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Sunlight curable boehmite/siloxane-modified methacrylic nano-composites: An innovative solution for the protection of carbonate stones

C. Esposito Corcione, R. Manno, M. Frigione*

Department of Engineering for Innovation, University of Salento, Via Arnesano, 73100 Lecce, Italy

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ABSTRACT

The application of hydrophobic polymers to stone materials is an effective way to preserve stone artifacts and to protect them from decay. To improve the characteristics and performance of water-repellent treatments, and to avoid the use of harmful solvents, new solutions have recently been explored. As a recent example, a sunlight photopolymerizable siloxane-modified methacrylic formulation, containing organically modified boehmite (OMB) nano-particles, was developed and characterized. In this paper, the protective characteristics of the latter nano-composite product applied on stone were assessed. To this aim, different analytical techniques (contact angle, colorimetric and water absorption measurements, ESEM-EDS analyses) were employed to characterize the water-repellent sunlight-polymerizable coating applied on two calcareous stone substrates typical of Apulia Region (Leccese stone, PL and Gentile stone, PG). A theoretical model able to predict the pores radius of each stone after the treatment, was proposed and verified. The experimental results evidenced that the properties of the innovative free-solvent sunlight-polymerizable protective coating, in terms of hydrophobicity and durability, are excellent and comparable to those of the commercial products.

1. Introduction

Stone monuments, artifacts and bas-relief represent an important part of our cultural patrimony, and they are continually subject to deterioration due to physical, chemical, biological and air pollution factors. In particular, stone substrates undergo chemical weathering due to different processes such as freezing and thawing cycles, crystallization of salt solutions and interaction with atmospheric pollutants (e.g., SO_2 and acid rain), when exposed to outdoor conditions. The deterioration rate of stone materials is strictly related to porosity features that affect surface interaction with harsh environment agents, including water. In particular, stones characterized by high open porosity and by wide and highly accessible pores (e.g., bio-calcarenite) are susceptible to a quite fast decay if exposed to a potentially aggressive environment [1].

Stone protection in the field of Cultural Heritage represents, consequently, an intricate challenge, because of the difficulty to meet all the criteria required. An ideal coating should be efficient, stable, durable, transparent, easy to apply, not-toxic and removable. Moreover, the protective coating should guarantee a high level of hydrophobicity, considering that moisture and rain water represent the main causes of degradation mechanisms. Nevertheless, the coating must also allow the transpiration of the stone in order to avoid that the water already present in the substrate can cause further degradation [2].

Both organic and inorganic protective agents have been employed to preserve historical monuments, including many synthetic polymers. However, poor durability, drastic change of the stone structural properties and poor physical-chemical compatibility with the substrate are often associated to treatments carried out with organic materials. Inorganic products seem to have some advantages such as good durability and a physical-chemical higher compatibility with the stone components but, on the other hand, they usually give insufficient penetration and, consequently, a poor strengthening effect [1].

Referring to organic materials, polymers based on acrylic and methacrylic monomers are widely used for the protection and conservation of stone elements, due to their ability to form water repellent and optically clear coatings. They present, however, severe durability issues concerning the outdoor use of such systems for the long term protection of archaeological artifacts and historical buildings.

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

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In order to overcome these deficiencies, water-borne silane-modified methacrylic resins and partially fluorinated acrylic copolymers have recently been proposed [2]. The free radicals for the initiation of the polymerization reactions of such systems are generally produced by the decomposition of a peroxide initiated by the heat generated through infrared (IR) lamps. Thus, this technique is not suitable for the protection of large surface areas [3].

Nanotechnology has recently provided promising materials for the protection and conservation of the cultural heritage. As an example, different scientists have recently proposed the application of sub-micrometric inorganic particles for the protection and/or consolidation of stone materials [1]. In particular, Kim et al. [4] analyzed the effects of the presence of inorganic nano-particles in tetraethoxysilane (TEOS) and experimented commercial available silicic acid esters mixed with silica nano-sols. TEOS-based products show excellent properties: due to their very low viscosity, alkoxysilane monomers are able to penetrate deeply into porous stone.

Dei and Salvatori proposed a dispersion of calcium hydroxide nano-sized particles (slaked lime) in alcoholic medium as protective for limestone, such as Gallina (a soft calcareous sandstone) and Alberese (a more compact limestone) stones. They observed that the treatment with nano-metric calcium hydroxide strongly affects the kinetics of capillary suction of Gallina lithotype during the first 30 min, but only a slight decrease of water absorption was measured at longer times [5].

In a recent work, Licchelli et al. [1] analyzed the protective effectiveness of some inorganic nano-particles dispersions (silica, calcium hydroxide and strontium hydroxide) when applied on a highly porous stone substrate, i.e. Leccese stone. They observed that the kinetics of capillary rise is affected to a certain extent by the nano-composite treatments only during the first 30 min. At longer times, the capillarity coefficients of treated and untreated stone are almost equal.

D'Arienzo et al. [6] applied a nano-composite system, based on a commercial blend of fluoro-elastomers and acrylic polymers, to Neapolitan tuff stone (a calcareous stones characterized by high porosity of about 50%). They observed that the application of a polymeric nano-composite coating strongly reduces both capillarity coefficient and water permeability values of the untreated porous stone. A fluorinated polyurethane based on Perfluoropolyethers (PFPEs) has been recently proposed to prepare a water-based montmorillonite nano-composite displaying good anti-graffiti properties for porous stones [1,7].

The authors of the present study have proposed several original nano-stuctured organic and hybrid (i.e. organic-inorganic) products for the protection of stone elements aimed at overcoming the limits associated with the use of acrylic based coatings and those related to the curing (hardening) process through the use of alternative energy sources [8–15]. Referring to this latter aspect, an innovative method based on the exposure to ultraviolet (UV) and visible radiations was proposed for the cure of methacrylate resin mixtures [8], widely used as protectives for the protection of stone [16–18]. To the best of our knowledge, the photo-curing technology was never used for the hardening of protective coatings employed on Cultural Heritage artworks. While UV source is widely used for the curing of coatings, inks and even adhesives [19,20], no use of this technique has been made so far for the curing of protective coatings for stone. In addition, a proper modification of the selected methacrylate monomer was performed, employing a methacrylate silane coupling agent, to enhance the adhesion to the inorganic substrate, and a high molecular weight polysiloxane unsaturated oligomer, to increase the hydrophobicity and to modify the viscosity of the mixture. A functionalization procedure with a mercaptosilane was also proposed in order to reduce the inhibition effect of oxygen towards the free radical photopolymerization reaction of the methacrylate resin [12]. Then, an attempt to optimize the characteristics and the performance of the polymeric photopolymerizable matrix was pursued by adding inorganic nano-sized particles [11,21] or by producing nano-structured O-I hybrid materials by sol-gel method [15].

In particular, organically—modified boehmite (OMB) nano-particles were proposed by the authors as inorganic filler for the production of a nano-composite. The boehmite nano-particles are colloidal plate-like crystals with a high anisotropy. They consist of double layers of oxygen octahedra partially filled with Al cations [22]. Their aqueous dispersions exhibit flow birefringence and thixotropy [23]. It was demonstrated that the presence of boehmite nano-particles does not affect the kinetics of photo-polymerization reactions of the siloxane-modified methacrylic resin and, in addition, OMB particles are able to greatly improve the physical-mechanical properties of the polymeric matrix [21,24]. Since for some applications, such as the protection of construction materials [25], the use of UV lamp could represent a technological limit, the possibility of using sunlight radiations to activate the photopolymerization reaction in the boehmite nano-composite formulation, was recently verified. Excellent results of the surface properties of the coating, in terms of hydrophobicity, transparency and hardness properties, were found [25,26].

Later, other researchers explored the possibility to use UV–vis radiations for the activation of in situ reaction of proper monomers, mainly intended for the protection of stones. Tulliani et al. [27] developed a novel cycloaliphatic epoxy based system, able to photopolymerize through a cationic reaction process, for stone protection, with conservation criteria as the main goal. They added an appropriate amount of PDMS to the resin, as both hydrophobic and rheological control agent. The authors evidenced the advantages related to the use of a cationic photopolymerization process over the radical one, such as avoiding the oxygen inhibition and the use of monomers that are less toxic and irritant than the acrylic monomers in radical processes. However, the hydrophobic properties of the epoxy-based coating are scarce, if compared to those displayed by commercial products or by methacrylic based systems [15].

The aim of the present paper was, then, the assessment of the protective properties of the sunlight-curable methacrylic/boehmite based system recently developed [26] when applied on calcareous stone substrates typical of Apulia Region—Italy (Leccese stone, PL and Gentile stone, PG). To this aim, water transport properties, color change and durability efficiency of each stone treated with the novel product were investigated. A theoretical model able to predict the pores radius of the treated stone was, finally, employed and verified.

2. Experimental

2.1. Materials

Trimethylolpropane trimethacrylate (TMPTMA) was chosen as the main component for the coating, due to its high reactivity. The product used was supplied by Cray Valley.

A trimethoxypropyl silane methacrylate monomer, produced by Dow Corning as Z6030 and known as MEMO, was used as a coupling agent to enhance the adhesion of the coating to the stone substrate.

A vinyl terminated polydimethylsiloxane (VT PDMS), supplied by Aldrich, was added to the methacrylic mixture to enhance the water repellence of the coating.

A 3-mercaptopropyltriethoxysilane (MPTS), supplied by Aldrich, was added to the siloxane modified methacrylic resin system in order to reduce the effect of inhibition of oxygen