Nanostructured material for durability and restoration of wooden surfaces in architecture and civil engineering

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NANOSTRUCTURED MATERIALS FOR DURABILITY AND RESTORATION OF WOODEN SURFACES IN ARCHITECTURE AND CIVIL ENGINEERING

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ABSTRACT: The present paper addresses to the latest technological innovations concerning nanostructured-materials, their wood surface protection functions, and describing the potential usage in the field of architecture, civil engineering and cultural heritage. The research briefly describes the existing nanomaterials, their classification and compatibility with the different wooden species. The technology used in this study is water soluble and water-borne organ-functional silane system which desires small depth of penetration by controlled molecular dimension. Defining operative procedures of application with the aim of testing the depth of penetration and the efficacy of the consolidation we find that a novel impregnation system for wooden surfaces could increase durability properties. Additionally, nanoparticles of silver and copper have extremely large relative surface area, increasing their contact with bacteria or fungi, and improving bactericidal and fungicidal effects by adversely affecting cellular metabolism and inhibit cell growth of xylophages agents. The present article reports on a joint research that involves University and SME's in the field of nanomaterials for wood restoration and conservation.

KEYWORDS: Nanotechnologies, coating, UV protection, water proofing, anti-bacterial, fire retardant

1 INTRODUCTION

Innovative technologies and, in particular, nanotechnology are multidisciplinary issues, involving various research topics: from molecular biology to chemistry, from materials science to physics, and engineering. Over the last decade the applications of nanotechnology have been developed rapidly, influencing several industry areas, having significant economic implications. Their pervasiveness is primarily due to their effect to the materials: from wood to textiles, up to self-cleaning cement materials, allowing them new features and unusual performance.

The last decade has witnessed an exponential growth of research activities based on the synergy between molecular and nano-sciences, giving rise to innovative functional inorganic and hybrid architectures exploiting the ultra-fine size effects due to their nano-organisation. Therefore fundamental understanding of synthesis, processing, and characterisation of functional nanosystems will render exceptional opportunities for their technological transformation to real applications.

The dissemination of knowledge on nanotechnology, nanomaterials and their use is now a necessary step by considering the enormous potential applications that nanotechnologies offer in terms of materials development, techniques and uses. In particular, including both new construction and Cultural Heritage, nanotechnology is providing a significant input to innovation in processes and products [1].

With this introduction, at present some industrial development researches are focused on the sector of coating of timber elements in constructions.

The use of nanotechnology is a real innovation in the development of wood coatings, particularly in relation to UV absorbing and biological decay. The effects of out-door exposure can degrade not only durability and physical wood properties, but its natural beauty as well.

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This last aspect is even more important if we are dealing with wooden elements belonging to our cultural heritage. Among the nanostructured products, already present on the market for wood protection, the most interesting appear:

- long-term outdoor performance, light stability, high transparency with ideal accentuation of the wood grain, as well as good mechanical and chemical resistances are major issues. UV protection is an important topic in nanostructured wood products development today, and a main factor for clear exterior wood coatings to fall below expectations.
- Nanotechnology opens a new world of opportunities and solutions in different areas. An example is copying of the water and dirt-repelling effect of Lotus leaves, and applying it on applications like self-cleaning windows and paints with water repellent function but, essential for wood, open-vapour.
- Nanostructured products with the aim of protecting wood surfaces from biological attacks as fungi, insects and bacteria.

Furthermore, the nanostructured materials should be addressed also to the preservation and durability not only of wood or ancient wood but also of its derivates that nowadays are considered as the sustainable future of this material.

2 STATE OF ART

In contrast with other fields of civil engineering and building recovery technology, the application of composite nanomaterials employed to reinforce wooden structures is a little known technique which requires, albeit partially, to be fully tested before being applied on a large scale. This holds true mainly for existing wood components (elements); with regards to new wooden elements, there is a much greater wealth of experience.

Wood is the product of the metabolic and physiological activity of woody plants. Because of its function in live plants, wood must be mechanically resistant (it sustains the weight of the crown, leaves, water, wind, snow etc.) and at the same time it must be porous: photosynthesis in the leaves requires water and inorganic substances (sap) to pass through the wood from the ground. Both these functions, mechanical support and sap conduction, are supplied by cells. Wood is composed of cells which are characterized by a solid wall surrounding a lumen. The wood cells are fusiform and about 90% of the cells in the wood have a vertical orientation. The cell wall has a good mechanical resistance to traction and compression, and the cell lumen can be covered by the sap.

The dimentions of cells vary a lot from different wooden species.

Pits permit the communication between adiacent conductive cells. This pits are holes in the cell wall, with a diameter of few microns. The pits are complex structured, with a permeable membrane that function as a filter.

This anatomical features influence the wood permeability properties, and they differ in different wooden species.

Mechanical properties of wood are usually tested on so called “clear sample”, it means small wood sample without strenght decresing defects.

Mechanical tests on full dimension beams are also common, and they show the high incidence of defect in wood strenght variability. Most recent researchs focus on the ways usefull for know the wood properties in structural beams without definitelly broke it. This non dissctructive tests can be applied in load bearing structures belonging to ancient and recent wooden structures as well.

In particular the reinforcement techniques for ancient degraded or broken beams is debated.

Nanotechnology could be very helpful in this field. In fact the use of nanomaterials and composite materials to strengthen wood was suggested few years ago by several American researchers who studied the effects of carbon nanotubes-based composites on the mechanical characteristics of reinforced wooden elements.

The tests were carried by applying these materials to newly constructed elements. Indeed BIBLIS [2] had proposed a strengthening technique using bi-component internal nanotubes; on the other hand, MITZNER [3] applied these materials for the external reinforcement of structural plywood.

Other tests dealing with reinforcing wooden structures using composite materials were carried out (and limited to) fabrics in carbon fibre (CFRP: Carbon Fibre Reinforced Polymers) by PLEVRIS and TRIANTAFILLOU [4] on a number of small, defect-free samples; they were subject to bending stress tests (length 0,75 m) and eccentric compression (sample dimensions 51x25x19 mm) in order to assess the increase in rigidity and resistance following reinforcement carried out by covering the taut area with unidirectional carbon fibre ribbons. The bending stress test results showed an increase in the last variable load by operation of the quantity of carbon fibre used compared to the section of the sample.

It must be stated that the results of tests on small scale wood samples can not yet be extended to real life situations; this does not hold true for wooden planks where any defects can significantly alter the mechanical behaviour. TRIANTAFILLOU (1997) studied the shearing stress behaviour of Glulam planks whose edges had been reinforced with carbon fibre ribbon. Other studies on the shearing stress reinforcement of wooden elements with composite materials were carried out by Swedish researchers. In the same field BLOM and BACKLUND [5] produced fibreglass-based (GFRP) and aramidic-based (AFRP) composites to reinforce Glulam planks. LARSEN et al. [6] increased the load bearing capacity of curved Glulam planks using GFRP materials following an experimental and numeric investigation.

In Italy, given the greater scope of recovery and conservation issues, research has focussed on methodologies for consolidating existing ancient structures.

Experiments carried out on antique timber and existing structures are complicated by the presence of wood defects (knots, oblique grain direction, failures, etc.) able to decrease the mechanical characteristics of the timber. However, experimental results have shown a clear trend

in terms of efficiency concerning said recovery techniques. GENTILE (2000) carried out bending stress tests on large planks (30x60x120 mm). Other tests were performed by BORRI [7,8,9], GIURIANI and FRANGIPANE [10], PIAZZA and TURRINI [11], RONCA (1991).
To the present interest on nanotechnological innovations, that is rapidly evolving, correspond a growing activity of publications and technical literature (i.e. "Journal of Nanotechnology") and international conferences and expos (i.e. Nanotech Conference and Expo) whose main topics involve the fabrication, characterisation, computational methods, simulation, software tools, nanostructure materials and devices and advanced material of different fields and sectors of application. In this wide framework, it should be highlighted that at present still few researches are focused on wood products.

3 NANOSTRUCTURED MATERIALS FOR WOOD PROTECTION: REQUIREMENTS AND PERFORMANCE

3.1 UV PROTECTION

The only way to slow the UV degradation of the surface is to incorporate a pigment or a UV stabilizer into the formulation. The colourless, UV-resistant, water-repellent preservative represents the broadest category of clear natural finishes on the market. Nanoscale UV absorbers offer good benefits in protecting coatings and coated substrates from being degraded by UV radiation. The small size of the particles makes it possible to offer high protection without affecting the transparency of the impregnation. This requirement is particularly important when dealing with ancient wooden handworks, often carved with decoration (Fig. 1). The water based nature of this typology of products is a functional and environmentally friendly solution against rot and moss build-up. Water absorption is significantly reduced as well.

Figure 1: *Decorated ancient floor system of XVIth century*

Utilizing this technology, the product absorbs the most damaging waves of the sun's spectrum, protecting wood for longer in the solar radiation around the world without the discolouring effect of these rays. This performance is particularly important considering weather climate changes.
Nanoscale UV absorber will protect the wood substrate from degrading UV radiation and will increase the lifetime of the coating. These products are most interesting in outdoor environments.
Nanoscale solutions are able to concentrate more active substance in a smaller volume of liquid. It is possible to use less product to archive better durability and the products are volatile organic compound (VOC) free and water based. This characteristic makes the product sustainable also in view of LCA.
This technology applies to multiple wood species and heat-treated wood. Hardwood with low permeability can be difficult to treat since they are not absorbing finishes well, not even solvent based oils. If a project foresees the use of these wood species it should consider a higher maintenance cost.
Until now, one of the best protection from the sun's ultraviolet radiation is obtained from pigmented products. These however, tend to hide the wood's natural grain and texture, creating challenges in balancing aesthetics with protection.
The use of nano-sized UV absorbers makes it possible to add the absorbers in much higher concentration without altering the transparency and the appearance of the coating. The primary crystallite size of approximately 10 nm is significantly smaller than other absorbers. This uniform particle size enables clear impregnating wood protection with unseen performance, while maintaining great aesthetics.
Blending combinations with light stabilisers and hydrophobic nanoscale components add to the performance: covering a wider spectrum of UV radiation, along with excellent moist regulating and water repellent properties.

3.2 WATERPROOFING

The nanostructured coating hereafter described is a multifunctional, nearly VOC-free, water-borne silane system. The coating system is suited for hydro and oleo phobic surface modification of wooden surfaces. It can also be used in formulations of translucent scumble paints with outstanding properties (Fig. 2). Once wooden surfaces are treated accordingly, formation of low energy surfaces leads to a prominent repelling effect towards almost all kinds of liquids. This strongly hydro and oleo phobic treatment reduces the pick-up of dirt significantly. As of such affection of wooden surfaces by microorganisms is reduced.

Figure 2: *Wooden board test – upper half of the surface was left untreated while the bottom part was protected with the nanostructured coating.*

The following images show two samples of pine boards, one of which is not protected, while the other was treated with nanostructured coating.

Figure 3: *Unprotected board*

In the top left corner of the image it is visible an oil drop, while in the bottom left corner it is a water drop.
The right side of the photo depicts the pine board after cleaning with damp cloth.
It can be observed that both water and oil deeply sunk into the unprotected surface, leaving difficult to remove stains.

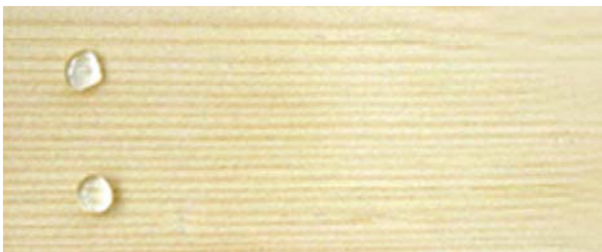

Figure 4: *Board protected with nanostructured coating*

In Fig. 4, the wooden board has been treated with the nanostructured coating. I the top left corner of the image it is visible an oil drop, while in the bottom left corner it is a water drop.

The right side of the photos depicts the pine board after cleaning with damp cloth.
It can be observed that the protected surface did not allow the penetration of liquids and after cleaning with the wet cloth did not leave any stains.
Dealing with wood, it is important to highlight that this kind on nanostructured coating based on water-borne silane system has good water repellent functions but, essential for wood, it is open-vapour.
This nanostructured coating exhibits its beneficial properties solely on the surface of the substrate. It may thus be appropriate to add biocides to the final formulation, e.g. agents against blue stain. This will actively prevent fouling caused by microorganisms. This surface modification is extremely resistant against weathering. Main reason is a severe stability of the fluoroalkylsilyl function as well as the chemical reaction of the silanols with the surface and the generation of a highly crosslinked siloxane network. These features make this nanostructured coating superior to standard fluorocarbon - based additive.

3.3 BIOTICAL DECAY

The wood can be attacked by the variety of insects, fungi and other organisms. These decay factors can successfully be tackled by using preparations based on nanoscale units of silver. The main advantages of this silver nanotechnology are its anti-bacterial and fungicidal properties. These are essential advantages over traditional specimens, disinfectants, which operate only at the time of use. Specimens coated with nano silver product leave on the surface active nanoparticles. While cleaning processes are effective at reducing bacteria, it is impossible to clean a wooden surface every minute of every day. Unfortunately, the minute cleaning stops, bacteria can begin to grow, and as bacteria grows, so does the risk of cross contamination and therefore in order to increase the sustainability, nanotechnology offers many supplements (including wood enhancement) such as silver-based nanocoatings. These supplements are integrated into a product at the time of manufacture, creating a concentration of silver ions on the surface of the product.

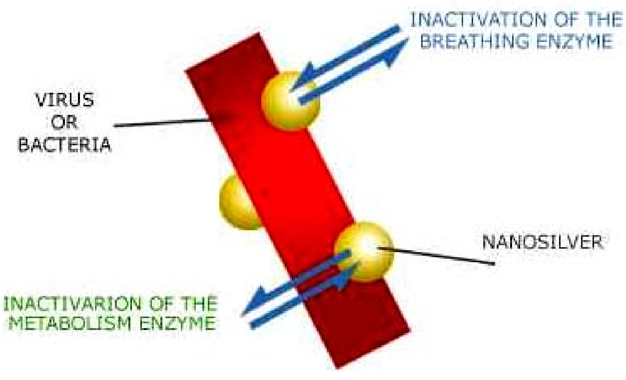

Figure 3*: Scheme of Silver nanoparticles*

When bacteria come into contact with the protected surface, the silver binds within the bacteria and causes their enzymes to breakdown, stopping the bacteria from multiplying and causing them to die.

Silver-based nanocotings become additives economically engineered into products, giving them protection against bacteria and fungi. Silver is a powerful, natural antimicrobial that has been used for many years to reduce infection rates. The properties of silver mean it will not break down or leach out of wood over time, making it safe and effective. Unlike other technologies, there is no known evidence to suggest that bacteria are currently resistant to silver, making it an ideal alternative to synthetic organic chemicals. Due to the properties of silver, silver-based nanotechnology can be incorporated into a vast array of materials including: powder paint, wet paint, coatings, varnishes fabrics, textiles, wood and plastics. The innovative technology can be easily integrated into the manufacturing process, alleviating increased production costs. The coatings which contain the nanoparticeles of silver will not change the aesthetics of wood, giving protection in-between cleaning practices, minimizing the risk of cross contamination.

3.4 FIRE RETARDANT

Nanostructured coatings can be effective also as fire retardant. Fire resistance can be increased through the use of products based on nanoparticles of titanium dioxite and silicon dioxite. These are a high performance thin film fire retardant coatings. They have been formulated to retard the flame spread across a wide variety of materials as well as suppress the generation of smoke. This proprietary flame retardant two-part epoxy coating creates a highly adherent fire retardant barrier on wood. In the event of fire, this coating produces water and gases, which snuff out oxygen and provides a cooling effect at the flame front. A dense char is formed, which further protects the surface from combustion. The product may be sprayed directly from the container, after proper mixing, using standard airless equipment.
Another nanostructured wood coating for fire resistance is almost a natural protection to water-based wood, particle board, plywood under dry inside. This coating is particularly environmentally friendly (odorless, halogen - free of solvents and metal), easy to apply (brush, roller or spray) and more perfectly transparent.

4 METHODS AND TOOLS OF APPLICATION

Nanostructured coatings by containing wood preservation agents can be painted, rolled or sprayed over the wooden surface. In a spray application it is mandatory to minimize the generation of Aerosol emissions by suited procedures e.g. application of HPLV spray processes, air driven low pressure spray processes. Consecutive application steps should be carried out wet-in-wet as a dried coat of the product will almost immediately exhibit a strong repelling effect. Consequently a second application step would therefore be much less effective.
The nano-based coating can be physically mixed with water at any desired concentration. Alcohols and ketons can be added as required to improve spreading on the wooden surface. However, compatibility of other usual coating additives for water-borne systems such as wetting agents, defoamers or binder systems has to be checked. It is recommended to draw special attention to the shelf life of such preparations. Sometimes conservation agents may have to be applied in order to prevent the build-up of microorganisms. The compatibility of additional biocides towards the nano-based coating needs to be evaluated.
In a quantity of 70 - 150 g/m² the water-borne silane coating system will exhibit a QUV-stability of 300 - 900 h with regard to hydro and oleo phobic surface activity (corresponding to approx. 1 - 3 years of exterior weathering in an average European climate). As a minimum concentration it is recommend a preparation of 1 part of product and 1 part of dilution agent (= organic solvent + water + additive). Temperature of treated substrates should stay in the range of 5 - 50°C. The nano-based product is sensitive to freezing temperatures. Frozen material can flocculate upon defrosting and may in part lose its beneficial properties. The coating, containing wood preservation agents, should not be applied on wet wood surfaces (wood moisture content < 18% recommended). Cross-linking on wet substrates will be incomplete and thus full efficiency may not be achieved. To a certain degree the water-borne silane coating will impart yellowing on bright wood surfaces. This will by no means influence the hydro /oleo phobic performance of the products. However, the issue must be taken into consideration once a certain optical appearance is of importance during the formulation of transparent, colorless wood preservation agents. As a fully cross-linked impregnating coating,
Full effectiveness of the coating is only reached at a minimum concentration of 50 wt.-percent in the final formulation. Thus lower concentrations are not recommended. Final statements on the realistic persistence of the final formulation can only be derived from respective outdoor weathering tests. Nevertheless, results of QUV testing according to EN ISO 11507 will exhibit a good correlation.

5 DURABILITY TESTS

The water-borne silane nano-coating enables the formulation of translucent scumble paints, which can withstand many years of exterior weathering once applied to a suited wooden surface. QUV-testing according to EN ISO 11507 (irradiation cycles by UVA-lamps (UVA-340) at 55°C, condensation cycles at 45°C plus intermittent rinsing with water) did show a permanent repelling effect of more than 800 h (corresponding to an approx. 2 years exterior weathering) when applying approx 100 g/m² in non-pigmented, transparent formulations. Elevated consumptions of up to 300 g/m^2 can further increase the durability of the treatment. Wood which is treated with the nanostructured coating stays completely air-permeable despite its strongly hydro and oleo phobic surface. Permeability of water vapour is only marginally influenced by the coating, much less than by most of the standard binder systems in the paint and coating industry.

Figure 4: *The durability test of pine board impregnation after 2 years: board protected with nanostructured coating (Top) and unprotected board (Bottom).*

The water-borne silane nano-coating is extremely resistant against all kinds of atmospheric exposure (UV-irradiation, rainfall, temperature changes) but imparts only a relatively weak UV-absorbing strength. Decomposition of lignin by UV light will be delayed but not prevented. Typical greying of wood under the influence of UV light may thus be delayed but will not be inhibited. If a strong UV-protection is desired in the final formulation, additional UV absorbers need to be introduced. With this regard the addition of pigments (e.g. most prominently iron oxides) can be recommended.

6 ENVIRONMENT AND NANOTECHNOLOGY

Nanostructured paints and coatings have the ability to reduce energy costs, and improve indoor air quality.
Surface treatments can significant reduce the use of chemical cleaners and save water and maintenance costs. Less cleaning cycles on a high rising building means also less risk for facade cleaners. While exposed surfaces still need cleaning the cleaning frequency can be expanded.
The over all appearance of the surface will improve. Furthermore, contamination can be removed much easier and the danger of permanent damage surface through pollution like acid rain is reduced.
Water repellent can use water as solvent. Being water based, the coatings are solvent and volatile organic compound (VOC) free.

7 CONCLUSIONS

In general the sectors of nanosciences and nanotechnology represents a strategic objective for European Union with socio-economical implications.
The continuous development in this sectors involves also the several construction fields.
The development of nanomaterials for cultural heritage and in particular for wood protection still needs deeper researches, involving also the productive sector.
The paper illustrates an activity of research that foresees the involvement of research centres and SMEs.

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