

## **NOVEL UV- CURED NANOCOMPOSITE USED FOR THE PROTECTION OF WALNUT WOOD ARTWORKS**

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### **ABSTRACT**

In the present paper, the properties and the effectiveness of an experimental solvent-free siloxane-modified acrylic - boehmite based nanocomposite as protective coatings for walnut wood artworks, were assessed. To this aim, a small amount (3 % wt.) of an organo-modified Boehmite (OMB) was added to the acrylic mixture. A novel methodology to apply and harden the coating, i.e. photopolymerization process, based on the supply of UV radiation, was employed. The novel nanofilled coating was applied on walnut wood specimens by brush and photopolymerized in air, using a UV lamp. The penetration of the protective product inside the wood substrate was analyzed using SEM and EDX techniques. Their hydrophobic capability was studied by water contact angle measurements. The colour change brought about by the coating applied on walnut wood substrates was estimate. The impact strength of the treated wood specimens was assessed. The water absorption behaviour of walnut wood elements coated with the novel organic photocurable nanocomposite was also evaluated. For comparison proposes, the same experimental measurements were also performed on walnut wood specimens treated with an unfilled acrylic system (i.e. control) and a commercial protective for wood, based on linseed oil. The experimental UV-cured nanocomposite displayed good protective characteristics with respect the commercial product, brought about by the presence of the nanofiller, and it can be proposed as a potential coating for a wood substrate.

**KEYWORDS:** Siloxane-modified acrylic resins; organo-modified Boehmite; nanocomposite, UV curing; photopolymerization; coatings for wood.

### **INTRODUCTION**

The application of hydrophobic polymers to wood and stone materials is an effective way to preserve the artefacts and protect cultural heritage structures and objects from decay. Wood and stone materials used in heritage and buildings generally deteriorate when exposed to environmental conditions. To limit the decay of such materials, the application of suitable

preservation remedies is required: in such a way, in fact, it is possible to avoid, or at least reduce, the contact between the substrate and the harsh environment.

The most widespread methodology for surface protection is the application of coating films able to confer a highly hydrophobic character to the surface of the artefacts (Poli and Toniolo 2000, Favaro et al. 2006, Amoroso and Caimati 1997, Horie 2010, Charola 2000). These materials most often consisted of synthetic organic polymers or copolymers dissolved in a proper solvent, being acrylic Poli and Toniolo 2000 (Amoroso et al. 1997, Tsakalof et al. 2007), fluorinated (Favaro et al. 2006, Tsakalof et al. 2007, Alessandrini et al. 2000, Torrisi 2008, Sadad-Shoai and Ershad-Langroudi 2009, Mazola et al. 2003, Piacenti et al. 1993, Poli and Toniolo et al. 2000, Aglieto et al. 1993), and silicon-based (Fassina 1994, Xu et al. 2011) polymers the most commonly used. The main problem caused by the use of polymers for the treatment of a wood substrate is related to their macromolecular nature, which leads to difficult penetration into and linkage onto the wood structure (Genco et al. 2011). This is due to the long chemical structure of the polymer backbone and, in turn, to the high viscosity that macromolecules impart to the solution. To overcome this difficulty, *in situ* polymerisation of suitable monomers has been proposed (Doehne and Price 2010, Bell and Coulthard 1990, Bell 1993). The smaller dimensions of the monomer molecules and the resulting lower viscosity of their solutions allow an enhanced sorption inside the wood substrate leading to protective layer more homogeneous and more strongly bonded to the wood substrate. One of the major drawbacks of this approach, however, is the need to heat the surface, possibly a large area, where the coating is applied for prolonged times, in order to induce the polymerization reactions (Vicini et al. 2001). This technological problem (Vicini et al. 2002, Pojman 1991) can be overcome by using frontal polymerization (Khan and Pojman 1996, Vicini et al. 2005) or photopolymerization (Mariani et al. 2002, Decker 1996) or using suitable catalysts able to active the reactions even at ambient temperature. In frontal polymerization, the heat released during the process by the exothermal reaction of the monomers is exploited to promote the formation of a hot travelling front, able to propagate quickly enough to avoid a prolonged warming of the treated surface (Vicini et al. 2002, Pojman 1991). In photopolymerization, on the other hand, the reaction between monomers starts by exposure to an UV/visible radiation in the presence of suitable photoinitiators. Both techniques are generally applicable to solvent-free systems.

In order to improve the characteristics and performance of the commercial water-repellent treatments, new solutions have been explored. In previous works (Esposito Corcione et al. 2010, Esposito Corcione and Frigione 2013), the authors developed novel photopolymerizable siloxane-modified acrylic/Boehmite nanocomposites, proposing them as protective coating for wood elements. The addition of a nanosized filler in a thermoplastic matrix has been widely demonstrated to be very effective in the improvement of scratch and impact resistance, Young's modulus and strength (Esposito Corcione and Frigione 2012, Greco et al. 2010). Flame, fire and moisture resistance seem to be also improved by when nanoclay is added to thermoplastic polymers (Greco et al. 2010): Their unique phase morphology, derived by layer intercalation or exfoliation, is able, in fact, to maximize the interfacial area between the organic and inorganic phases and to enhance the bulk properties.

The examples of nanocomposite based thermosetting matrices are more recent but equally promising (Greco et al. 2012a, Chen and Curliss 2003, Chin et al. 2001, Yu et al. 2004, Liu et al. 2004, Dorigato et al. 2011). Epoxy and acrylate thermosetting resins are extensively used as matrices for composites and nanocomposites as well as adhesives and coatings, due to their exceptional adhesive properties and overall performance. The most used nanofillers for such matrices are aluminum oxide ( $Al_2O_3$ ), clay, calcium carbonate ( $CaCO_3$ ), silica ( $SiO_2$ ) and

titanium dioxide (TiO<sub>2</sub>). Montmorillonite exfoliation in epoxy polymer has also been the main issue of many investigative studies (Ray and Bousmina 2006, Yu et al. 2004). Only few examples related to the incorporation of Boehmite into polymers to prepare nanocomposites have been reported in the literature (Zheng et al. 2005, Esposito Corcione et al. 2007, 2008, Blaszcak et al. 2010). The Boehmite particles are colloidal plate-like crystals with a high anisotropy. They consist of double layers of oxygen octahedra partially filled with Al cations (Esposito Corcione et al. 2009). Their aqueous dispersions exhibit flow birefringence, thixotropy and elasticity (Klopprogge et al. 2002).

A valuable advantage of Boehmite nanoparticles is their availability on a large industrial scale coupled with a tailorable interface (either hydrophobic, hydrophilic or silane treated) able to promote their dispersion in a large number of resins (Kornmann 2001).

Only recently protective nanocomposite coatings have been proposed for the protection and the surface resistance enhancement of wood substrate (Sow et al. 2010, Blanchard and Planchet 2011). Some of the reported papers described the use of radiations (UV or others) for the polymerization of the resin, demonstrating the efficiency of a proper combination of UV-curing technology and nanotechnology in such applications. To the best of our knowledge, however, the introduction of Boehmite nanofillers in a UV-cured thermosetting resin applied on wood specimens has not yet been explored.

In order to improve the hydrophobicity of wood elements Lesar et al. recently also proposed linseed- and tung-oil and to preserve Norway spruce and beech wood against wood-decay fungi (Humar and Lesar 2013). In addition hydrophobicity can be also achieved with modification, as explained by Militz (1993), and Rowell et al. (2009).

In this study, a photopolymerizable siloxane-modified acrylic/Boehmite nanocomposite, previously developed (Esposito Corcione and Frigione 2012, Esposito Corcione et al. 2012), was applied on walnut wood elements. The walnut wood was selected as experimental substrate since it is extensively used due to its attractive timber, which is hard, dense, tight-grained and polished to a very smooth finish. An integrated approach based on the data collected by different analytical techniques (FTIR and ESEM-EDS analyses, contact angle and colorimetric measurements, resilience, water repellence) to acquire a deep knowledge of the behaviour of the innovative hydrophobic product as protective outdoor coating, was adopted. The same experiments were also carried out on a commercial product, in order to evaluate and quantify the possible advantages of the proposed product over a commercial one.

## MATERIAL AND METHODS

Trimethylolpropane trimethacrylate (TMPTMA, supplied by Cray Valley), was chosen as the main polymeric component of the coating.

Organically modified Boehmite (OMB, supplied by Sasol as Disperal-MEMO), was selected to produce the nanocomposite. The organic stabilizer for the nanoparticles is trimethoxypropyl silane methacrylate (MEMO).

The same silane methacrylate monomer, MEMO (Dow Corning) was also used as a coupling agent to enhance the dispersion of the nanofiller into the organic coating.

A vinyl terminated polydimethylsiloxane (VT PDMS, supplied by Aldrich), was added to the acrylic mixture to enhance the water repellence of the cured coating.

The photoinitiator, Irgacure 819 supplied by Ciba, is able to catalyze the reaction under UV radiations. All the mixtures produced contained 1wt part per hundred (pph) of the photoinitiator.

The chemical formula of each component employed, as well as the projection of Boehmite crystalline structure, are reported elsewhere (Esposito Corcione et al. 2010, Esposito Corcione and Frigione 2012).

The innovative photopolymerizable protective, with or without the addition of OMB, was applied, in the liquid state, on walnut wood specimens in order to verify if the presence of the coating would be able to reduce the water absorption and to enhance the superficial characteristic of this kind of wood. An amount of about  $1\text{g} \cdot 25\text{ cm}^{-2}$  of the product was applied by brush on walnut substrate.

A novel methodology to apply and harden the experimental coatings, i.e. photopolymerization process, based on the supply of UV radiation, was employed: The filled and unfilled coatings were applied on walnut wood specimens by brush and photopolymerized in air, using a UV lamp, obtaining a film with a thickness of about  $30\text{ }\mu\text{m}$ . The procedure used to UV-cure each mixture applied on wood specimens is described in details in the following section.

For comparative purposes, a commercial protective impregnating coating for wood, commercialized by GEAL (Agliana, Pistoia, Italy) as LINFOIL, was also used. This product is based on linseed oil in white spirit solution, containing small amounts of long-oil alkyd resins, natural and mineral derived waxes (Lionetto and Frigione 2012) and posses a low viscosity of about  $0.01\text{ Pa}\cdot\text{s}$ . LINFOIL was applied according to the procedure recommended by the producer: it was applied on the surface of the specimens by brush with three subsequent treatments, each of them repeated after 24 h.

Walnut wood type was selected because it is frequently used for its attractive timber, which is hard (about 80 Shore D), dense (about  $600\text{ kg}\cdot\text{m}^{-3}$ ), tight-grained and polishes to a very smooth finish.

### **Preparation of the nanocomposite mixture**

In order to improve the dispersion of OMB in the methacrylic-based mixture and, in turn, to obtain a true nanocomposite, two different modifications of the conventional “solvent dispersion method” were proposed in a recent paper (Esposito Corcione and Frigione 2012). Following these procedures, OMB was firstly dispersed in MEMO silane, because of its high compatibility with modified Boehmite, and subsequently added to TMPTMA resin and VT PDMS. The method that employs a magnetic stirrer for 24 h, using a rate of 1500 rpm at ambient temperature ( $23^\circ\text{C}$ ), was found to be more effective to disperse the Boehmite than the simple sonication technique. With this procedure, a more homogeneous and more stable dispersed nanofilled system was obtained, both in the liquid and cured conditions (average dimension of the particles in the liquid: about  $80\text{ nm}$ ) (Esposito Corcione and Frigione 2012) Starting from these findings, the optimized procedure employing a magnetic stirring was selected to prepare the nanocomposite.

Details of composition of the organic control system, i.e. the mixture with the same composition of the nanocomposite but not containing OMB nano-particles, as well as of the nanofilled suspension produced, are reported in Tab. 1. The compositions used were optimized during several studies performed in recent years, being able to guarantee high surface properties, in terms of hydrophobicity, transparency, hardness and suitable viscosity for the specific application. In particular, the effect of the presence of OMB nanoparticles on the viscosity of the experimental mixtures was also analyzed in a previous paper, showing that even in presence of the nanoparticles the viscosity of the mixture remain almost equal to  $0.03\text{ Pa}\cdot\text{s}$ .

Tab. 1: Composition of the liquid mixtures produced.

Sample	Weight composition
67 T-30 M-3 PDMS <sub>819</sub>	67% TMPTMA, 30 % MEMO, 3 % PDMS, 1 pph Irgacure
67 T-30 M-3 PDMS-3 OMB <sub>819</sub>	67% TMPTMA, 30 % MEMO, 3 % PDMS, 1 pph Irgacure, 3 pph OMB

Once prepared, the liquid formulations were applied on walnut substrate and photocured using a medium pressure Hg UV lamp (UV HG 200 ULTRA), with a radiation intensity on the surface of each sample of  $9.60 \mu\text{Watt}\cdot\text{mm}^{-2}$ . The maximum time necessary to achieve the complete curing of the films, working in air atmosphere, was found to be 6 hours. A quantity of about  $1 \text{ g} \cdot 25 \text{ cm}^{-2}$  of the experimental product was always applied on the walnut wood. In the case of the commercial coating, on the other hand, the complete evaporation of the solvent occurred after 7 days from the application on wood substrate.

### Experimental techniques

The neat walnut specimens were firstly characterized by XRD and FTIR analyses. To this aim, Wide - Angle X-ray diffraction was collected on a PW 1729 Philips, using Cu K $\alpha$  radiation in reflection mode ( $\lambda = 0.154 \text{ nm}$ ). The wood specimens were step-scanned at room temperature from  $2\theta$  values of  $1.3^\circ$  to  $60^\circ$ . Fourier Transform Infrared (FT/IR-6300 Jasco) Spectrometer was used to analyze the chemical composition of the wood. The untreated wood sample was placed on a KBr support and analyzed in the FTIR instrument, in order to determine its characteristic peaks.

In order to study the distribution of the nanofilled treatment on the walnut surface, Scanning Electron Microscopy (SEM, Model Jeol JSM-6550F) was employed. Energy dispersive spectroscopy (EDX), allowing traceability of suitable elements, was also employed to detect the penetration depth of the different treatments within the wood by performing qualitative/quantitative elemental analyses. Aluminium (Al) was chosen as indicator of the presence of the nanofiller.

The evaluation of colour change of the coated walnut substrates was carried out by means of a Konica Minolta CR-410 in total reflectance and double channel mode, using a Xenonlamp light source. The determinations were carried out according to the standard Normal protocol 43/93 (Normal Protocol 43/93, 1993) The colour changes were evaluated by the CIE L\*a\*b\* system (ASTM D-1925, (1988), CIE 1976) and expressed as  $\Delta E$ . Twenty colour determinations were carried out on different spots of each wood specimen, before and after each treatment performed. The instrument was calibrated on a standard white plate reference before each measurement.

Dynamic contact angle measurements of the different coatings applied on walnut substrate were performed in order to evaluate the water repellence efficiency of each. To this aim, a COSTECH instrument, equipped with a video camera and an image analyzer, was employed. The analyses were performed at room temperature by means of the sessile drop technique, using distilled water as measuring liquid. Twenty measurements were performed on each sample, averaging the results.

The glass transition temperature ( $T_g$ ) of unfilled and nano-filled UV-cured coatings were measured by using thermal analysis (Mettler Toledo DSC1 StareSystem), heating 10–20 mg of each sample from  $-10$  to  $250^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  in nitrogen atmosphere. At least three samples for each formulation were tested and the results averaged.

Impact strength of treated walnut samples was determined using Charpy method (using an IMPACT 15 ATS FAAR). The sample size used for the test was 80x10x4 mm. The wood samples were firstly oven dried at  $105 \pm 2^\circ\text{C}$  until a constant weight was achieved. The impact test was carried out at room temperature ( $25^\circ\text{C}$ ) and the impact energy (calculated from the area of the load versus deformation curve) was reported in  $\text{J}\cdot\text{cm}^{-2}$  as the average of five tests.

The effect of the different treatments used towards the absorption of water was, finally, assessed. Sets of 10 coated and uncoated specimens ( $20 \times 20 \times 20$  mm) of walnut wood were oven dried at  $105 \pm 2^\circ\text{C}$  until a constant weight was achieved; they were, then, placed in a tank and filled with deionized water for 21 days. During this immersion period, water was daily replaced with fresh one. The immersed specimens were periodically removed from the tank, shaken to eliminate residual water, and weighed, calculating the Water Absorption ( $WA_t$ ) according to the following equation:

$$WA_t = \frac{W_t - W_0}{W_0} * 100 \quad (1)$$

where:  $W_t$  - weight (in grams) of the specimen soaked in water for time  $t$ ,  
 $W_0$  - the initial dry weight of the specimen (i.e. the oven dried mass before impregnation).

## RESULTS AND DISCUSSION

### Neat walnut wood characterization

The XRD spectrum of untreated walnut wood shows the presence of two peaks related to the crystalline planes of the cellulose,  $15$  and  $22^\circ$  respectively, comparable with those reported in the literature for this arboreal specie (Franceschi et al. 2008, Jia et al. 2011, Ma et al. 2011, Wang and Liu 2011).

The FTIR spectrum determined on a walnut sample shows all the characteristic peaks of the base components of the wood can be observed. In particular, the following peaks are visible:  $3450\cdot\text{cm}^{-1}$ , that corresponds to the broad band of OH groups;  $3000\cdot\text{cm}^{-1}$  (peak of CH groups);  $1735\cdot\text{cm}^{-1}$  (peak of the carboxylic group C=O, typical of the hemicelluloses);  $1370\cdot\text{cm}^{-1}$  (typical peak of the cellulose group, C-O-C); and  $1200\cdot\text{cm}^{-1}$  that can be attributed to the CO group (Lionetto et al. 2012).

The presence of cellulose is generally detectable with multiple peaks at different wave numbers, i.e. at  $1370$ ,  $1160$ ,  $1110$ ,  $1050$  and  $898\cdot\text{cm}^{-1}$ . However, among them, the main peak is around  $1370\cdot\text{cm}^{-1}$  related to the bond stretching (C-O-C) of carbohydrates (Giachi et al. 2012).

In Fig. 1, a SEM image of a section of an untreated walnut wood specimen is shown.

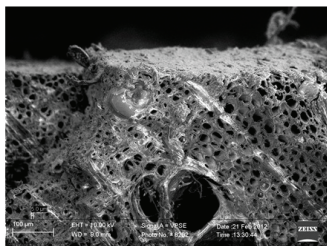


Fig. 1: SEM picture of untreated walnut wood specimen.

The picture reported in Fig. 1 evidences the typical structure of the deciduous open-grained hardwood wood, composed by a dense network of fibers and channels. Some tylosis are also visible, able to limit the penetration of water as well as of liquid products inside the wood specimens.

As reported in literature the standard walnut wood has a porosity of about 0.11 % (Franceschi et al. 2008).

### Treated walnut wood characterization

The untreated and treated walnut wood specimens were first characterized by SEM and EDX. In Fig. 2, the SEM images of the surface of walnut wood specimens treated with the nano-filled (a and b), unfilled c) photopolymerizable formulations, compared to the SEM picture of the same wood coated with a commercial product d), are shown. From the SEM images it can be noticed that the experimental polymer-based treatments appear homogeneously distributed on the walnut wood surface. Furthermore, from the observation of Figs. 2 a) and b) it is not possible to clearly identify the presence of Boehmite nanoparticles. Referring to the treatment based on the commercial product, shown in Fig. 2 d), small micrometric particles are visible on the surface of the wood specimen, whose chemical nature is not reported on datasheet.

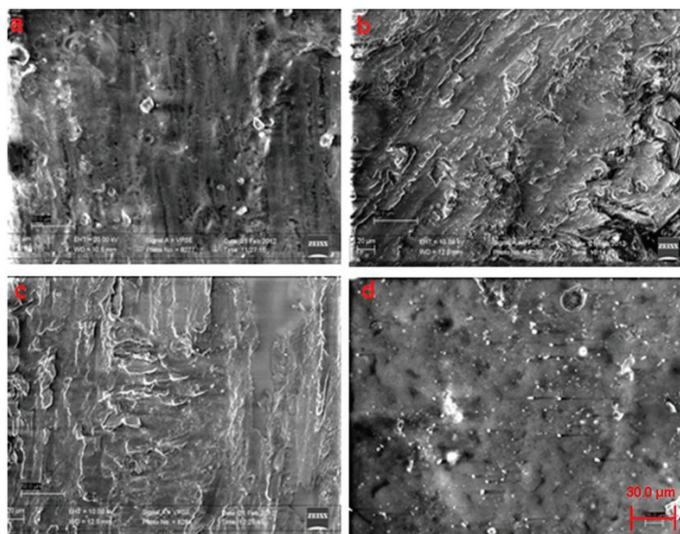


Fig. 2: SEM pictures of walnut wood specimens treated with a) Boehmite-based photopolymerized nanocomposite; b) Boehmite-based photopolymerized nanocomposite; c) unfilled photopolymerized system; and d) commercial product.

An elementary analysis, through EDX technique, was then performed on each specimen at different depths, starting from the surface until its inner part. In this way, the penetration of each liquid treatment was assessed along with the main chemical components entered in the wood substrate.

In Tab. 2, the value obtained from EDX analysis performed on the walnut wood specimens coated with the control organic formulation or with the commercial product, are reported.

Tab. 2: Results from EDX analysis performed on wood specimens treated with commercial product and control organic formulation.

Commercial system			Control system 67 T-30 M-3 PDMS819		
Distance from the surface	Chemical elements	(wt. %)	Distance from the surface	Chemical elements	(wt. %)
0 $\mu\text{m}$	Carbon Oxygen Aluminum	56.56 $\pm$ 0.9 36.67 $\pm$ 0.8 5.77 $\pm$ 0.4	0 $\mu\text{m}$	Carbon Oxygen Silicon	56.27 $\pm$ 1.2 41.87 $\pm$ 0.9 1.18 $\pm$ 0.03
400 $\mu\text{m}$	Carbon Oxygen Aluminum	56.15 $\pm$ 0.7 43.01 $\pm$ 0.9 0.83 $\pm$ 0.05	400 $\mu\text{m}$	Carbon Oxygen Silicon	60.49 $\pm$ 0.8 39.13 $\pm$ 0.4 0.28 $\pm$ 0.005
1.6 mm	Carbon Oxygen Aluminum	56.03 $\pm$ 0.8 43.46 $\pm$ 1.2 0.46 $\pm$ 0.01	1.4 mm	Carbon Oxygen Silicon	57.18 $\pm$ 0.9 48.68 $\pm$ 1.2 0.10 $\pm$ 0.002

Referring first to the commercial product, from the data reported in Tab. 2 it is evident that the linseed oil-based protective contains aluminum. Comparing, then, the Al content measured at different distances from the surface of the specimens, it was possible to have an indication of the penetration depth of this product. The high value of aluminum on surface, about 6 % wt., found for Linfoil protective is significantly reduced at 400  $\mu\text{m}$  from the surface (becoming lower than 1 % wt). This value further decreases at 1.6 mm from the surface (i.e. 0.46 wt. %). The high viscosity of the linseed oil-based system can justify this result: The liquid product, being not able to penetrate easily inside the wood element, rather remains on its surface.

Tab. 3: Results from EDX analysis performed on wood specimens treated with Boehmite-based photopolymerized nanocomposite.

Nanocomposite system 67 T-30 M-3 PDMS-3OMB819 (2012)		
Distance from the surface	Chemical elements	(wt. %)
0 $\mu\text{m}$	Carbon Oxygen Aluminum Silicon	65.00 $\pm$ 1.1 31.17 $\pm$ 0.51 3.10 $\pm$ 0.01 0.74 $\pm$ 0.03
400 $\mu\text{m}$	Carbon Oxygen Aluminum Silicon	59.04 $\pm$ 1.3 39.95 $\pm$ 0.76 0.71 $\pm$ 0.01 0.30 $\pm$ 0.009
1.3 mm	Carbon Oxygen Aluminum Silicon	61.84 $\pm$ 1.5 37.22 $\pm$ 0.9 0.61 $\pm$ 0.08 0.33 $\pm$ 0.03

The control unfilled photopolymerized formulation evidences a penetration depth even lower. A value of its characteristic element, the Si, around 1.20 % wt. was measured on the surface of the specimens treated with the control formulation. However, at 400  $\mu\text{m}$  from the surface, only



0.28 % wt. of Si can be still detected. Furthermore, it appears in small traces when performing the EDX measurement at a higher distance from surface. These observations again suggest a poor penetration of the liquid formulation into the cavities of wood.

In Tab. 3, the results found from EDX analysis performed on walnut wood specimens treated with the Boehmite/nanocomposite, are reported. The results reported in Tab. 3 were averaged on about twenty measurements for each sample.

The data reported in Tab. 3 evidence that both chemical species, i.e. Al, the characteristic element of Boehmite nanoparticles, and Si, characteristic of the siloxane components composing the polymeric matrix of the nanocomposite, gradually decrease from the surface of the wood specimens, even if their presence is still measurable at 1.3 mm from the surface. This observation suggests that the ability of the nanofilled suspension to penetrate inside the walnut wood sample is at least comparable to that of the commercial product, although it possesses an higher viscosity than the control organic system (Esposito Corcione et al. 2007). The presence of nanometric Boehmite particles, not aggregated in micrometric agglomerates, allows to achieve a good penetration depth in the wood structure, which in turn guarantees a great protective effect for wood specimens. The introduction of such particles, on the other hand, is expected to provide other important advantages to the protective. The authors have, in fact, already verified the improvement of surface properties of Boehmite/nanocomposite coatings applied on glass substrate (Esposito Corcione et al. 2008).

The ability of a protective product to penetrate in the wood substrate is one of the most important properties required to a novel coating to be proposed for this specific application. This latter capability is in fact always investigated by experts of wood protection. Smulski and Côté 1984 for example analyzed the possibility to penetrate in the first and second order void volumes of *Tilia americana* L. and *Pinus strobus* L. of a novel water-borne alkyd resin (Smulski and Côté 1984). Penetration of the gross capillary system of both species was evidenced by the creation of high resolution, negative alkyd resin replicas of cell lumina, pit openings and cell wall surface detail. Infiltration of the transient cell wall capillaries present in saturated wood elements was also demonstrated by the achievement of moderate antismell efficiencies of up to 37 % in small wafers of basswood and 27 % in Eastern white pine wafers.

In order to assess the other characteristics of the experimental formulation developed, color change, contact angle and impact strength were measured on the untreated and treated walnut wood samples. The experimental results are summarized in Tab. 4.

Tab. 4: Results of color change, contact angle and impact strength measurements performed on untreated and treated with different products walnut wood specimens.

Sample	$\Delta E$	Contact angle (°)	T <sub>g</sub> (°C)	Resilience (kJ.m <sup>-2</sup> )
Untreated	-	57.0 ± 1.8	-	0.25 ± 0.01
Commercial	10.6	92.7 ± 3.8	-	0.46 ± 0.01
67 T-30 M-3 PDMS <sub>819</sub>	18.2	87.0 ± 2.8	50.2 ± 2.1	0.34 ± 0.01
67 T-30 M-3 PDMS-3OMB <sub>819</sub>	8.4	98.2 ± 0.7	54.8 ± 0.9	0.42 ± 0.02

Referring first to the color change of the walnut wood substrate, it is noticed that the organic control formulation causes a very high alteration of the natural color of wood, excluding its usage in the protection of cultural heritage artworks. On the other hand, the nanocomposite formulation causes a color alteration even lower than that measured in the case of the commercial product. In addition, a very high optical transparency of the coating filled with 3 % wt. of OMB

nanoparticles has been found in a previous study (Esposito Corcione et al. 2008), being its light transmittance at 900 nm nearly equal to 90 %. The UV-cured nanocomposite could eventually be used, therefore, for the protection of wood artworks. The color of the walnut substrate observed after the experimental nanofilled coating is, in fact, very similar to that of the old wood.

The contact angle measurements performed on the walnut wood specimens, untreated and treated with the different formulations, evidence that the nanofilled coating is able to grant the highest hydrophobic performance, even when compared to the commercial product.

On unfilled and nano-filled coatings, UV-cured but not applied on wood substrate, the glass transition temperature ( $T_g$ ) was also measured and reported in Tab. 4. The  $T_g$  can be regarded, in fact, as the limiting service temperature for any polymeric coating. An increased  $T_g$  was measured on the nanocomposite with respect to that found for the reference unfilled organic formulation. This result is in line to what found in other studies performed on nanocomposite used as protective coatings for wood. An enhancement of  $T_g$  of UV-waterborne polyurethane-acrylate coatings for wood was obtained with the addition of alumina and silica nanoparticles, able to hinder the mobility of macromolecular chains at the interface with the nanoparticles (Kornmann et al. 2001). In a different paper, commercial organoclays were dispersed in an epoxy-acrylate oligomer, which was subsequently UV-cured and proposed as protective for wood substrate. DMTA analysis proved that nanocomposite coatings possessed a higher  $T_g$  (in the range 72-75°C) compared to that measured on unreinforced coatings (i.e. 71°C). The restriction of polymer chains mobility, due to the presence of layered silicate nanoparticles, explained the increase of glass transition temperature related to the decrease of the free volume (Nkeuwa et al. 2014a). Similarly, an appreciable increase in  $T_g$  was also found on organo-modified montmorillonite and an unmodified Boehmite added to acrylic latex dispersions, typically employed for wood applications, to obtain nanocomposite coatings (Malucelli et al. 2013).

The Charpy impact strength measured on the wood specimens coated with the novel photopolymerizable nanocomposite is fairly comparable to that displayed by the specimens treated with the commercial product. The application of the organic control formulation, on the other hand, only slightly improves the toughness performance of the wood.

Finally, the water absorption behavior of uncoated and coated specimens of walnut wood, determined by using the procedure previous described, is shown in Fig. 3. Each point represents the average weight measurement of each set of ten specimens.

A thorough understanding of wood permeability is essential for proper wood drying and treatment. The goal of most silvicultural practices is to increase tree height and diameter growth. However, very little is known about the effect of different growth rates on hardwood or sapwood permeability. Yin (Yin 1998) deeply analyzed the relationship between the permeability of wood and the part of wood studied, i.e. heartwood or sapwood. They cut twelve trees of the same age and divided them into three diameter growth classes of four trees each for northern red oak, black walnut, and yellow-poplar. Vessel lumen area and the longitudinal and radial permeabilities of the sapwood of each species were measured to evaluate the effect of diameter growth rate on vessel lumen area percentage and on the intrinsic permeability. The longitudinal permeability of the outer heartwood of each species also was also determined to evaluate the effect of growth rate on the decrease in longitudinal permeability following sapwood conversion to heartwood (Yin et al. 1998).

As expected, the water absorption capacity of the coated samples was generally reduced with respect to uncoated wood specimens. In particular, the samples treated with nanocomposite coating absorb less water not only respect to the uncoated wood but also respect to wood coated with the control unfilled coating, i.e. 67 T-30 M-3 PDMS<sub>819</sub>, (2012) especially in the first immersion period. This different behavior was quantified by determining the final water

absorption values (WA) reported in Tab. 5 for treated and untreated wood specimens. The tortuous path created by the nanofiller well dispersed into siloxane-modified acrylic matrix, able to hinder the transport of water, can explain the decrease of water absorption, as also found in other studies performed on UV-cured clay/boehmite-based nanocomposite coatings for wood (Nkeua et al. 2014b).

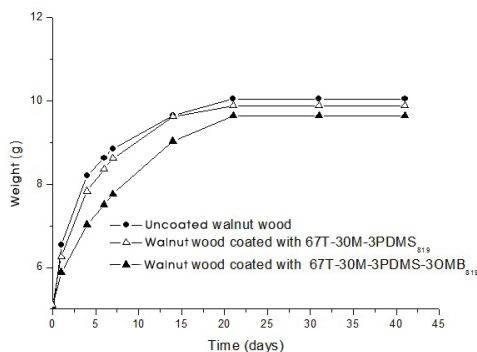


Fig. 3: Water absorption behavior of walnut wood specimens, untreated and treated with Boehmite-based photopolymerized nanocomposite and unfilled photopolymerized system.

Tab. 5: Results of water absorption measurements.

Wood sample	WA (%)
Uncoated	108
Coated with 67 T-30 M-3 PDMS <sub>819</sub>	94
Coated with 67 T-30 M-3 PDMS-3 OMB <sub>819</sub>	90

## CONCLUSIONS

An experimental photopolymerizable siloxane-modified acrylic nanocomposite, containing a small amount (3 % wt.) of organo-modified Boehmite, was applied on walnut wood specimens in order to assess its protective capability. For comparison purposes, an unfilled photopolymerized product, with the same composition of the nanocomposite matrix, and a commercial linseed oil-based protective were applied on wood specimens, performing the same characterization.

SEM and EDX techniques allowed to quantify the penetration of the different protective products inside the wood substrate. The experimented siloxane-modified acrylic nanocomposite displayed a high penetration depth, comparable to the unfilled organic and commercial products. Contact angle measurements performed on the coated walnut wood substrates revealed a great hydrophobic capability of the nanofilled coating. The colour change brought about by the nanocomposite was found to be even lower than that measured in the case of the commercial product. Comparable values of impact strength were measured on wood specimens treated with the nanocomposite and with the commercial product. Walnut wood elements coated with the novel organic photo-curable nanocomposite were found to absorb the smallest amount of water. The T<sub>g</sub> of the nanocomposite, finally, was increased with respect to the control unfilled formulation.

In conclusion, the Boehmite-based photopolymerized nanocomposite system proved to

posses the essential characteristics required to a protective coating for a wood substrate and to behave even better than a commercial linseed oil-based product. As further applicative advantages, the novel nanocomposite system allows to reduce the set time of the protective, from 7 days in the case of commercial product, necessary for the evaporation of the solvent, to 6 hours in the case of photopolymerization process, and to eliminate completely the use of solvents.

Further studies are in progress to assess the durability of the nanocomposite coating applied on wood specimens against UV radiations and weathering to verify its effectiveness also for outdoor applications.

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