

# Waterborne Hybrid Silica-Alumina Coating to Increase Poplar Wood Application Opportunities

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## ABSTRACT

Environmental sustainability and health issues are important factors to be considered in developing new coating materials. In this context, sol-gel is a widely studied procedure that represents also a sustainable one, due to the mild process temperature and conditions.

In the panorama of soft wood applications, the combined advantages of using an abundant and inexpensive natural source and an environmental friendly technological process, are expected to offer promising breakthroughs.

This work aims at developing and testing under different conditions a waterborne hybrid silica-alumina coating to increase poplar wood wear performances, without compromising on aesthetical qualities.

**Keywords:** poplar wood, waterborne sol-gel, wear resistance, natural wood color

## 1 INTRODUCTION

Wood has played a substantial role throughout the human history. It has been used for thousands years due to its resistance and easiness in manufacturing. Moreover, wood is a sustainable, renewable and versatile raw material as well as aesthetically appreciated [1].

Today friendly environmental bioresources are becoming a very important subject of research [2] and biomaterials such as wood can be a potential alternative to non renewable materials. Moreover, biomaterials are attractive for industries, which must comply with increasingly restrictive legislative provisions about environmental sustainability [3].

Nevertheless, wood components deriving from cellulose, hemicellulose and lignin, have a very soft and hydrophilic nature, and wooden manufactures often undergo surface damage as their natural composition [2]. Despite conventional wood coatings such as oil finishing, shellac, varnish and laquer increase material durability, wood is a highly abrasive and non homogeneous material [4], [5].

In this scenario, several methods and procedures for wood modification and functionalisation have been

purposed [2], [6], [7]. Adding specific nanoparticles (NPS) to the coating matrix is one of the most common used procedure in coating industry. However dispersion and suspension techniques are required, and NPS disaggregation and dispersion in the air during elaboration processes may represent hazards for human health [8].

An interesting way to modify wood for improved properties is the sol-gel procedure. The process is applicable to natural and heat-sensitive materials, and allows for a versatile non-toxic surface treatment method [9]. The starting solution can be composed of water instead of alcohol according to the final coating performances. With a view to an easy scale-up of the sol-gel preparation, the use of water implies a reduced volatile organic compounds (VOC) emission during the evaporation of the solvent phase, improving the air quality and concurrently reducing health and fire hazards [10].

One of the key factor that influences coating performances of fibrous porous materials is the temperature of the process throughout the coating application phase [3]. However, typical low process temperatures make the sol-gel treatment to be considered as a sustainable one as well as applicable to bio and heat-sensitive materials. Moreover, with the increase in treatment temperature and time wood suffers of colour variation. Color variation has a relevant role concerning the final application of wood materials. In some cases it is the determining factor in the selection of a specific type of wood, since the aesthetical properties are often crucial, as for wood flooring [6].

In this work, we describe a simple and economic way to functionalize wood surface by the sol-gel procedure, aiming to improve mechanical properties of poplar veneers. The main focus of this work is devoted to the correlation of process parameters with final material features. Considering the functional properties by the solely coating side it was not enough to effectively improve the properties of the final system. Indeed, wood possesses some inherent characteristics, as porosity and thermal sensitivity, that required to consider it as an active component during the coating preparation process. Thus, an equivalent attention is devoted in this work, to the chemical and functional properties of the coating and of the substrate, analyzing the properties of the final composite as a result of a dialogue

between the two components. Moreover, a particular attention is addressed to the aesthetical outcome of the final system. Indeed, the combined advantages of using an inexpensive natural source, as poplar wood, and an environmental friendly technological process, as the aqueous sol-gel, expected to offer promising alternative in the panorama of construction materials, creating positive breakthroughs.

## 2 MATERIALS AND METHODS

### 2.1 Reagents and Materials

Glycidoxypropyltrimethoxysilane  $\geq 98\%$  (Glymo), and aluminium tri sec butoxide 97% (ASB), were purchased by Sigma Aldrich and used as precursors. Deionized water was used as solvent. The hydrolysis reactions were catalysed by nitric acid  $\text{HNO}_3$  (65% Honeywell Riedel-de Haën). All chemicals were used without further purification. Poplar wood veneers substrates, with standard thickness 1.5 mm and diameter 30 mm, were used as specimens. Before applying, the coating substrate was pre-treated with XHC20 water-based penetrating sealer (IVM Srl, Italy).

### 2.2 Sol Synthesis

300 ml of sol-gel were prepared according to the following procedure: Glymo 0.267 mol were mixed with ASB 0.145 mol, simultaneous addition of hot water (60 °C) 203 ml and  $\text{HNO}_3$  0.028 mol, vigorous stirring. After about 30 minutes the sol was homogeneous and colourless. On the next day the preparation was used for wood treatment.

### 2.3 Wood Specimens Preparation

Poplar wood veneers specimens of 30 mm diameter and 1.5 mm thickness were prepared for morphological and physical characterization and following mechanical tests. Samples were identified and labelled depending on treatment conditions they were subjected and on total heating time and temperature when they were applied. Uncoated and air-dried samples (UncoatAD) were used as control. Air-drying was performed under environmental conditions (relative humidity of  $67 \pm 5\%$  and temperature of  $25 \pm 2$  °C). All substrates, CoatAD, 1hCoat100 and 2hCoat100 were pre-treated by 1 h soaking in XHC20 before sol application. The pre-treatment with sealer was intended to better simulate a commercial wood finishing, since commercial wood surface treatments often combine both base and top coatings [6]. Samples were soaked in 10 ml of sol for 1 hour after different drying methods were applied to XHC20 sealer. Final sol drying processes have been applied in order to stabilize the silica network. Table 1 resumes all the preparation steps for poplar specimens, details on the applied drying procedures are shown for both the first sealer impregnation and consequent sol-gel treatment.

### 2.4 Chemical-Physical and Morphological Coating Characterization

Optical absorption of the hybrid coatings was analysed by a UV/VIS spectrophotometer CM2600d (Konica Minolta Inc. Optics Company).

Surface colour variation,  $\Delta E^*$ , was evaluated referring to  $L^*$   $a^*$  and  $b^*$  coordinates ( $L^*$  stays for lightness,  $a^*$  and  $b^*$  stay for the colour opponents green-red and blue-yellow, respectively) according to CIELAB model [11].

The morphology of wood structure was evaluated by Scanning Electron Microscopy (SEM) observations (Zeiss evo 50 EP). The instrument was equipped with Oxford INCA 200 detector LZ4 10 mm for Energy Dispersive X-ray Spectrometry (EDX) analysis.

### 2.5 Mechanical Characterization

Abrasion resistance tests were performed using Mini-Martindale (James Heal) equipped with 600 grit abrasive paper applying a load (9 kPa) on sample holder. The mass loss was measured after 10, 100, and 1000 cycles on both treated and untreated samples.

Surface hardness was evaluated according to BS EN 1534:2010 (British Standards Institution, Wood flooring - Determination of resistance to indentation - Test method BS EN 1534:2010), specific for wooden materials. For the purpose, a Brickers 220 (Gnehm Switzerland) indentation system was equipped with 10 mm of diameter indentation sphere and the test was conducted applying a force of 1 kN.

## 3 RESULTS AND DISCUSSION

### 3.1 Physical and Morphological Results

In order to evaluate the effect of applied coatings on colour variation ( $\Delta E^*$  value),  $L^*$ ,  $a^*$  and  $b^*$  values of treated specimens vs UncoatAD color data ( $L_0=89,66\pm 0.20$ ,  $a_0=0,54\pm 0.08$  and  $b_0=18,05\pm 0.19$ ) were compared.

Considering the just noticeable difference as  $JND=1$  [12], the visible color variation has been evaluated. The obtained values are reported in Table 2 and a visual comparison between samples is shown in Figure 1. Human eye senses a variation in colour at  $\Delta E^* > 1$ . In Table 2, all samples reported higher values. However a relevant color variation from UncoatAD can be observed in 2hCoat100 samples, reporting  $\Delta E^* = 8.9$ . The noticeable darker color in comparison with 1hCoat100 and CoatAD samples was attributed to higher lightness loss ( $L^*$ ) compared to untreated samples. To the same reasons are due the average color changes of 1hCoat100 vs CoatAD. Although the obtained results of  $\Delta E^* = 5.2$  and  $\Delta E^* = 5$ , respectively, are higher than the JND value, appearance was similar to uncoated wood. No statistical significance ( $P = 0,336$ ) between 1hCoat100 and CoatAD  $\Delta E^*$  values has been verified for a P value  $< 0.05$ .

Name	Coating	Impregnation Time (h)	Drying Temperature (°C)	Drying Time (h)
UncoatAD	Uncoated	No impregnation	No coating drying	No coating drying
CoatAD	XHC20 sealer	1	AD	24
	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> sol	1	AD	24
1hCoat100	XHC20 sealer	1	AD	24
	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> sol	1	100 ± 2	1
2hCoat100	XHC20 sealer	1	100 ± 2	1
	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> sol	1	100 ± 2	1

Table 1: Summary of specimens preparation procedure.

Name	L*	a*	b*	ΔE*
CoatAD (n = 10)	88.43 ±0.25	0.76 ±0.12	22.88 ±0.63	5.00 ±0.56
1hCoat100 (n = 10)	84.87 ±0.40	2.35 ±0.40	17,94 ±0.85	5.21 ±0.32
2hCoat100 (n = 10)	84.25 ±0.21	2.74 ±0.10	24.75 ±0.61	8.90 ±0.38

Table 2: Average colorimetry results for CoatAD, 1hCoat100, and 2hCoat100 treated specimens in CIEL\*a\*b\* colour system. *N* corresponds to the number of measurements.



Figure 1: Visual analysis of samples colour variation. From left to right samples UncoatAD, 2hCoat100, 1hCoat100 and CoatAD are showed.

The darker tonality of heat-treated wood was often attributed to the formation of coloured degradation products deriving from hemicelluloses and to extractives that seemed to participate in the colour formation of heat-treated wood [13].

The morphology of wood treated and untreated samples was evaluated, both prior to the immersion and after the treatment, by SEM (scanning electron microscopy) observations (StereoScan 360, Cambridge Instruments), while coating composition was mapped through EDX analysis (Energy Dispersive X-ray Spectrometry). Figure 2 confirms that the coating was successfully deposited on wood samples surface. In CoatAD wood sample (Fig 2b), coating presented higher homogeneity and less surface defects if compared to 1hCoat100 specimen (Fig 2c). The occurrence of surfaces bubbles and imperfections was attributed to the thermal treatment after sol-gel immersion. Since it is higher in heat-treated samples (CoatAD and 1hCoat100), it is probably due to the faster solvent evaporation and forced drying of samples in the oven.

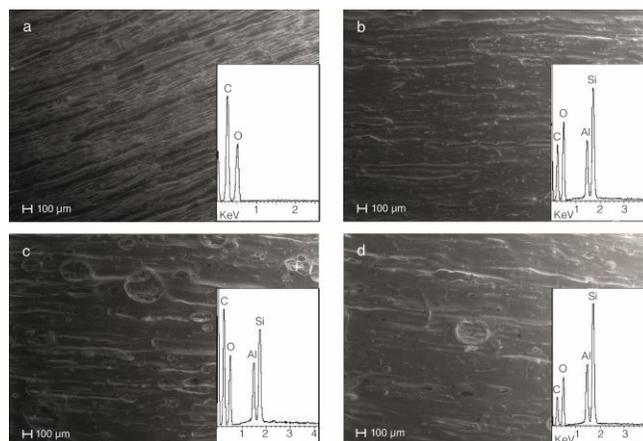


Figure 2: Surface SEM micrographs and EDX analysis of UncoatAD (a), sol-gel treated wood specimens CoatAD (b), 1hCoat100 (c), and 2hCoat100 (d).

### 3.2 Mechanical Results

Brinell hardness (HB) has been calculated to evaluate the consolidation of the wood surface in differently treated samples. In Figure 3 a histogram shows the obtained results on wood veneer samples, after indentation test. The Brinell hardness of treated specimens was higher compared to that of uncoated wood. This was attributed to silica and alumina sol-gel content, which are well-known for their hardness and stability, as a result of their special structure of three-dimensional networks [15].

Abrasion resistance of uncoated and coated wood samples was evaluated by abrasion test, recording the mass loss after 10, 100 and 1000 cycles, as shown in Figure 4. Lower weight loss was related to higher abrasion resistance materials as for lower observed curve slope. The increase of the surface abrasion resistance in treated samples in comparison with the uncoated one can be therefore attributed to the modification imparted by the sol application. Abrasion resistance properties depend both on the hardness and the flexibility of the film [6]. Nevertheless, some differences in final performances can be deduced depending on the applied process parameters.

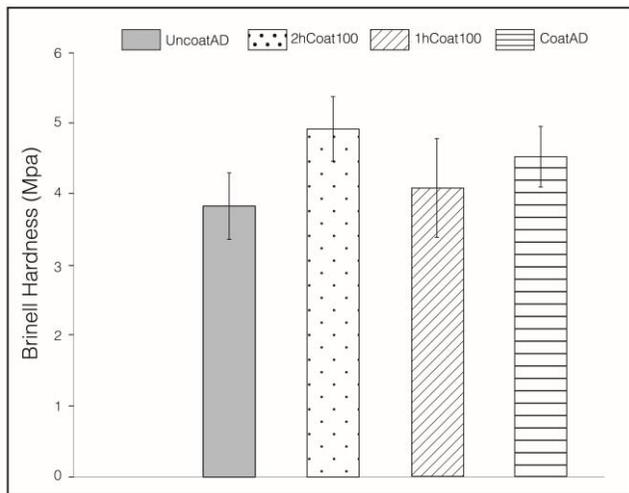


Figure 3: The Brinell hardness HB values relative standard deviations, before and after silica/alumina sol treatment

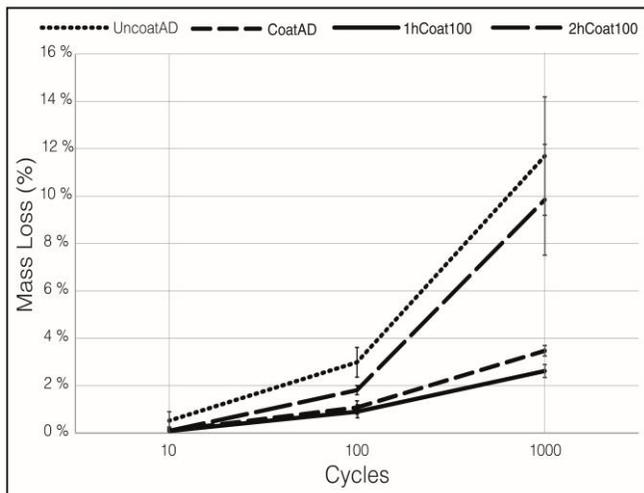


Figure 4: Mass loss and relative standard deviation of uncoated and treated wood samples calculated after 10, 100 and 1000 cycles of abrasion cycles

#### 4 CONCLUSIONS

Wood functionalization was performed on poplar wood veneers through an easily implemented water-based sol-gel treatment. The interlock of the silica/alumina component within the 3-D wood natural porous structure led to better mechanical performances, namely, abrasion resistance and hardness, with reduced effect on the aesthetical outcome. Particularly, despite the chemical component, the process parameters itself was found to play a major role in determining the final properties of the treated wood. The possibility to enhance the performances of naturally renewable bio-resources, as soft woods, that nowadays lack of performances for convenient industrial application, could

be a cost-effective alternative both from an environmental, sustainable and a technological point of view.

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