrier frequency of 400.13 MHz (1H) equipped with a double resonance probe. Before analysis, the specimens were dried (120 °C × 24 h) and ground using a M20 Universal Mill (IKA). Samples were packed in 4 mm zirconia rotors and spun at 6 kHz. ^{29}Si CPMAS spectra were obtained with pulse length 4.3 μs, scan delay 10 s; 6 k scans with contact time of 5 ms. SP sequence was used for quantitative analysis. Q_8M_8 was used as an external secondary reference. Si units were labelled according to the usual NMR notation: Qn, Tn, with capital letters referring to the number of Si–O– bonds and *n* being the number of oxo-bridges. ^{13}C CPMAS spectra were acquired with 90° pulse length of 3.36 μs, contact time of 2 ms, 2000 scans and scan delay of 5 s. Adamantane was used as a secondary external reference.

Determination of silicon was carried out using Agilent 7500ce Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent Technologies). Before analysis, the wood samples were dried (120 °C × 24 h) and ground using a M20 Universal mill (IKA). Acid digestion of wood powder was performed in PTFE vessels using ultrapure nitric acid (69.5%, Merck) and hydrogen peroxide (30%, Merck). A rhenium solution (800 μg/L) was added as internal standard. Mineralization was performed in a high-throughput microwave reaction system (MARSXpress™, CEM) using the following thermal cycle: 12 min at 100 °C, 15 min at 150 °C, and 22 min at 210 °C.

2.4. Microorganisms and biological tests

The microorganisms belonged to the German Collection of Microorganisms and Cell Cultures (DSMZ), the Industrial Yeast Collection (DBVPG), and the ARS Culture collection (NRRL). Fermentation tests were performed at 25 °C in Yeast Medium broth