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Protective properties and durability characteristics of experimental and commercial organic coatings for the preservation of porous stone

Carola Esposito Corcione [a], Nicoletta De Simone [b], Maria Laura Santarelli [b], Mariaenrica Frigione [a,*]

[a] Department of Engineering for Innovation, University of Salento, Lecce, Italy
[b] Department of Chemical, Materials and Environmental Engineering, University of Rome La Sapienza, Rome, Italy

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ABSTRACT

The application of hydrophobic polymers to stone materials is an effective way to preserve stone artefacts and protect Cultural Heritage from decay. To improve the characteristics and performance of water-repellent treatments, and to avoid the use of harmful solvents, innovative solutions have been widely explored. As recent examples, organic nano-filled photo-polymerizable systems were proposed as free-solvent efficient protective coatings for porous stones. In this paper, the nano-filled coating, based on a methacrylate mixture matrix optimized in previous studies, was applied on two calcareous stone substrates, typical of Apulia Region (*Pietra Leccese*, PL, and *Pietra Gentile*, PG). Its characteristic protective properties (in terms of water-repellency, chromatic modification, capillary water absorption, transmission of vapor water, penetration into the stone) were assessed and compared to the same characteristics displayed by two commercial organic water-borne hydrophobic coatings. Natural exposure and accelerated weathering tests were performed to estimate the long-term behavior of the coatings. The characteristic protective performance displayed by the experimental free-solvent photo-polymerizable coating was found greater than those recorded for the commercial organic products.

1. Introduction

The degradation of objects, monuments and buildings made by stone is a natural and irreversible process. The water ingress in stone is considered the main responsible of its degradation, especially for porous lithotypes [1]. Once water penetrates the stone, it can carry out its deleterious effects through: the chemical dissolution of the carbonate component of the stone; physical processes, such as freezing/thawing cycles, crystallization/precipitation of salts; biological degradation. Thus, to preserve objects, monuments and buildings made by stone from the natural decay, it is mandatory to limit the penetration of water into porous substrates. This can be achieved by applying a highly hydrophobic protective coating on the surface of the stone [2–4].

Any protective coating for stone, or for other inorganic substrates, must be: compatible with the substrate, water-repellent, capable to avoid the ingress of chemicals or other harsh agents, permeable to vapor water, transparent, durable and reversible or, at least, the surface where it is applied must be re-treatable [5–8].

Many are the examples of the use of either organic, natural or synthetic polymers, or inorganic protective coatings for the preservation of objects and structures made by stone [4,9]. Limited durability, modification of the structural properties of the stone and scarce physical-chemical compatibility with the substrate are often observed when organic materials treatments are used. Inorganic-based protectives, conversely, seem to have some advantages in terms of good durability and a greater compatibility with the stone substrate, but they usually are not able to penetrate sufficiently inside the stone resulting, thus, in a poor consolidating effect with respect to polymeric coatings [10].

Referring to organic products, acrylic and methacrylic monomers are typically employed to protect and consolidate stone objects and structures, due to the water repellence and the optically clear appearance of the coatings based on such polymers [11]. On the other hand, severe durability issues arise when such acrylic systems are used for the protection of stone objects and historical structures outdoor located. Furthermore, protectives based on acrylic resins exert a scarce adhesion to porous substrates and provide insufficient water drainage from

* Corresponding author.
E-mail address: mariaenrica.frigione@unisalento.it (M. Frigione).

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the coated surface [9]. Additional concerns refer to the use of solvents, possibly harmful, employed during the application of the resins. Finally, the curing (hardening) process of the coating takes place at ambient temperature with a consequent slow, and even possibly incomplete, development of the final properties.

In order to avoid the mentioned limits, water-borne silane-modified methacrylic resins and partially fluorinated acrylic copolymers have been also experimented. The polymerization reactions of such systems are generally initiated by free radicals produced by the decomposition of a peroxide, generated by IR lamps heat. In the case of the protection of large surface areas, this method is not applicable [9].

Novel and promising materials for the protection and conservation of the Cultural Heritage have been also provided by nano-technology. Recently, the application of inorganic nano-particles, incorporated or in situ formed inside a polymeric matrix, has been proposed by different scientists for the protection and/or consolidation of object and structures made by stone: several advantages were found also in this field by the inclusion of nano-sized multi-functional particles [10,12–19].

During the last years, the authors of the present paper have proposed different experimental, both unfilled and nano-filled, methacrylate systems for the protection of stone elements in the view to overcome the limits observed for acrylic based coatings [20–26]. In particular, a methacrylate monomer was modified with a methacrylate silane coupling agent to enhance its adhesion to the inorganic substrate. In addition, a high molecular weight polysiloxane unsaturated oligomer was used to enhance the hydrophobicity and properly modify the viscosity of the methacrylic-silane mixture; this latter was functionalized with a mercaptosilane in order to limit the inhibition effect of oxygen towards the free radical photo-polymerization reaction of the methacrylate resin [27]. A curing technique based on the exposure of the methacrylate resin mixtures to ultraviolet (UV) or visible radiations was proposed for the first time in the field of protection and conservation of Cultural Heritage [28]. The performance of the photo-polymerizable methacrylate mixture matrix was optimized with the addition of inorganic nano-sized particles, i.e. organically-modified boehmite nano-particles [21,29], or by the production of nano-structured O-I hybrid systems by the sol-gel method [24].

Boehmite nano-particles are colloidal plate-like crystals with a high anisotropy, consisting of double layers of oxygen octahedra partially filled with Al cations [30]. Their dispersion in water exhibits flow birefringence and thixotropy [31]. The same authors have been previously demonstrated that the presence of boehmite nano-particles does not influence the UV-curing reactions of the siloxane-methacrylic resin; furthermore, they are able to significantly improve the physical-mechanical properties of the polymeric matrix [29,32].

In this paper, an experimental photo-polymerizable nano-filled coating, previously developed, was applied on two typical Apulian carbonate stones.

The nano-filled formulation was already experimented as protective coating for the same stones selected in the present study, as reported in previous papers [25,26]. In those cases, however, the photo-polymerization reactions were activated by solar radiations, using a mixture of proper photo-initiators. It was found that the nano-filled formulation applied on the two porous stones was able to confer an excellent hydro-repellence character to the stone substrate, with an acceptable chromatic alteration. If on one hand, an additional advantage in that case was the use of a solar (natural) exposure to photo-polymerize the protective coatings, on the other, the use of UV-radiations as light source for the photo-polymerization of the nano-filled coating pose concerns about the influence of the environmental conditions (such as solar radiation, temperature and humidity levels, geographic location) on the performance of the coating. The use of solar radiations, furthermore, limits the application of such coating to outdoor.

The aim of the authors in the present paper was to compare the protective performance of the photo-polymerizable nano-filled coating with that displayed by two commercial products, used either in indoor or outdoor applications. In order to avoid the influence of environmental conditions on the results, the UV-radiation was selected as the only means to photo-polymerize the nano-filled coating applied on stone substrates.

After the identification of the more appropriate amount of the experimental product to apply on each kind of stone, the protective properties displayed by the novel coating were determined and, then, compared with those of two commercial water-repellent products, applied on the same stone substrates.

2. Experimental

2.1. Materials

2.1.1. Stone substrates

Two calcarenitic stones, known as "P*ietra Leccese*" (Leccese stone, PL) and "*Pietra Gentile*" (Gentile stone, PG) were selected in the present study. They are widespread employed in Apulian region (Italy) both in ancient and modern buildings and churches, as well as to realize statues and monuments. Although possessing a similar mineralogical composition, i.e. mainly composed of calcite (natural calcium carbonate, $CaCO_3$), they were selected on the basis of their different porosity. The experimental nano-filled photo-polymerizable system was, thus, applied on the two stone substrates and its protective characteristics assessed.

Leccese stone, PL, is extracted from quarries located in Salento area (Cursi-Lecce). It is whitish-yellow stone, composed of fossil fragments and numerous little grains of glauconite and phosphatic nodules. The size of bioclasts is around 150 μm and the micritic matrix is composed of clay minerals. Porosity, Φ (%) = 33.5 ± 0.5 [26],

Gentile stone, PG, also known as "*Pietra di Ostuni*", is extracted from quarries of Brindisi Area (i.e. Carovigno and Ostuni). It is composed of fossil seaweed residues and calcareous litoclasts (size 200 μm) in a micritic matrix with a small quantity of microsparitic cement. Porosity, Φ (%) = 21.9 ± 0.6 [26].

2.1.2. Experimental UV-cured nano-filled formulation

The organic nano-filled formulation was composed by: Trimethylolpropane trimethacrylate (TMPTMA, supplied by Cray Valley), as the main component for the coating; a trimethoxypropyl silane methacrylate monomer (MEMO, produced by Dow Corning), a coupling agent; a vinyl terminated polydimethylsiloxane (VT PDMS, supplied by Aldrich), to improve the water repellence of the coating; a 3-Mercaptopropyltriethoxysilane (MPTS, supplied by Aldrich), to reduce the effect of inhibition of oxygen towards radical photo-polymerization; diethylamine (DTA, again supplied by Aldrich) has been employed to aid the functionalization of VT PDMS with MPTS, obtaining a product indicated as mPDMS. Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (purchased by Ciba as IRGACURE 819) was selected as photo-initiator for the UV-cure. Finally, an organically modified boehmite (OMB, supplied by Sasol as Disperal-MEMO) was added to the organic mixture as nano-filler. The complete method to produce the mixture can be found in [27].

2.2. Preparation of the nano-filled coating

A detailed description of the procedure employed to produce the experimental liquid nano-filled formulation, whose composition is summarized in Table 1, can be found in a previous paper [22].