

Article

Removing Aged Polymer Coatings from Porous Stone Surfaces Using the Gel Cleaning Method

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Abstract: Acrylic polymers were extensively used in past restoration practices, usually as consolidants or protecting agents. Their removal is often required because polymer coatings can improve some decay processes of stone substrates and, after ageing, may generate undesirable materials on the surface of artifacts. Therefore, the removal of old polymer coating from the surface of artifacts has become a common operation in the conservation of cultural heritage. As with other cleaning operations, it is a delicate process that may irreversibly damage the artifacts if not correctly carried out. The main aim of this study was to determine the appropriate cleaning procedure for efficiently removing old acrylic polymers (e.g., Paraloid B-72) from the surface of historical buildings. For this purpose, a polymer was applied to two different porous stone substrates (bio-calcarenite and arenaria stone). The hydrogel cleaning approach was used for the present study, as preliminary results suggested that it is the most promising polymer-removing method. The considered hydrogel (based on a semi-interpenetrating polymer network involving poly(2-hydroxyethyl methacrylate) and polyvinylpyrrolidone) was prepared and characterized using different techniques in order to assess the gel's properties, including the gel content, equilibrium water content, retention capability, hardness, Young's modulus, and morphology. After that, the hydrogel was loaded with appropriate amounts of nano-structured emulsions (NSEs) containing a surfactant (EcoSufTM), organic solvents, and H₂O, then applied onto the coated surfaces. Moreover, plain EcoSufTM in a water emulsion (EcoSuf/H₂O) was also used to understand the polymer-removing behavior of the surfactant without any organic solvent. A comparative study was carried out on artificially aged and unaged polymer-coated samples to better understand the cleaning effectiveness of the considered emulsions for removing decayed polymer coatings. The experimental results showed that the NSE-loaded hydrogel cleaning method was more effective than other common cleaning procedures (e.g., cellulose pulp method). In fact, only one cleaning step was enough to remove the polymeric material from the stone surfaces without affecting their original properties.

Keywords: gel materials; characterization; polymer coatings; eco-friendly surfactant; nano-emulsions; cleaning process; SEM-EDS; micro FTIR-mapping



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1. Introduction

Cultural heritage includes artifacts, monuments, and buildings that have a diversity of values, including symbolic, historic, artistic, aesthetic, ethnological or anthropological,

scientific, and social significance. It includes tangible heritage (movable, immobile, and underwater), intangible cultural heritage embedded in culture, and natural heritage artifacts, sites, or monuments. Hence, the conservation of cultural heritage, particularly of tangible elements, is a common operation to maintain their original structure against degradation processes [1,2]. Cleaning, i.e., removing undesired materials from the substrate surface, is an essential step of the conservation process. It represents a delicate operation because, if is not correctly performed, it may irreversibly damage the heritage [3]. The undesired materials to be removed from the surfaces of artifacts may include deposits of pollutants, grime or dirt, soil materials, and aged polymeric coatings (and related degraded materials) applied in previous conservative interventions. Synthetic polymers have been widely used in past restoration practices, usually for consolidation and/or protection purposes. The removal of aged polymeric and other undesired materials without damaging the substrates and preserving their original properties is a challenging task [3]. A traditional methodology involves the use of organic solvents and a cleaning intervention based on mechanical action or solubilization processes. This method has many drawbacks such as poor selectivity, health and environmental risk, uncontrolled penetration, alterations of the substrate's original properties, and re-deposition of the undesired materials inside the pores of the substrate [3–6]. In order to overcome these problems, water-based nano-structured materials have been proposed for removing old coatings [4,5,7–9]. For instance, nano-emulsions (NSEs) can be used as an alternative to non-confined organic solvents. They are water-based fluids containing small amounts of organic solvents dispersed as nano-droplets, which are stabilized by the addition of a surfactant. Due to the nanometric size of the solvents/surfactant droplets and their consequently large surface area, the cleaning effect can be significantly enhanced [4].

There are different methods to apply nano-structured emulsions for removing undesired coating and related materials: they can be placed into direct contact with the surfaces to be treated, or they can be supported on proper transporting mediums, e.g., cellulose pulp poultice or hydrogels. In a previous work, we thoroughly investigated and discussed the cleaning performances of the direct contact method as well as the cellulose pulp poultice method [10]. In the present work, we mainly focused on the hydrogel method. In the last decades, scientists have introduced physical gels in which a cross-linking process is obtained via non-covalent interactions, (i.e., xanthan gum, gellan gum, agar, chitosan, sodium alginate-calcium) and chemical gels based on covalently cross-linked polymers (e.g., polyacrylamide gels) [3,11–13]. The chemical gels had better performances than the physical gels due to their good mechanical properties, well-defined shape, and swelling properties [3,14–17].

The main aims of the present study were the synthesis, characterization, and application of a gel material that could load water-based cleaning systems, particularly nano-emulsions. Such a hydrogel would behave as a suitable transporting medium of NSEs for removing aged polymer coating from stone artifacts. For this purpose, a semi-interpenetrating polymer network involving poly(2-hydroxyethyl methacrylate) and polyvinylpyrrolidone was selected and synthesized following a method reported in the literature [18]. Poly(2-hydroxyethyl methacrylate), often crosslinked with N,N-methylenebisacrylamide (HEMA-MBA copolymer), has been used as main component of various hydrogels due to its good biocompatibility, and it has found different applications including drug delivery systems, porous sponges, and the manufacturing of soft contact lenses and artificial corneas [19–24]. Moreover, in combination with the highly hydrophilic polyvinyl pyrrolidone (PVP) [25], a HEMA-MBA copolymer was used to make hydrogels that displayed excellent properties and suitability for the preparation of cleaning tools for cultural heritage items. In particular, highly retentive hydrogel materials based on this polymeric matrix were prepared and used in the cleaning of different water-sensitive substrates [3]. Nevertheless, the effectiveness of the HEMA-MBA copolymer/PVP hydrogel in the removal of aged coatings from stone artifacts has been poorly explored [4].

The properties of the investigated hydrogel were studied in detail using different techniques to verify its suitability for cleaning applications, including its gel content, equilibrium water content, retention capability, hardness, Young's modulus, and morphology (via SEM observations). Moreover, the properties were compared with well-known agar gel. To our knowledge, a full characterization of this type of hydrogel has not been reported elsewhere.

The cleaning effectiveness of the NSE-loaded hydrogel was tested for the removal of an aged acrylic polymer (e.g., Paraloid B-72) that was widely employed in the past for restoration processes [26–34] from the surface of two different stone substrates (a bio-calcarene and an arenaria stone). Cleaning tests using the same hydrogel loaded with an emulsion containing only the surfactant were also carried out for comparison. For the present study, Lecce stone (LS) was used as the bio-calcarene, which has been highly employed for different buildings and artifacts in the south of Italy, especially in the Puglia region during the Baroque period [35–39]. Due to its high open porosity (>30%), and high content of calcite (~95), it has been facing many deterioration problems compared to other stone materials [1,35]. The considered sandstone is an arenaria (AS, mainly composed of SiO₂ and silicates) used as a building material (e.g., palaces and churches) mainly in the surroundings of Pavia (North Italy). The magnificent façade of the San Michele Maggiore church (XI century) and other representative buildings in Pavia were made using this Arenaria stone. It is a soft stone with a low surface cohesion and high open porosity (around 15%) that shows a heterogeneous morphology because of its chemical composition. Due to its heterogeneous structure and high open porosity, this sandstone is also affected by many decay problems [10,40].

Previous restoration interventions performed on LS and AS using synthetic polymer materials have badly affected the stone substrates (strong variation in the original surface properties, water capillarity and vapor permeability reduction, alterations in surface wettability) [5]. As the old coatings must be removed prior to any new possible conservation action, i.e., consolidation using a more appropriate material [1,35,41], investigations on suitable methods for the removal of the aged polymer materials are highly desired.

In order to investigate the decayed polymer cleaning process as in the real cases, polymer-treated specimens were exposed to artificial ageing cycles (up to 35 days) at a high temperature (inside an oven, 70 ± 2 °C), corresponding to more than 50 years of natural ageing of the polymer material [5,42]. The cleaning ability for the aged polymer samples (12, 25, and 35 days) of a hydrogel loaded with two different emulsions (different chemical proportions of surfactant, organic solvents, and water) was evaluated using different experimental techniques. Chromatic variations and the surface wettability were determined to evaluate the effects of the cleaning process on the original stone properties, while the surface morphology and cross-sectional properties were studied using an optical microscope and SEM (scanning electron microscopy). Moreover, the EDS (energy dispersive X-ray spectra) technique was used to obtain semi-quantitative analyses of the stone substrate before and after the cleaning process. Finally, the presence of possible residual coatings or any other organic residue on the stone surfaces after cleaning was examined using micro-FTIR (ATR mode) spectroscopy and mapping experiments.

The experimental results showed that the investigated cleaning tool based on the NSE-loaded hydrogel was able to efficiently remove the old polymer coatings from the surface of the very porous stones. Therefore, it can be considered as a promising alternative to other traditional cleaning methods (e.g., cellulose pulp, agar gel) for the conservation of stone cultural heritage items.

2. Materials and Experimental Methods

2.1. Chemicals and Lithotypes

The selected polymer material was Paraloid B-72 (100% acrylic resin, Bresciani s.r.l., Milan, Italy). Nano-emulsions were prepared using the surfactant (ECOSURF™ EH-6, C₈H₁₈O·(C₃H₆O)_x·(C₂H₄O)_y, non-ionic surfactant, Sigma Aldrich, St. Louis, MO, USA)

and the organic solvents 2-butanol (purity 99% BuOH, C₂H₅CH(OH)CH₃, Fluka Chemicals, Buchs, Switzerland) and 2-butanone (purity 99%–101% CH₃C(O)CH₂CH₃, BDH Chemicals Ltd., Poole, UK). Ethyl acetate (ACS reagent, purity ≥ 99.5% CH₃COOC₂H₅, Sigma Aldrich, St. Louis, MO, USA) was used for preparing the polymer solution. The HEMA-MBA/PVP hydrogel was synthesized using different chemicals: 2-hydroxyethyl methacrylate (HEMA, CH₂=C(CH₃)COOCH₂CH₂OH, Sigma Aldrich, St. Louis, MO, USA), N,N-methylenebisacrylamide (MBA, (H₂C=CHCONH)₂CH₂, Sigma Aldrich, St. Louis, MO, USA), polyvinylpyrrolidone (PVP, (C₆H₉NO)_n, Sigma Aldrich, St. Louis, MO, USA), and α,α'-azobisisobutyronitrile (AIBN, (CH₃)₂C(CN)N=NC(CH₃)₂CN, purity 98%, Sigma Aldrich, St. Louis, MO, USA). Agar (Agarose, 3,6-Anhydro-α-L-galacto-β-D-galactan, Sigma Aldrich, St. Louis, MO, USA) was used to compare the properties of the synthesized hydrogel. Water was purified using a Millipore Organex system: R ≥ 18 M cm (Burlington, MA, USA).

One month before the coating application, the stone samples were cleaned according to the standard method (UNI 10921 Protocol) [43]. In brief, Lecce stone (LS, supplied by Tarantino and Lotriglia, Nardò, Lecce, Italy), and Arenaria stone (AS, taken from a quarry in Monte Arzolo, Province of Pavia, North Italy) samples (5 cm × 5 cm × 1 cm and 5 cm × 5 cm × 2 cm) were smoothed using abrasive carbide paper (No: 180 mesh). After that, they were washed with deionized water, dried in an oven at 60 °C, and stored in a desiccator until they reached room temperature. The dry weights of the samples were recorded every day until they were constant [44].

2.2. Synthesis of the Hydrogel

The HEMA-MBA copolymer/PVP hydrogel was synthesized according to a modification of a method reported in the literature [18]. A resistant, transparent, and highly retentive semi-interpenetrating polymer network was created by embedding PVP into a poly HEMA hydrogel network. In a typical preparation, PVP and water (25.1 and 57.9% *w/w* of the final mixture, respectively) were accurately mixed in a round-bottom glass flask until a solution was obtained. Then, a mixture made of 2-hydroxyethyl methacrylate monomer (HEMA) and a N,N-methylenebisacrylamide cross-linker (MBA) was prepared (16.8 and 0.2% *w/w* of the final mixture, respectively) and added to the PVP aqueous solution. Nitrogen (N₂) gas was passed through the resulting solution for some minutes to remove the oxygen, then a radical initiator α,α'-azoisobutyronitrile (10⁻² mol with respect to the HEMA) was added into the reaction mixture. After that, the mixture was gently sonicated in an ultrasonic bath for 30 min to eliminate gas bubbles. In order to complete the polymerization reaction, the mixture was heated to 60 °C for 4 h under a nitrogen atmosphere. Then the resulting gel was separated and washed several times with distilled water. It was stored in water in a beaker, and the water was replaced every day (up to 7 days) to remove the unreacted materials.

2.3. Characterization of the Synthesized Hydrogel

Several experimental analyses were performed to study the properties of the synthesized hydrogel material. Moreover, some of the properties were compared with the agar physical gel.

2.3.1. Gel Content

The gel content (G) was calculated according to the following equation [18,45]:

$$G (\%) = (W_d/W_0) \times 100 \quad (1)$$

where W_d is the dry weight of the synthesized hydrogel and W_0 is the weight of the starting components (i.e., HEMA and PVP for the investigated material) in the initial reaction mixture.

2.3.2. Water Content and Release Capacity

The equilibrium water content was determined according to Equation (2) [18,45]:

$$(EWC) \text{ EWC} = [(W_w - W_d)/W_w] \times 100 \quad (2)$$

where W_w is the water swollen hydrogel (at least 7 days immersed in water) and W_d is the dry weight of the hydrogel as previously indicated.

The retention capability (RC; capacity of releasing water) was calculated considering a gently dried (vacuum dried at 25 °C for 1 h) fully swollen gel sample (about 12.5 cm² and 2 mm thickness gel film). It was kept on a filter paper (five sheets of Whatman®) inside a covered petri dish. The sheets were weighed before applying the gel and after 30 min from the application. The retention capability was obtained based on the weight difference with respect to the surface area of the gel film, as indicated in Equation (3). The solvent-releasing capacity was calculated similarly.

$$RC = (W_{wf} - W_{df})/SA \quad (3)$$

Here, W_{wf} is the weight of the wet filter paper due to the releasing of water from the gel film, W_{df} is the dry weight of the filter paper, and SA is the surface area of the gel film.

2.3.3. Rheological Properties

The mechanical properties (compression strength and Young's modulus) of the HEMA-MBA/PVP hydrogel were measured, compared with physical gel (agar), and examined considering their possible relationship with the texture, the durability, and the usability of the gel materials. All the considered measurements were performed on the prepared gels without drying them. The considered gel samples were prepared in cylindrical molds (30 mm × 30 mm, diameter × height) and were subjected to a compression test using a TA.XT plus Texture Analyzer (Stable Micro Systems, Godalming, UK) equipped with a 5 kg load cell and a P/10 measuring system consisting of a cylindrical probe with a diameter of 10 mm [46–48]. The probe was lowered with a test speed equal to 1.00 mm/s in order to determine a 70% sample deformation. The following parameters were determined: (a) hardness; that is, the maximum compressive force per unit area required for sample destructuring; (b) Young's modulus (YM), calculated as the slope of the tangent at the first part of the compressive stress–strain curve. Stress–strain curves were also produced. Three replicates were carried out for each gel. The experimental values of the various types of measurements were subjected to statistical analysis, which was carried out using the statistical package Statgraphics 5.0 (Statistical Graphics Corporation, Rockville, MD, USA). In particular, a *t*-test was carried out to evaluate whether the difference between the mean of the two groups was statistically significant.

2.4. Preparation of Coated Stone Specimens

Polymer coatings were applied to the considered lithotypes in a similar way as previously reported [10]. In brief, commercially available Paraloid B-72 was dissolved in ethyl acetate to prepare a 10% (*w/w*) polymer solution, which was then applied to the LS and AS specimens. In particular, one half of each specimen surface (half of the available surface, 2.5 cm × 5 cm) was treated with the polymer solution (600 µL) using a small pipette, and the other part was kept without any treatment and used as a reference surface. Some stone specimens were fully coated and used for specific analyses. The treated samples (LSPB, and ASPB) underwent different ageing cycles in order to obtain artificially weathered coatings before testing the removing ability of the emulsion-loaded hydrogel as in the real cases. In the artificial ageing process, the coated specimens were divided into three groups, which were then stored in an oven (70 ± 2 °C) for 12, 25, and 35 days, respectively. Some coated samples were kept without exposing them to ageing cycles for comparison with the aged samples and were named as unaged LSPB and ASPB.

2.5. Preparation of Nano-Structured Emulsions and Application of the Emulsion-Loaded Gels

After completing several preliminary trials, two different emulsions were chosen with different compositions (*v/v* ratio): (i) EcoSurf/H₂O: H₂O 95.0%, surfactant (ECOSURF™ EH-6, non-ionic surfactant) 5.0%; (ii) NSE: H₂O, 65.9%, surfactant, 3.5%, BuOH, 9.7%, and butanone 20.9%. The NSE was prepared according to the literature [4] and analyzed using dynamic light scattering (DLS) using a MALVERN ZS90 apparatus (Malvern Panalytical Private Limited, Malvern, UK) to assess the dimensions of the droplets in the emulsion [49]. The emulsion was well mixed, and a small portion (1 mL) was placed into the plastic stub. The measurements (time = 10 s) were performed at 25 °C. The analysis was repeated three times in order to obtain an accurate measurement.

The prepared emulsions were loaded in the synthesized hydrogel before being applied to the surfaces of the stones. Thin hydrogel films (2 mm thickness) were properly cut to fit the area of the treated specimen surface (about 12.5 cm²). The correctly shaped hydrogel films were gently dried (vacuum at 25 °C for 1 h) and then immersed into the envisaged emulsion (NSE or Ecosurf/H₂O, 2.1 mL) for 24 h. Then, they were applied to the surface of the stone specimens to be cleaned for 15 min. After removing the gel film, the stone surface was gently cleaned using a wet cotton swab to remove any possible residues. This procedure was performed on three samples of each specimen group to collect accurate results.

The cleaning performances of the emulsion-loaded hydrogel were evaluated using different analyses, as reported in Section 2.6.

2.6. Instrumental Techniques

A Nicolet iN10 Thermo Fischer μ FT-IR spectrometer was used to collect micro-FTIR spectra in attenuated total reflectance mode (ATR, germanium crystal, Thermo Fisher Scientific, Waltham, MA, USA) and to perform μ -FTIR mapping experiments on the cleaned stone surfaces. A total of 64 scans were collected for each spectrum.

Chromatic variations after ageing and after the cleaning processes were evaluated using a Konica Minolta CM-2600D spectrophotometer (Konica Minolta, Inc., Tokyo, Japan) considering the L*, a*, and b* coordinates of the CIELAB space and the global chromatic variations, expressed as ΔE^* according to the UNI EN 15886 protocol [50]. In order to obtain accurate results, 15 different measurements (3 specimens for each kind of sample and 5 measurements on each specimen) were performed, and the average values were determined as recommended in the literature [44,51].

The contact angle measurements on the treated surfaces as well as after the ageing and cleaning processes were performed using a Lorentzen and Wettre instrument (Zurich, Switzerland) according to the UNI EN 15802 Protocol [52]. A total of 15 different measurements of each group of samples were used to calculate the average values, as previously reported [53].

The morphological features were observed using optical microscopy using a light polarized microscope Olympus BX51TF equipped with the Olympus TH4-200 lamp (Olympus Corporation, Tokyo, Japan) and using scanning electron microscopy (SEM) using a TESCAN FE-SEM apparatus (MIRA XMU series, TESCAN, Brno, Czech Republic). The elemental composition of each material (semi-quantitative analysis) was determined using energy dispersive X-ray spectrometry (EDS) using a Bruker Quantax 200 instrument (Bruker, Billerica, MA, USA) combined with the SEM apparatus. The SEM-EDS instrument operated at both low and high vacuum settings and was located at the Arvedi Laboratory, CISRiC, University of Pavia, Pavia, Italy. The gel samples were examined after drying in a vacuum at room temperature (20 ± 2 °C).

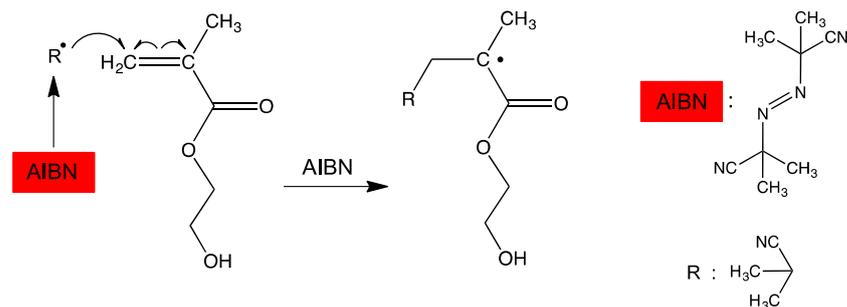
3. Results and Discussion

3.1. Characterization of the Synthesized Hydrogel

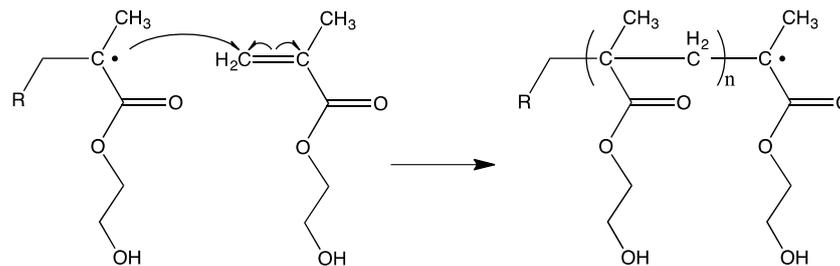
A semi-interpenetrating hydrogel network was created by synthesizing the HEMA-MBA copolymer in the presence of linear PVP polymer chains, as reported in Scheme 1. The

copolymer was synthesized via free radical polymerization with α,α' -azobisisobutyronitrile (AIBN) as a radical initiator. It is known that the HEMA monomer and MBA cross-linker react very fast in the presence of radical initiators due to their double bonds [54–58]. On the contrary, no reactivity is expected for PVP in these experimental conditions, and it only interacts via H-bonds contributing to the interpenetrated structure. The synthesized hydrogel was washed very well with water and stored for up to 7 days in water in order to remove any unreacted substances. It appeared as a soft and transparent gel material, whose properties were investigated using different techniques, as mentioned in the experimental section.

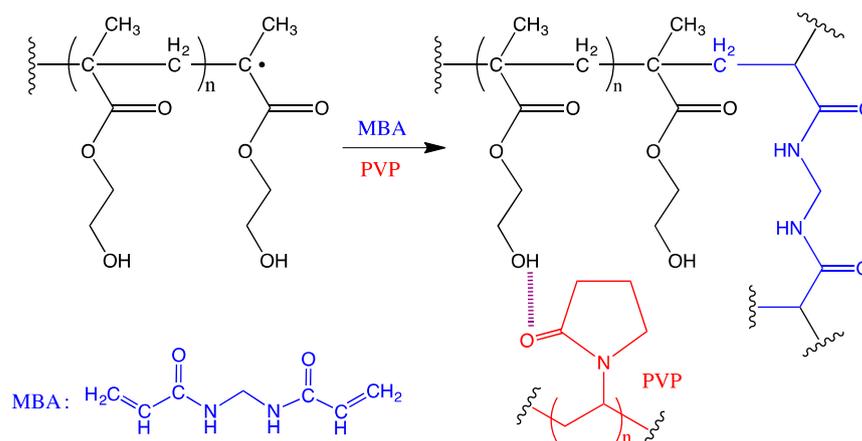
Initiation:



Propagation:



Crosslinking and gelation:



Scheme 1. Reaction steps of the synthesis of the HEMA/MBA/PVP hydrogel.

The gel content, the equilibrium water content, and the retention capability are summarized in Table 1 and compared with the corresponding properties of agar and other commonly used gels. Investigating the equilibrium water content (EWC) as well as the capacity of water release (RC) of the hydrogel is very important, especially when its application concerns the cleaning of water-sensitive substrates. The EWC and RC values determined for the HEMA-MBA/PVP hydrogel (81%, and 13 mg/cm², respectively) were similar to those already reported [3]. Both parameters were distinctly lower than the agar

gel (used as a reference) and other common hydrogels (see Table 1). The lower values of water content and water release displayed by the HEMA-MBA/PVP material were more acceptable, considering its possible use for the cleaning of water-sensitive artefacts. In particular, the amount of released water for the agar gel was more than double with respect to the HEMA-MBA/PVP material. The RC values reported for Kelcogel or acrylamide (soft) were even larger (Table 1) [3].

Table 1. The physicochemical properties of the HEMA-MBA/PVP copolymer compared to other common hydrogels [3].

Samples	Gel Content (G, %)	Equilibrium Water Content (EWC, %)	Retention Capability (RC, Water Released, mg/cm ²)
HEMA-MBA/PVP ^(a)	76 ± 5	81 ± 2	13 ± 2
Agar ^(a)	-	95 ± 2	28 ± 2
Acrylamide (soft) ^(b)	88	97	56
Kelcogel ^(b)	-	97	33

^(a) This work. ^(b) from ref. [3].

After being left to rest in cylindrical molds and stored at 4 °C, the HEMA-MBA/PVP and agar gels were subjected to a compression test. An evaluation of the gels' mechanical properties is useful to deeply investigate the gels' inner microstructures and to investigate their durability and usability. Figure 1a shows that the hardness of the HEMA-MBA/PVP gel, measured as its resistance to compression, was slightly higher than the agar gel, although the observed differences were poorly significant from a statistical point of view. On the contrary, the two materials displayed a strongly different behavior when their Young's modulus values were considered. In Figure 1b, the compressive strength vs. strain profiles of the two specimens are reported. It can be observed that the agar gels and HEMA-MBA/PVP hydrogel were characterized by completely different mechanical behaviors when they were subjected to a uniaxial compressive force: the former showed a fracture zone (peak stress) at low strain values [59], while the latter exhibited a delayed fracture only at the higher level of the considered strain range. Therefore, the agar gel appeared to be more brittle, quickly breaking down, with respect to the HEMA-MBA/PVP hydrogel, which instead showed a longer duration without easy de-structuring [6,59–61]. Based on these experimental data as well as the literature data, agar was not considered for the preparation of the emulsion-loaded hydrogels to be applied to the removal of the aged coatings on the stone substrates.

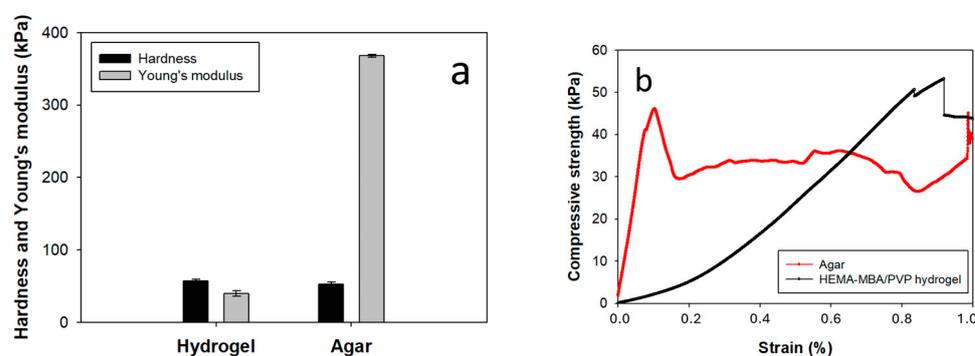


Figure 1. (a) The hardness and Young's modulus values of the HEMA-MBA/PVP hydrogel with respect to the agar gel (mean values ± S.E.; $n = 3$); (b) Stress–strain graphs of the considered gels.

The SEM micrographs of the HEMA-MBA/PVP material reported in Figure 2 show the porous structure at a microscopic level. The EDS analysis confirmed the presence of nitrogen due to the PVP component, in addition to carbon and oxygen, which are the most abundant elements, as expected for the organic nature of the polymer.

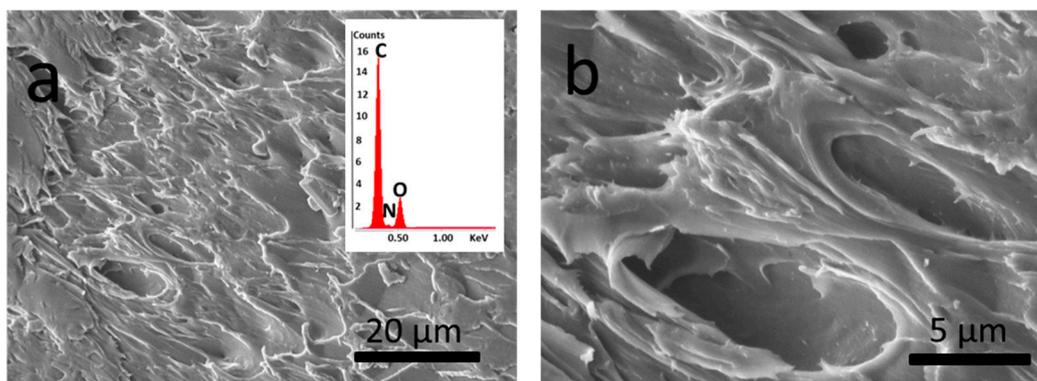


Figure 2. SEM images of the HEMA-MBA/PVP hydrogel with different magnifications (a,b). EDS spectrum in the inset.

3.2. Characterization of the Aged Polymer (Paraloid B-72) Coating

The polymer-coated stone specimens (LS and AS) were exposed to artificial ageing cycles, as explained in the experimental section, before investigating the cleaning ability of the gel-supported emulsions towards the artificially weathered polymer, which could be considered representative of naturally aged protective coatings on artifacts. The coated LS and AS specimens were artificially aged at different extents (0, 12, 25, and 35 days at $T = 70 \pm 2 \text{ }^\circ\text{C}$) in order to correlate the cleaning effectiveness with the ageing degree of the polymer. The Paraloid B-72 ageing process was thoroughly investigated and reported in a previous paper [10]. In particular, the prolonged exposure to the artificial ageing conditions affected the physical appearance and the texture of the polymer coating, inducing color darkening (Figure 3), gloss decrease, and the partial loss of adhesion to the substrate. The effects of ageing were quite different on the two examined stones, most likely due to the distinct features of the original substrates. In any case, these property variations indicated that polymer decay, involving changes in its structure and chemical composition, occurred during the ageing process (both artificial and natural). The variations were particularly evident in the most aged samples. It should be noted that 35 days of ageing in an oven under the above-mentioned conditions could correspond to 50 years of natural ageing [5,42].

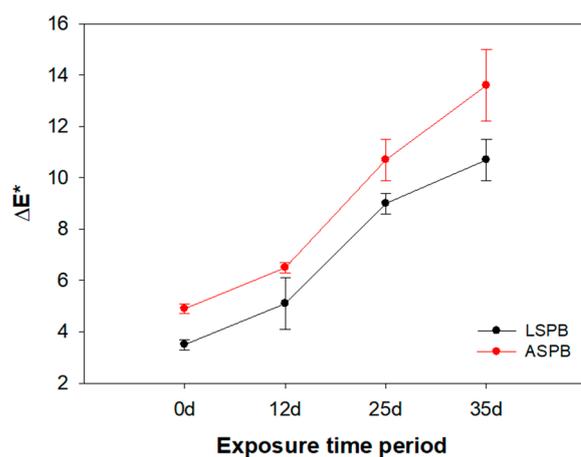


Figure 3. Overall chromatic changes (ΔE^*) observed on the coated stones before and after the ageing cycles (variations compared to uncoated/natural surfaces).

3.3. Cleaning Performances of the Loaded Hydrogels

Prior to loading them into the hydrogels, the nano-structured emulsions were analyzed using DLS in order to evaluate their droplet sizes. The analysis showed that 99% of the droplets contained in the NSEs had a size ranging between 90 and 120 nm (average size: $110.5 \pm 6.3 \text{ nm}$, Figure S1). As reported in the literature, nano-sized droplets induce an

improvement in the emulsion cleaning effectiveness [4]. Thin films of hydrogel loaded with emulsions (EcoSurf/H₂O and NSE) were used to test their ability to remove polymer coating from the surfaces of the LS and AS. The films (thickness of about 1 mm, area of about 12.5 cm²) were applied to the coated stone specimens as described in Section 2.5. After removing the gel films from the surfaces, they were gently cleaned using a cotton swab to remove any possible residue. An initial naked-eye observation could determine the different behaviors of the two cleaning systems (Figure 4). In fact, the Paraloid B-72 coating seemed to be completely removed from both stones using the NSE-loaded hydrogel system, as can be clearly seen in Figure 4 (LSPB_NSE and ASPB_NSE). Meanwhile, in the other case, the polymer coating was still present on the stones' surfaces.



Figure 4. Coated LS and AS before and after exposure to the cleaning process using two different emulsions (EcoSurf/H₂O and NSE). For each specimen, the vertical bar demarcates the coated area (**left**) and the area treated with the emulsion-coated hydrogel (**right**).

To better characterize the surfaces of the LS and AS after the application of emulsions-loaded hydrogels, more investigations were performed using different experimental techniques, such as optical microscopy, SEM-EDS, chromatic and wettability measurements, and micro-FTIR (ATR mode).

3.3.1. Optical and Electron Microscopy

The morphological and micro-structural changes induced by the cleaning process on the coated stone specimens were examined using optical microscopy and SEM-EDS experiments. The OM images after the polymer removal process from the LS surface are reported in Figure 5 and Figure S2, while the corresponding images for the AS are reported in Figures S3 and S4. Images taken of the original stones and the coated stones before cleaning are also reported in both cases for comparison. After the application of the NSE-loaded hydrogel, the removal of the polymer coating from the Lecce stone surface appeared to be complete, regardless of the ageing degree (0–35 days ageing) of the considered specimens (Figure 5e,f and Figure S2e–h). On the contrary, residues of the polymer coating could be still observed on the surface of all the LS specimens (both unaged and aged) after the application of the hydrogel loaded with the EcoSurf/H₂O system, indicating that the emulsion prepared without using any organic solvents displayed distinctly lower cleaning

performances than the NSEs (Figure 5c,d and Figure S2a–d). Similar results were obtained after carrying out the cleaning procedure on the AS specimens. The Paraloid B-72 was exhaustively removed both from the unaged and aged specimens (Figures S3e,f and S4e–h) after the application of the NSE-loaded hydrogel, while EcoSurf/H₂O was poorly effective, even on the arenaria specimens (Figures S3c,d and S4a–d).

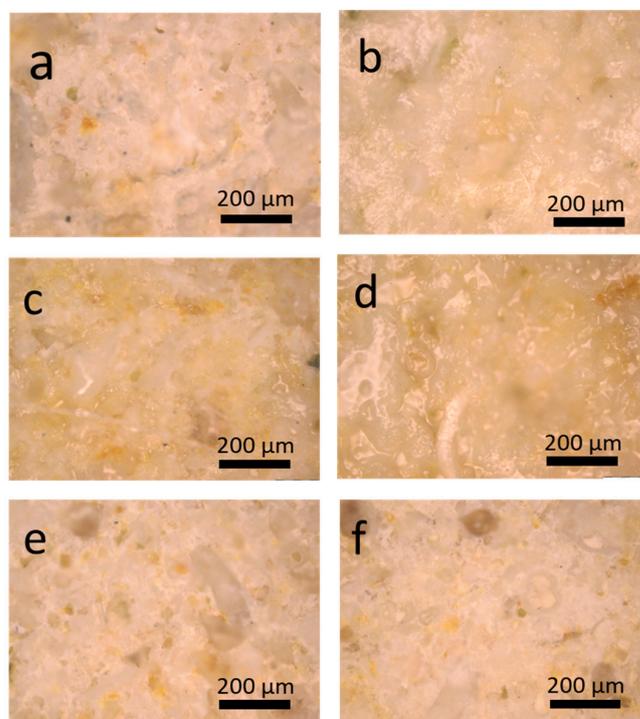


Figure 5. Optical microscope images of LS: (a) original/natural LS; (b) coated LSPB before cleaning; (c) unaged LSPB; (d) 35 d aged LSPB cleaned using EcoSurf/H₂O; (e) unaged LSPB; (f) 35 d aged LSPB cleaned using NSE.

The polymer removing process was further investigated via SEM-EDS analyses both on the surface and on the cross-section of the stone specimens. The results were used to understand the morphological, micro-structural, and compositional changes that occurred in both lithotypes due to the hydrogel cleaning process. The SEM-EDS experiments were performed on unaged and 35-day-old specimens, as well as on plain and coated-uncleaned stones for comparison. Observations of the aged specimens were particularly considered because they were closer to real cases in which naturally weathered polymer coatings need to be removed during conservative operations.

The microphotographs taken of the LS specimens and the corresponding EDS spectra are reported in Figure 6. The cleaning system EcoSurf/H₂O/hydrogel showed a very poor ability to remove the Paraloid B-72 coating (both unaged and 35-day aged) from the LS surface, confirming the results obtained via OM. In fact, the stone surface after the application of this hydrogel (Figure 6c,d) appeared to be quite similar to before the cleaning system was applied (Figure 6b). The polymer material can be clearly observed over the stone matrix. On the contrary, the NSE-based cleaning system was able to completely remove the polymer layer from the LS specimens, and the cleaned surface displayed the almost the similar morphological features to the original uncoated LS (Figure 6e,f). Moreover, no polymer residues could be observed on the stone surface (e.g., inside the pores).

The behavior of the emulsion-loaded hydrogel cleaning systems was also investigated via EDS measurements. The EDS spectra acquired for the uncleaned and cleaned LS specimens are reported in the insets of Figure 6. They show a drastic decrease in carbon content on the surfaces of the stone specimens that were cleaned using the NSE-containing hydrogel compared to the uncleaned surfaces due to the satisfactory removal of the organic

coating. At the same time, an increase in the calcium content was observed on the cleaned surface because the main component of the LS (calcium carbonate) was no longer covered by the organic layer. Also, peaks corresponding to the minor components of LS (Mg, Al, Si, P) can be observed in the EDS spectra taken after the cleaning process (insets of Figure 6e,f), and the overall elemental composition was very similar to that of the plain LS (inset of Figure 6a). The EDS spectra taken after the application of the hydrogel loaded with EcoSurf/H₂O displayed an almost unaltered content of carbon and only a small increase in the calcium content with respect to the uncleaned specimen surface, suggesting that the polymer removal (if any) occurred only at a low extent.

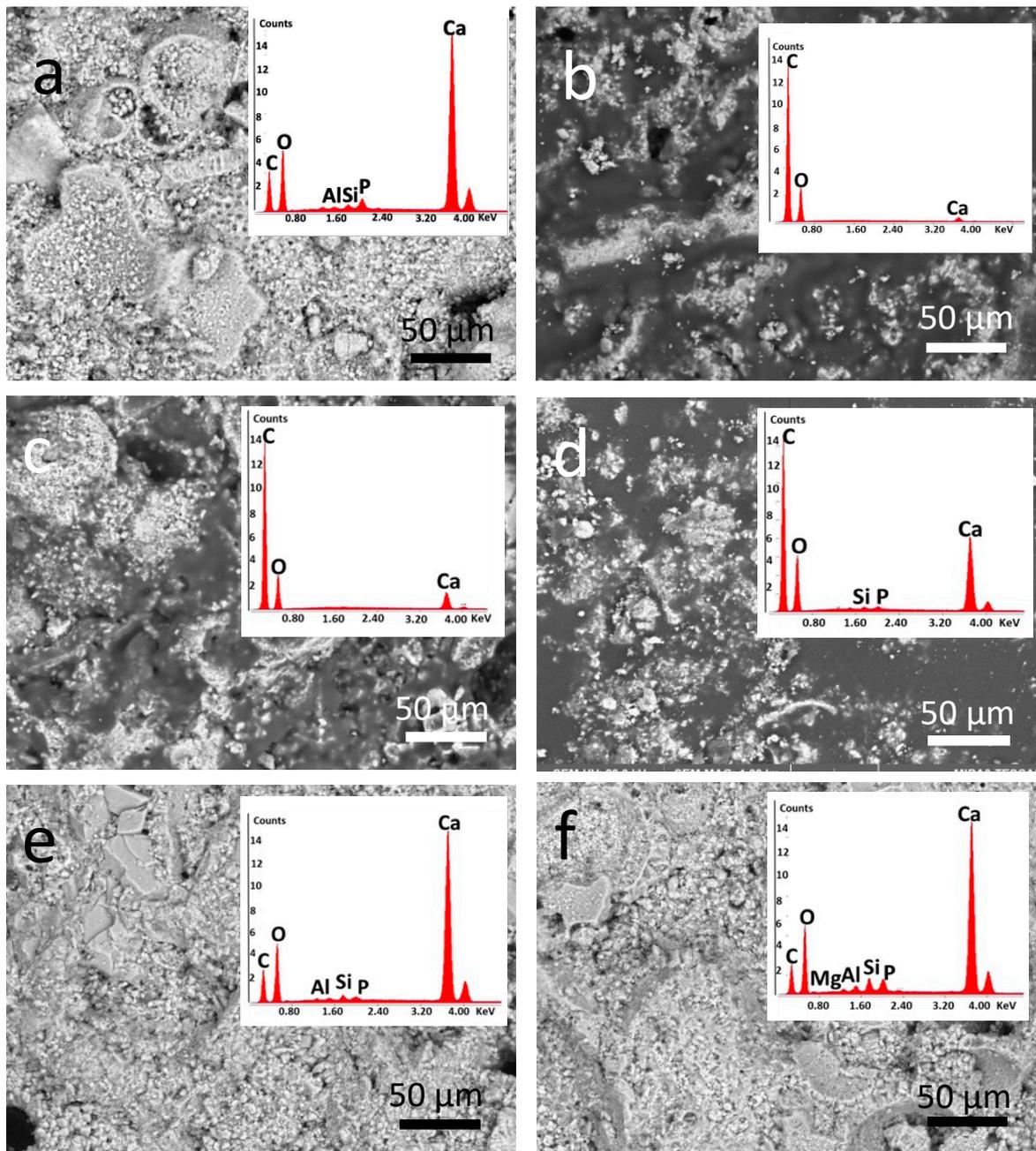


Figure 6. SEM images of the LS surfaces: (a) original/natural LS; (b) coated LSPB before cleaning; (c) unaged LSPB; (d) 35 d aged LSPB cleaned using the EcoSurf/H₂O hydrogel; (e) unaged LSPB; (f) 35 d aged LSPB cleaned using the NSE hydrogel. Corresponding EDS spectra are reported in the insets.

Similar results were obtained via the SEM-EDS experiments performed on the AS specimens. The homogeneous coating surfaces on the arenaria were not (or very poorly) affected by the cleaning procedure involving the EcoSurf/H₂O-hydrogel system, while the original appearance of the AS surface was completely recovered after the cleaning performed using the NSE-hydrogel system (Figure 7). In this case too, a drastic reduction in carbon content was observed after cleaning using NSEs, and the elemental composition was very similar to the original arenaria stone, indicating a satisfactory coating removal. The other cleaning system based on the EcoSurf/H₂O emulsion, on the contrary, did not induce significant variations in the elemental composition, confirming that the polymer remained on the surface.

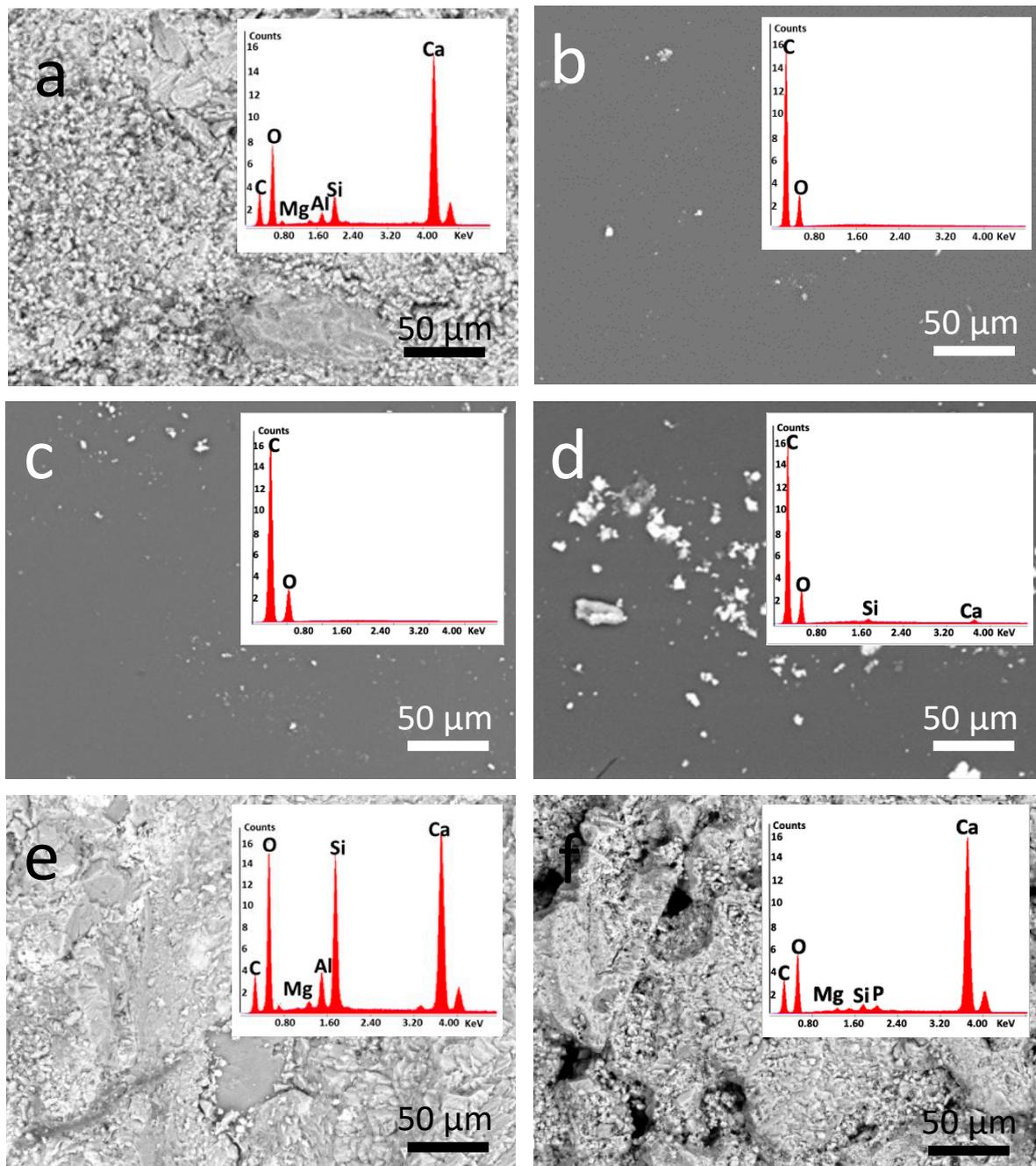


Figure 7. SEM images of AS surfaces: (a) original/natural AS; (b) coated ASPB before cleaning; (c) unaged ASPB; (d) 35 d aged ASPB cleaned using EcoSurf/H₂O; (e) unaged ASPB; (f) 35 d aged ASPB cleaned using NSEs. Corresponding EDS spectra are reported in the insets.

In addition to the qualitative observation of the EDS spectra, the results of the semi-quantitative analyses can also be considered to further explain the behavior of the cleaning systems. The C contents (weight %) are presented in Table 2, while Table S1 reports the results of the same EDS analyses expressed as carbon/calcium content ratios.

Table 2. The results of the EDS semi-quantitative analysis of both LS and AS (wt% of carbon): uncoated, coated, and after cleaning with two different emulsions (unaged and 35 d aged).

Stones	Carbon wt%						
	Uncoated	Coated		Cleaned—EcoSurf-H ₂ O		Cleaned—NSE	
		Unaged	35 d Aged	Unaged	35 d Aged	Unaged	35 d Aged
LS	11.3 ± 0.7	64.8 ± 0.9	46.8 ± 1.2	59.1 ± 0.7	43.7 ± 0.2	10.7 ± 0.5	10.2 ± 0.3
AS	10.5 ± 1.4	67.4 ± 0.7	67.4 ± 0.5	66.3 ± 0.2	65.2 ± 0.9	11.1 ± 0.2	11.7 ± 0.4

Furthermore, cross-section analyses were also performed to assess the effectiveness of the cleaning process carried out using the emulsion-loaded hydrogels. The SEM images taken of cross-sections of the coated LS and AS specimens (35 days-aged) before and after the cleaning process are reported in Figure 8 and Figure S4, respectively. Before the hydrogel application, the polymer layer was clearly visible on the outer stone surface (Figure 8a and Figure S5a), while the morphological features of the original stone substrates were completely recovered after the cleaning process (Figure 8b and Figure S5b,c).

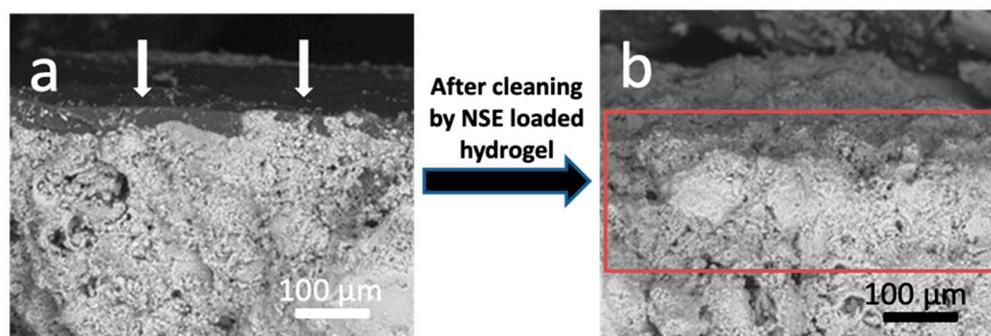


Figure 8. SEM images of the cross-section of 35 d aged LS before and after polymer removal using the NSE-loaded hydrogel: (a) before cleaning LSPB; (b) after cleaning LSPB (the red box indicates the cross-section area from the cleaned surface to a few micrometers depth).

These results further confirm the effectiveness of the NSE-loaded hydrogel as an appropriate cleaning tool for removing both the unaged and aged acrylic polymer coatings from the surfaces of the porous stone substrates.

3.3.2. Chromatic and Wettability Measurements

The chromatic variations induced by the investigated cleaning processes measured on both the LS and AS specimens and expressed as ΔE^* values (calculated with respect to the original stone materials) are reported in Figure 9. The variations in the single chromatic coordinates L^* , a^* , and b^* determined for the coated (35-days aged) and cleaned stone specimens are presented in Table S2. The presence of the aged polymer coating on the stone surface significantly affected the chromatic properties of both the LS ($\Delta E^* = 10.7 \pm 0.8$) and AS ($\Delta E^* = 13.6 \pm 1.4$). In particular, a color change towards yellow (positive Δb^* values compared to the untreated stones) and a decrease in surface brightness (negative ΔL^* values, Table S2) can be observed.

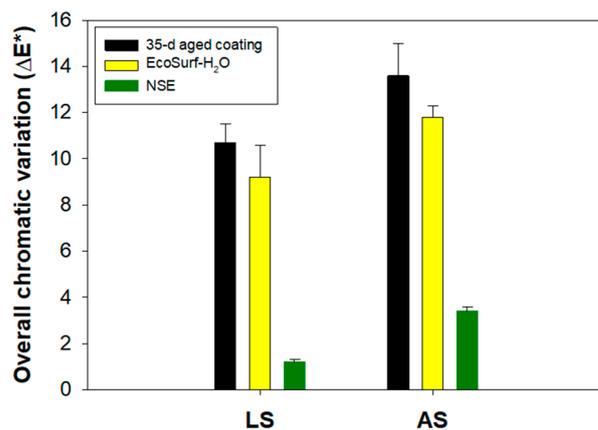


Figure 9. The overall chromatic variation (compared to natural stones) observed for the LS and AS surfaces coated with aged Paraloid B-72 coatings and after its removal using hydrogel loaded with two different emulsions (EcoSurf/H₂O and NSE).

After application of the EcoSurf/H₂O-loaded hydrogel, the chromatic properties of the treated stones were still very different from the original lithotypes and quite similar to those observed on the coated specimens. In fact, the ΔE^* values underwent only a small decrease (by about 2 units for both stones), suggesting an unsatisfactory removal of the aged polymer layer from the stone surface. On the contrary, the chromatic properties observed after the application of the NSE-loaded hydrogel were closer to those of the original lithotypes. Consequently, the overall chromatic changes calculated for the cleaned LS and AS (1.2 ± 0.1 and 3.4 ± 0.2 , respectively) corresponded to color variations which could be hardly detected by the naked eye (ΔE^* values lower than 5) [62]. This indicates again that the NSE-based cleaning system efficiently removed the aged polymer coating from the stones' surfaces.

The wettability of the stones' surfaces was also assessed at the different stages of the cleaning process by carrying out contact angle (α) measurements (Table 3). The values of α were higher than 90° when the coated stones were considered, confirming the water-repellent behavior of the polymer coating. A decrease in the water-repellant character was observed after ageing due to the decay process undergone by the coating. The application of the EcoSurf/H₂O-loaded hydrogel induced only a moderate reduction in the α value measured on the LS surface (both unaged and aged specimens), while in the case of the AS, the decreased contact angle was very low and almost within the experimental error range. This strongly suggests that the coating removal (if any) was very unsatisfactory. The contact angle values could not be measured on the surface of the LS and AS after cleaning using the NSE-loaded hydrogel because water droplets were quickly absorbed by the stone matrix (Figure S6), as already observed in the case of untreated natural stones. This clearly indicates that the polymer coating was efficiently removed, restoring the original hydrophilic character of the stone surface.

Table 3. The contact angle measurements, α ($^\circ$) of the coated stones before and after the ageing cycles (35 days) and after cleaning using the two different emulsions.

Stones	Contact Angle, α ($^\circ$)					
	Coated		Cleaned—EcoSurf/H ₂ O		Cleaned—NSE	
	Unaged	35 d Aged	Unaged	35 d Aged	Unaged	35 d Aged
LS	95 ± 2	80 ± 3	78 ± 1	72 ± 3	n.d.	n.d.
AS	115 ± 5	95 ± 3	106 ± 3	90 ± 1	n.d.	n.d.

3.3.3. Micro-FTIR Mapping

The chemical composition of the stone surfaces after applying the polymer-removing tools (compared to the coated one, i.e., before the cleaning processes), was also investigated using the micro-FTIR technique, particularly by performing mapping experiments in the ATR mode. A picture of the examined LS specimen used for testing the NSE-loaded hydrogel, the related microscope image showing the examined area, the corresponding μ -FTIR map, and the related spectra are reported in Figure 10. The examined surface included both a coated area (left side of the specimens in Figure 10a,b) and a cleaned area (right side). The spectra were registered every 100 μm along an overall distance of around 0.5 mm so that measurements from 0 to 200 μm referred to the still coated surface and from 300 to 500 μm corresponded to the surface that underwent the cleaning treatment. The peaks observed at about 1750 and 1200 cm^{-1} in the spectra taken on coated stone can be ascribed to the acrylic polymer (C=O and C-O stretching, respectively). Bands corresponding to the main inorganic components of the LS (i.e., CaCO_3) were also present. When the area treated with the NSE-loaded hydrogel was examined (right side in Figure 10a,b), the representative peaks of the polymer and particularly the one ascribed to the C=O group (about 1750 cm^{-1}) [63–65] were no longer observed, and the main absorptions were only due to CaCO_3 (1425 and 873 cm^{-1}) [1,64,66–70], as expected for the cleaned surface. The false-color map (Figure 10c) graphically displays the results discussed above for the single FTIR spectra.

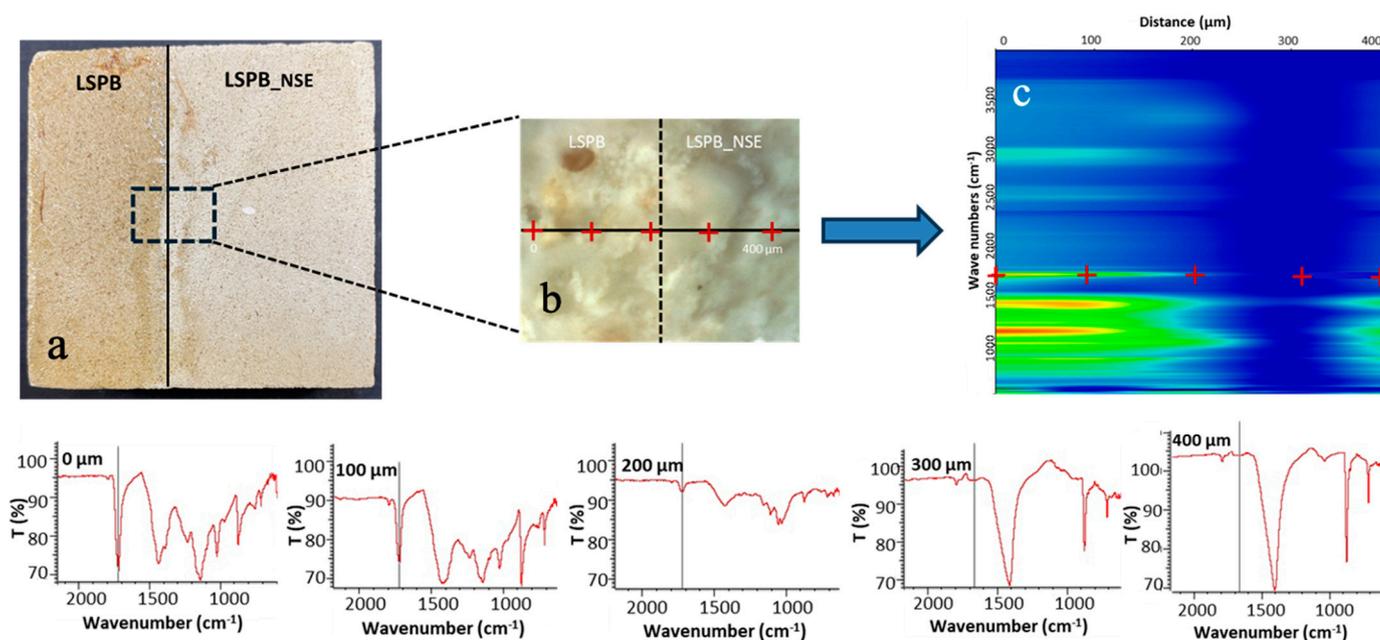


Figure 10. Micro-FTIR (ATR mode) mapping analysis performed on the 35 d coated LS surface before and after applying the NSE-loaded hydrogel. Upper side from the left: (a) the examined specimen with a vertical bar separating the coated surface on the left from the cleaned one on the right; (b) the examined area with the analysis points and their distances; (c) the resulting false-color μ -FTIR map. Lower side: FTIR spectra taken at different points in the examined area (from 0 to 400 μm distance); vertical bar indicates the position of the carbonyl stretching peak characteristic of the polyacrylate coating.

The same experiment was also performed on another LS specimen after the application of the EcoSurf/ H_2O -loaded hydrogel (Figure S7). In this case, the strong peaks at about 1750 and 1200 cm^{-1} , ascribed to the polyacrylate polymer, were still detected on the treated area as well as on the coated area, confirming again the poor ability of this cleaning system to remove the coating from the stone surface.

The results of the micro-FTIR experiments also suggested that no residues of organic substances remained on the cleaned area after removing the polymer coating using the NSE-loaded hydrogel. In fact, the FTIR spectra did not show any absorption related to organic compounds (e.g., gel material, surfactant). In particular, no peaks in the carbonyl-stretching region (expected at about 1731 cm^{-1} for the HEMA-MBA/PVP copolymer) or in the C-H absorption region (both stretching and bending) were observed.

Similar experiments performed on the AS specimens did not provide useful results because their rough and irregular surfaces were not particularly suitable for the μ -FTIR-ATR technique. In fact, owing to its inhomogeneity, a satisfactory contact between the stone surface and germanium crystal could not be attained to the same extent across all the considered areas.

4. Conclusions

The present work was mainly focused on evaluating the effectiveness of the gel cleaning method for removing aged polymer coating (e.g., Paraloid B-72) from the surface of very porous stone substrates (Lecce stone, LS and arenaria stone, AS).

For this purpose, hydrogels based on the HEMA-MBA/PVP copolymer were prepared, and their properties were compared to those of agar gel, which is commonly used in the cleaning procedures that are currently applied to conservation of cultural heritage items. The considered hydrogel displayed a lower equilibrium water content (EWC) and retention capability (RC) than agar and other common hydrogels. This could be desirable when its application to water-sensitive artefacts is considered. Moreover, the investigated hydrogel was slightly harder ($57.2 \pm 2\text{ kPa}$) than the physical gel of agar ($52.3 \pm 2\text{ kPa}$), and at the same time, it showed lower Young's modulus values, indicating that it was more elastic than the reference gel.

To evaluate its applicability to the cleaning of stone surfaces, the HEMA-MBA/PVP hydrogel was loaded with a nano-structured emulsion (NSE) formed by the surfactant EcoSurf™ EH-6 and limited amounts of organic solvents (2-butanol and butanone). A hydrogel loaded only with EcoSurf™ EH-6 and water was also prepared and tested for comparison.

Stone specimens (LS and AS) which had been previously coated with Paraloid B-72 were artificially aged in an oven to simulate the natural ageing (and consequent degradation) of the polymer coatings. After application of the emulsion-loaded gels on the stone specimens, the effectiveness of the polymer removal was assessed using different experimental techniques. The results showed that the NSE-loaded hydrogel allowed for satisfactory removal of the polymer, regardless of the aging time. This result was particularly demonstrated by the SEM-EDS and FTIR-mapping experiments as well as the colorimetric and wettability measurements. On the contrary, the hydrogel loaded only with EcoSurf/H₂O was not effective in coating removal, as the polymer was still present on the surface of both stones after the application of this cleaning system. The presence of emulsified organic solvents, although in limited amounts, seems to be essential in providing a good performance of the gel cleaning system.

In conclusion, the cleaning method based on the HEMA-MBA/PVP hydrogel and nano-structured emulsion can be considered as a promising cleaning tool that allows for the complete removal of the polymer coating from the surface of even porous stone substrates. Based on this study, this method is more effective than other common cleaning practices (e.g., cellulose pulp) because aged polymer removal is obtained after just one application without affecting the original properties of the stone substrate.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings14040482/s1>, Figure S1. Dynamic light scattering (DLS) analysis of prepared NSE. Figure S2. Optical microscope images of unaged and aged LS after polymer removal using emulsion-loaded hydrogels: (a) unaged LSPB; (b) 12 d LSPB; (c) 25 d LSPB; (d) 35 d LSPB using EcoSurf/H₂O; (e) unaged LSPB; (f) 12 d LSPB; (g) 25 d LSPB; (h) 35 d LSPB using NSE. Figure S3. Optical microscope images of AS: (a) original/natural AS; (b) coated ASPB before cleaning; (c) unaged ASPB; and (d) 35 d ASPB cleaned using EcoSurf/H₂O; (e) unaged ASPB; (f) 35 d ASPB

cleaned using NSE. Figure S4. Optical microscope images of unaged and aged AS after polymer removal using emulsion-loaded hydrogels: (a) unaged ASPB; (b) 12 d ASPB; (c) 25 d ASPB; (d) 35 d ASPB using EcoSurf/H₂O; (e) unaged ASPB; (f) 12 d ASPB; (g) 25 d ASPB; (h) 35 d ASPB using NSE. Table S1. The results of the EDS semi-quantitative analysis of both LS and AS (carbon/calcium wt%): uncoated, coated, and after cleaning with two different emulsions (unaged and 35 days aged). Figure S5. SEM images of the cross-sections of 35 d aged AS before and after polymer removing using NSE-loaded hydrogels: (a) before cleaning ASPB; (b) after cleaning ASPB; (c) at a higher magnification of (b). Table S2. Chromatic coordinates of coated (Paraloid B-72) stone specimens after being exposed to 35 days of ageing cycles and after being removed by hydrogels loaded with two different emulsions (EcoSurf/H₂O and NSE): variations refer to the uncoated/natural stone surfaces. Figure S6. Deposition of water droplets on coated stone specimens (LSPB and ASPB) and on the same specimens after cleaning using NSE-loaded hydrogels. Figure S7. Micro-FTIR (ATR mode) mapping analysis performed on 35 d coated LS surface before and after applying EcoSurf/H₂O-loaded hydrogels. Upper side from the left: (a) the examined specimen with a vertical bar separating the coated surface on the left from the cleaned one on the right; (b) the examined area with the considered points and their distances; (c) the resulting false-color m-FTIR map. Lower side: FTIR spectra taken at the different points in the examined area (from 0 to 400 mm distance); vertical bar indicates the position of the carbonyl stretching peak characteristic of the polyacrylate coating.

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