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Original article

Consolidation of Vicenza, Arenaria and Istria stones: A comparison between nano-based products and acrylate derivatives

Giulia Gheno [a], Elena Badetti [b,*], Andrea Brunelli [b], Renzo Ganzerla [a], Antonio Marcomini [b,*]

[a] DSMN, Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Scientific Campus, Via Torino 155, 30172 Mestre, VE, Italy
[b] DAIS, Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Scientific Campus, Via Torino 155, 30172 Mestre, VE, Italy

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ABSTRACT

Nano-based formulations are emerging as successful materials besides the use of conventional products for the consolidation of carbonate works of art e.g. stone, mortars or mural paintings. In this work, the physico-chemical characteristics, performances and consolidation efficacy in terms of external appearance of commercial NanoRestore $Ca(OH)_2$ and NanoEstel SiO_2 dispersions were investigated and compared with two commercial acrylates derivatives, Acril 33 and Acril ME. The colloidal stability of the different consolidants was investigated by dynamic light scattering (DLS) and centrifugal separation analysis (CSA) techniques. As expected, acrylate emulsions showed a higher colloidal stability than the inorganic nanoparticle dispersions, with sedimentation velocity from 10^{-4} to 10^{-2} μm/s. The examined consolidants were applied on three different stones, widely used in historical buildings in Venice: Vicenza, Arenaria and Istria stones, representing macro-, meso- and microporous materials, respectively. The absorption capacity, color and gloss variation of the different stone materials were comparatively evaluated after the consolidants application. An accordance among porous structure of the substrates, hydrodynamic particle size and amount of consolidants absorbed was observed for nano-based formulations. The weathering resistance under natural and UVB aging conditions were also investigated for the consolidated stone samples, and recorded as changes of color, gloss and surface morphology. NanoRestore and NanoEstel showed the best performances under the natural aging while the UVB irradiation seemed to not induce significant modification in the surface morphology of the treated stone samples.

1. Introduction

The persistent exposure to the combined action of natural weathering and anthropogenic pollution over time can cause several damages to lime- and silica-based porous materials used in both artworks and architectural manufacturing. Air pollution, the presence of soluble salts and biodeteriogens [1–5] can induce flaking of the surface layers, powdering, formation of small blisters and loss of large area of the artefact [6,7]. In this context, one of the main challenges in conservation and restoration field is the use of compatible consolidants, which can avoid deterioration without altering the main characteristics of the stone materials restored. Furthermore, the durability of the treatment and the long-term stability of the consolidated substrates should be ensured [8–15].

In the field of stone conservation, calcium hydroxide is one of the most promising products suitable for consolidating calcareous materials (e.g. stone sculptures, monuments or wall paintings) because it is converted into calcium carbonate as a result of carbonation, when exposed to atmospheric CO_2 under moist conditions. $Ca(OH)_2$ is generally applied as a saturated aqueous solution, however, due to its low solubility, large amount of solution is needed. Consequently, the treatment of stone materials with large amounts of water could be detrimental to porous matrices, favoring the pore collapse through freeze–thaw cycles and the transport of soluble salts [16]. Additional drawbacks are the incomplete conversion of calcium hydroxide into calcium carbonate, as well as the post treatment chromatic alteration and the low penetration depth [17]. Moreover, the stability of aqueous $Ca(OH)_2$-based dispersion is not always ensured, although few exceptions are reported in literature [18]. Fast clustering and sedimentation of the hydroxide particles can in fact occur, with scarce penetration and veiling of the treated surface [19].

To enhance the consolidant performances of $Ca(OH)_2$, engineered nanomaterials (ENM) based formulations have been developed [20]. In detail, dispersions of $Ca(OH)_2$ nanoparticles (NPs) in water or short-chain alcohols have been largely studied to establish their potential use for consolidation of limestone and carbonatic painted surfaces [16,21–23], wood [24], paper and

* Corresponding authors.
E-mail address: elena.badetti@unive.it (E. Badetti).

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canvas deacidification [25], as well as for archaeological bones treatment [26]. The nano-size of the particles eases the penetration of the product through porous substrates and increases the particle reactivity with respect to CO_2 by turning into calcium carbonate. Several methodologies of $Ca(OH)_2$ NPs synthesis have been reported [27–32], and the related formulations showed different features like degree of dispersibility, particle size distribution and particle structure, which are expected to affect the consolidation process. Literature studies showed that $Ca(OH)_2$ NPs dispersed in short-chain alcohols exhibited a higher colloidal stability than using water as dispersant, significantly improving the degree of consolidation by decreasing agglomeration rate of particles [21,33,34].

As far as silica-based stones consolidation, commercial products containing alkoxysilanes, such as tetraethoxysilane (TEOS), are commonly used [35]. These products, polymerizing in situ via a sol-gel process within the porous structure of the stone to be consolidated, increase the mechanical properties of the materials. However, they can form a dense microporous network of gel that tend to become brittle and susceptible to cracking. Moreover, this network can obstruct the porous of the materials promoting a significant reduction of water permeability [36]. To improve consolidation performances, nanosilica-based products were synthetized by a template synthesis in which a surfactant was used as structure-directing agent during the polymerization process. Following this procedure, silica nanoparticles with uniform size and ordered mesopores were obtained. The presence of surfactants avoids the cracking of the gel during the drying phase because of a coarsening of the gel network that reduces the capillary pressure [37,38]. Furthermore, the advantage of using nanosilica-based product with respect to the traditional solvent-based TEOS is the non-hazardous solvents employed and the reduced time necessary to obtain the gel network. In this case in fact, the hydrolysis step is skipped and the film is formed by condensation of the silica NPs. On the other hand, the capability of silica nanoparticles to penetrate porous materials with respect to the solvent-based silica product have not been jet deeply investigated [39].

Acrylic resins have also been largely used in conservation practice. They are thermoplastics copolymers based on monomers derived from acrylic and methacrylic acid. Depending on the ratio of the monomers, it is possible to structure a resin with specific molecular weight and physico-chemical characteristics [40]. During the early 1930s, acrylic polymers started to be used as picture varnishes because of their initial resistance to yellowing, their solubility in hydrocarbons solvents, their ability to form flexible and transparent films and their glass transition temperature, preventing the dirty pick-up. Unfortunately, these resins resulted unsuitable for long-term uses, due to the unexpected cross-linking, cracking and yellowing exhibited when the polymers were exposed to natural light [41]. At the end of the 1940s, a more stable acrylic resin system was introduced with the commercial name of Paraloid. This acrylic polymer applied in solution was recommended for a wide range of applications, such as textile, wood and pigments consolidants, as adhesives for paper and, due to its hydrophobicity, as consolidant and water repellent for stones [42]. In particular, Paraloid B72, a copolymers of methyl methacrylate and ethyl acrylate [P(MMA/EA)] soluble in organic solvents, showed an improved stability at different aging conditions [43,44]. After their application, transparent films are formed by coalescence of the particles in the dispersion. In the last years, the growing attention towards human health and environment has led to water-based emulsions safer than the original formulations.

In this context, four different stone consolidants NanoRestore, NanoEstel, acrylic-based emulsion Acril 33 and micro emulsion Acril ME were investigated. The physico-chemical characterization of the commercial suspensions was performed by means of dynamic light scattering (DLS) and centrifugal separation analysis (CSA). The consolidants were then applied on three different stones, i.e. Vicenza, Arenaria and Istria stone that are representative of macro-, meso- and microporous materials. These stones have been selected for their abundance in architectural decorative apparatus of numerous venetian palaces and churches such as the Basilica of San Marco and Palazzo Ducale [45]. To the best of our knowledge, the application of consolidants on these stones is still scarcely investigated, as well as their use on historic surfaces which is still limited and mainly confined to scientific research [46,47]. Before the application step, Brunauer-Emmet-Teller (BET) analysis was carried out to evaluate the specific surface area and the total pore volumes of the three different stone materials. Afterwards, the consolidated stones samples were investigated under natural aging and laboratory test conditions, i.e. UVB aging. In fact, it is recommended to run both accelerated and natural aging tests in parallel to accurately evaluate materials durability [21]. Stereomicroscopic measurements were carried out to observe the variations in the physical and morphological characteristics of the treated surfaces, while colorimetric and gloss [48] measurements were performed to evaluate the chromatic variations which can occur on the surfaces after the consolidation treatments due to natural and artificial aging. Beside the consolidation effectiveness, the knowledge of the aesthetic variations occurring on historic surfaces treated with different consolidants after aging is of interest for a large community of end-users (e.g. architects, curators, conservators). Moreover, only few studies have been focused on the effect of venetian environment on weathering of the stone investigated [49,50]; with still a lack of knowledge on their consolidation and aesthetic surface variations before and after aging testing.

2. Experimental

2.1. Materials

All the commercial products tested were provided by CTS (Altavilla Vicentina, Italy). NanoRestore is a 2-propanol dispersion of $Ca(OH)_2$ NPs (5 g/L solid concentration). NanoEstel is an aqueous colloidal dispersion of nano-sized silica (solid content 30%) stabilized with sodium hydroxide (NaOH < 0.5%). Acril 33 is an aqueous emulsion (solid content 46%) of ethylacrylate and methylmethacrylate copolymer while Acril ME is a water based micro emulsion (solid content 41%) of the polymer poly(butyl methacrylate).

Vicenza, Arenaria and Istria stones $5 \times 5 \times 2\,cm^3$ were provided by Laboratorio Morseletto (Vicenza, Italy), with a porosity of approx. 27, 5 and 0.7%, respectively, which confirmed data already reported in literature [51–53]. Vicenza stone is a light ivory calcareous rock, principally composed by calcite and dolomite, extracted from the Oligocene horizons in Colli Berici (Vicenza, Italy). It is the result of the sedimentation of innumerable minute fossils, which create its texture. Arenaria is a clastic sedimentary rock composed mainly by sand-sized minerals or rock grains with a dark grey color. Istria stone is instead a sedimentary compact rock with a micritic structure and a whitish color, formed during the lower Cretaceous. According to their features, the stones types described above have been extensively used as building materials in venetian architectures.

2.2. Nano-based and acrylates consolidants characterization

The dispersion stability of each consolidant was carried out by dynamic light scattering (DLS) and centrifugal separation analysis (CSA). Hydrodynamic particle diameter was measured by DLS by means of a multi-angle Nicomp ZLS Z3000 (Particle Sizing System, Port Richey, FL, USA) with an optical fiber set at 90° scattering angle