Use of nanocoatings for the restoration of matte paintings

Carlotta Beccaria[1], Annalisa Colombo[2], Francesca Gherardi[3], Valentina Mombrini[1], Lucia Toniolo[3]

[1]Conservation studio Carlotta Beccaria, Milan, Italy, [2]CIFE Foundation, Milan, Italy, [3]Politecnico di Milano, Milan, Italy

Nanotechnology has been used with promising results for the conservation of cultural heritage. Nanotechnology completely modifies some properties of pure polymers, such as their gas permeability and mechanical or optical properties, by the introduction of apposite nanoparticles into the organic matrix to yield novel and innovative nanocomposite materials. For example, optical properties — such as ultraviolet (UV) and infrared absorption, light diffusion, and refractive index — can be improved and modulated by dispersing suitable nanoparticles in existing polymers, while preserving the transparency and flexibility of the material (Colombo *et al.*, 2010).

The present study reports on novel nanocoatings that are able to mimic the diffuse surface properties of matte painted surfaces. These have been obtained by exploiting the bulk scattering phenomenon created by the presence of nanoparticles with tailored optical properties (high refractive index and optical transparency in the visible range), suitably dispersed in a polymeric matrix. Three different coatings based on titanium dioxide (TiO_2) nanoparticles dispersed in poly(2-ethyl-2-oxazoline) (Aquazol 200®, CTS s.r.l.) were prepared, producing transparent nanocomposites that are notable for their tuneable optical properties (Colombo *et al.*, 2012). In particular, the films showed ultraviolet (UV) filtering up to the edge of the visible range and tailored refractive indices, up to about 1.67, controlled by the increasing concentration of nanoparticles in the polymeric matrix. Moreover, although the nanocomposite films were optically transparent, they showed a loss in transmittance attributed to Rayleigh scattering, due to the presence of nanoparticles clusters in the matrix. As it was possible to tune the amount of diffused light by changing the nanoparticle concentration in the polymer, a novel application of this material has been found for the treatment of matte artworks (Colombo *et al.*, 2015).

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Correspondence to: Carlotta Beccaria, Conservation studio Carlotta Beccaria, Via Conservatorio 30, 20122 Milan, Italy.
Email: beccaria.restauro@gmail.com

The optical performance of this material has been tested on a black acrylic monochrome painting, in order to simulate its application in the conservation of artworks. Fibre-optic reflectance spectroscopy (FORS) was used to measure the optical appearance of replica paintings after treatment with the nanocoatings, revealing that it is possible to match the reflective properties of the pristine painted surface by tailoring the number of nanoparticles in the polymeric matrix to produce the appropriate bulk scattering (Fig. 1).

The requirements of stability and reversibility of this material once cast onto painting models have been checked after two years of natural aging. Fourier transform infrared (FTIR) measurements showed a slight aging of the polymer revealing that, in natural indoor conditions, TiO_2 nanoparticles do not cause extensive degradation. This has been demonstrated for the naturally aged samples by dissolving the material with aqueous solutions of a non-ionic surfactant (TWEEN 20, CTS s.r.l.) and a weak chelating agent (tribasic ammonium citrate, CTS s.r.l). The removal efficacy was ascertained using FTIR and scanning electron microscopy with energy dispersive X-ray analysis (SEM–EDX) to study micro-samples collected from the painted surfaces, showing that almost complete removal of both the polymer and TiO_2 nanoparticles is possible.

The encouraging performance of the material has been exploited in the restoration of a white, inverted monochrome sculpture, created in the 1960s and attributed to Agostino Bonalumi (1935–2013). This artwork was realized using a canvas made of cotton fibres and phthalate polyvinylchloride (PVC), assembled on a wooden frame measuring $35 \times 35 \times 11.5$ cm. The coloured layer is characterized by the presence of titanium white as the pigment, kaolin as an extender and vinyl glue as the binder. The restoration process began with surface cleaning (Cremonesi & Signorini, 2004) and repair of an L-shaped tear (Borgioli & Cremonesi, 2005). Finally, the painting was retouched using Gamblin colours, particularly titanium white,

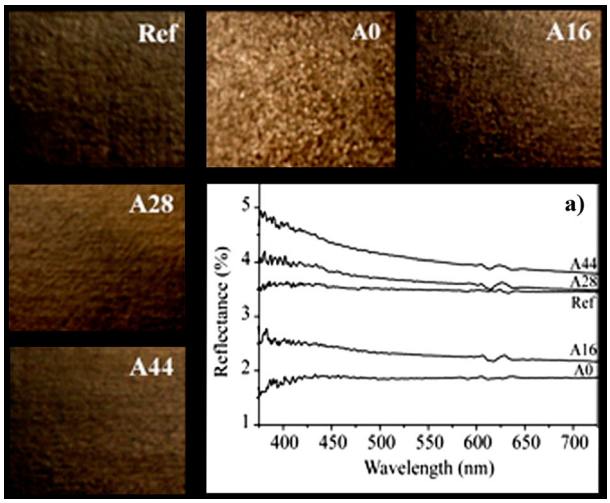

Figure 1 The black painted surface before and after the application of the coatings: pristine poly(2-ethyl-2-oxazoline) (C0); nanocomposite films with 16, 28 and 44 wt% TiO2 in the polymeric matrix (C16, C28 and C44, respectively). (A) FORS measurements.

with an aldehyde resin medium (Dunkerton, 2010). These were chosen in order to avoid any interactions with the nanocomposite consolidants that were used to preserve the matte appearance of the painting. In this case, the best result — from an aesthetic point of view — was obtained with a nanocomposite containing 40% by weight TiO_2 in the polymeric matrix. The material was applied with a brush using water as the diluent (Fig. 2).

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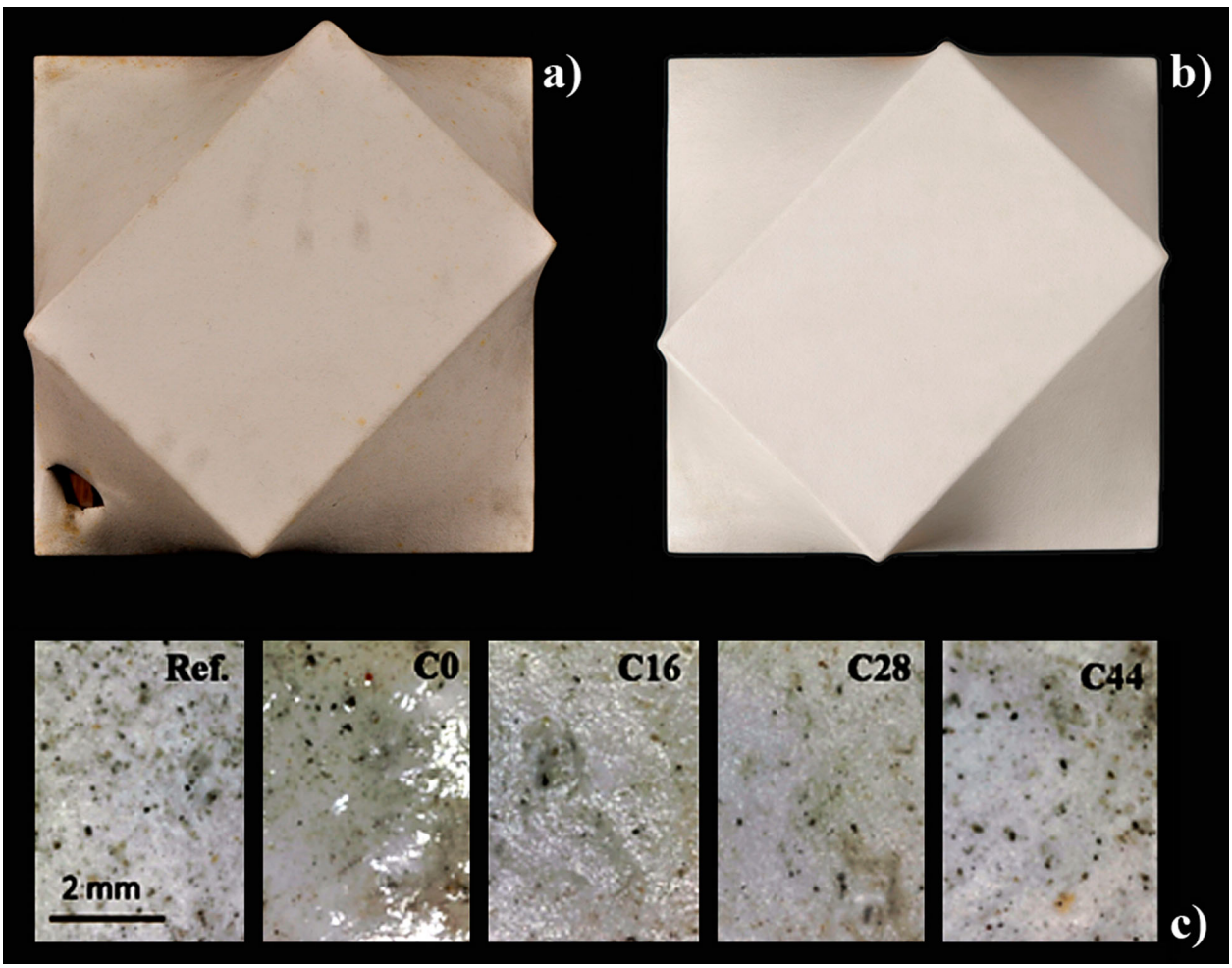

Figure 2 White monochrome painting seen from above: (A) before; (B) after conservation treatment; and (C) the treated areas viewed with a portable digital microscope.