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Comparison of TiO_2 and ZnO nanoparticles for the improvement of consolidated wood with polyvinyl butyral against white rot

Danial Harandi*, Hossein Ahmadi, Mohsen Mohammadi Achachluei

Faculty of Conservation of Historic and Cultural Property, Art University of Isfahan, P.O. Box 1744, Isfahan, I.R. Iran

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ABSTRACT

Synthetic polymers are widely used in the conservation of historical relics. These materials are attacked and deteriorated by microorganisms. The environmental factors also accelerate their deterioration. In this study, the antifungal properties of TiO_2 and ZnO nanoparticles in Polyvinyl butyral (PVB) were assessed. In three groups, samples were prepared from *Poplar* wood and they were treated with the nanocomposites under vacuum condition. Two groups were incubated separately in darkness and light conditions with rainbow fungus (*Trametes versicolor)* for 7 weeks according to the Bravery method. The third group was studied after the accelerated aging due to temperature, humidity and UV light irradiation. Treated samples with 1% of nano-TiO_2 and nano-ZnO in 5% of PVB in darkness conditions, did not show antifungal properties. But 2% of these nanoparticles protected the wood against fungal in darkness conditions.

There was an appropriate antifungal properties all treatments in light condition. The accelerated aging of the treated samples with the nanocomposite indicated the protective effect of this latter treatment against aging factors compared to the treated samples with the consolidant lacking nanoparticles.

1. Introduction

Synthetic resins are widely used as consolidants for conservation treatments and the protection of cultural heritage. These materials have little resistance against biological factors and the consolidated artworks having these materials are still invaded by fungus and mold. This deterioration is accelerated by environmental factors and ultraviolet light. Therefore, there is a crying need for a method to prevent the invasion of microorganisms to the synthetic polymers, consolidants, and the adhesives used in the conservation of artistic-historical objects. Hence, the study of preventive methods against biodeterioration of consolidant polymers was necessary for conservation purposes.

Wood as an organic material is deteriorated by microorganisms, especially by the wood-decay fungus which alters the physical and mechanical properties of wood artifacts. Wood biodeterioration cannot be stopped with consolidation materials, although treatment with Paraloid and Regalrez consolidants against fungal colonization of wood led to general slowing of fungal growth in treated samples (Clausi et al., 2011). As wood consolidants, synthetic polymers could be invaded by rottes due to the organic structure of these polymers (Heyn et al., 1996). PVB and Paraloid B-72 have been widely used for the consolidation of wood (Wang and Schniewind, 1985; Schniewind, 1998), but PVB has better properties against biodeterioration than Paraloid B-72 (Koestler and Santoro, 1998). Studies about the presence of fungi in the vinyl materials such as polyvinyl acetate, polyvinyl chloride and polyvinyl butyral indicated the growth of fungi on them (Inoue, 1983; Roberts and Davidson, 1986; Hamilton and Barry, 1983).

Synthetic polymers could be deteriorated by microorganisms (Gu, 2003; Mohan, 2011; Leja and Lewandowicz, 2010; Bastioli, 2005). They will also be destructed due to chemical, physical and environmental effects (Corning, 1998). Synthetic resins are widely used as adhesives and consolidants in the conservation of historical relics and it is assumed that compared with natural resins, these resins are less degradable by biological factors. However, there has been many reports about the degradation of synthetic polymers by microorganisms used for conservation treatment as adhesives, consolidants, and protective coating (Cappitelli et al., 2007, 2008; Leja and Lewandowicz, 2010; Kawai and Hu, 2009).

Many of the synthetic polymers are appropriate sources of carbon and energy required for the growth of microorganisms.

* Corresponding author.
E-mail addresses: danial.harandi@gmail.com (D. Harandi), h.ahmadi@aui.ac.ir (H. Ahmadi), mohsen.mohammadi@aui.ac.ir (M. Mohammadi Achachluei).

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When temperature and humidity conditions are appropriate, they attack these polymers and deteriorate natural and synthetic polymers in an enzymatic and chemical process. Studies conducted on the consolidants such as acrylic polyurethane and epoxy resin indicate that none of these consolidants are resistant to microorganisms (Gu, 2003; Mohan, 2011). Assessments showed that the poly-isobutyl methacrylate and polylauryl methacrylate that are used as stone consolidants are susceptible to fungi growth (Cappitelli et al., 2004).

The protection of UV light and antifungal activity of ZnO nanoparticles were identified in cellulosic materials and they are used as additives in the cotton fibers and sheets of paper (Ghule et al., 2006; Moafi et al., 2011; Sricharussin et al., 2011). Furthermore, ZnO nanoparticles are used to protect oil paintings on paper support against dirt, fungal attack, and UV light (El-Feky et al., 2014) and protection of wooden objects against UV (Clausen et al., 2009).

Studies on photocatalytic properties of TiO_2 in anatase structural form show that it is the most effective industrial photocatalyst (Ohama and Van Gemert, 2011, 1–2). TiO_2 with 2.3eV energy gap can absorb the Uv light (De Filpo et al., 2013) and it results in the production of hydroxyl radicals and superoxide ions. These products can decompose the polluting molecules and disinfect the microorganisms (Sequeira et al., 2012). Therefore, TiO_2 is used as an antifungal and antibacterial substance (Kangwansupamonkon et al., 2009; Maness et al., 1999; Sunada et al., 2003; Kim and Yoon, 2008; Maneerat and Hayata, 2006).

Titanium dioxide is multifunctional and it is used as the films on cellulose fibres (Snyder et al., 2013; Uddin et al., 2007), and self-cleaning building materials (Benedix et al., 2000; Stamate and Lazar, 2007). Recently, the application of nano-Ti_2O in the conservation of historical relics has been assessed showing acceptable results for the conservation purposes (De Filpo et al., 2013; Afsharpour et al., 2011, 2014; Wang et al., 2013). As far as the application of synthetic resins and their deterioration is concerned, biological stabilization of consolidants has a great importance for conservation purposes. In this study, the application of TiO_2 and ZnO nanoparticles has been evaluated to improve the nanoparticle consolidants applied to wood to guard it against white rot and environmental effects.

Regarding the considerable use of synthetic materials in the restoration of historical relics and the deterioration of which by the environmental factors and microorganisms, modern methods of preventing the invasion of fungi and the effects of biological factors and also making antifungal consolidants are necessarily needed. Based on the multifunctional features of the photocatalyst activity of TiO_2 and ZnO nanoparticles, in this study, they were used to improve the characteristics of PVB consolidant against white rot fungi (*Trametes versicolor*as) and environmental factors.

2. Material and methods

2.1. Wood sample preparation and treatment

All samples are obtained from poplar wood (*Populus alba L.*). For the biological evaluation, samples were prepared in 15*10*5 mm dimensions according to Bravery guideline (Bravery, 1979).

TECNAN nano-Ti_2O in anatase structural from (10–15 nm) and Houston nano-ZnO (10–30 nm) were used for nanocomposite production. 5% (w/w) solution of PVB in ethanol (Scharlau) was stirred at room temprature for 6 h. Subsequently, the nanoparticles were added in the following percentages: 1% and 2% (w/w) of TiO_2 and ZnO nanoparticles were separately added to 5% solution of PVB and for more assessments, a combination of nano-TiO_2 and nano-ZnO (0.5%: 0.5% and %1:1%) was assessed in PVB.

Wood samples were treated under vacuum condition (7 mbar) and they were placed after treatment at room temperature. Afterwards, the samples were dried in 103 ± 2 °C for 24 h.

2.2. Biological assessment

Samples were cultivated with malt extract agar medium and exposed to *Trametes versicolor* (rainbow fungus) as a white rotter. They were incubated at 22 °C and 60% Relative humidity. Each test has 5 times frequency and is separately conducted in two conditions of light and darkness applied for fungus cultivation for 7 weeks and fungal growth and the durability of samples were calculated regarding NF-EN 350-1 (Table 1**).**

Mass loss of sample (A) was measured using the following equation (Jones and Worrall, 1995)

$$\%A = [(OW - DW) \times 100]/OW$$

Where, OW and DW refer to dry original mass and past decay dry mass.

2.3. Accelerated aging

The samples were located at 60 °C and 75% RH for 20 days and then were irradiated by UV (365 nm) for 120 h according to Mohammadi Achachluei method (2010).

2.4. Structural analysis

Structural changes were assessed in the cross section of samples by scanning electron microscope (SEM) and Nicolet 470 Fourier Transform Infrared Spectrometer (FTIR) equipped with PIKE Miracle attenuated total reflectance (ATR).

2.5. Color measurement

Color variations during the aging procedure were measured by solution Colortector Alpha colorimeter and CIE L^* a^* b^* system. Five points of samples were measured before and after the accelerated aging. Parameters L^* (lightness), a^* (red-green) b^*(yellow-blue) were measured and each average was calculated (Aydin and Colakoglu, 2005; Matsuo et al., 2011). Color changes were evaluated according to the following equations.

$$\Delta L^* = L_2^* - L_1^* \quad (1)$$

$$\Delta a^* = a_2^* - a_1^* \quad (2)$$

$$\Delta b^* = b_2^* - b_1^* \quad (3)$$

$$\Delta E^* = \left(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\right)^{1/2} \quad (4)$$

Table 1
Natural durability of wood is rated from very to not durable, according to the percentage reduction in mass after fungal attack (European standard NF-EN 350-1 guidelines (AFNOR, 1994).

Durability rating	Description	Reduction in mass *x* (%)
1	Very durable	$x \le 5$
2	Durable	$5 < x \le 10$
3	Moderately durable	$10 < x \le 20$
4	Slightly durable	$20 < x \le 30$
5	Not durable	$x > 30$