Original article

A visible and long-wavelength photocured epoxy coating for stone protection

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A B S T R A C T

An epoxy coating modified by PDMS hydroxyl terminated is presented in this paper in order to evaluate its potential use as a protective of a stone surface. With a view to its use in restoration sites, visible and long-wavelength photoinitiated cationic polymerization is proposed here. The system investigated is based on a crosslinking mechanism which shows remarkable advantages for stone protection, such as the low toxicity of the products and facility of mixture preparation. Furthermore, the visible light exploitation represents the most important advantage, because it is easy to apply in a restoration site, with or without irradiation instruments. Besides coating characterization through FT-IR, DMTA analyses and contact angle measurement on glass slides, analyses were also carried out on coated plaster samples. These analyses were performed in order to evaluate the effectiveness of the protective, in relationship to hydrophobicity (contact angle measurement, capillary water absorption) and morphology surface changing (SE/SEM observations, colorimetric measurements) before and after polymer application and UV aging test of coated samples. The overall characterization makes it possible to consider it a suitable coating for stone protection.

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1. Research aims

The aim of this research is to take advantage of the good results obtained with visible and long-wavelength photoinitiated cationic polymerization, to introduce this process into the conservation field. In fact, we considered that some of the benefits that this polymerization process has shown in another sector, such as the absence of any solvent and the easy *in situ* mixture and application, could also be successfully exploited with a modified epoxy resin to develop new protectives for stones.

2. Introduction

It is a well-known fact that stone protection in the field of cultural heritage represents an intricate challenge, because of the difficulty to meet all the criteria required. In fact, an ideal coating should be efficient, stable, durable, transparent, easy and safe during application and removal [1]. Moreover, the protective coating should guarantee a high level of hydrophobicity, considering that rain water represents the main medium for degradation mechanisms [2]. Nevertheless, *transpirability*, or rather water vapor

transmission, should be guaranteed, allowing the removal of water due to rain or capillary rise [3]. Silicone resins and acrylic-fluorinated compounds are the products most commonly proposed as protective coating [4–7]. Silicones and especially acrylic resins have been widely used in the restoration field also for other kinds of interventions, such as consolidation treatments [8].

On the contrary, epoxy resins have been considered *dangerous* for a long time, due to some inherent features namely stiffness, yellowing and low reversibility (or better retreatability) [9,10]. Thus, applications for aesthetic reasons have been totally banned. Further studies have demonstrated that yellowing processes are due to the presence of chromophores groups, but as with other polymers, the choice of the epoxy system together with the means of application and post application conditions have a strong influence on the results [11]. On this basis, interesting studies have been carried out over the past years also on epoxy resin systems, especially on cycloaliphatic epoxy resins as consolidant treatment for stone conservation [12–14]. Yellowing which can be ascribed to the aromatic moieties of bis-phenol-A based epoxy monomers usually employed, can be avoided using a cycloaliphatic monomer.

The system presented here is a visible and long-wavelength photoinitiated cationic polymerization of a dicycloaliphatic epoxy resin (CE) and a diglycidyl ether (HDGE) cured in the presence of a polysiloxane hydroxyl terminated oligomer (PDMS-OH) as an additive. On the basis of some of our previous studies [15,16], this system has been specifically developed and tested for its feasibility for stone protection, with conservation criteria as the main goal. For

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this reason, the addition of HDGE as the reactive diluent was tested to flexibilize the polymer, in compliance with conservation requirements [17]. The addition of an appropriate amount of PDMS-OH was tested as both hydrophobic and rheological controller, keeping the protective coating on the surface.

Few applications of the photopolimerization process have been exploited in the stone protection field. A photo-curing system has been recently studied, but it concerns a radical UV-cured siloxane-modified acrylic coating [18,19]. Due to its advantages, the UV curing process is widely used in different fields, such as solvent-free formulations and lower energy required with respect to thermal curing [20]. In particular, the cationic photopolymerization presents other relevant advantages, such as avoiding the oxygen inhibition, and uses monomers that are less toxic and irritant than the acrylic monomers in radical processes.

Cationic curing polymerization is a multistep process that starts with the photoexcitation of dyaryliodonium or triarylsulfonium salts, followed by the decay of the resulting excited singlet state with both, heterolytic and homolytic cleavages. The initiator of cationic polymerization is the Brønsted acid generated by a reaction among the very reactive cations and aryl-cations with monomers. Initiation of polymerization takes place by protonation of the epoxy monomer, and then by the addition of further monomer molecules through a chain growth reaction [21]. In this work, the PDMS-OH was added to the formulation and thus, the so-called activated monomer (AM) mechanism took place together with the usual mechanism for the ring-opening polymerization of epoxies known as ACE (Activated Chain-End Mechanism) [22]. The AM mechanism is active when the cationic polymerization of epoxies is carried out in the presence of alcohols. In our case, this was achieved through the PDMS hydroxyl terminated. During the polymerization, the growing ionic chain end undergoes a nucleophilic attack by the alcohol to give a protonated ether. Deprotonation of this ether by the epoxy monomers results in the termination of the growing chain and the proton transfer to the monomer can start a new chain. The polymer now has an alcohol fragment as an end group. As a consequence of the chain transfer reaction, there is an increase of flexibilization of the cured film with a consequent delay in vitrification.

Several studies have been carried out on dyaryliodonium or triarylsulfonium photoiniators salts, in order to extend their absorption bands, because they have their principal absorption bands in the short-wavelength (220–310 nm) region of the UV spectrum. The number of photosensitizers operative in the long wavelength are limited and, generally, they suffer from poor solubility in a wide variety of monomers. Therefore, in our investigation, we selected the so-called free-radical promoted cationic polymerization to extend the wavelength range of onium salt photodecomposition by using camphorquinone (CQ) as previously reported [23–25]. These free-radicals can be produced by using CQ which exhibits a strong absorption in the wavelength region between 420 and 500 nm. The choice of this compound was made on the basis of its high absorption coefficient and long-wavelength absorption as well as its excellent solubility and low toxicity. Camphorquinone is well known to undergo n-p* excitation on long-wavelength irradiation and to initially generate the excited singlet state that rapidly undergoes efficient intersystem crossing to the excited triplet. Due to the diradical character, there is a strong tendency for excited triplet carbonyls to abstract hydrogen atoms from an appropriate donor, in our case the monomer itself. At this point, the onium salt can oxidize this carbon-centered radical. The generation of an aryl radical by the decomposition of the diaryliodide free radical closes the cycle by providing a species that again can abstract a hydrogen atom from the monomer. Carbocation is formed and it is reactive enough to start the cationic ring opening polymerization.

The epoxy system investigated in this paper was cured by using a long wavelength emission lamp in order to simulate solar-light emission in the laboratory. The curing conditions were studied and the protective coating fully characterized.

Finally, the effect of natural light on the developed composition was checked through the outdoor exposition of a few samples during favorable environmental conditions. It was verified that the cationic photopolymerization was effective, since the gel content was close to the values measured for the samples polymerized by means of the lamp (data not reported).

3. Experimental

3.1. Materials

The bis(cycloaliphatic) diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (CE), the hydroxy-terminated PDMS (viscosity of 1,800–2,200 cSt), as the cationic photoinizator, triphenyliodonium hexafluoroantimonate (PI) and the photosensitiziers 2,3-bornadione (Camphorquinone, CQ), were purchased from Sigma-Aldrich (Milan, Italy). The 1,6-hexanediol diglycidyl ether (HDGE) was purchased from EMS (Switzerland). All the products were used as received without any further purification.

In the frame of the more general research project "Re-frescoes" [26,27], the so-called artificial stones [28] as plaster samples were formulated in our laboratory and employed to test the protective efficiency. A magnesian lime has been purchased from La Calce del Brenta (Padua, Italy) and employed as slaked. Its water content is 50 wt%. Silica sands have been employed as aggregates with the following grading curve: 15% (0.075–0.150 mm), 25% 0.150–0.300 mm, 35% (0.300–0.600 mm), 25% (0.600–1.120 mm). They were sampled from the Sesia river (Varallo, Italy). The binder/aggregates ratio was 1:3 in volume. The plaster specimens ($5 \times 5 \times 2$ cm^3) were slightly polished using carborundum paper of 400 mesh in order to reduce the degree of roughness preparatory for contact angle measurement. They were then washed with water, dried in an oven at $60\,°C$ and kept to constant weight in a dryer.

3.2. Preparation methods

The photocurable formulations were prepared by mixing CE and HDGE in 1:1 molar ratio. Different amounts of the siloxane additive were added to the epoxy resins in the range between 2–8 per hundred resin (phr). The cationic photoiniziator (PI) and the photosensitizier (CQ) were added in 0.5 and 4 phr respectively. The formulations were coated both on glass slides by means of a wire-wound applicator and on one of the wider surfaces of the plaster samples by brush. The average amount of polymer applied range from 0.48 to 0.64 mg/cm^2 (determined by weight difference). Then, the prepared samples were exposed to visible light irradiation by using a lamp set up as follows: six neon lamps purchased from Osram were placed inside a plastic box (generally used for electric panel) of standard dimensions (50×30 cm^2) at a regular distance of 5 cm to each other. The radiation intensity was approximated to be 134 mW·cm^{-2}, assuming a point source lamp and considering the following selected parameters to achieve a comparable intensity with standard instruments: the distance between samples and lamps (4 cm), the power of each lamp (9 W) and the placing of each sample regularly under the box, in order to be irradiated homogeneously by the three lamps. Moreover, this lamp was selected for its spectrum emission, especially for its maximum wavelength equals to 435 nm, close to the CQ λ_{max} absorption of 478 nm, to optimize the light absorption and the curing process consequently.

Fully cured films were obtained on glass slides (thickness of about 100 μm) and on plaster samples (thickness ranging from 10 to 100 μm).

3.3. Characterizations

3.3.1. Coating film characterization

FT-IR spectroscopy was performed by means of a Thermo-Nicolet 5700 instrument. The liquid formulations were coated onto silicon wafers and exposed to the lamp. During irradiation, every 30 minutes, the silicon wafers were rapidly removed from the lamp in order to collect FT-IR spectra and again exposed to the lamp until the fully cured film formation. In this way, the real time FT-IR methods were approximated, in which extent of the reaction is controlled through the simultaneously exposure to UV and IR beams. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Specifically, epoxy group conversion was followed by monitoring the decrease in the absorbance in the region 760–780 cm^{-1} and normalized it to the ester band at 1670 cm^{-1}.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration.

Dynamic contact angle measurements were performed with a Krüss DSA10 instrument, equipped with a video camera. Analyses were performed at room temperature by means of the sessile drop technique. Three to five measurements were performed on every film on glass slides and the values were averaged. The measuring liquid was double distilled water (γ = 72.1 mN/m). Contact angle measurements were performed also on the polished plaster samples according to the UNI 10921 standard. Since plaster sample surfaces are characterized by roughness and heterogeneity due to lime and sand grain distribution, both advancing and receding angle measurements were carried out. It is recognized that dynamic contact angle measurements provide more information on the relation between the coating and the stone substrate respect to static ones [29].

The assessment of the advancing contact angle was achieved by enlarging the water drop at a rate of 1.5 μL·s^{-1} until it increased in volume from 6 to 20 μL. The assessment of the receding contact angle was achieved by shrinking the water drop volume from 20 to 6 μL, at a rate of 1.5 μL·s^{-1}.

3.3.2. Characterization methodologies to the evaluation of the protective efficacy

Artificial ageing tests of the polymer were performed using a QUV Tester/Se Accelerated Weathering Tester (Q Panels Lab Products). Irradiance was kept at 0.75 W/m^2/nm, and the temperature fixed at 55 °C for 500 h of exposure. Glass slides and the treated plaster samples were placed in the chamber. FT-IR spectra and colorimetric measurements were collected before and after the ageing test.

Colorimetric measurements were performed according to the Italian Recommendation Normal 43/93, using a spectrophotometer Minolta CM 700d, operating with the CIE-L*a*b* system. Color changes were expressed in terms of ΔL*, Δa*, Δb*, where delta values are the differences between chromatic values of treated and untreated samples and as such and aged samples. The global difference in color is expressed by the ΔE* value (equation (1)):

$$\Delta E* = \left[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2 \right]^{\frac{1}{2}} (1)$$

Capillary water absorption tests and total imbibitions tests were performed according to the UNI 10921 method. The dried samples were placed on a multilayer pack of filter paper soaked in distilled water, putting the treated surface in contact with paper, for capillary water absorption tests. A non-treated sample was also used as a reference. The amount of water absorbed by capillarity forces was determined by weighing samples before and after keeping them on the soaked filters at determinate time intervals (10 min, 20 min, 30 min, 60 min, 4 h, 6 h, 24 h, 48 h, 72 h). For total imbibitions tests, samples were completely immersed in distilled water and weighed after 10 min, 30 min, 1 h, 4 h, 8 h, 24 h, 48 h until constant mass. The amount of absorbed water at time T_i ($\sqrt{s}$) is expressed by equation (2):

$$Q_i = (m_I - m_O)/A \times 1000 (2)$$

where m_0 is the capillary water uptake of the untreated stone sample (g), m_I is the capillary water uptake of the treated sample (g) and A is the treated surface (cm^2) in contact with the filter paper.

We report also the protection efficacy against capillary water absorption in order to compare the formulation with literature data. The protection efficacy, or P.E., is described as follows (equation (3)):

$$P.E.\% = \left[(A_{nt} - A_t)/A_{nt} \right] * 100 (3)$$

where A_{nt} is the mass of the water absorbed by the untreated sample, and A_t is the mass of the treated sample at a specific time of the absorption test.

The evaporation trend was measured according to the NORMAL 29/88 standard, placing the samples completely soaked in an oven at 40 °C until the initial weight was recovered. The water evaporation from the untreated surfaces was avoided covering all the samples surfaces with parafilm except for the treated one.

The plaster samples coated with a graphite film were observed by means of a Scanning Electron Microscope (SEM, Hitachi S2300-D), acquiring an SE (Secondary Electron) signal. The aim was to observe any eventual morphology and texture changing before and after polymer application, as well as after ageing and removal tests.

Removal tests were conducted applying a poultice of cellulose pulp saturated with pure acetone on the coated plaster samples. The poultice was covered with parafilm, to avoid the solvent evaporation, for 3 hours. After the removal of the poultice, the partially swelled coating was removed by means of a bistoury.

4. Results and discussion

4.1. Coating preparation and characterization

4.1.1. Photopolymerization

The photopolymerization process was monitored collecting FT-IR spectra every 30 minutes, as described above. The epoxy conversion curves as a function of the irradiation time for the pure CE monomer, the CE and HDGE mixture (1:1 molar ratio) and in the presence of increasing amount of PDMS-OH additive are reported in Fig. 1. The slope of the curve indicates the polymerization rate, while the plateau value indicates the final epoxy group conversion. As already reported in literature [15,16], the pristine CE presented a high initial rate of polymerization, and the epoxy group conversion levels off to a value of about 65%, due to the formation of a glassy polymer network which hindered the mobility of the reactive species. However, the addition of the HDGE monomer caused a slight increase of the conversion to 74%, due to a flexibilization of the polymer matrix, as shown below by DMTA analysis. As expected, a relevant increase of the epoxy group conversion was obtained by the addition of the PDMS-OH, reaching the value of 94%. This value is not proportional to the amount of PDMS-OH added.
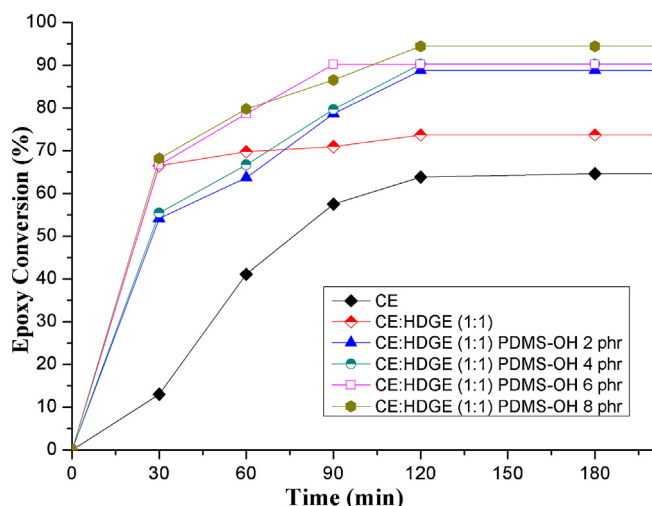
Fig. 1. FT-IR conversion as a function of irradiation time for the pristine CE, the CE:HDGE mixture (1:1) and in presence of growing amount of PDMS-OH.

These results are explained on the basis of the chain transfer reaction involving the Si-OH group. The chain transfer reaction leads to a more flexible structure, in which the mobility of the reactive species increases and the polymerization can be almost completed, as proved also by the high gel content values, always above 99%.

4.1.2. Thermal properties/Viscoelastic characterization

Thermo-dynamic-mechanical characterization (DMTA) was performed on cured films in order to evaluate the viscoelastic and thermal properties of the polymer network. The technique determines the elastic (E′) and viscous (E″) components of the modulus of the materials in a large temperature range. The E″/E′ ratio gives the tan δ value, which maximum corresponds to the Tg of the material. The evolution of tan δ in function of the temperature, for the pristine CE-cured system, is reported in Fig. 2a. The curve shows a single peak at 180 °C with a shoulder attributable to the presence of heterogeneous species. When HDGE is added to the CE in a 1:1 molar ratio, the tan δ value dramatically decreases to 108 °C, indicating a flexibilization of the polymer matrix, in accordance with the FT-IR results.

In addition, as previously verified [15], when PDMS-OH is mixed with the epoxy resin, the curve presents two distinct tan δ values, defining a biphasic cured polymer: the first one (at 96 °C) related to the epoxy resins and the second one attributable to the PDMS chains (at −16 °C). As an example, in Fig. 2b, the CE-HDGE 1:1 molar ratio cured system containing 8 phr of PDMS-OH is reported.

This bi-phasic system indicates that the PDMS-OH is covalently linked to the network. This finding supports the chain transfer mentioned previously [15].

The addition of the HDGE halved the Tg value of the pristine CE, although it should be reduced more for the targeted application.

4.2. Evaluation of the protective efficacy

4.2.1. Hydrophobicity and traspirability evaluation

Dynamic contact angle measurements were performed both on glass slides and on plaster samples. The advancing and receding contact angle values of the pristine CE and of the CE:HDGE surface formulations are lower than 90°, indicating a low hydrophobicity degree of these surfaces. The addition of 2 phr of PDMS-OH causes an increase of both the advancing and the receding contact angle value, leading to equilibrium contact angle values near 90°. The addition of a higher amount of PDMS-OH from 2 phr to 8 phr does not further enhance the hydrophobicity of the film (Table 1), as it
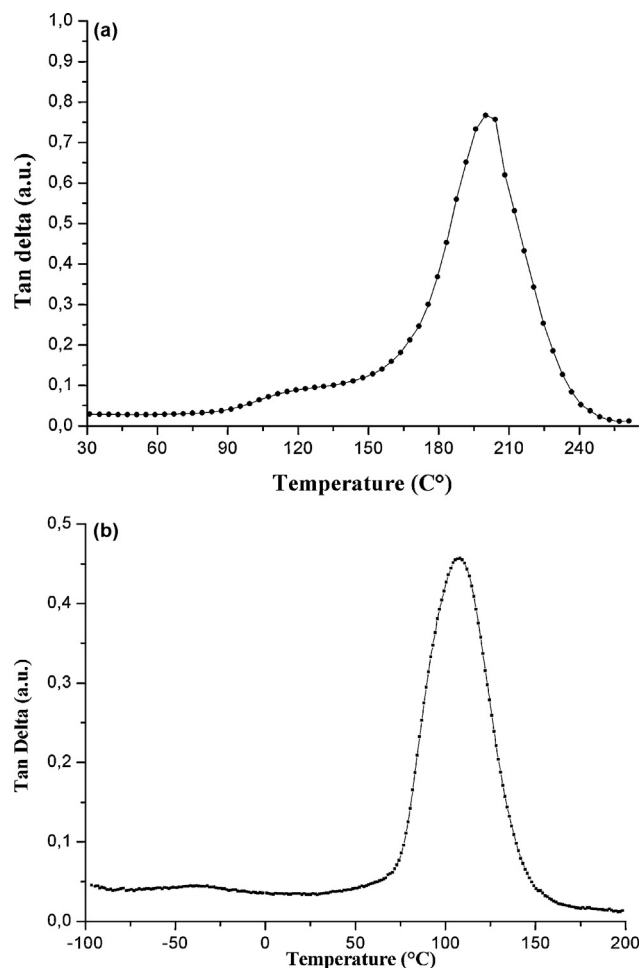
Fig. 2. DMTA tan δ curves: a: pristine CE; b: CE:HDGE (1:1) + PDMS-OH 8 phr.

has already reached a plateau value, so that the surface of the cured films could be considered completely siliconized.

It has been reported in a previous paper [15] that the addition of a lower amount of 2 phr of PDMS-OH in an epoxy matrix is sufficient to cause its migration on the surface, enhancing the contact angle values. However, further amount of PDMS-OH were also added to compare these formulations with that applied on plaster samples. The PDMS-OH was also employed as a rheological controller, since the formulations with 2 phr of PDMS-OH were not viscous enough to remain on the plaster surface before curing. The formulation with

Table 1
Dynamic contact angle measurement of polymer coating on glass slides[a,b].

	Advancing contact angle	Receding contact angle
CE	97 ± 0,8	46 ± 3
CE	97 ± 2	45 ± 3
CE:HDGE (1:1)	98 ± 1	58 ± 1,3
CE:HDGE (1:1)	98 ± 2	57 ± 1
CE:HDGE (1:1)PDMS-OH 2 phr	104 ± 1,5	72 ± 2
CE:HDGE (1:1) PDMS-OH 2 phr	104 ± 1	62 ± 2
CE:HDGE (1:1)PDMS-OH 4 phr	106 ± 3	76 ± 1
CE:HDGE (1:1) PDMS-OH 4 phr	106 ± 2	86 ± 2
CE:HDGE (1:1)PDMS-OH 6 phr	102 ± 2	72 ± 1
CE:HDGE (1:1) PDMS-OH 6 phr	106 ± 2	88 ± 2
CE:HDGE (1:1)PDMS-OH 8 phr	102 ± 3	72 ± 3
CE:HDGE (1:1) PDMS-OH 8 phr	104 ± 2	88 ± 2

[a] Before artificial aging.
[b] After artificial aging.
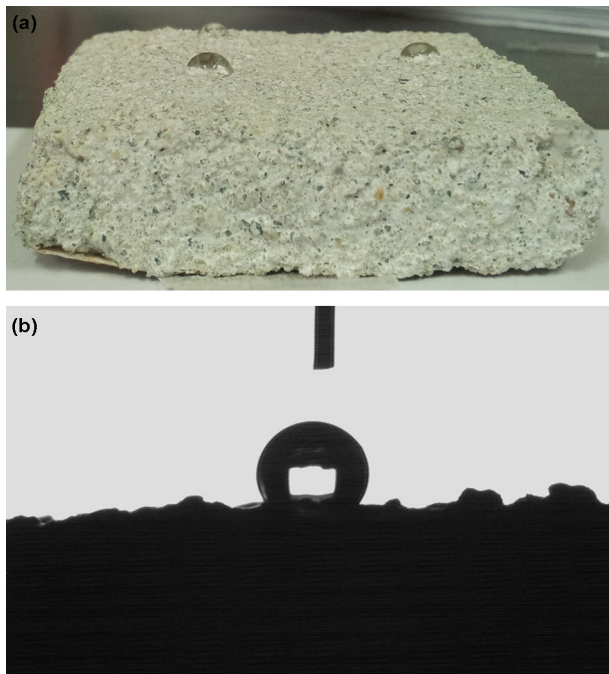
Fig. 3. a: deposition of water drops on a plaster sample treated with CE:HDGE (1:1) + PDMS-OH 6 phr; b: water drop on a plaster sample during the dynamic contact angle measurement.

4 phr was sufficiently viscous, but we also added 6 and 8 phr to verify a potential wettability difference between them (Fig. 3a, b).

The general result on plaster samples is that both advancing and receding contact angle values are lower than the contact angle values measured on glass slides (Table 2). This result can be attributed to the interaction with the stone substrate. It has been already verified that dynamic contact angle values are different when the same products are applied on stone substrates characterized by different physico-chemical and mineralogical properties, especially from their degree or porosity and structure. As a matter of fact, the dynamic contact angle values differ of 30° for each protective polymer applied on two very different stones: a very porous stone, a bio-calcareous fossiliferus stone (called the Noto stone) and a less porous stone, a metamorphic marble called Candoglia Marble [29].

The different amount of PDMS-OH seems not to affect the wettability of the surface. The variation between the contact angle values of the different formulations falls inside the standard deviation values, and it may be related to the different coating distribution on the plaster surfaces caused by brush application and to the chemical heterogeneity of the substrate.

The interesting result is that all the advancing contact angle values are higher than 90°, while the receding ones are ranging from 56° to 75°, even after the UV aging test, so the

Table 2
Dynamic contact angle measurement on treated plaster samples[a,b].

	Advancing contact angle	Receding contact angle
Untreated plaster sample	0	0
CE:HDGE (1:1)PDMS-OH 4 phr	88 ± 5	62 ± 3
CE:HDGE (1:1) PDMS-OH 4 phr	87 ± 3	63 ± 4
CE:HDGE (1:1)PDMS-OH 6 phr	95 ± 3	75 ± 5
CE:HDGE (1:1) PDMS-OH 6 phr	96 ± 5	75 ± 5
CE:HDGE (1:1)PDMS-OH 8 phr	92 ± 4	72 ± 4
CE:HDGE (1:1) PDMS-OH 8 phr	92 ± 4	72 ± 6

[a] Before artificial aging.
[b] After artificial aging.
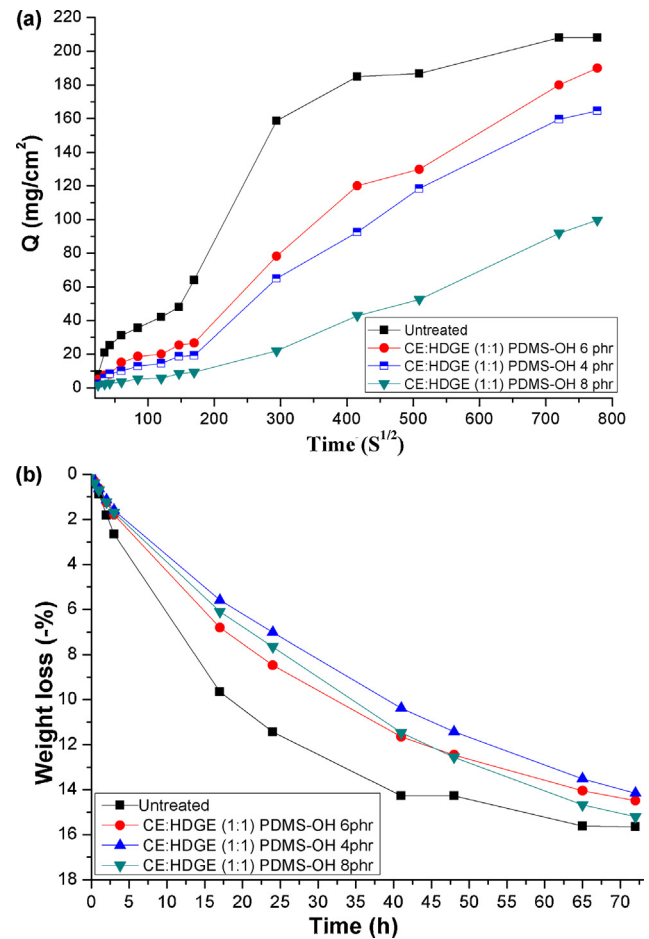
Fig. 4. Capillary rise curve (a) and evaporation trend (b) of the untreated and treated sample.

wettability of the surface samples seem to remain unchanged after the UV exposure. In comparison with the untreated sample (the contact angle value is 0°), the coating is able to delay the water penetration, but not to completely avoid it. The hydrophobicity has been demonstrated also by the capillary water absorption test on plaster samples (Fig. 4a). The coated plaster samples with the photocured epoxy formulation showed a steadily reduction of the amount of absorbed water by capillarity with respect to the untreated samples. After 14 h (170 $\sqrt{s}$), the absorption degree of the untreated samples rapidly increased, reaching the plateau value after 24 h (300 $\sqrt{s}$).

The coated samples show a lower water absorption with respect to the untreated ones. Two groups can be identified. The first one includes samples with a similar trend, treated with 4 and 6 phr of PDMS-OH. They absorb less water than the untreated samples, but more water than the samples treated with 8 phr PDMS-OH. In order to compare this water protection with literature data, the protection efficiency against water absorption by capillarity after 3 hours of absorption was calculated. Considering this short time, we can assume that the absorption is related to the surface properties and not to the porosity inside the plaster samples. The protection efficiency for the coating with 4, 6 and 8 phr of PDMS-OH was 67, 45 and 85%, respectively. We can point out two consequences from this result. The first one is that the formulation with 8 phr of PDMS-OH is the most efficient and is comparable with literature data regarding protective coating applied on stone. As an example, the protective efficacy for acrylic and siloxane formulations applied on stones (marbles, bricks and sandstone) ranges from 60 to 90%,
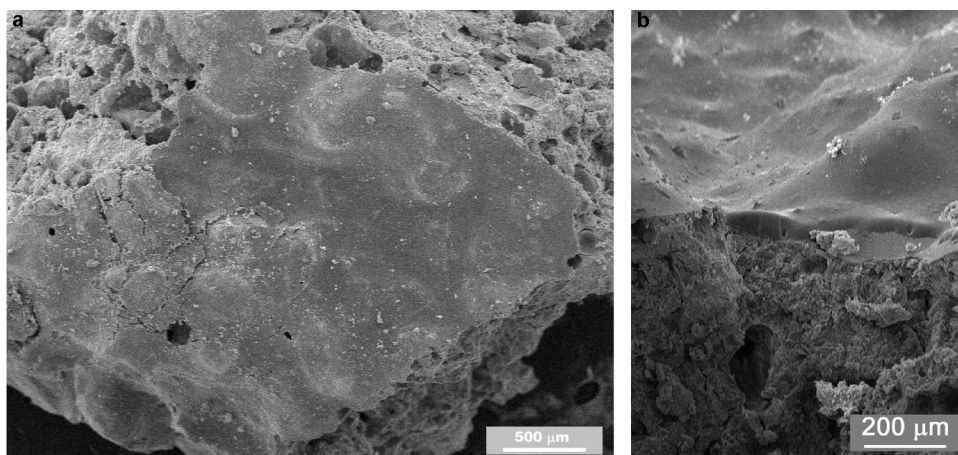
Fig. 5. SEM micrograph of the treated sample. a: surface, 30×; b: cross section 100×.

with a prevalent value of 80%. [7]. The second one is that there is not a linear correlation between water absorption and the PDMS-OH content, since the formulation with 6 phr of PDMS-OH is less efficient than the formulation with 4 phr.

We must consider that the brush application on an heterogeneous substrate influences the polymer amount applied and the coating thickness on the substrate. For these reasons, the actual distribution and migration of the PDMS-OH toward the coating surface can be in fact variable and independent from the added amount in the photocurable formulation.

A deeper investigation on a larger sampling and the optimization of the application procedure could verify the relation between the PDMS-OH amount and the absorption of water from plaster samples. We remind that the contact angle measurements have not shown an improvement of the hydrophobization through higher amount of PDMS-OH, although we know that several researches [29–31] stated the difficulty to establish a relation between capillary water absorption and contact angle measurements.

The total immersion test showed that untreated samples underwent a higher and faster weight increment than the treated ones in less than 1 h, while the treated samples reached a stable value after 8 h. The completely soaked samples after the total immersion test have been used to check their evaporation trends. The untreated samples have completely recovered the initial weight through a faster weight loss than the treated samples (Fig. 4b). So, the coating layers are able to delay but not to prevent water evaporation from the inside to the outside of the plaster samples.

4.2.2. Morphology surface characterization, optical properties and changing

SEM observations conducted on treated samples revealed a relevant texture modification of the plaster sample since porosity drastically decreased as few pores could be detected on the surface. Morphology seems to be less affected by polymer application, as the coating follows/keeps the sample roughness (Fig. 5a). Therefore, from this point of view, the protective application presents the typical disadvantages related to the polymer application on stone materials [32], especially on very porous and heterogeneous ones as plaster samples here tested. Considering the possible application on real masonries, the main problem could be in fact the hindrance of salts crystallization (transported by water) present in these porous materials. The interaction among protective efficacy and salts in plasters has then to be verified. Salts characterization, desalination procedures and residual salts checking are obviously preliminary activities to plan before any protective application. Moreover, the protective efficacy could be tested on less porous stone materials

such as marble ones [33]. On the other hand, the section observation has shown that the polymer doesn't have a deep penetration, but it rather forms a superficial layer, with a thickness of 10–100 μm (Fig. 5b), depending on the application step and sample roughness.

SEM observations of treated aged plaster show some fissured and detached bubble areas, related to cracking phenomena that usually occur [32] during aging test (Fig. 6). The observation of the treated unaged and aged samples after removal test have confirmed that a partial removal after the poultice application is possible (Fig. 7). As a matter of fact, the poultice application causes a partial softening and swelling leading to a possible detachment of the coating film. The detached film can be actually removed through bistoury, reaching the removal rate of about 40% of the coating (average value of different samples by weight difference of the applied amount). However, the use of the bistoury has to be limited to avoid surface plaster damaging.

Finally the mean value of five measurements for each sample has been calculated to verify its colorimetric coordinates variation (Table 3). Delta E variations of treated samples, ranging from 0.90 to 2.26, can be considered a good result, since literature data consider the value of five as the limit value for compatibility with the substrate [34]. Treated aged samples showed higher but acceptable values (from 2.43 to 5.79) that rarely exceeded the value of five. The brightness coordinates that are responsible for visible yellowing changing have not reached a relevant increase. As verified in other tests described previously, there isn't a clear distinction between
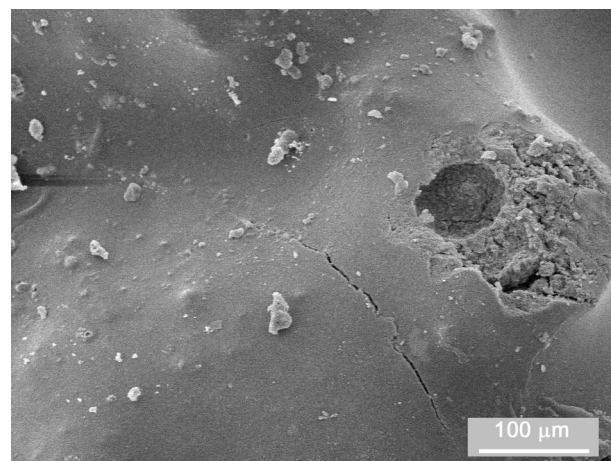

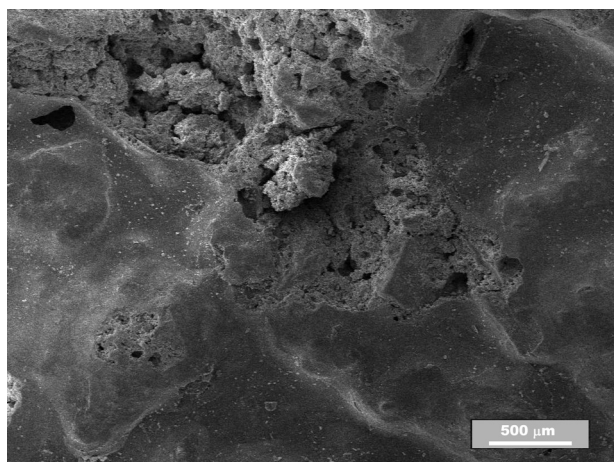**Fig. 6.** SEM micrograph of a treated aged sample: bubbles and cracking phenomena occurred after aging (200×).

Fig. 7. SEM micrograph of the treated sample surface after removal test, 100×.

Table 3
Variation of the chromatic parameter of the treated plasters[a,b].

	ΔL^*	Δa^*	Δb^*	ΔE^*
CE:HDGE (1:1) PDMS-OH 4 phr	1.59	−0.15	−0.62	1.71
CE:HDGE (1:1) PDMS-OH 4 phr	*2.39*	*−0.17*	*−0.39*	*2.43*
CE:HDGE (1:1) PDMS-OH 6 phr	0.42	0.62	0.50	0.9
CE:HDGE (1:1) PDMS-OH 6 phr	*3.22*	*−0.32*	*−0.75*	*3.32*
CE:HDGE (1:1) PDMS-OH 8 phr	−1.55	0.34	−0.88	1.82
CE:HDGE (1:1) PDMS-OH 8 phr	*5.66*	*−0.37*	*−1.19*	*5.79*

[a] Before artificial aging.
[b] After artificial aging.

the different formulations, probably due to the different amount applied, or to the surface distribution or roughness.

5. Conclusions

An epoxy system cured in the presence of a polysiloxane hydroxyl terminated oligomer (PDMS-OH) has been presented here as a potential protective coating for stone conservation.

This system presents a number of innovative features for stone conservation that makes it very easy to use. First of all, the photopolymerization is carried on at room temperature through the exploitation of visible light and is not inhibited by oxygen. These features allow an easy application in a restoration site, with or without irradiation tools.

Then, this paper demonstrates that a hydrophobic epoxy-siloxane coating on glass substrate is also an effective hydrophobic agent on plaster samples. In addition, coating yellowing did not occur after the UV aging test. We are aware that the aging phenomenon require further investigation, given the complexity of the process. Nonetheless, results obtained confirm our selection and mixture of materials for the formulation developed.

Finally, the coating presented in this paper has undoubtedly some limits, such as the higher Tg value than the ideal value near room temperature. However, this coating is very promising, taking into account that environmental and safety criteria are acquiring an increasingly important role in the field of conservation. Our coating perfectly fits these criteria, since it is characterized by low toxicity, a solvent free approach and an easy *in situ* mixture and application.

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