Chapter 5

Polymeric Micro- and Nanosystems for Wood Artifacts Preservation

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Additional information is available at the end of the chapter

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Abstract

The complex methods of diagnosis investigation of the wood artifacts state and proper materials for their protection against decay are very important goals in cultural heritage. This chapter focuses on the recent trends in micro- and nanostructured polymer systems for application in cultural heritage and on wood preservation, especially. The synthesis, properties, and applications, as well as the relevant analysis techniques to reveal the structures and properties of polymer systems, are discussed, too. To overcome the specific problems that exist for wood artifacts, some aspects should be treated: effects of the environmental factors, as moisture and pollutant absorption into the wood fibers, over-exposure effect of sun or artificial light sources, biological attack of different microorganisms, and the effects of the protective and decorative coatings.

Keywords: polymers, nanoparticles, PEG, SEBS, ZnO

1. Introduction

The conservation of cultural heritage is essential for humanity in order to preserve the cultural background of a people. Under this context, since most often old wooden objects present serious biological or chemical degradation which affects more or less the structural integrity, the mechanical resistance of the wooden material and their level of the authenticity are reduced [1, 2]. As a natural polymer, wood is composed of cellulose, hemicellulose (rich in free hydroxyl groups, being able to contribute to the hygroscopicity of wood), and

lignin (hydrophobic heteropolymer). The delignification will weaken the water resistance capacity of wood. By heating, the hygroscopicity, moisture uptake rate, and sorption hysteresis will be reduced, due to hemicellulose degradation [3].

Also, wood is an environmentally friendly material, a structural organic tissue, which consists of cellulose fibers embedded in a lignin matrix together with some minor components: terpenoids, resin and fatty acids, pectin, proteins, and inorganics [4].

Wood is hydrophilic; the physico-mechanical properties decrease with increasing the relative humidity below the saturation point, and the surface degradation is accelerated in weathering conditions. Wood quality is mainly influenced by the following external factors: high humidity and oxygen presence, (micro)biological organisms such as fungi, molds, insects, temperature, and electromagnetic radiation (UV, IR, high-energy β or γ, and so forth) [5].

Taking into account these principles, the traditional conservation-restoration methods that in some cases can produce irreversible effects on wooden objects over time have been replaced with modern procedures due to the intensive development of nanotechnologies [6]. The wood protection with micro- and nanopolymeric systems exceeds the disadvantage of multilayer coatings that could affect the optical properties and the surface quality and also reduce the water vapor transmission rate (WVTR) [7].

The degradation induced by UV light represents the main drawback and induces the organic compound decomposition due to the increase in photon's energy that breaks the chemical bonds. An inefficient polymer coating can lead to loss in mechanical properties and integrity of the matrix and wood discoloration due to lignin degradation. New composite materials were developed, as aromatic impregnating agents (insecticides or fungicides) such as creosote, halogenated carbamates, benzothiazoles, pentachlorophenol, (alkyl) imidazoles, bis (tributyltin) oxide, or salt-based impregnates such as borates, quinolinolates, naphthenates of copper, zinc or chromated copper arsenate-based preservatives (CCA) in several commercial variants and so forth [8–10], fluoroalkyl functional oligomeric silane system [11], short-chain amino silicones [12], alkoxysilanes with different organic groups [R'Si(OR")] [13], zinc oxide (ZnO) nanoparticles dispersed in maleic anhydride-modified polypropylene (MAPP) [14], and titanium dioxide (TiO_2) nanoparticles [15–19].

During the last decades, an intensification of historical wood artifacts preservation researches has intensified, and the new materials should present reversibility, must be compatible with all the materials encapsulated by the object, must not leech from wood, must be ecologic and biodegradable, and the "artistic" materials are to be treated as a whole [20]. Nanotechnology may provide interesting alternatives to develop new and efficient wood treatments to overcome technologies less feasibly used in the past decades to improve wood properties like heat treatment, chemical modification and impregnation, methods that can expand the dimensional stability, and resistance against microorganism [16]. Due to their very small dimensions (less than 100 nm), the nanomaterials have new properties, especially improved chemical reactivity and high mechanical properties. The nanostructures confer hardness and high wear resistance to the protected wood artifacts in some measure due to the increased density of the material [21, 22].

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2. Conservation of the recovered marine shipwrecks

The unanimously used method of conserving the marine shipwrecks consisted of water replacing from the wooden material with polyethylene glycol (PEG), obviating the uncontrolled dehydration that would cause drastic damage of artifacts by fracturing the fragile wood cells [21, 23–25]. In such preserved shipwrecks, an accumulation of sulfur and iron compounds was observed, leading to the acidity increase which facilitates the cellulose depolymerization by the destruction of cellular wood walls and residual lignin degradation [23, 26, 27]. The increase of the system acidity can also produce PEG degradation into acidic byproducts that can act as ionic transporters [28–30]. For the preservation of these shipwrecks, the wood deacidification by using neutralizing alkaline compounds was required. The studies established that the maximal effect of acidity neutralization of archeological wood is achieved with nanodispersed alkaline hydroxides (20–150 nm) in alcoholic or PEG solutions, the most used being Na and Mg hydroxide. The alkaline nanoparticles dispersed into the polymer solution (low-molecular weight PEG: 200–2000 g/mol) deeply penetrate the degraded cellulosic cells, completely neutralizing the acids resulted from the wood degradation and further inhibiting the cellulose hydrolysis [21, 31, 32]. The deposition of calcium and magnesium hydroxide nanoparticles in the wood wall cells inhibits the oxidation of wood, thus increasing the conservation degree of the shipwrecks [22].

3. Historical wood artifacts conservation

The historical wood artifacts show different degrees of chemical and biological degradation that weakens the material resistance, and their physical and structural consolidation is essential in preserving these objects. The use of polymeric resins, which must have a good compatibility with the wood material and a high stability to environmental degradation, has an important contribution in the old wood objects consolidation [33–36]. The consolidation effect of the polymer resins is significantly improved by the nanodispersion in these solutions of mineral materials with reinforcing effect (especially metal oxides) [37]. The nanoinsertions of these nanocomposites into the wood support, besides the role of physical consolidation, also provide an important increase in resistance to oxidative and biological degradation (fungus mildew) and increased flame retardancy [38–41]. The most suitable polymers for wood preservation are aliphatic and aliphatic epoxy acrylic resins due to their stability to oxidative degradation, their adhesion, and processability. The most intensely used polymers for the preservation of modern and archaic wood articles are the polyacrylates, the low-molecular weight ethyl acrylate (Paraloid B 72) a metallic copolymer, recently used as composites with nanometric materials, being representative [42, 43]. The most used nanocomposites of polymeric resins are obtained with metal oxide nanoinsertions mainly ZnO, MgO, TiO_2 and metals Cu, Au and Ag [44–47].

4. Study case

Under such context, poly(styrene-ethylene-butylene-styrene) has the advantage of being able to be used as the base material for polymer films on the one hand and the advantage of high

stability, good mechanical properties, and resistance to biological attack. Also, its composite with ZnO increases the efficacy of this polymer. ZnO has been reported as a substance that provides an increased wood stability against degradation due to UV radiation because ZnO has the ability to block UV rays, both UVA and UVB, acting as physical filters that reflect or disperse UV radiation.

For the polymeric composition, poly(styrene-ethylene-butylene-styrene) block copolymer (SEBS) grafted with maleic anhydride (MA), mixed with ZnO, has been used for the preservation of wood surfaces by spraying the pretreated wood surfaces. A slight color change could be observed at the fir wood treated with SEBS-MA sample, because the consolidant retention, the penetration depth, and the uniformity of the consolidant distribution into the material are parameters that influence the consolidation effectiveness.

The protective behavior of these polymers on these samples was put into evidence by specific analytical techniques: Fourier-transform infrared spectroscopy (FTIR), chromatic analysis, and gloss index analysis [48–51].

The first change that indicates the wood degradation is identified by lignin degradation, through quinone compounds formed responsible for a yellowed surface. These compounds increase the surface roughness, the chemical bonds are weaker, and macroscopic cracks are formed [52]. The treatment of wood with different consolidants causes the alteration of the spectra aspect by the appearance or intensification of some characteristic absorption bands.

The temperature aging is characteristic to a reduction in hydroxyl groups, an increase of the unconjugated carbonyl groups, and an apparent slight increase of lignin. The different behavior of the studied wood species may be explained by their different chemical composition, especially hemicelluloses, lignin, and extractives content.

The color parameters that can indicate the wood change are L^* (degree of color lightness), a^* (green-red chromatic coordinate), b^* (blue-yellow chromatic coordinate), and ΔE (color variation and stability) that can be calculated using Eq. (1)

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔE^*, Δa^*, and Δb^* are the differences between the sample specimens and the reference specimen; ΔL^* is the change of the light in the point, on different time intervals, compared with the initial value: $\Delta L^* = L_1^* - L_{initial}^*$; Δa^* is the chromatic deviation of the a^* coordinates (red and green colors) of the same point, on different time intervals, compared to the initial value: $\Delta a^* = \Delta L^* = a_1^* - a_{initial}^*$; Δb^* is the chromatic deviation of the b^* coordinates (yellow and blue colors), respecting the same mathematic formula: $\Delta b^* = b_1^* - b_{initial}^*$ [53].

ΔE^* value is an evaluation criterion of the overall change color. If the value is smaller than 0.2, the difference is not visible. A small difference in color is given by a value between 0.2 and 2. Between 2 and 3, respectively, between 3 and 6 highlight a color change visible with high-quality, respectively, a medium-quality filter. At a value over 6 of ΔE^*, the color is highly changed or even different [54].

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The positive values of Δa^* after 120 h of irradiation indicate a tendency of both wood surfaces to become reddish. But when the exposure time increases, the values of Δa^* become negative, which is associated with a tendency of both wood surfaces to become greenish. Lignin degradation leads to chromophoric groups formation, carbonyl, and carboxyl groups, which affect the color change mechanism [55]. The process of lignin degradation is accentuated by oxygen and moisture presence, decreasing the coating adhesion due to low-molecular degradation products. In these conditions, an efficient coating must respect more requirements, namely enough filter efficiency until 440 nm, oxygen barrier, water vapor permeation, and abrasion, scratch and impact resistance [56].

The color changes in time can be highlighted by the chromatic variations, namely ΔL^*—variation of lightness and Δb^*—variation of the blue-yellow chromatic coordinates. In [56], the authors presented these variations of acrylic-ZnO coating for wood. ΔL^* increase from −20.09 for the wood sample to −5.66 for the sample of impregnated wood with 4% ZnO, Δb^*, the coordinate that marks the wood yellowness after UV exposure, a decrease from 15.27 until 0.99 after impregnation with the UV absorber (**Figure 1**).

Under such context, the gloss parameters could reflect the polymer quality, by irradiation, a small decrease is observed, most probably due to the polymer degradation, faster for SEBS-MA than SEBS-MA + ZnO (**Figure 2**).

Auclair et al. concluded during their study [57] that ZnO is a more efficient photo-protector for wood than CuO. As polymer matrix, urethane-acrylate systems were used. In case of polymer-ZnO nanocomposites, the discoloration of clear-coated wood exposed outdoors was reduced and the higher increase in gloss was obtained.

The photo-yellowing and UV degradation of wood surfaces were overcome by coating with ZnO-maleic anhydride-modified polypropylene (MAPP)-polyurethane transparent

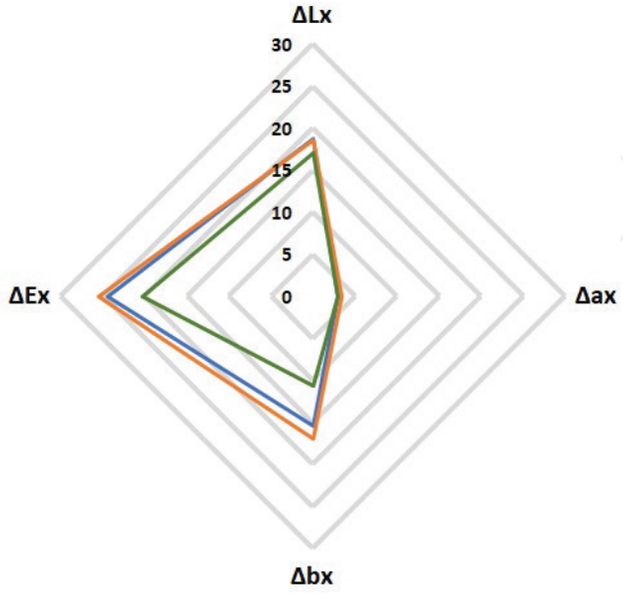

Figure 1. Chromatic parameters of fir wood samples after irradiation (60 min).

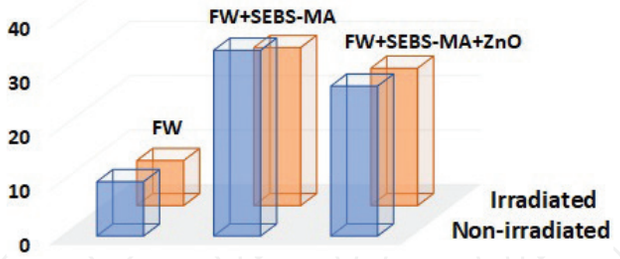

Figure 2. Gloss parameter of fir wood samples under different conditions.

nanosystems [14]. The acid anhydride groups of MAPP ensure the compatibility with OH groups from wood.

FTIR analysis can be used for solid wood samples being a fast-spectroscopic method and requiring an easy sample preparation. Information regarding the wood degradation can be obtained based on composition, functional groups, and molecular structure [52, 58, 59]. The degradation mechanism depending on the wood chemical composition (hemicellulose, lignin, and extractives content) is reflected in the chemical changes regarding the reduction of OH groups, increasing of unconjugated carbonyl groups, and formation of aromatic carbonyl conjugated groups as quinoid structures [60] (**Table 1**) (**Figure 3**).

Using polymeric micro- or nanosystems, the moisture content decreases. Humidity along with density is the physical factor that influences the physical, mechanical, and dimensional properties of wood and also influences the wood structure degradation. According to ISO 13061-1 [61] and Eq. (2), the moisture content is calculated for both native and treated wood:

$$w = \frac{m_w - m_0^*}{m_0} 100 \tag{2}$$

where w is the moisture content [%], m_w is the sample weight measured at a certain moisture [kg], and m_0 is the weight of the sample oven-dried [kg].

As the humidity increases in the wood cell membranes, most of the mechanical properties of wood decrease, except for elasticity which increases. In the saturated air, the steady-state humidity will reach a maximum, which is precisely the same saturation humidity (the saturation point of the fiber). At this point, the sorption stops as a phenomenon of wood hygroscopicity, and the desorption begins if the external environment conditions change. Because relative air humidity is a function of temperature and humidity pressure, it results that the equilibrium humidity is directly dependent on relative humidity and temperature and, depending on them, there is a whole range of equilibrium humidities. Curves describing the evolution of sorption and desorption processes of water are not overlap, leading to the hysteresis area. Hysteresis indicates less water retention of dried capillaries as compared to those of the membrane in the wet state, due to the fact that the cell membranes suffer some deformations remaining during sorption. Hysteresis has a special role in drying and steaming wood as well as explaining the internal tensions. Water repellency can be improved by coating with natural wax [62], paraffin wax [63], palm oil [64], and esterified organosolv lignin [65].

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Main absorption bands, cm^{-1}	Peak assignment [58]
3300	Stretching of —OH groups
2895	C—H aliphatic
1730–1740	Stretching of carbonyl group
1638	Bending of water (the moisture content)
1596 and 1512	Lignin aromatic ring
1423	Asymmetric C—H deformation
1364–1375	Symmetric bending of methyl groups in lignin and hemicellulose, bending of hydroxyl groups of polysaccharides
1157	Symmetric stretching of bridging oxygen
1025–1029	C—O in cellulose pyranose ring
898	Cellulose
809 and 670	Aromatic C—H from lignin

Table 1. Main FTIR absorption bands of wood.

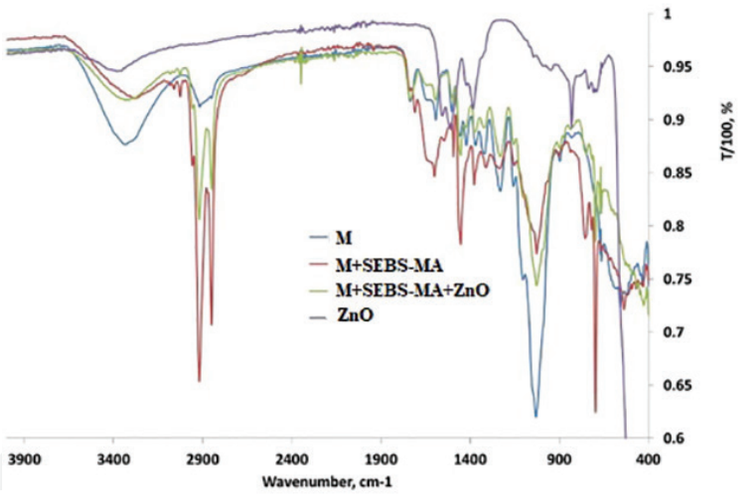

Figure 3. FTIR spectra of fir wood samples.

ZnO is a suitable component for UV protection in coatings. Dispersion in acrylic polymers leads to a reduced yellowing and improved optical properties after artificially weathering for up to 1500 h [56]. Shellac nanosystems were studied in [66] as wood coating and different property modifications were observed using various nanofillers. For shellac-ZnO systems, the inhibition or the slowing down of the UV degradation was obtained. ZrO_2 ensures an increased coating hardness. In both cases, the color, film-forming ability, water repellence, and adhesion were preserved.

UV-waterborne polyurethane containing different nanoparticles in order to increase the wood coating was studied. Thus, alumina, silica, ZnO, and CuO were used [7, 67]. The PU coating glass transition temperature is enhanced using alumina and silica that decrease the chains mobility at nanoparticles interface. The water and UV barrier properties are also increased. ZnO ensures a good photo-protection and clear-coated wood.

The coatings without nanoparticles in their composition present photo-yellowing and wood surface degradation when exposed to UV light. Dispersion of ZnO nanoparticles in MAPP and PU coatings restricted the color changes and photodegradation of wood polymers [14].

TiO_2 nanoparticles can impart hydrophobic or hydrophilic properties to the material, fungicidal, and bactericidal protection and present photo-catalytic activity. Using TiO_2 as coating for wood items ensures anisotropy, wettability, and UV protection [46, 68–71].

Zanatta et al. obtained the nanoparticles by a hydrothermal method using microwaves, and then the wood pretreated with chromated copper borate was coated with TiO_2. The wood maintained the natural color and the fungi resistance was improved [15].

The improvement of UV resistance using anatase TiO_2 was demonstrated in [17] when micro- and nanoparticles were impregnated on acacia hybrid wood. The exposure of the treated wood at UV radiation 960 h did not lead to color changes.

Obtaining stable and uniform dispersed coating is an effectiveness indicator. Polypropylene glycol can be considered a good solvent for metal oxides (ZnO, CeO_2 and TiO_2) nanoparticles films. An increased UV resistance and thus a decrease in lignin degradation were observed [72] (**Figures 4–6**).

TiO_2 coatings are a good moisture barrier for wood. If the treated wood is exposed to a 20–60% relative humidity (RH), the weight maintained constant, and at an RH between 60 and 90%, the mass increased with only 6%. TiO_2 coatings drastically decreased the change in anisotropic swelling of wood [19]. Obtaining films with controlled physico-chemical characteristics broadens their field of application. TiO_2 films may have different morphologies and wettability depending on the precursor pH (1–14). This characteristic may be a great advantage in using the nanoparticles coatings in various humidity environments [16].

Impregnation with micronized copper quaternary (MCQ) and UV absorbing acrylic resin (UVA-acrylic) was found to be a good method to increase the wood resistance to weathering conditions, and good visual, physical, and chemical properties were obtained [73].

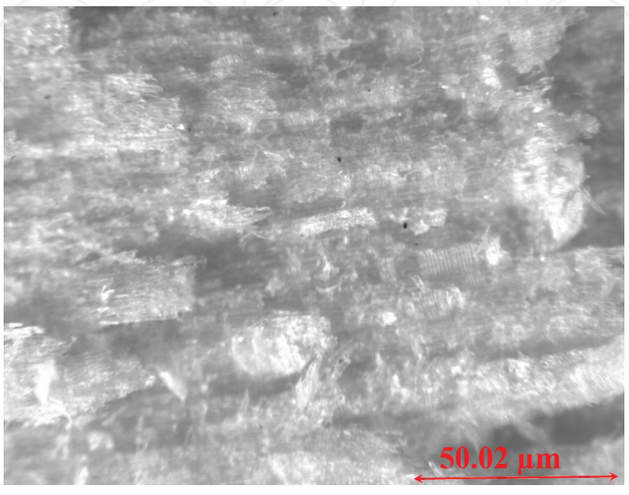

Figure 4. The fracture of the polymeric film from fir wood.

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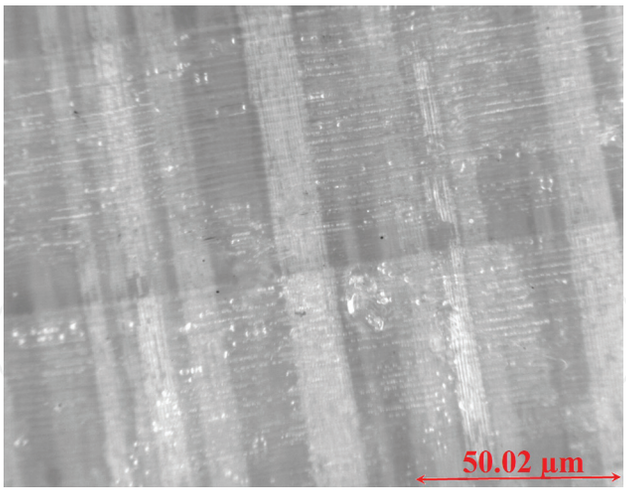

Figure 5. The fracture of the polymeric film from fir wood + SEBS-MA.

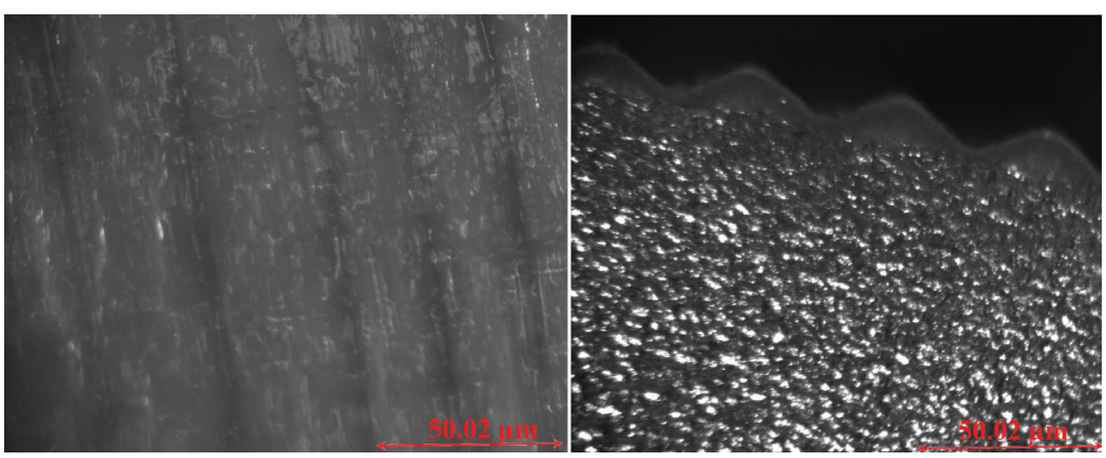

Figure 6. The fracture of the polymeric film from fir wood + SEBS-MA + ZnO.

Nkeuwa et al. [7] studied the behavior of UV-cured multilayer coatings where only the top coat consists of a nanoparticle—nanoclay with the RH variation. The color and gloss of initial, during, and after accelerated aging coatings were investigated. The color of coated samples does not present visual changes during and after aging. The studied color parameters (ΔL^*, Δa^*, Δb^*, and ΔE^*) increase with increasing RH while the gloss retention is lowered. At high RH, significant changes are observed.

Other additives used for wood protection are the fire retardants (FR). A good flame retardancy can be obtained using phosphorous, boron, and silicone. Phosphorous FR can exhibit both condensed and/or gas phase action and can generate less toxic gases and smoke during combustion [74]. Systems containing both phosphorous and nitrogen components are good substitutes for halogenated FR due to their synergistic effect [38, 39]. In [40], nitrogen-phosphorous FR dispersed in poly(sodium silicate-aluminum dihydrogen phosphate) (PSADP) was used to reduce poplar wood hygroscopicity and to improve its fire resistance. These two components present a synergic effect on the two properties being distributed over the inner surface and penetrate the cell cavities of wood.

5. Microbial degradation of wood

The degradation of wood materials depends on physico-chemical and biological factors such as temperature, humidity, nutrients, and the type of wood (hardwood or softwood), specific to the environment in which they are exposed. Among the biological factors, insects, macro- and micromycetes, and bacteria, the microbial load of the environment, corroborated with humidity and temperature, plays an important role in the biodegradation processes of this material. Of the microbiological agents, the most common types of biodegradation are those caused by fungi and bacteria, which manage to degrade the wood through enzymatic mechanisms with the enzymes they are secreting. The fungi types that attack wood materials are divided into three classes:

1. White-root fungi can degrade all cellular components by using nonspecific enzymes that they secrete, but in a first stage, they degrade the lignin using hemicellulose as a carbon source. Following the degradation with these types of fungi, the attacked surfaces get a whitish appearance [75]. This class includes macromycetes such as *Phanerochaete chrysosporium* (*Sporotrichum pulverulentum*), *Phanerochaete sordida*, *Phlebia radiata*, and *Phlebia tremellosa* [76] which is able to degrade wood lignin to CO_2 and water.
2. Brown-root fungi generally degrade cellulose and hemicellulose from wood, but they also degrade lignin. The mechanisms used by brown rot fungi in the biodegradation of wood are both enzymatic and non-enzymatic. These micromycetes do not produce lignin degradation enzymes but have a mechanism that results in lignin modification and slow reduction of lignin content in the attacked wood. This class includes macromycete species as *Serpula lacrymans*, *Postia placenta*, *Gloeophyllum trabeum*, *and Tyromyces palustris*. Surfaces attacked by fungi of this class get a brownish look [77]. Studies on wood sample of *Pinus sylvestris* and *Populus euramericana* showed that after vacuum treatment with inorganic or organic preservatives, which contain Cr^{6+}, Cu^{2+}, As^{5+}, organic salts of ammonia and N-alkylbenzyldimethylammonium chloride, inoculated with macromycetes from the species *S. lacrymans 1*, *S. lacrymans 2*, *P. placenta*, *G. trabeum*, *and T. palustris*, reveal a substantial reduction in wood loss due to the inhibition of the biological activity of the macromycetes tested [77].
3. Soft root fungi, or micromycetes, from which the most popular are *Penicillium chrysogenum* and *Aspergillus niger*, perform deterioration from edge to center of wood. In a study of wood artifacts from Islamic Art Museum, the Grand Egyptian Museum and Saqqara necropolis [78], two species of of the genus *Alternaria*, 15 species of *Aspergillus*, three species of the genus *Cladosporium*, six species of *Penicillium*, two species of *Trichophyton*, along with species of the genus *Cladosporium*, *Chaetomium*, *Phoma*, *Stemphylium*, *Ulocladium*, and *Syncephalastrum*, were found most of them with cellulolytic enzymatic activity, able to degrade the wood [78]. Their frequency on the analyzed artifacts was between 7.1 and 35.7%; the most common fungal species being (**Figure 7**) *Aspergillus. brasiliensis*, *Aspergillus flavus* var. columnaris, *Penicillium* sp.2, *Aspergillus parasiticus*, *Aspergillus terreus*, *Aspergillus versicolor*, *Cladosporium* sp.1, *and Penicillium* sp.3, the rest being encountered at a frequency of 7.1% [78].

In vitro tests performed in order to establish the biological action of three types of inorganic nanomaterials with Ag, Ti, and Cu (AgNPs, CuNPs, TiNPs) on fungi and bacteria (*Bacillus alvei*, *Short Bacilli*, *Bacilli Spore Former*, *Aspergillus niger*, *Aspergillus flavus*, *Aspergillus fumigatus*)

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isolated from funerary masks of degraded wood from Saqqara showed that the most effective of the tested materials is AgNPs, followed by CuNPs and TiNPs [79], both for fungi and bacteria (**Figures 8** and **9**). The action mechanism of AgNP includes processes such as adherence to microbial cells, penetration into cells, free radical generation, DNA and RNA damage [79, 80].

Another study performed on China's degraded wood objects [81] found in the Dingtao King Mausoleum during the Dynasty West Dynasty (206 BC-25 AC) revealed a massive degradation of the wooden objects. Determinations have shown that the degradation is caused by fungi. DNA sequencing of isolated fungi showed that there are 114 genres of fungi. However, in all samples, the most abundant genus was *Hypochnicium* sp., which represent 98.61–99.45% of the total of the fungal community.

Wood objects exhibited in museums are subject to deterioration of biological agents. The wood Jesuit sculptures from South America exposed at the Museum of Natural Sciences of La Plata, Buenos Aires Argentina, are subject to the biodegradation [82]. Determinations made on a strip of degraded wood of the *Cedrela fissilis* species led to the identification of two fungi species*: Nigrospora sphaerica* and *Chaetomium globosum*. *Chaetomium* is a recognized macromycete for its ability to destroy wood, but for *Nigrospora sphaerica*, very few things are

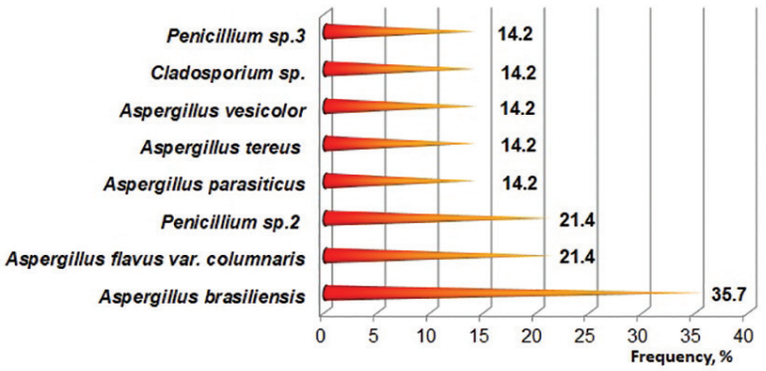

Figure 7. Fungal species frequency (%) (micromycetes) identified on biodeteriorated wood artifacts, from Islamic Art Museum, Saqqara necropolis, Grand Egyptian Museum, Cheops Solar Boat [78].

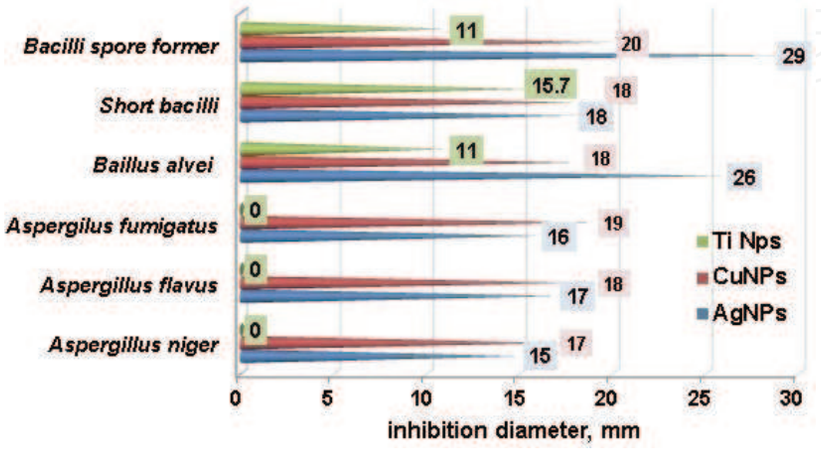

Figure 8. Effect of inorganic nanomaterial with AgNPs, CuNPs, TiNPs, on some fungal and bacterial strain isolated from wood artifacts from Saqqara necropole. Concentration of nanoproduct applied: = 10 μg/mL [79].

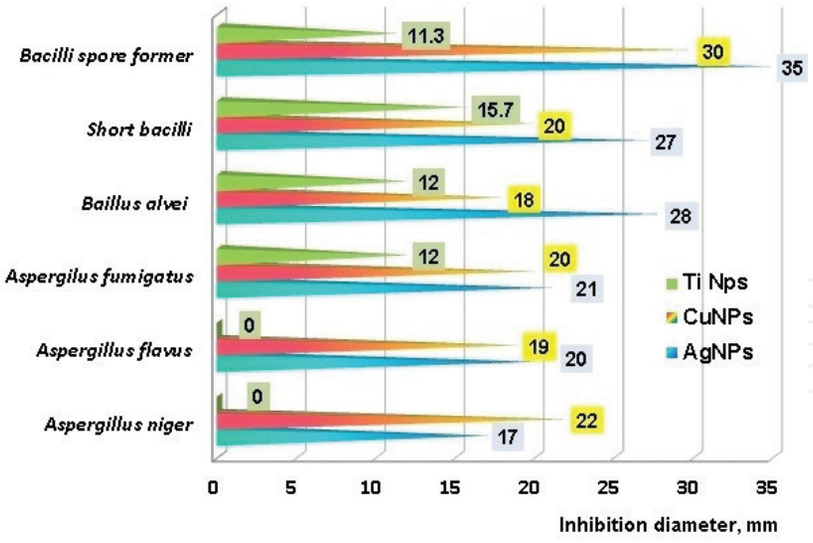

Figure 9. Effect of inorganic nanomaterial with AgNPs, CuNPs, TiNPs, on some fungal and bacterial strain isolated from wood artifacts from Saqqara necropole. Concentration of nanoproduct applied: = 15 μg/mL [79].

known regarding its effects on wood [82]. Bacteria are another class of biological agents that can affect the structure of the wood. Thus, in studies conducted to find an optimal method of disinfection and protection of wood surfaces in the historical area of Auschwitz-Birkenau II, bacterial species such as *Pseudomonas fluorescens*, *Staphylococcus equorum,* and *Bacillus cereus* have been isolated from this site. In terms of fungi, the following species have been identified on the wood surfaces: *Alternaria alternata*, *Chaetomium globosum*, *Cladosporium cladosporioides*, *Engyodontium album*, and *Penicillium citreonigrum*.

In vivo tests, made on new pieces of white poplar wood, previously sterilized and treated with a mixture of cultures of bacteria and/or fungi, were aimed at the evaluation of the number of living microorganisms on the surfaces (bacteria) and the estimation of the percentage from the wood surface altered by fungal activity, as well as the changes in color and luminance of the treated samples. The study reveals that the best commercially available biocidal products are B, ABM-1, and R 101 (**Figure 10**) (product B containing 24% benzyl alkyl (C12–16) dimethyl-ammonium chlorides, 5% boric acid ABM-1 contains N-3-aminopropyl-1,3-propanediamine, N,N-dialkyl (C10–C16)-N-methyl N-polyoxyethylene ammonium propionate, N,N-dialkyl (C10–C14) [3-dodecanoylamino)] propyl dimethyl ammonium acetate; product R101 contains 40–60% N,N-dodecyl-N,N-dimethylammonium chloride and 20–25% isopropanol). The best results were obtained for product R101, followed by AM-1, applied by spray or fogging exposure. The color (ΔE) and luminance (ΔL) tests showed that for the treatments chosen, no remarkable differences compared to the untreated control were observed (**Figure 11**). In another study, the effects of some aqueous dispersions of silver or zinc nanoparticles (AgNPs, ZnNPs) to air and liquid permeability of *Paulownia* wood samples exposed to *Trametes versicolor* were assessed [83]. The wood samples were heat treated at 100 and 150°C, after which they were exposed to *T. versicolor*. Permeability values were measured before and after exposure to fungal activity. The results obtained showed significant decreases in permeability in all treatments after exposure to fungi (**Figure 12**). The permeability difference was related to the growth and accumulation of fungal hyphae along the lumen vessels, which block the fluid transfer. The best results were obtained by heat treatment at 150°C, followed by impregnation

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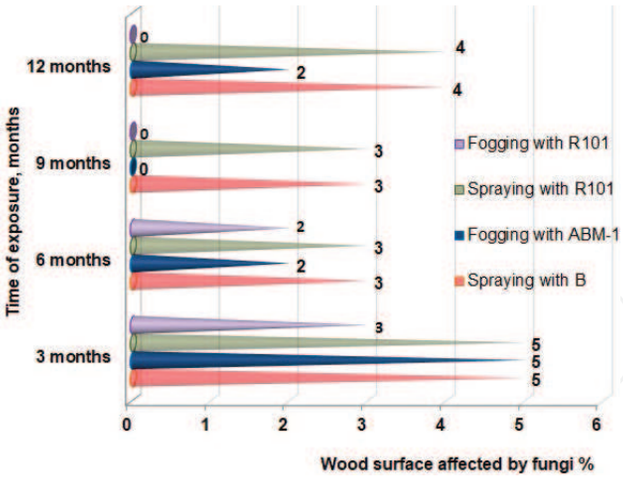

Figure 10. Biocidal effect of some commercial products on the wood samples inoculated with fungal strains, by spraying or fogging [84].

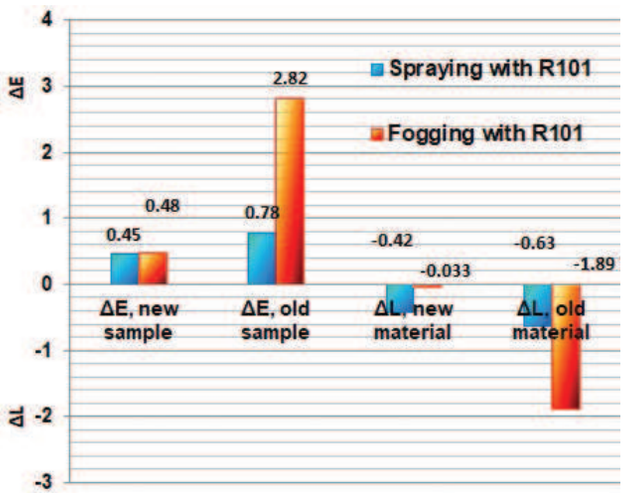

Figure 11. The color and luminance difference of wood samples after biocidic product applications. ΔE = difference of color; ΔL = difference of luminance [84].

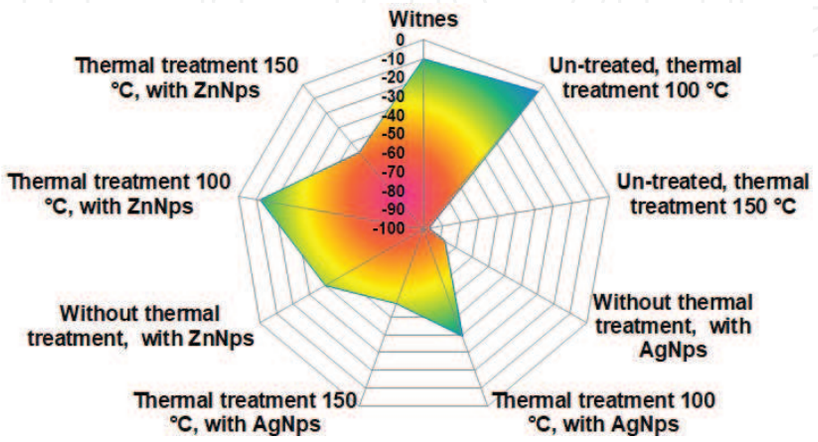

Figure 12. Specific air permeability in wood samples treated with ZnNps and/or AgNps nanomaterials after exposure to action of rot-white fungus *Trametes versicolor* [83].

with ZnNps or AgNps which significantly inhibited the growth of the microorganism, reducing the mass loss of impregnated wood samples subjected to fungal attack [83].

Regarding methods of treatment against wood degradation, there are currently several methods of protection against decomposition caused by biological agents. From these, organic compounds based on quaternary ammonium salts were the most used. Studies conducted to determine the antimicrobial activity of three biocides against *Pseudomonas fluorescens*, *Staphylococcus equorum*, *Bacillus cereus*, *Bacillus muralis*, *Sporosarcina aquimarina*, *Rhodococcus fascians*, and some fungi species such as *Chaetomium globosum*, *Penicillium citreonigrum*, *Cladosporium cladosporioides 1*, *Acremonium strictum*, *Aspergillus fumigatus* and *Cladosporium cladosporioides 2*, all isolated from wood or brick surfaces, showed that species such as *Staphylococcus equorum*, *Bacillus cereus*, *Sporosarcina aquimarina*, *Rhodococcus fascieni*, *Cladosporium cladosporioides*, and *Acremonium strictum* have a high susceptibility to quaternary ammonium biocides [85]. Thus, the wood objects with a historical value can be efficiently disinfected by three times application of a biocide (30% v/v) which contains dodecyl dimethyl ammonium chloride, citric acid, propiconazole, and propanol [85]. The mechanism of action of ammonium quaternary salts is based on the dissolution of certain sites from cell walls, which results in the loss of microbial cell integrity, followed by exposure of cell content and release of the material out of the cell, followed by degradation of proteins, of nucleic acids, and cell lysis, the latter caused by autolytic enzymes [85].

Protecting degradation of wood by biological agents can also be done without biocides based on quaternary ammonium salts. A wood protection variant is based on the application of a titanium isopropoxide gel and ammonium cerium nitrate as a stabilizer for wood treatment [86]. As a mechanism of action, it is assumed that the hydrolysis of titanium isopropoxide is initiated by the wood-based OH groups as well as by the moisture in the cellular wood wall resulting in a layer of cerium-doped TiO_2 which seals the wood surface and thus limiting the direct exposure of micro- or nanopores of wood to fungal hydrolytic enzymes. Studies conducted on Norway spruce have shown that this method can be protected against degradation by biological agents such as *Gloeophyllum trabeum*, *Rhodonia placenta,* and *Coniophora puteana*.

6. Conclusions

The maintaining of wood quality in time is usually achieved with the help of preservatives. These are individual chemical compounds or mixtures that make wood less susceptible to attack from a large variety of degradative factors or organisms. These organisms include insects, marine borers, and various types of fungi such as stain and decay. Some of these chemicals are effective against a wide range of organisms, while others are very specific and protect wood from only one type of organism.

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Conflict of interest

The author(s) declared no potential conflicts of interest.

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