

Review

# Innovative Wood Surface Treatments Based on Nanotechnology

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**Abstract:** This work reviewed innovative wood surface treatments based on nanotechnology. It is well documented in the literature that the cell walls of wood present significant porosity; this porosity is on a molecular scale. The main reason for the use of nanotechnology in wood science and technology is the unique characteristic of nano-based materials to effectively penetrate deeply into wood substrates, which, in turns, results in the alteration of their surface chemistry. This subsequently causes an improvement in wood properties. Any potential change in the wood properties due to treatment with nanomaterials is based on the higher interfacial area which is developed due to the treatment. This occurs because the number of particles is significantly reduced to the nanoscale. The nanomaterials improve the properties of wood as a raw material and alter its original features to a limited extent. However, their potential impact on both health and the environment should be addressed by applying tools such as life-cycle assessments. This will avoid mistakes being made in which new technologies are released on the market prior to an impact assessment having been carried out.

**Keywords:** surface treatments; wood; nanotechnology; additives

## 1. Introduction

Wood can be used in indoor applications, and with proper treatment, also in outdoor application. The transformation of wood as a raw material into an engineering material with industrial applications requires a refining process which combines other materials, so-called additives [1–3]. The majority of wood and wood products in their final states contain additives; these may include protective coatings, coatings to improve aesthetic appearance, preservatives for protection against fire or biological factors like fungi and insects, or even plastics to successfully create new types of products [4,5]. When wood is used in outdoor applications, its surface is exposed to many agents, and protection is imperative. Protection, therefore, can be achieved in an efficient manner through the use of a coating or modification, which can be done with surface or bulk treatments.

A coating applied to a wood surface is referred to as a substrate. Varnishes, lacquers, and paints are common coatings applied to wood surfaces; their role is both protective and decorative. This means that they can protect the substrate as well as the surface of the treated material, and should possess an attractive color and retains a natural appearance. The basic properties of a coating are determined by its main components, namely binders, pigments, solvents, fillers, and additives [6]. The binder sticks pigment particles to the wood surface and to each other, creating a protective layer. Pigments give color and, at the same time, contribute to making the surface layer opaque. Solvents give the coating the necessary viscosity for its application to the wood substrate. Fillers are used to modify the

color strength and the gloss of the coating. Additives prevent mold and decay, make the color drip-free, help the drying procedure, improve the adhesion characteristics, and control finishing. Coatings which are currently applied to wood surfaces can be categorized as air-drying, reaction-curing, water-soluble, stains, and oils and waxes [6–8].

The aim of this paper is to review innovative treatments for wood surfaces based on the science of nanotechnology and, thereby, to improve the fundamental wood properties, namely, durability, water absorption, mechanical properties, UV absorption, and fire resistance.

Nanotechnology is an attractive science, which seems to have a great potential in the production of a new generation materials with improved properties [9]. The first part of the word, “nano”, refers to materials with dimensions of less than 100 nm. The basic and unique characteristic of nanomaterials is that they have a high surface–volume ratio, which endows them with higher activities in surface-related phenomena compared to bulky systems of an identical mass [9]. In a way, nanotechnology is not a new idea. Many chemical substances or even chemical processes have special properties at the nano level. Chemists, for instance, have worked for decades to synthesize polymers which are structured by microscopic subunits. Also, nanotechnology has been successfully used to incorporate microscopic features into microchips for computers. Indeed, we can see nanoscale structures everywhere, as for example in milk, which is a colloidal nanoscale substance. Another example is proteins, which can play an important role in biological activities.

The exposure of wood in an outdoor setting can negatively influence not only its durability and physical properties, but also its natural beauty. The latter becomes very important if we are talking about the wooden structures which comprise our cultural heritage. It is well documented in the literature that the wood cell wall possesses significant porosity; this is of molecular dimensions [9,10]. The main reason to use nanotechnology in so-called wood science and technology is the unique characteristic of nano-based materials to penetrate deeply into wood substrates in an effective way, which, in turns, results in the alteration of the material’s surface chemistry. This subsequently causes an improvement in the wood properties. Currently, nano-based materials may be effectively applied to wood through in following distinctive ways:

- through the impregnation of nano-based materials,
- as polymeric nanocarriers through the impregnation of nano-based materials,
- as coatings [10,11].

Nanosized metals can be synthesized by applying one of the following chemical approaches:

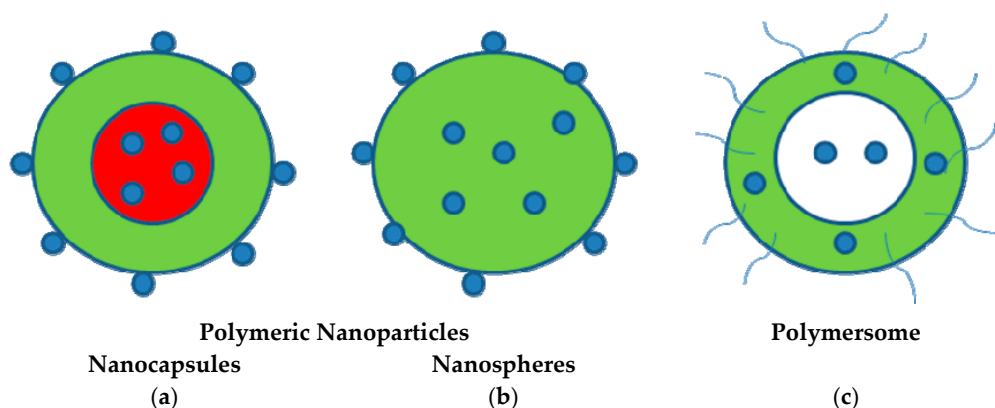
- solution-based synthesis (like sol-gel or sonochemical)
- vapor-based synthesis; i.e., combustion and chemical vapor deposition) [11–16].

The unique characteristics of nanosized metals are determined by the synthesis method [14]; these characteristics include a uniform size distribution of the particles, great stability, and a high surface-to-volume ratio [17–19]. Their application in wood science aims to enhance the biological, physical, and mechanical properties of wood [14,19,20]. Nanosized metals are usually dispersed in an organic polymer resin such that a nanocomposite is formed. Proper dispersion in this case is a very important factor in terms of maximizing the improvements to the wood properties. Thus, it is crucial to investigate possible interaction of metals with wood substrates, since deviations can result in phase separation. On the other hand, a possible accumulation of nanosized metals due to their high surface energy can result in the creation of various micro-composites inside the wood substrate, which can act as weak zones [20].

In the case of polymeric nanocarriers, an encapsulation of the active ingredient into polymeric nanocarriers can be conducted by several techniques, such as nanoprecipitation [19]. Several types of polymeric nanocarriers that may be used for active ingredient delivery are depicted in Figure 1 [9,11,19–22]. The incorporation of organic biocides into polymeric nanoparticles and the subsequent introduction of the nanoparticles into wood may be advantageous. Conventional biocides, even those with low solubilities,

can be easily dispersed in a solid polymeric nanoparticle that can, in turn, be suspended in water and then applied to wood using conventional water-borne treatments. In this way, biocides with a particularly low solubility that, until now, had a limited presence in the market, may now find a place in the wood preservation industry. In this case, polymer wood substrates will act as storage reservoirs which will control the release rate of the biocide, and at the same time, will protect the unreleased biocide from exposure to the environment. This may lead to the protection of the material for long periods [23].

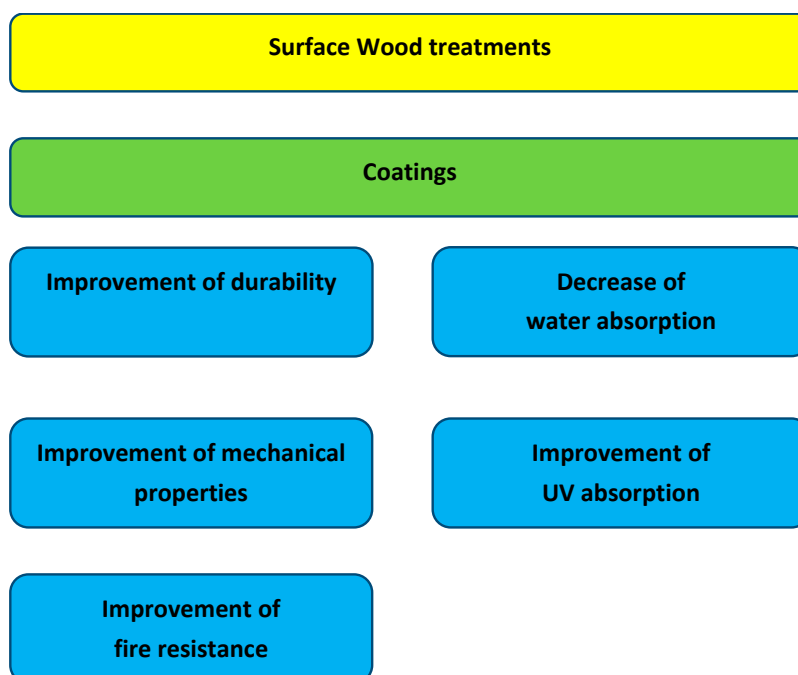
The third distinctive way, namely coatings, is presented and reviewed in the following section.



**Figure 1.** Types of polymeric nanocarriers: (a,b) Polymeric nanoparticles whose active ingredients are conjugated to, or encapsulated in, polymers. (c) A polymersome composed of hydrophilic-hydrophobic block copolymers, arranged in a lipophilic bilayer vesicular system and with a hydrophilic inner core [9].

## 2. Surface Treatment of Wood Based on Nanotechnology Coatings

The effective protection of wood can be achieved through coating or surface modification, as depicted in Figure 2 [9,24,25]. An excellent critical review on surface modifications of wood was authored by Petric [25]; his major findings are summarized in Table 1. Those based on nanotechnology are reviewed herein.



**Figure 2.** Classification of wood surface treatments.

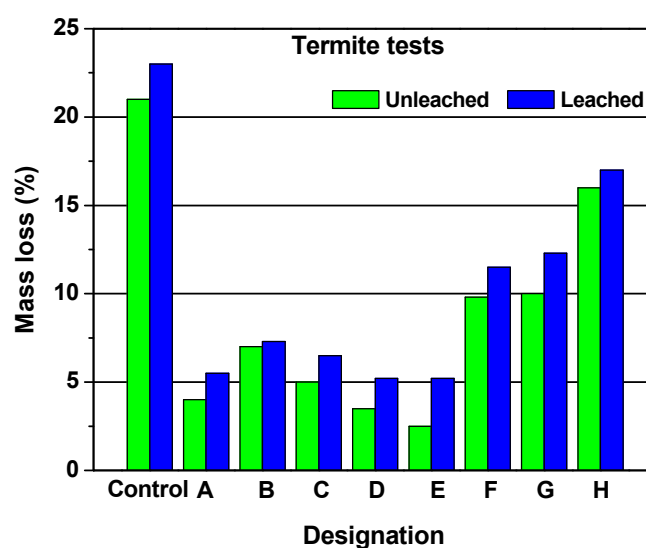
**Table 1.** Methods applied for the surface modification of wood, and key improved wood properties [25].

Method	Key Wood Properties
Chemical or enzymatic grafting	Resistance to weathering
	Decay resistance
	Activation of wood surface
	Wettability
Plasma treatments	Hydrophobicity
	Wettability
	Hydrophobicity
	Activation of wood surface
Exposure to microwaves	Improved penetration
Mechanical treatments (surface densification)	Hardness, resistance to abrasion
	Wettability
Surface chemical modifications	Hydrophobicity
	Activation of wood surface
	Resistance to weathering
Sol-gel methods and deposition of nanoparticles	Decay resistance
	Fire retardancy

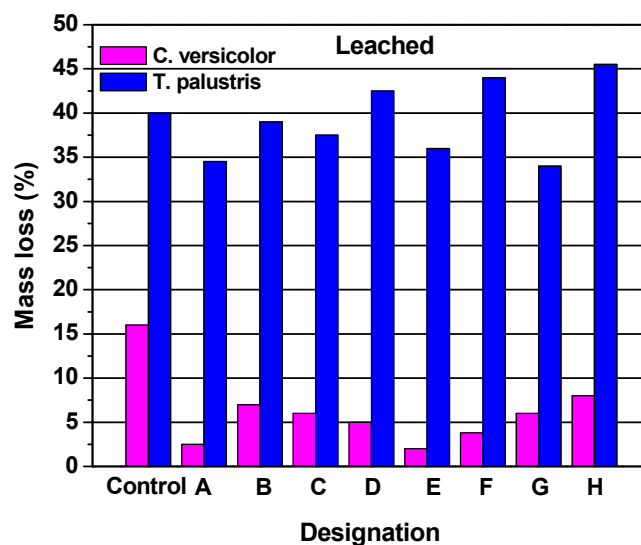
### 2.1. Increased Durability

The prevention of the growth of various microorganisms is an objective of wood coatings. It is well established that some elements, and mainly their ions, can be successfully applied for protection against various types of microorganisms like fungi and bacteria. Silver and copper, both in elemental form or as salts, are characteristic examples. The decrease of their size to the nano scale results in an increased surface area and a consequent increase in their catalytic activity [26]; this combination gives rise to interactions of the nano-based material with the cell membranes of microorganisms. The advantages of this silver nanotechnology are its antibacterial and fungicidal properties. This is a great advance compared to traditional treatments, which operate only at the time of use.

Recently, nano-based compounds (zinc and copper) have been applied wood surfaces in order to investigate resistance against termites and mold [27–30]. It has been shown that zinc-based compounds appeared to be more effective in terms of termite mortality and decay resistance against fungus, i.e., white-rot (Figures 3 and 4). Bak and Nemeth [31,32] reported on the effectiveness of different nanoparticles against fungi. It was revealed that treatments which contained borate were more effective. Their main conclusion was that only a formulation that contained zinc-oxide provided full protection of wood samples after leaching.



**Figure 3.** Mass loss following termite resistance of pine wood: (A) nanozinc oxide; (B) nanozinc oxide with binder 1; (C) nanozinc oxide with binder with binder 2; (D) nanozinc borate; (E) nanozinc borate with binder 1; (F) nano-copper oxide; (G) nano-copper oxide with binder 1; and (H) nano-copper oxide with binder 2 [9].



**Figure 4.** Mass loss following resistance of pine wood: (A) nanozinc oxide; (B) nanozinc oxide with binder 1; (C) nanozinc oxide with binder 2; (D) nanozinc borate; (E) nanozinc borate with binder 1; (F) nano-copper oxide; (G) nano-copper oxide with binder 1; and (H) nano-copper oxide with binder 2 [9].

A wide spectrum of organic, photocatalytic, and silver ion antimicrobial agents have been applied to date as coatings [33–51]. This includes silver nanoparticles [52], combinations of various metal ions and various metallic nanoparticles [53,54], and combinations of all of the above [55–69]. Photocatalytic agents (e.g., titanium dioxide, ZnO) require conditions of water and oxygen and UV light, and are activated by ultraviolet light [52,68,70]. The use of titania nanoparticles for the protection of surface treatments comprises the formation of a thin film of water on the surface of wood [52–54]; this, in turn, prevents biological growth. Both nano TiO<sub>2</sub> and ZnO can also remove microorganisms from wood surfaces due to their photocatalytic behavior. In these cases, reactive free radicals are produced which are able to attack and kill potential microorganisms. Nanozinc borate has also been used to reduce microbial activity [53–55].

Based on the above, it appears that silver, copper, and titanium dioxide particles [9,55] offer a broad range of protection features which make these potentially useful antibacterial materials.

## 2.2. Improvement of Water Absorption

The incorporation of inorganic particles into organic polymers as fillers is a common practice to improve the water absorption of wood and to make its surface hydrophobic. A first approach is to make the surface of the wood water-repellent; in this case, the water which exists on the wood surface is in the form of a spherical drop. With this approach, any potential water-soluble contaminants can be moved away from the surface. The second approach is the use of a treatment which makes the surface of wood hydrophilic; the treatment in this case acts as a barrier which prevents water from penetrating the wood substrate. With this approach, a thin homogeneous film of water is created, which can run off the surface and dry. This is advantageous, since no residual contamination is left on the surface [6].

Polymeric coatings which are filled with nanoparticles are used to improve the water absorption of wood surfaces; these may include spheres or tubes. Nanosized materials can be incorporated into the formulation of a potential coating by two very distinctive approaches, namely, solution blending, or in situ [9,11]. In the first approach, which is referred to as “physical”, a suitable solvent is added to the polymer and then force is applied to ensure dispersion. Following this, the application of the coating to the wood surface can be done by three ways, namely dipping, brushing, or spraying [55,71]. The second way, namely in situ addition, which is referred to as the “chemical approach”, involves compound addition directly to monomers and subsequent polymerization. In this way, the nanomaterials are synthesized in situ by chemical reactions on the wood surface. These may include hydrothermal

methods or sol-gel deposition. This method is advantageous because the very small molecules diffuse easily between nanoparticles.

Silver nanoparticles have been used to improve the water absorption characteristics of wood. Mantanis and Papadopoulos [56] applied a nano-silver compound and examined its effect on the sorption characteristics of pine wood. It was revealed that 2 min immersion significantly reduced the water vapor sorption, as depicted in Figure 5. Similar findings were also reported elsewhere [57,72].

Another nanoparticle with promising potential is nanosilica. This material, with proper modification, improves the compatibility with the polymer and is able to improve the sorption characteristics [55,58–61]. These improvements are more evident when nanoclays are applied. Nanoclays have a platelet structure and possess a high aspect ratio. The sorption characteristics of the wood surface is improved, since a route for molecules is produced; molecules have to track a long distance through the coating. Nanoclay, which is hydrophilic, provides excellent dispersion and interaction with polar polymers.

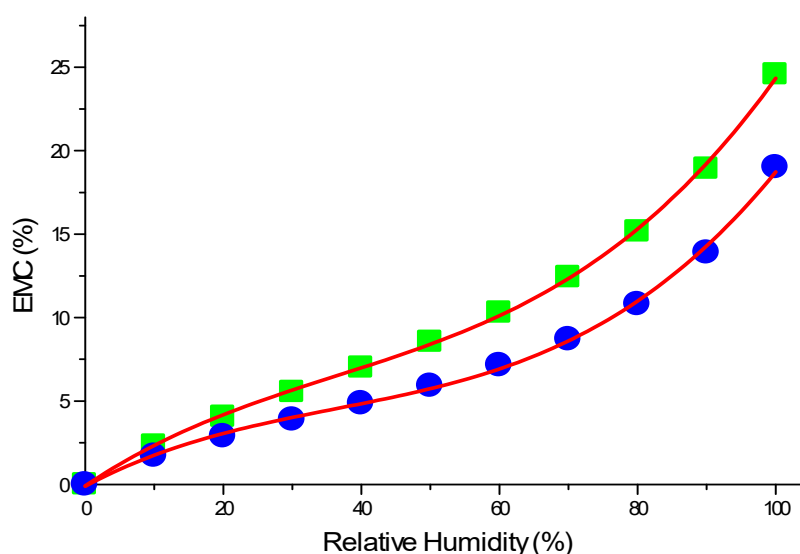


Figure 5. Adsorption isotherms for untreated (■) and treated (●) wood. [40], Copyright MDPI, 2019.

### 2.3. Improvement of Mechanical Properties

The incorporation of inorganic particles into organic polymers as fillers is a common practice which is applied to improve the mechanical properties of wood. With this approach, the rigidity and hardness of the inorganic particles is combined effectively with the polymer's processability [62]. The dispersion of inorganic materials to nanosize causes an increase in the surface area, and consequently, the ratio of the interfacial area is also increased; this significantly influences the properties of the material [63]. In the case whereby the compatibility between the inorganic particles and the polymers is suitable to avoid accumulation, an improvement in the mechanical properties occurs, since this type of interaction causes a reduction in the movement of the polymer's chain segments [64]. Again, nanosized materials can be easily incorporated into the formulation of a potential coating following two approaches, namely through solution blending and in situ [9,11].

Recent studies have investigated the mechanical performance of heat-treated wood. After heat treatment, wood was impregnated with a nano-silver suspension. It was found that such impregnation fortified the effects of thermal modification. This was attributed to improved thermal conductivity which, in turn, improved the mechanical performance of the wood [65,66].

Another common nanoparticle that is applied for the improvement of mechanical properties is nanosilica. The main advantage of using nanosilica is its high hardness. Furthermore, nanosilica can easily be chemically modified in order to improve its compatibility with the polymer [67]. It has been reported that the modification of silica with a series of silanes can improve scratch and abrasion resistance [61,73].

Resistance in surface scratching is a desirable property, since it prevents damages and prolongs the aesthetic value. The use of ceramic nanoparticles increases scratch resistance [74–77].

#### 2.4. Improvement of UV Absorption

The use of UV radiation absorptive coatings serves to prevent lignin degradation from UV light. Nanoscale UV absorbers protect the wood surface and consequently increase the lifetime of the coating. The small size of the nanoparticles offers a high level of protection against UV without affecting the transparency of the surface [55]. In this way, damaging solar rays are absorbed by the coating and the wood surface is protected. UV absorbers can be added in higher concentrations without altering the transparency of the coating, since their size is significantly smaller than that of other absorbers [78,79]. Currently used UV absorbers comprised mainly titanium and ZnO particles [80–82], i.e., photocatalytics.

#### 2.5. Improvement of Fire Resistance

The application of nanoparticles, either alone or in combination with traditional fire retardants, serves to reduce the ignitability of wood. The nanomaterials used for fire resistance can be categorized as follows [83]:

- nanoclays (layered aluminosilicates). It has been reported that montmorillonite, a variety of bentonite clay, is the most effective and promising among the layered silicates. Its main characteristic is that it is able to split into individual nanosized plates [83].
- nano oxides. Nanoparticles of titanium have applied for this purpose [84]. They create a fire retardant barrier on the wood surface which retards the spread of flame and suppresses smoke generation. Additionally, they produce water and gases when exposed to fire, which provide a cooling effect by snuffing out the oxygen. At the same time, char is created which, in turns, protects the wood surface from combustion [85–87]. Another nano-oxide with promising potential is ZnO [88].
- nanosilica sol and silicon compounds. Nano-SiO<sub>2</sub> has been applied to wood by the sol-gel method and has demonstrated great potential [89].
- nanostructured carbon materials. Information on carbon nanotubes and graphenes as potential fire retardant materials is limited.

### 3. Summary of Points Raised and Advantages of Nanomaterials in Surface Treatment of Wood

The treatment of wood surfaces with nanomaterials provides products with better performance compared to those with conventional wood treatments. Treatments can improve a variety of properties, as shown in Figure 2. A variety of nanomaterials, including nanoxides, metal nanoparticles, and nano-clays, have been applied. The basic advantages of nanomaterials are presented, and compared to the potential disadvantages, in Table 2. A summary of the nanomaterials described in the literature, as identified in this paper, is depicted in Table 3.



**Table 2.** Basic advantages of nanomaterials [9].

Property	Advantages	Disadvantages
Water absorption	The impregnation of nanomaterials reduces the pore size and space available within the cell wall, which is used for the absorption of water molecules. In this way, a rough hydrophobic surface is created.	There is increasing concern about the environmental risks of nanomaterials. Experience from the past reminds us that new breakthrough technologies may not be more environmentally friendly than traditional technologies. It is certain that incomplete knowledge about nanomaterials delays their broad application. Their potential impact on both health and the environment should be addressed by applying tools such as a life-cycle assessment.
UV-protection	Damaging solar rays are absorbed by the coating and the wood surface is protected. UV absorbers can be added in higher concentrations without altering the transparency of the coating, since their size is significantly smaller than that of other absorbers	
Fire resistance	The application of nanoparticles, either alone or in combination with fire retardants, is able to reduce the ignitability of wood. They create a fire retardant barrier on the wood surface which retards the spread of flames and suppresses the generation of smoke.	
Durability	Nanoparticles increase the decay resistance of wood by reducing moisture availability. This happens either by preventing the absorption of moisture or by blocking the flow path of liquid.	
Mechanical properties	The incorporation of inorganic particles into organic polymers, as fillers, is a common practice applied to improve the mechanical properties of wood. In this way, the rigidity and hardness of the inorganic particles is combined effectively with the polymer's processability. The dispersion of inorganic materials causes an increase in the surface area, and consequently, the ratio of the interfacial area is also increased; this significantly influences the properties of the raw material.	

**Table 3.** A summary of the nanomaterials described in the literature.

Property Improved	Nanomaterial Used	Reference
Water absorption	nano-elulsion	[45]
	TiO <sub>2</sub>	[46,48]
	nano silica	[32,47,51,55,58]
	spherical metal oxide	[49]
	SiO <sub>2</sub> , ZnO, TiO <sub>2</sub>	[50,57]
UV-protection	AgNPs	[52,57,72]
	CuO	[19]
	TiO <sub>2</sub>	[46,48,78,79]
	ZnO	[80–82]
	acrylate nanoparticles	[61]
Fire resistance	nano silica	[67]
	TiO <sub>2</sub>	[84,85]
	ZnO	[88]
	SiO <sub>2</sub>	[89]
Durability	Ag	[36]
	Ag, TiO <sub>2</sub>	[37,38]
	Ag, TiO <sub>2</sub> , ZnO	[39,59]
	ZnO, B <sub>2</sub> O <sub>6</sub> Zn <sub>3</sub> , CuO	[14,19,27–32,51]
	AgNPs	[15,30,52,59]
Mechanical properties	TiO <sub>2</sub>	[18,20,53–55]
	AgNPs	[65,66]
	nano silica	[67,73]
	CuO	[58]
	ceramic nanoparticles	[75–77]

#### 4. Future Prospects of Nanotechnology

It appears that nanotechnology will herald the next generation of wood-based products with hyper-performance and advanced service abilities when used in outdoor applications. Nanotechnology



seems to present a tool to extend structural performance and the serviceability of wood, allowing scientists and researchers to manipulate and perhaps eliminate the formation of random defects. New non- or low-toxicity nanomaterials such as nano-dimensional zinc oxide, silver, titanium dioxide, and even possibly clays might be used as either preservative treatments or moisture barriers. In addition, resistance to fire might be enhanced by the use of nano-dimensional materials like titanium dioxide and clays. It is therefore of vital importance to understand the synthesis-structure-property relationships of nanocomposites in the development of advanced polymer nanocomposites with enhanced material properties.

However, it has to be mentioned that there is increasing concern about the environmental risks of nanomaterials. Experience from the past reminds us that new breakthrough technologies may not be more environmentally friendly than the traditional technologies. It is certain that incomplete knowledge about nanomaterials has delayed their broad application. Their potential impact on both health and the environment should be addressed by applying tools such as a life-cycle assessment (LFA) [90,91]. Therefore, regulations and many tests are required to be carried out before the commercialization and industrialization of such products can occur, especially for those designed for indoor applications. As concluded by Bauer et. al. [91], the issues and elements of a common framework for LCA and nanotechnology can be summarized as: *'(i) the structuring of typical functions as the basis for common system boundary definitions to enable comparisons, (ii) establishment of modular LCI models to describe the variety of materials and manufactured properties, (iii) to agree on provisional procedures to document the release of nanoparticles even without applicable impact assessment models'*.

The impact of nanotechnology on construction was recently investigated [91]. Since wood can be considered a valuable engineering material, the authors of this paper choose to cite the major findings of the aforementioned study, i.e., *'(i) the construction industry has high expectations of nanotechnology to solve some of the industry's most difficult problems; (ii) low literacy level on nanotechnology topics and disconnect from ongoing R&D efforts is a major barrier, although expectations are high; (iii) to overcome such limitations, systematic construction industry- or companywide approaches such as roadmaps and strategic plans must be undertaken to profit from the benefits nanotechnology offers and to gain a competitive advantage in selected application areas and product categories'*.

Significant concerns are also related to the effect that nanomaterials may have on human health and on the environment. Due to their small size, nanomaterials may have a negative effect the respiratory and digestive tracts, or even on the eyes and or the skin surface [92,93]. However, very few studies have been carried out to offer solutions to the environmental and social issues that are associated with the use of nanomaterials [94].

Last but not least, the economic perspectives of nanotechnologies, as an emerging technology, are based on the opportunity to enhance material properties in a more refined way. So, the competitiveness of a company, and therefore its growth, may depend, in the near future, on its ability to apply nanotechnologies and to use nanomaterials. According to Teizer et al. [90], the coatings industry consists of approximately 1400 companies; their sales are estimated to comprise about of US\$20 billion per year. Coatings based on nanotechnology were proved to be 20 times more effective concerning water repellency [90]. It is estimated that the global market of nanomaterials will, in the next two decades, reach a value of \$340 billion [17].

## 5. Conclusions

The main reason to use nanotechnology in wood science and technology is the unique characteristic of nano-based materials to penetrate deeply into wood substrates in an effective way, which, in turn, results in the alteration of the wood's surface chemistry. This subsequently causes an improvement in the wood properties. Any potential change in the wood properties due to treatment with nanomaterials is based in the higher interfacial area which is developed. This happens because the number of particles is significantly reduced. Nanomaterials improve the properties of wood as a raw material and alter its original features to a limited extent. However, their potential impact on both health and the environment should be addressed by applying tools such as a life-cycle assessment.

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