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Conservation of tuff-stone with polymeric resins

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Abstract

In this work, the experimentation of protective treatments on yellow and grey tuff-stones, characteristic materials of the historic buildings of Salerno (Italy), was performed. Tuff-stones, due to their high porosity, are often interested by damage phenomena from salt crystallization and other deterioration mechanisms mediated by water. As a consequence, they show a weak durability and require frequent maintenance and restorations. The study was carried out using several commercial polymeric resins, with different chemical composition, as protective coatings suitable for prevent water from entering into the porous material. In particular, siloxane, silicon and fluorinated resins, in solvent and/or in water solution, were considered. The protectiveness of the treatments was evaluated performing capillary absorption and total immersion tests and salts crystallization cycles, both on untreated and treated samples. Moreover, the hydrophobic properties of the surface were determined by static contact angle measurements on the treated samples. In order to estimate the over time effectiveness of the treatments, colorimetric measurements and UV weathering tests were also carried out. Finally, using the experimental data, a static durability indicator was calculated as proposed in the literature, in order to evaluate the effectiveness of each treatment on the potential durability of the treated tuff samples. On the whole, silicon resins in water solution represent the best choice for a protection treatment of tuff-stone, since they showed a good compromise among eco-compatibility, reduction of absorbed water, yellowing of the original substrate, weathering resistance after UV exposure.

Keywords: Tuff-stones; Water absorption; Rock durability index; Photo-oxidative weathering; Efficacy of protective treatments; Polymeric resins

1. Introduction

In the last years, in the field of Cultural Heritage, a great deal of attention was devoted to the use of polymeric substances for protecting and reinforcing incoherent materials. In particular, it was shown that the polymeric impregnation of a stone can reduce weathering of the treated material. Actually, a protective surface treatment, aimed to reduce the rate at which water and any pollutants transported by it infiltrate and move through a stone, can significantly enhance the durability of a stone material [1–3]. It is known, in fact, that water is the most aggressive factor responsible for weathering, because the deterioration mechanisms of building materials are largely mediated by it [4–7].

Nevertheless, different polymeric resins have been often employed as coatings in the conservation of stone materials without adequate knowledge of the polymer/stone system properties. As a result, either insufficient protection efficacy, poor weatherability, or both, were usually observed. Polymeric materials, in most cases, can strongly reduce water permeability of treated stones, arising, as a consequence, interstitial condensation or water vapour originating inside a building. Moreover, polymeric materials could provide short-term water repellence of the coated surface, and could be unstable in photo-oxidative conditions typical of outdoor exposure [8–14].

The most widely used materials for the protective treatments of a stone are silicone and siloxane resins, acrylic resins and fluorinated polymers. Silicon and siloxane resins

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are among the first synthetic polymers used for waterproofing masonry and preservating historic and artistic monuments. The advantage of silicone-based treatment is due to the fact that these polymers render the impregnated material water repellent but not water-proof [1,4]. The acrylic resins, on the other hand, had a fast development in the field of Cultural Heritage due to their remarkable transparency, clarity and weathering characteristics. Furthermore, they resist sunlight, heat and adverse weather conditions quite well even if over long times their protective action cannot be satisfactory [9,13,14]. In the last years, in order to improve the outdoor stability of acrylic polymers, fluorinated ones from acrylic monomers were prepared. Moreover, fluorinated polymers are under experimentation because up today they did not result in the expected improvement of the coating properties [8,10–12].

In the literature, a lot of papers evidence that the new impregnation products, as well as those which already exist, must be viewed with caution and be subjected to laboratory research before they can be used on historic buildings [15–17]. At the present time, specific evaluations on synthetic resins in terms of durability over time have not always been carried out; such evaluations could provide a good safety margin for the integrity of the repair works. Moreover, few studies are reported on the modifications of the intrinsic properties of the stone due to the impregnation with polymeric resins.

In this work, the experimentation of protective treatments on tuff stone by using of different polymeric products was performed. Tuff stone is a volcanic rock that crops out over large parts of central-southern Italy; it usually displays a huge variability in the lithological features within the different outcrops. Campania's architecture has been characterized for centuries by the use of the local tuff stone as a building material, as it is shown by its presence in numerous Greek and Romans ruins [18]. The most commonly used lithotypes are the Neapolitan Yellow Tuff (NYT) in the Neapolitan area, and the Campanian Ignimbrite, either in the grey and yellow *facies*, mainly used in Salerno area [19]. Since the historic centre of Salerno is located near the coast, materials in buildings are interested by marine aerosol and transport phenomena of salts [20–22].

Tuff stone, due to its high porosity, has a weak durability. Therefore, it requires frequent maintenance and restorations, which are often carried out without a deep knowledge of its weathering mechanisms and compatibility with materials for conservation. Despite the in-depth studies on the characteristics of the tuff stone, only few works were aimed at using that knowledge to choose and successively apply the best treatment to slow down the deterioration processes of masonries. So, these repair interventions have had often given very unsatisfactory results.

In this study, in order to evaluate the features of the original substrate, yellow and grey tuff-stones, coming from the areas that provided building materials for the historic centre of Salerno, were submitted to a preliminary chemical, physical, mechanical and microstructural characterization. This step was of fundamental importance because the lithotypes of tuff stone coming from the different quarries of Campania region can show a huge variety of composition and properties. After, in order to achieve a first evaluation of the polymeric protection effectiveness, capillary absorption and total immersion in water tests and salts crystallization cycles were repeated on untreated and treated samples. Moreover, static contact angle measurement on treated samples were conducted to evaluate the surface water repellence. Finally, quantitative colorimetric measurements and UV exposure tests have been performed with the aim to estimate the over time effectiveness of treatments. In the last part of the work, a semi-empiric equation proposed in the literature [23] to assess the durability of the original and treated stone will be tested using the obtained experimental data.

2. Experimental

2.1. Materials

The study concerned yellow (YTQ) and grey (GTQ) tuff-stones coming from quarry located in Comiziano (NA), near Salerno, and on some commercial polymeric materials, having water repellent properties, used as protective agents for the tuff stone material.

The commercial polymeric resins analyzed were reported in Table 1. Stone samples were treated with polymers by paint-brushing, according to the suggestions reported in the technical sheets of each resin.

2.2. Methods

Mineralogical and morphological characterization was carried out both by means of X-ray powder diffraction analysis (Philips PW1710, Cu Kα + Ni filtered radiation, 2θ range from 5 to 50°, step size 0.03°/2θ and 5 s counting time per step) and SEM observation (Assing mod. LEO 420).

The pore-size distribution was measured by means of a mercury porosimeter Autopore III 9420 Micromeritics. Tests and data evaluation were performed according to the Italian Recommendation NORMAL 4/80 [24]. In particular, the mercury pressure range was from 1.50 to 60,000 psi. The pore diameter (d) was measured in μm and the "integral open porosity" P [%] was determined using the following formula:

$$P\,[\%] = 100\frac{V_{\mathrm{Hg}}}{M}\rho_{\mathrm{s}} \quad (1)$$

where V_{Hg} is the volume of mercury penetrated into the sample, M and ρ_{s} mass and bulk density of the analyzed stones, respectively.

The amount of water absorbed (Q) as a function of time (t), on both treated and untreated stones, was measured according to the Italian standard UNI 10859 [25]. The