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Original article

Preventive protection of paper works by using nanocomposite coating of zinc oxide

Maryam Afsharpour [a,*], Saleh Imani [b]

[a] Chemistry & Chemical Engineering Research Center of Iran, 14335-186 Tehran, Iran
[b] Conservation Department, Art University of Isfahan, Isfahan, Iran

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ABSTRACT

In this work, we investigate the role of zinc oxide nanoparticles in the inherent protection of paper works against damaging effects of ultraviolet radiation, pollutant gasses, mold, and bacteria. For this purpose, the cellulosic nanocomposite of ZnO was used as protective coating on the surface of the paper. This nanocomposite can act as a consolidant as well. To determine the protective potential of this coating, the chemical and physical properties of treated papers after light and heat accelerated aging were measured. Results showed good stability of papers with nanocomposite coating. Also, a good light stability was shown in the colored paper that was treated with this nanocomposite. Furthermore, to demonstrate the degree of antifungal and antibacterial properties of coated papers, sample papers were treated with two common fungi and bacteria, and the positive preventive effect of coated paper against fungi and bacteria was observed.

Research aims

Paper is subjected to numerous deterioration processes, which may cause irreversible degradation of important manuscripts and works of art. In this study, we investigate the role of ZnO in the inherent protection and preservation of paper works against damaging factors. A cellulosic nanocomposite of ZnO was used as protective coating on the surface of paper fibers. This nanocomposite can protect paper from damaging effects of UV light, air pollutants, bacteria, and fungi. A degradation of mechanical properties of paper during thermal aging has been detected with tensile strength of papers. Mechanical tests revealed that the ZnO nanocomposite coating had the best resistance to tensile strength compared with other papers. This is due to the fact that the layer structure of polymeric nanocomposites can improve ZnO fiber bonding. Also, the UV-blocking property of coated paper was investigated by measuring the fading percent of colored paper under UV irradiation. The fading process in nanocomposite coated paper is also slowed down over time. This finding can be explained by the absorption of UV light through ZnO nanoparticles; hence, the color embedded under the layer of cellulosic polymer remains intact. Furthermore, to demonstrate the degree of antifungal and antibacterial properties of coated papers, samples were treated with two common fungi and bacteria, and the preventive effect of ZnO coatings against fungi and bacteria is described.

1. Introduction

Cultural heritage such as old manuscripts are susceptible objects which are influenced by environmental conditions such as climate, pollution, biological agents, and mechanical stresses [1–4]. In order to slow down these degradation processes, it is necessary to carry out preventive conservation that is an important element of museum policy in taking care of collections. So, conservation science focused on chemical compounds that are able to protect the artistic substrate.

In the last few years, nanostructured materials have been frequently applied to solve the problems in restoration and conservation of artworks such as paper, wood, textile, stone and wall paintings [5–19]. Due to their particular characteristics, nanomaterials seem to be very suitable for new conservation treatments. The most common nanomaterials used in conservation science are inorganic nanomaterials such as calcium and magnesium hydroxide [5–10], metal oxides (such as SiO_2, TiO_2, ZnO, and Fe_2O_3), and their nanocomposites [11–19].

Calcium and magnesium hydroxide nanoparticles are helping to de-acidify paper and wood artifacts and diminish acid formation. The smaller size of the particles improves the material spreading and penetration, and a very weak white glazing forms after application. Also, it reduces the rate of oxidative degradation of cellulose

* Corresponding author. Tel.: +98 21 44787758; fax: +98 21 44787712.
E-mail address: afsharpour@ccerci.ac.ir (M. Afsharpour).

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and enhances the preservation of old paper documents [5–7]. These nanoparticles are now being used as effective agents in wall painting restorations [8,9].

Metal oxides, because of their unique physico-chemical characteristics (e.g., high surface area, photocatalytic effect, color tone modification, good optical properties, higher penetration depth, and thermal expansion coefficient) exhibit improved performance over traditional chemical compounds in the conservation field [10–19].

Titanium dioxide nanoparticles can be used as an active and preventive protection system in order to implement transparent self-cleaning coatings on paper [11] and stone [12–14] surfaces. Also, the display boxes that are coated by TiO_2 nanoparticles can be used for the conservation of historical and artistic objects by controlling the microclimate in which they are stored [15]. The efficacy of SiO_2 nanoparticles was examined as a consolidate agent for stone [16,17] and a magnetic nanoparticle gel system was used to clean a painting [18].

Since ZnO is broadly used in modern and contemporary pictorial art, acting as a pure white pigment [19,20], the present paper is trying to investigate the ZnO role in the protection of paper works of art. Nanostructured ZnO has received much attention as a photocatalyst in practical applications such as environmental purification, self-cleaning, gas and chemical sensing, and catalysis [21–25]. Furthermore, ZnO appears to be strongly resistant to microorganisms [26–28] and nano-ZnO is now widely used as an antimicrobial agent in the restoration of cultural heritages [29–32].

Over the past decade, a variety of physical and chemical approaches have been used to prepare nano-ZnO coatings, including the sol-gel method, wet chemical synthesis, microwave synthesis, hydrothermal synthesis, and chemical vapor deposition [33–37]. However, the use of these sort of coatings in substrates with low thermal and mechanical resistance, such as old manuscripts, deserves more attention. In this study, a non-impact spray-based technique (recent/novel technique) has been developed to coat sample papers via a cellulosic nanocomposite of ZnO. This nanocomposite can act as a consolidate material as well as protect papers from UV light, air pollutant, mold, and bacteria.

To find materials which can be safe for long-term use, avoiding the degradation of treated papers, two accelerated aging tests, due to light and heat, were designed. The degradation of mechanical properties of paper with thermal aging has been measured via tensile strength of papers. Furthermore, to determine how well nanocomposites screen papers from the damaging effects of ultraviolet radiation, a selection of colored papers was exposed to light and the fading of color is discussed by using diffuse reflectance spectra of samples before and at intervals during the UV exposure experiment. The traditional artists' colorant, Alizarin Lake, as a model of a fugitive organic pigment [38], was applied in coloring the paper samples.

Also, this study is mainly aimed at verifying the antifungal and antibacterial properties of the ZnO coating. Biodeterioration processes may cause irreversible degradation of important documents and works of art and fungi or bacteria seem to play a key role in the biodeterioration of paper works. To demonstrate the degree of antifungal and antibacterial properties of the coating, papers were treated with two common fungi and bacteria, and the preventive effects of the coating are discussed.

2. Experimental

2.1. Material and methods

ZnO nanoparticles (mean size = 150 nm) and ethanol were purchased from Merck and used without further purification. Klucel G (hydroxypropyl cellulose) with molecular weight of 370,000 was used as consolidate material in composite. All reactions were carried out at room temperature in air. Fourier transform infrared spectroscopic (FTIR) measurements were conducted using a Bruker, Equniox 55 spectrophotometer. The spectra were recorded in the range of 600–4000 cm^{-1} with a resolution of 2 cm^{-1} by using Golden Gate Micro-ATR accessory. Scanning electron microscopy was performed on a Philips XL-300 instrument with inbuilt EDS. After coating the sample with gold by sputtering coater, samples connected to the sample holder by a conductive carbon tape. Thermal analysis of paper sample (5.3 mg) was carried out using in a PL STA-1500 apparatus with heating rate of 10 °C min^{-1} in air over the range of 25–700 °C. UV–Vis spectrophotometric analysis was obtained on the Aventes UV4200 Avaspec spectrometer equipped with an integrating sphere. The spectra were recorded at room temperature in the wavelength range of 200–900 nm. The mechanical properties of the fiber samples were measured on Gotech, GT-6018-B strength measurement instrument according to ISO1924-2:1995 method. The tensile properties of paper strip with 15 mm in width were measured in the machine (MD) and cross directions (CD) of papers.

Accelerated aging was performed in Binder KBF115 ageing chamber according to the ASTM D6819-02 at 90 °C, and for light aging, the fiber sample was irradiated by a 30 W Philips UV ray lamp (wavelength 270 nm) at a distance of 15 cm.

2.2. Conservation procedure

To demonstrate the suitability of our coating method for protection of paper, we have firstly chosen a standard filter paper (Whatman) to test the coating procedure. Many pieces were cut from standard paper and one set was reserved without any treatment for comparison (S). Another set of samples was prepared by coating the surface of the paper by spraying an ethanolic Klucel suspension (0.7 g of Klucel in 100 ml of ethanol) twice (K).

ZnO nanoparticles (0.2 g) were dispersed in 100 ml of ethanol by using an ultrasonic instrument for 5 min. The second set of papers was coated by spraying this ZnO nanodispersion on the surface of the papers. To obtain coated papers of better quality, the procedure was repeated twice. Then, all paper samples that had been coated with ZnO nanoparticles were dried at room temperature (A).

To prepare sample B, first, one layer of the Klucel suspension was sprayed on the surface of the paper and dried at room temperature. Then, the second layer of nanocomposites prepared by adding 50 ml of the ZnO nanodispersion (0.2 g of ZnO in 50 ml of ethanol) to 50 ml Klucel suspension (0.7 g of Klucel in 50 ml of ethanol), was sprayed on the surface of the Klucel layer.

All of the paper samples (coated and uncoated) were aged thermally. The accelerated aging tests were performed in a closed system at 90 °C according to the ASTM D6819-02e3 method.

Also, we prepared another set of colored papers to investigate the fading effect (C). These samples were prepared by coloring the papers with Alizarin using a traditional technique. Two grams (2 g) of Alizarin madder were boiled in 200 ml of water for about 15 min to dissolve the dye. After filtering the madder, sample papers were put in the hot color solution for about 10 min. Then, the dried colored papers were coated by Klucel (C–K), ZnO nanoparticles (C–A) and ZnO nanocomposites (C–B) according to previous procedures. The coated and uncoated (C–S) colored papers were aged in a chamber with a UV lamp (270 nm, 30 W) to test the degree of fading in colored papers. The distance between the UV source and the samples was fixed at 15 cm.

Furthermore, to demonstrate the degree of antifungal and antibacterial properties of coated papers, samples were treated with two common fungi (*Aspergillus niger* ATCC16404 and *Candida albican* ATCC) and two bacteria (*Staphylococcus aureus* ATCC6580 and *Escherichia coli* ATCC1330). All experiments were performed