Performance of Nanomaterials for the Conservation of Artistic Stones

In the last few years nanocomposites have been frequently applied for restoration and conservation of artworks. In fact, it has been demonstrated that inorganic oxide nanoparticles, such as silica and titania, may improve the performance of materials used in the conservation field. The experience in the synthesis and characterization of nanoparticles within UTTMAT at ENEA, combined with the experience in conservation materials in terms of durability of the conservative products, fostered a research investigation on nanocomposites applied to cultural heritage. In this study, performances of nanocomposites composed by an acrylic resin and a polyalkylsiloxane with nanosilica and nanotitania will be comparatively presented. Artificial aging to verify the positive effects of nanoparticles were carried out on stone specimens treated with nanocomposites

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In the last few years, nanoparticles and nanostructured materials have been frequently applied to restoration and conservation of artworks [1,2]. In fact all cultural heritage undergoes aging processes with final degradation effects, due to their intrinsic material properties and deterioration phenomena, which are influenced by environmental conditions such as climate, pollution, biological agents, and mechanical stresses. In order to slow down these degradation processes it is necessary to carry out conservative interventions, consisting in restoration and preventive treatments. So far, conservation science focused on chemical compounds, in general polymers and copolymers, able to consolidate and protect the artistic substrate (e.g. coating, adhesive, water repellent and biocide materials). Nowadays the application of nanomaterials and nanotechnology is enabling new functionalities that promise to improve the properties of traditional commercial products.

Inorganic nanoparticles (such as Ag, SiO_2, TiO_2, ZnO_2, ferrites and other metal oxides) due to their unique physico-chemical characteristics, such as cohesive forces arising from high surface area, photocatalytic effect, colour tone modification, good optical properties, higher penetration depth, thermal expansion coefficient, etc., exhibit improved performance over traditional chemical compounds for the conservation field [3,4]. The modulation of physical chemical properties of a protective coating (such as polymer based paints) can be obtained by a proper blending of the coating material with suitably chosen nanoparticles. This way, the developed nanocomposite can be accurately tailored to the different purposes required from the considered application [5].

The Technical Unit for Materials Technologies (UTTMAT) at ENEA possesses a consolidated knowledge in

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nanomaterials synthesis and characterization. The ENEA Technical Unit Materials Technologies (UTTMAT) possesses a consolidated knowledge in nanomaterials synthesis and characterization. In the Unit advanced diagnostic expertise and instrumentation [Scanning Electronic Microscopy (SEM), Transmission Electronic Microscopy (TEM), Optical Microscopy (OM), X Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), X Ray Fluorescence (XRF), Ultra Sound (US), Termogravimetry (TG), Differential Thermal Analyses (TDA), Raman spectroscopy, light scattering and N_2 adsorption at 77K to explore nanomaterials surface characteristics, zeta potential to measure nanofluid stability] are conjugated with nanopowder synthesis capabilities. Nanosized powders are obtained by conventional and unconventional methods, such as by precipitation from water, organic and micellar solutions or by laser pyrolysis from liquid precursors. Nanoparticles are usually obtained by mechanochemistry, inducing near-room-temperature solid state reactions by Ball Milling[1]. Furthermore, since 1984 diagnostic evaluations and in situ interventions on more than 1300 artworks have been performed by UTTMAT researchers. Paintings of Michelangelo, Raffaello, Leonardo, Antonello da Messina, Beato Angelico, Piero della Francesca, Tiziano, Tibetan thangkas, frescoes, wall paintings, mosaics, bronzes, mortars and stones have been characterized [6,7,8].
In order to evaluate the compatibility and durability of conservation materials and methodologies, we have conducted diagnostic analyses on cultural materials, studies on nanoparticles and nanocomposites appropriate for the cultural heritage field, and comparisons of methodologies and materials according to different environmental parameters (temperature, humidity, solar light and simulated aerosols).
In this technical report, the results from a study about polymer-based nanocomposites and about their efficiency in protecting stones frequently found in cultural heritage are reported.
White marble (statuary and veined Carrara, Proconnesio and Pentelic), travertine and biocalcarenite samples were considered as substrates on which the nanocomposites were tested. Before treatment, all specimens were aged with natural and/or artificial weathering. Two different commercial products: Paraloid B72, an acrylic resin (methylmethacrylate/ethylmethacrylate copolymer MA/EMA 30/70 w/w%) (sold by SINOPIA) and Rhodorsil RC80, a polyethysiloxane (produced by Rhodia Silicones), were chosen as polymers for this research. As nanoparticles, SiO_2, TiO_2 and their mixture were applied; they were synthesised by CO_2 laser pyrolysis of two liquid precursors, $Si(OEt)_4$ and $Ti(i\text{-}OPr)_4$, respectively, delivering on average a mean size around 15 nm with low polydispersity [9]. In general, the synthesis of nanocomposites to obtain a final homogenous dispersion is a tricky step, depending on the type of: chosen preparation method, solvent, and particles concentrations. In our case, several preliminary laboratory tests were carried out to obtain a homogenous dispersion, without formation of protruded aggregates. SEM micrographs were used to check the results with nanoparticles at different concentration (fig.1) and the selected dispersions are shown in Table 1.
To simulate a treatment, as it happens in a real situation, the obtained suspensions were applied on the surface of the stones by brushing until visible refusal and repeating the treatment after 4 hours [10].
The nanocomposite performance was tested after submitting all the specimens to accelerated weathering by artificial sunlight and freeze-thaw cycles. This step is very delicate due to the lack of specific standard practice or regulations (national or international) ruling the tests to assess the durability of the consolidant/protective materials. Only few regulations exist and for artificial solar irradiation, the NORMA UNI 10925-2011 – which concerns the methodology for artificial solar light test applied on natural and artificial stones – was applied. Following this standard method, a climatic chamber (SOLARBOX 1550 E) equipped with a xenon arc light source, 1500 W, with spectral range from 280 to 800 nm, was used and samples underwent constant irradiation at $1000 W/m^2$ for 556 hours. The irradiation time was sufficient to ensure $2000 MJ/m^2$, the specific irradiation conditions required by the above standard norm. For freeze-thaw resistance, due to the lack of any specific standard, the UNI EN 539–2 issued for tiles was applied. Tests were performed in

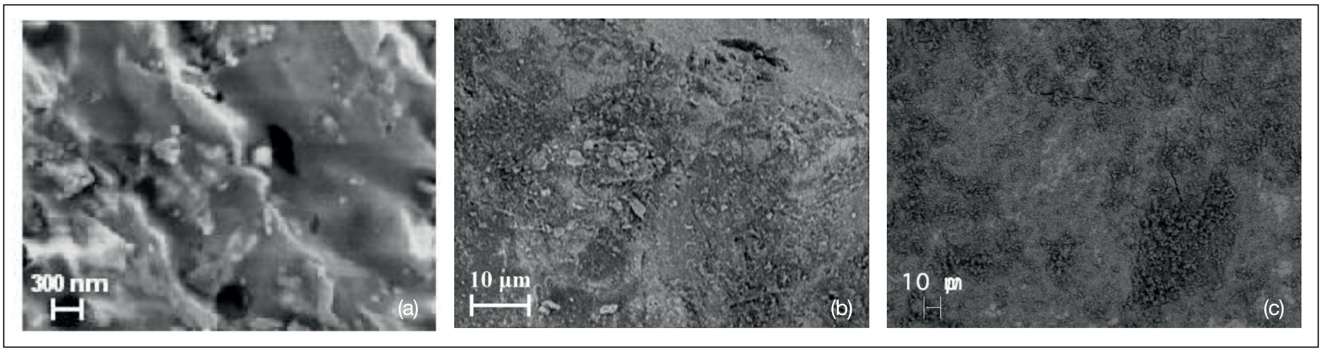

FIGURE 1 SEM images of statuary Carrara marble treated with Rhodorsil RC80 and 0.2% (a), 1% (b), 2% (c) w/v silica nanoparticles
Source: ENEA

an Angelantoni climatic chamber and samples were first immersed in water for 7 days until complete imbibition of water. About the artificial aging step, it is also possible to carry out other kinds of weathering processes simulating, for instance, the marine aerosol effect (hazard for outdoor stones), the temperature (T) and the relative humidity (RH) effects. In fact the aging processes to different environmental parameters (T, RH, sun, spray marine) must be done when a new chemical compound is commercialized. In particular, these kinds of qualifications are fundamental when considering works of art, where compatibility is a very important concept [11].
The consolidant and protective nanocomposite behaviour was tested checking some properties before and after the accelerated aging. With SEM micrographs it was possible to investigate the nanoparticle composite film morphologies and to evaluate the influence of nanoparticles on the integrity of surface coatings after the aging processes. The microstructural investigations were performed with a FEG-SEM LEO 1530 (Zeiss, Obercoken-Germany) equipped with

Polymer	Nanoparticles Concentration
RC80 and Paraloid B72	SiO_2: 1%
	TiO_2: 0,2%
	SiO_2 (0,2%) - TiO_2 (0,2%)
	SiO_2 (1%) - TiO_2 (0,1%)

TABLE 1 Final concentrations used to prepare the nanocomposites
Source: ENEA

In-lens secondary electron detector, conventional secondary electron detector and scintillation detector for backscattered electrons (Centaurus), and the higher magnification SEM image revealed that the nanoparticle aggregate morphology induces a micro- and nano-scale roughness at the surface of the films.
The wettability properties of the nanocomposite coatings were assessed by static water contact angle measurements to evaluate the local water repellence of the surface. The measurements were carried out through a home-made apparatus, in compliance with standard UNI EN 15802 – 2010 (Conservation of cultural property - Test methods - Determination of static contact angle). The measurements showed the increase in static water contact angle (θs) as a function of SiO_2 particle concentration for Rhodorsil and Paraloid B72 composite films. Fig. 2 shows the image of a water drop on a treated marble sample. The addition of both titania nanoparticles and silica and titania mixture gave comparable positive results for both kinds of investigated polymer coatings. These data suggest that nanoparticles induce a significant enhancement in hydrophobicity and impart highly water repellent properties to protective films. In particular, Paraloid B72 protective layers change their character from hydrophilic ($\theta s<90°$) to hydrophobic ($\theta s>90°$) surface [12].
The capability to protect stone materials was verified also by measurements of water absorption by total immersion. The absorption curve and the relative Imbibing Capacity (I.C.) was measured for

each sample by means of the gravimetric method. These results were used to calculate the protection ratio percentages, P.R.%, defined as the percentage variation between the imbibing capacity of untreated and coated stone, according to UNI Document 10921 (Natural and artificial stones – Water repellents – Application on samples and determination of their properties in laboratory). For both RC80 and Paraloid, the water absorption data have demonstrated the enhanced efficiency of nanoparticles for marble and travertine protection.

Ultrasound method (US), a non-destructive technique that measures the velocity of elastic waves through a solid medium, stones in our case, was also carried out to provide information concerning the effect of treatments on the mechanical properties (integrity and cohesion of the protective film on the stone surface) of the specimens. A portable instrument, a Krautkramer USM 23 with low frequency using a probe of 50 KHz through transmission method, was used and no sample preparation was necessary. Ultrasonic wave velocity was measured in all specimens in the three directions X, Y, and Z. For each direction, four values were recorded and the average was calculated. A thin layer of water was used as acoustic coupling medium between the stone and the transducer. The obtained measurements were processed by a home-made software, operating in Windows XP system and able to measure the propagation time in the tested sample. This time corresponds to the interval between the initial ultrasonic pulse and the instant at which the signal exceeds a threshold in amplitude. After the consolidation treatments all the samples showed an increase of ultrasonic velocity with respect to the untreated specimens due to the improvement of structural cohesion and mechanical resistance of marble and travertine substrates.

The US results for both marbles and travertines show a significant variation with siloxane treatment, while Paraloid B72 increase reached only 5% (Fig. 3). This effect can be attributed to the low penetration capacity of the acrylic resin, partially ascribed to its high macromolecular dimensions. For Rhodorsil RC80 dispersions, the best performances were recorded with the addition of the silica and titania mixture at the same nanoparticle concentration of 0.2% w/v (an ultrasonic velocity variation of more than 25% with respect to the pure siloxane application).

Finally, colorimetric measurements were executed to calculate colour changes induced by photochemical and photothermal degradation of nanocomposites. Colour values, reported in the CIEL*a*b* space, were obtained with a Minolta CM-

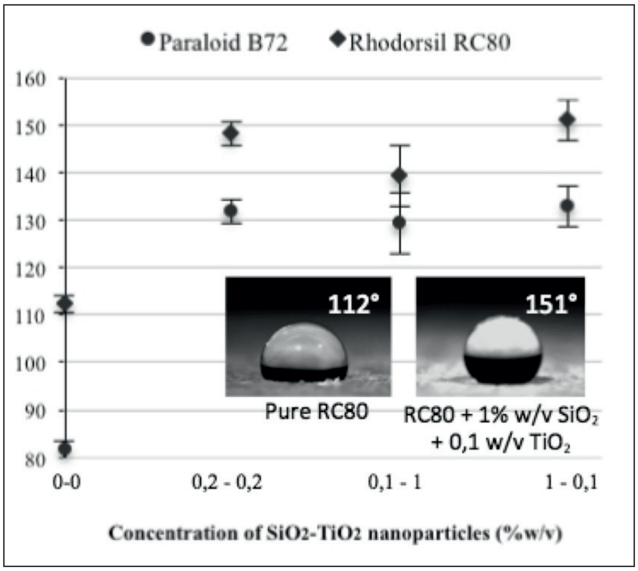

FIGURE 2 Static contact angle vs. concentration of SiO_2 and TiO_2 nanomixture
Source: ENEA

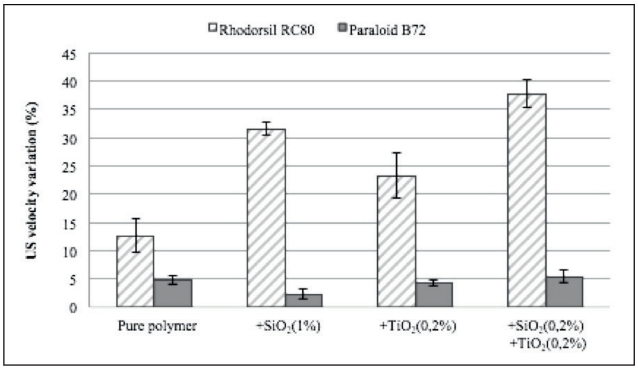

FIGURE 3 Ultrasonic velocity variation (%) in marble samples after the consolidation treatment
Source: ENEA

525i Spectrophotometer using a D65 illuminant. The colorimetric variations, measured before and after the accelerated aging processes, revealed that the optical surface alterations remain acceptable (ΔE value is always under 5).

The results show that some properties of conservation materials can be improved with the presence of nanomaterials. Research must be continued, mainly with respect to the reversibility and compatibility of the new products. Nanotechnology can be also applied to other kinds of cultural heritage materials, such as - for instance - the restoration of wall paintings, wood and paper [1].

Note

1. Mechanochemical technique allows, in particular, a low cost production of ferrites, coloured mixed metal oxides. Starting from the particle dimensions (≈ 5nm) of as synthesized material, nanoparticles size can be modulated by simple heating up to 100 nm and above, thus obtaining a color tone modulation.

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