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Consolidation of Stone Materials by Organic and Hybrid Polymers: An Overview

Alberto Mariani and Giulio Malucelli*

Historic stone buildings and monuments undergo a gradual, unstoppable, and episodic deterioration due to environmental or climatic impact, biological or mechanical deterioration, or, in the case of better-preserved structures, inadequate maintenance. Water infiltration, freezing and thawing, carbonation, wind erosion, acid rain, and graffiti/vandalism are the key “environmental” issues that strongly impact cultural heritage and therefore must be limited or even prevented. This interaction leads to the occurrence of different phenomena, possibly involving blistering phenomena on the stone surface, its gradual weather away, leaving a sound surface behind, or the dropping away of the bulk material, because of prolonged weathering, in a single event. It is noteworthy that, quite often, the stone may appear perfectly intact to the naked eye, though it is losing its cohesion beneath its surface. Therefore, it becomes necessary to either efficiently protect the stone substrates to prolong their life, or to fix the damage that already occurred by means of effective, reliable, and long-lasting consolidation/restoration strategies. This work aims at summarizing the current state-of-the-art referring to the use of monomeric/oligomeric or polymeric consolidants, providing the reader with some perspectives for the next future.

In particular, the problem is especially evident in those structures too large to be preserved in museums or, more generally, in protected places.

This makes them particularly sensitive to the atmospheric and environmental conditions in which they are, too often including human activities. This makes their conservation particularly burdensome and expensive.

Due to various effects, including wind, rain (especially acid rain), smog, freeze-thaw cycles, telluric movements, or more simply vibrations and mechanical effects linked to human activities, the presence of microorganisms, mosses, lichens, and drought affect the degree of conservation of stone materials. Their systematic recovery and conservation, therefore, represent a necessity both in terms of historical-artistic importance and environmental protection and, finally, for the safety of the population itself.

To protect and consolidate the stones from corrosion and deterioration caused by

chemical, physical, and biological effects, they are generally treated with a protective agent. Ideally, this latter must be permanent, transparent, easy to use, nontoxic, removable, and compatible; besides, of course, it must be such as to avoid becoming a problem itself.

In addition, since the humidity of the air and rainwater can cause deterioration of the stone, the protective material must be very hydrophobic, and must ensure that the stone “breathes,” to prevent the remaining water in the substrate from damaging the stone.^[1]

To this aim, several protective and consolidating materials have been proposed. Among these, polymeric materials such as epoxy, acrylic, and silicone resins are often used.^[2]

English dictionaries define the term consolidation as the process to join into one whole, or to form into a compact mass. More specifically, it is the operation that aims to increase consistency and resistance of materials. Thus, a material able to restore a degraded one is named “consolidant.”


For what concerns the matter of interest of this review, consolidants must be able to penetrate the stone homogeneously, quickly, and in-depth. The treated material should retrieve properties as close as possible to the original ones. Treatments must be long-lasting, not cause deterioration, and not rule out possible future actions. Moreover, consolidation treatments should be as cheap, easy, and safe as possible.^[3]

1. Introduction

For thousands of years, stones have been used to construct houses, buildings, monuments, streets, and various day-life objects. Although many of them have survived the passage of time and bad weather, their state of conservation is not always adequate to the historical, artistic, touristic, or simply civil importance that characterizes them.

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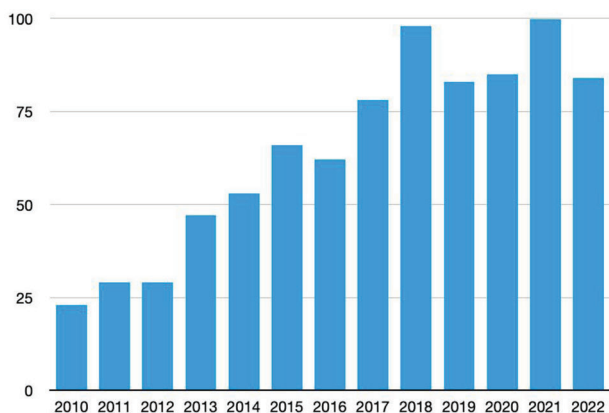


Figure 1. Number of publications (from 2010 to 2022) in peer-reviewed journals, dealing with the consolidation of stone (data collected from Web of Science database, accessed on April 1, 2023).

However, simultaneous satisfaction of these requisites is not always easy to achieve, thus justifying the continuous research effort to accomplish them.

For example, penetration may be increased by increasing compatibility, reducing viscosity, and lowering the molecular dimensions of the consolidant or those of its precursors.

Up to now, the research performed by the academic community on the consolidation of stone materials has grown a lot, as witnessed by the increasing number of papers appeared in the scientific literature (Figure 1).

This review intends to focus on the use of these polymeric materials, considering their role as consolidating agents.

2. Stone Materials: Types and Uses

Stones have broadly been exploited in the construction sector as they are naturally abundant and exhibit suitable mechanical properties and durability; further, they can be quite easily manufactured according to different shapes and geometries (such as beams, arches, slabs, blocks, and columns, among others). To classify the stone materials, it is possible to exploit their geologic origins (i.e., geological classification), their structure (i.e., structural – or physical – classification), or their chemical composition (i.e., chemical classification).

According to the geologic origins, stone materials can be classified, consistent with their geologic formation, into sedimentary, igneous, and metamorphic.^[4,5]

Sedimentary stones are derived from the sedimentation of disintegration products derived from eroded/weathered materials; they include dolomite, sandstone, limestone, and shale, among others. Igneous stones originate from cooling and crystallization processes that involve magma, i.e., a volcanic originally hot and molten material. Based on the solidification depth, igneous stones can be further divided into extrusive (volcanic) and intrusive (Plutonic) stones. The former undergo a quick cooling process as they originate on the earth's surface, even in the oceans, hence giving rise to the formation of fine-grained structures; conversely, the intrusive stones originate from 2 to 10 km below the earth's surface. This way, they are coarse-grained stones, as they undergo a slow cooling process. Extrusive stones comprise

Trachyte and Basalt, while intrusive stones include Gabbro and Granite.

Metamorphic stones are either sedimentary or igneous stones that underwent structural and mineralogical changes due to the action of heat, pressure, or both. Some examples of metamorphic stones include Marble, Slate, Quartzite, and Gneiss, among others.

The chemical classification of stone materials is based on their dominant constituent. Therefore, three main groups can be considered, namely: calcareous stones (such as marble, limestone, and dolomite), for which the main components are carbonates; siliceous stones (such as granite, quartzite, and gneiss), whose main component is silica; argillaceous stones, for which clay is the main component. Sedimentary argillaceous stones include siltstones, clay stones, and shale, while metamorphic comprise slates and phyllites.

The structural classification categorizes stone materials based on the absence or presence of layered morphologies: in the latter case, the classification also considers the type (nature) of layered structures. Accordingly, there exist three different groups: the unstratified (massive) stones (such as gabbro and Granite), the stratified (layered) stones (such as shale, limestone, and sandstone), and the foliated stones (such as schists, gneiss, and slate), which show a parallel arrangement of certain mineral grains that provide these stone materials with a striped appearance.

Table 1 collects the main stone materials with their peculiarities and some uses.

3. Deterioration of Stone Materials

Despite their quite high durability, stones are “living” materials that significantly interact with the surrounding environment; the interactions that take place may shorten the duration of stone materials, hence leading to a progressive alteration of their surface and bulk properties, which may result in mechanical failures and collapses. The deterioration extent is strictly related to the chemical composition, mineralogical features, and microstructural characteristics of the stone materials.^[6,7] Stone degradation may involve both natural and anthropic factors, as schematized in Figure 2.

The next paragraphs will summarize the main characteristics of each type of stone deterioration.

3.1. Chemical Degradation

Chemical reactions are the main responsible for the chemical degradation of stone materials. Specifically referring to calcareous stone materials, the chemical conversion of CaCO_3 into $\text{Ca}(\text{HCO}_3)_2$ is the so-called Karst effect: the high solubility of the bicarbonate in rainwater accounts for the progressive removal of the surface layers of the stone material that underwent the transformation.^[8] The Karst effect is further intensified in very polluted environments, where the concentration of carbon dioxide in the air is remarkably high. Indeed, the dissolution of CaCO_3 is always associated with an increase in pH, because of the formation of H_2CO_3 ^[9] that, in turn, releases CO_2 into the surrounding atmosphere.

Table 1. Main types of stone materials with some characteristics and uses.

Stone	Characteristics	Uses
Basalt	<ul style="list-style-type: none"> - Igneous stone - Fine-grained structure - Dark or light dark color - High mechanical strength - High weather resistance - Low permeability 	Construction material
Granite	<ul style="list-style-type: none"> - Igneous stone - Coarse-grained structure - Dark or light dark color - High mechanical strength - Excellent durability - Good resistance to frost and weathering - Least porous - Poor fire resistance 	Construction material
Limestone	<ul style="list-style-type: none"> - Sedimentary stone - Usually stratified - Color changes from white to grey & dark - Poor resistance to chemical deterioration 	Construction material when fine textured and free from cavities and cracks
Marble	<ul style="list-style-type: none"> - Metamorphic stone - Often layered - Available in different colors - Least porous - Good mechanical strength 	Construction and ornamental material
Sandstone	<ul style="list-style-type: none"> - Sedimentary stone - Usually stratified - Medium to fine grained texture - Available in different colors 	Construction and ornamental material

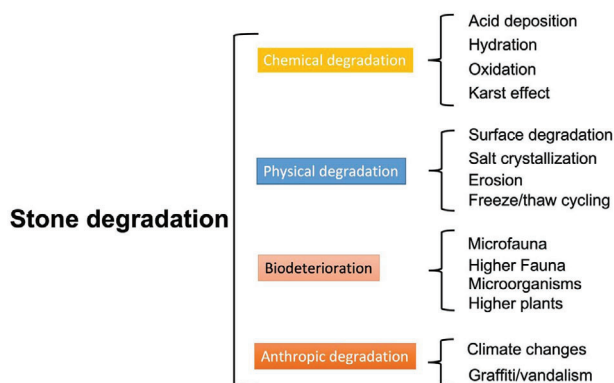


Figure 2. Scheme of the possible stone deterioration phenomena.

Another frequent chemical cause of stone deterioration regards acid deposition; this phenomenon may take place both in wet and dry conditions: wet conditions require the action of acid rain, while the latter derives from the adsorption of gaseous pollutants (such as NO_x or SO_2) on the stone surface. Therefore, acid deposition promotes the formation of acidic species, able to react with the stone components, hence giving rise to soluble products that can effortlessly be leached out from the degrading stone. This process never comes to an end, as the exposure of a new stone layer to acid deposition allows for the occurrence of new

reactions between the acidic species and the stone substrate. The Karst effect is quite common in several different types of stones, namely: calcareous stones (with the formation of calcium sulfate dihydrate, i.e., the so-called gypsum), granites, and marbles (for these two latter, two phenomena, namely efflorescence and appearance of porosity, occur).^[10]

Oxidation phenomena are also very common for stone materials such as granites,^[11] limestones,^[12] and marbles:^[13] they involve any oxidizable metal present in the stone, which, in the presence of air (oxygen) and water, increases its oxidation number, leading to the formation of brittle oxidation stains. A typical metal that undergoes oxidation is iron.

Hydration represents another chemical degradation process affecting stone materials; however, it generally does not compromise their integrity, but it may be considered an initial stage of hydrolysis reactions: in this context, some typical hydration phenomena refer to the transformation of iron oxides into iron hydroxides and the conversion of anhydrous calcium sulfate to gypsum.^[14]

3.2. Physical Degradation

It is well-known that natural agents including temperature changes, wind (and particles embedded in), and water can promote physical deterioration phenomena in any stone material.^[15] In particular, very frequently, the combined effects provided by such natural agents result in the so-called surface erosion of the stone materials, i.e., the progressive removal of their surface layers. This degradation process can be further promoted because of the presence of water that, according to a freeze/thaw mechanism, promotes the swelling/shrinkage of the stone material (Figure 3), leading to the formation of cracks as well as the occurrence of other surface degradation phenomena such as contour scaling (i.e., detachment of mm- to cm-thick surface layers following the contour of stone surface features), delamination (i.e., detachment of multiple thin stone layers sub-parallel to the stone surface), surface flaking and scaling (i.e., detachment of sub-mm to mm-thick surface layers totally independent of the stone structure, Figure 4).^[10,16,17]

Surface erosion usually requires stone materials showing extended porosity: this is the reason that justifies the occurrence of this phenomenon typically in sedimentary stones (i.e., limestones and sandstones);^[18] conversely, it is less frequent in granites, as they show better mechanical behavior with respect to sedimentary stones.^[9]

Physical degradation of stone materials can also be promoted by salt crystallization, due to the increase in the concentration of salt solutions derived from anthropogenic events (e.g., agricultural activities), from the migration of soil ions on the stone materials, using the capillarity of the latter, and from the composition of the stone materials, which promotes crystallization phenomena, with the concurrent lowering of relative humidity (RH). Conversely, the RH increase rehydrates the crystallized salts: the repetition of these crystallization/rehydration processes accounts for the appearance of mechanical stresses in the stone materials, which may lead to their deterioration (surface flaking, Figure 5).^[19]

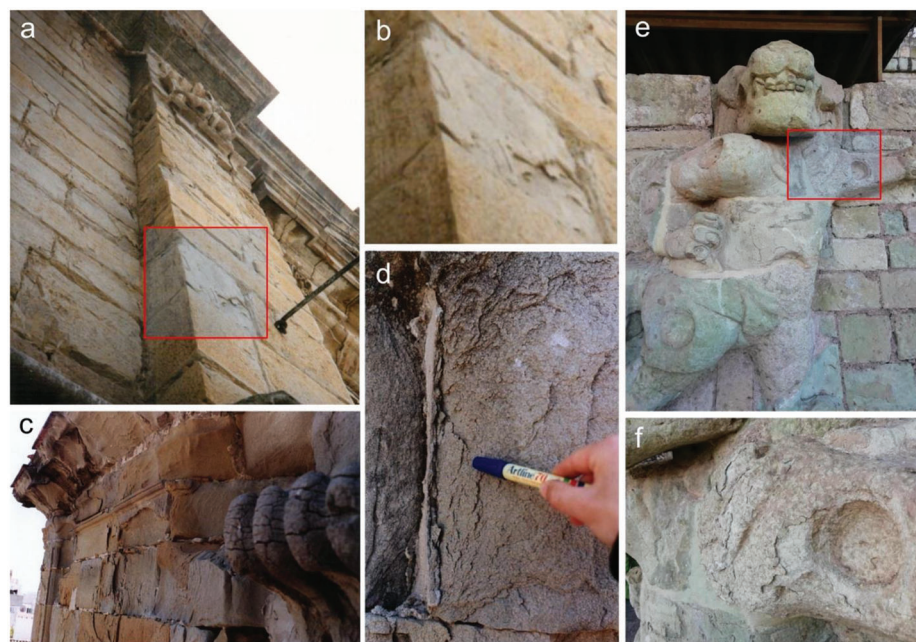


Figure 3. Examples of stone damage associated with swelling/shrinkage of stones. a) Micritic limestone at Jaen's Cathedral (Spain) showing scaling and delamination. b) Detail of the squared area in (a) showing scaling of the surface of the stone block. c) Massive fracturing and scaling of sandstone at Tarifa (Spain). d) Detail of scaling in Tarifa sandstone. e) Carved tuff stone figure at the Maya site of Copan (Honduras) showing scaling and loss of surface relief. f) Detail (squared area in (e)) of scaling damage. Reproduced under terms of the CC-BY license.^[17] Copyright 2022, the Authors. Published by Elsevier.

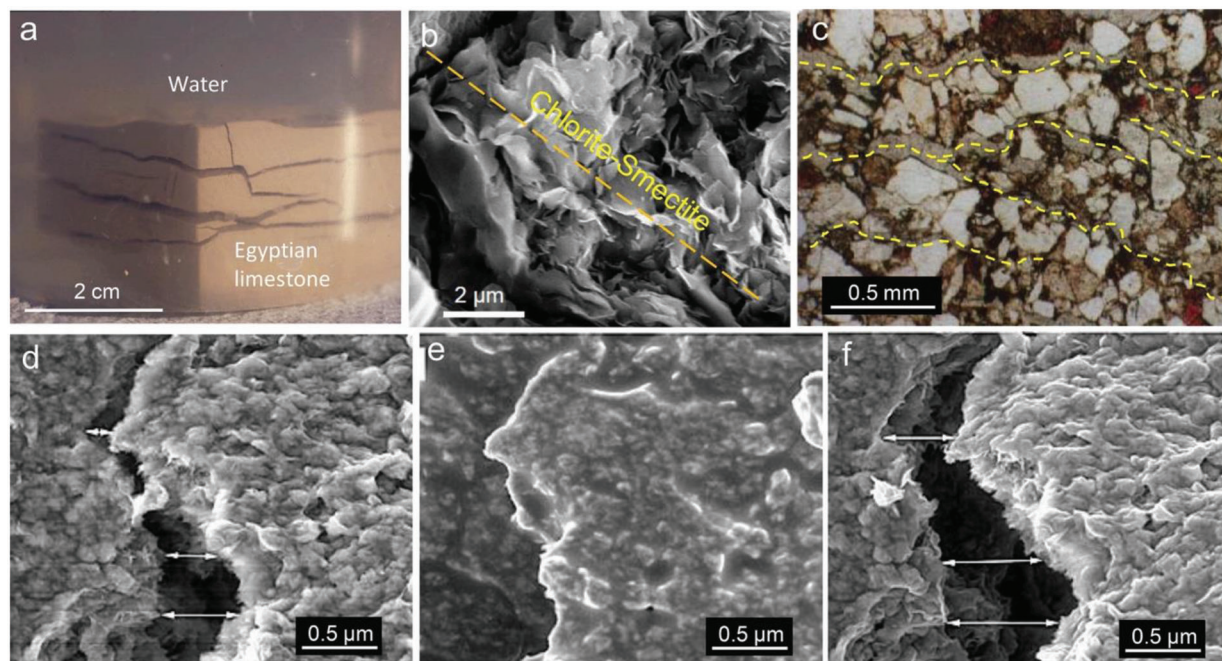


Figure 4. Swelling damage development from the macro- to the microscale. a) Egyptian Limestone block (remains of a fully degraded stela from the Egyptian collection of the Phoebe Hearst Museum, Berkeley, USA) developing multiple macroscale cracks subparallel to the bedding planes after immersion in distilled water. b) Scanning electron microscopy (SEM) image of Tarifa Sandstone showing chlorite-smectite mixed layer clay aggregates with a preferred orientation sub-parallel to the stone bedding plane (marked by the dashed line). c) Tarifa Sandstone observed under the polarizing microscope (plane light) showing extensive cracking. d–f) Sequential environmental SEM (ESEM) images of Egyptian Limestone from the Phoebe Hearst Museum showing expansion upon the increase of partial pressure of water and temperature decrease within the ESEM chamber, resulting in water condensation (transition from (d) to (e)) followed by a decrease in partial pressure of water and temperature increase, resulting in drying (transition from (e) to (f)). Note the significant widening of the crack in (d) after a full wetting/drying cycle (f), demonstrating a permanent deformation (residual strain) and associated stone damage at the microscale. Reproduced under terms of the CC-BY license.^[17] Copyright 2022, the Authors. Published by Elsevier.

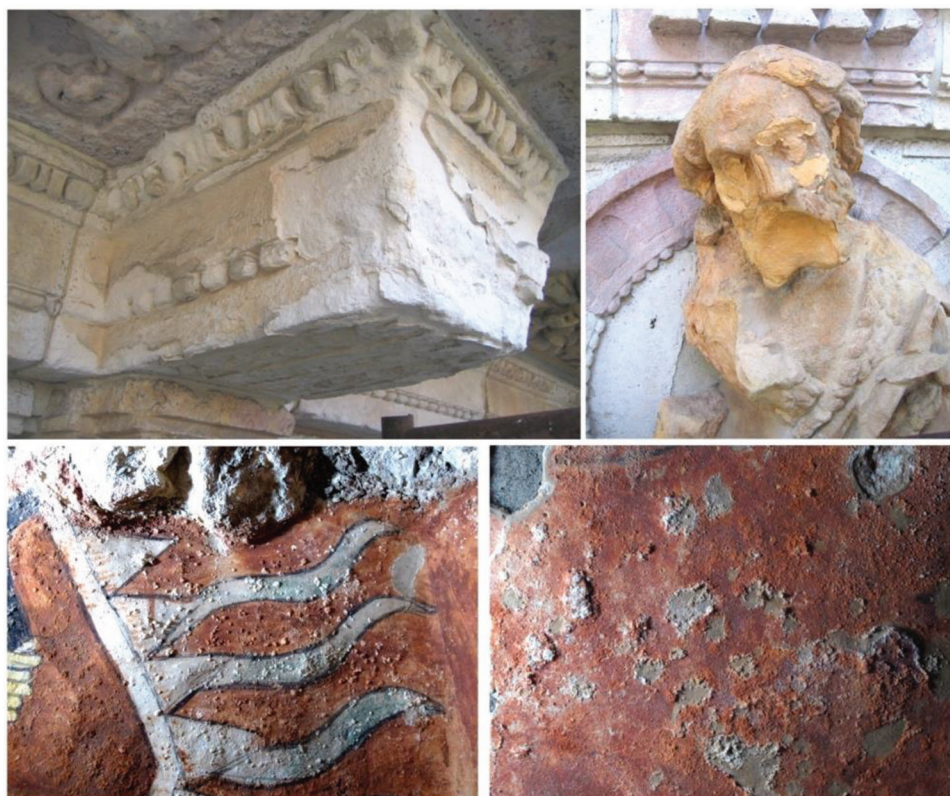


Figure 5. Effects of salt crystallization on the surface of works of art. (Top row) 17th-century limestone works (Angera stone) from the Ca' Granda Palace in Milan (Italy) showing delamination induced by salts in outdoor environment. (Bottom row) Mesoamerican wall paintings were recently discovered in tombs near Puebla (Mexico), where salt efflorescence causes surface flaking. Reproduced with permission.^[19] Copyright 2016, Elsevier.

3.3. Biodeterioration

Biodeterioration is defined as the degradation undergone by stone materials because of the action of (micro)organisms.^[20–23] This type of degradation is suffered by any stone material, in any climate condition, although each stone material may have a different bio-receptivity, i.e., a diverse susceptibility to be colonized by (micro)organisms, which depends on the structure, composition, and morphology of the hosting material, on its porosity and permeability, pH, conservation conditions, as well as on the anthropogenic eutrophication of the atmosphere.^[21,23,24] Besides, several biodeteriogens, usually classified as microorganisms, micro- and higher fauna, and higher plants,^[23] can be involved in the stone degradation processes. Because of biodeterioration, different effects can be observed on the stone substrate, which are strictly related to the type of deteriogen. More specifically, biodeterioration by microorganisms can promote the formation of a biofilm, changes in color, chemical modifications, and dissolution/recrystallization phenomena as well. Two typical examples of biodegradation of a stone material are presented in **Figures 6** and **7**.

Conversely, the biodeterioration promoted by higher plants, micro- and higher fauna is usually associated with physical outcomes, including erosion phenomena and the appearance or the development of cavities within the stone substrate.^[25]



Figure 6. Influence of biodeterioration processes occurred on an angel statue at the "Peters"-Portal on the Cathedral of Cologne (Germany): a) original object in 1880 photograph; b) the respective weathered statue in 1993. Reproduced with permission.^[23] Copyright 2000, Elsevier.

3.4. Anthropogenic Degradation

Anthropogenic degradation is usually present in all the degradation phenomena affecting stone materials. In particular, different

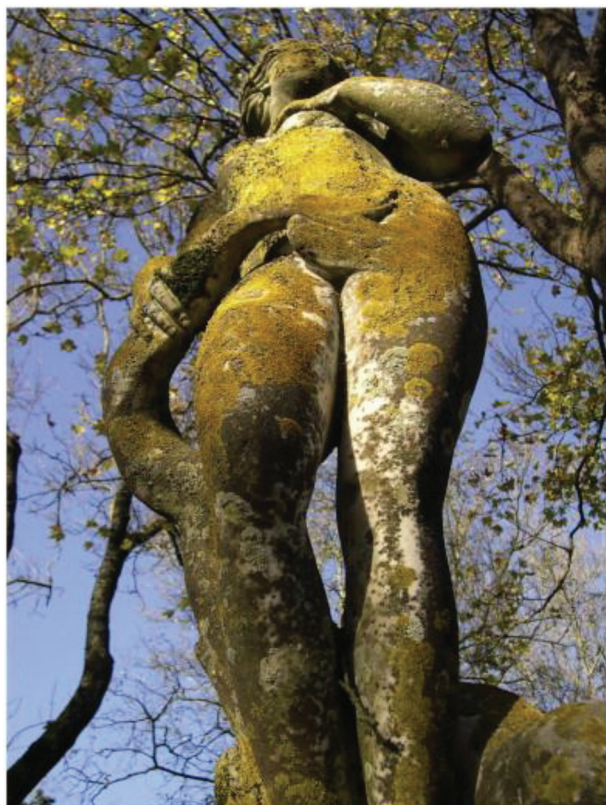


Figure 7. Marble statue from the gardens of Palácio Nacional de Queluz (Portugal) with extensive lichen colonization. Reproduced with permission.^[24] Copyright 2012, Elsevier.

anthropic factors can contribute to the deterioration of the stones. First, the moisture that derives from obstructed drains, inappropriate water management, or system failures can play a key role in the decay of stone materials.^[26] Then, human activities undoubtedly can provide a significant contribution to environmental pollution that, in turn, may affect both the chemical and physical deterioration of the stone materials. Wrong or unsupervised conservation, restoration, and consolidation efforts can further impact the stone's integrity.

Among the anthropic factors, climate changes exhibit a double role in stone deterioration: on the one hand, they are capable to increase the kinetics of already occurring degradation processes; on the other hand, they can make the previous restoration activities ineffective.^[27,28]

Fire is another anthropic, tremendous, and catastrophic event that can promote instant, severe, shock outcomes, ascribable to differential thermal expansion caused by compactness,^[29] and mineral composition,^[30] leading to fracture and spalling phenomena, accompanied by a significant material loss. Besides, the appearance of microcracks, surface soot-covering, and changes in permeability features can promote further deterioration.^[31]

Last but not least, graffiti and vandalism (**Figure 8**) constitute a dramatically impacting anthropic factor for stone materials. Apart from the very negative appearance of stone materials when sullied by graffiti, it is important to consider that the components of graffiti (such as chalk, lacquers, waxes, paints, and



Figure 8. Spray-painted graffiti on a concrete wall at the University of Milan (Italy). Reproduced with permission.^[33] Copyright 2014, Elsevier.

enamels, among others) may promote both physical and chemical deterioration of the stone substrates. Further, removing the graffiti may require the use of abrasive products, capable to cause surface modifications, mineralogical changes, and chemical contamination as well.^[32]

4. Stone Consolidation

4.1. Monomers/Oligomer/Polymers

Figure 8 shows the main consolidants used for carbonate-based and silicate-based stones and their frequency of use. It is evident that alkoxysilane (AS) polymers are the most used in practice and those, on which most research is focused. They are materials that are used both in carbonates and silicate-based stones, and that—in addition to mere consolidation—can impart waterproof, biocidal, and self-cleaning properties, just to name a few properties. Among the polymers, lesser importance is paid to acrylic polymers (used for both carbonate- and silicate-based stones), and epoxy resins (for carbonate-based stones).^[34] Indeed, acrylic and epoxy polymers had been among the most used and studied, especially in the past. However, despite possessing excellent reinforcing properties, which make them particularly useful in the case of erosion and detachment of material, their importance has gradually decreased, especially due to problems related to their incompatibility with some stone substrates (**Figure 9**).^[35,36]

More specifically, epoxy resins (e.g., EP2101), despite being characterized by strong bonds and high mechanical resistance, have poor resistance to atmospheric agents and are prone to yellowing, due to exposure to UV radiation.

On the other hand, acrylic polymers (e.g., Paraloid B72), although generally transparent and colorless, and exhibiting good resistance to atmospheric agents and transparency, are prone to degrade in the presence of water, especially in acidic or alkaline conditions. In addition, both epoxy resins and acrylic polymers are characterized by relatively high viscosities even in solution, which makes the stone consolidation processes more difficult.

As for AS, these react to give rise to the corresponding silicone polymers, which are widely used in the consolidation of stones. In particular, the commercial products Conservare OH

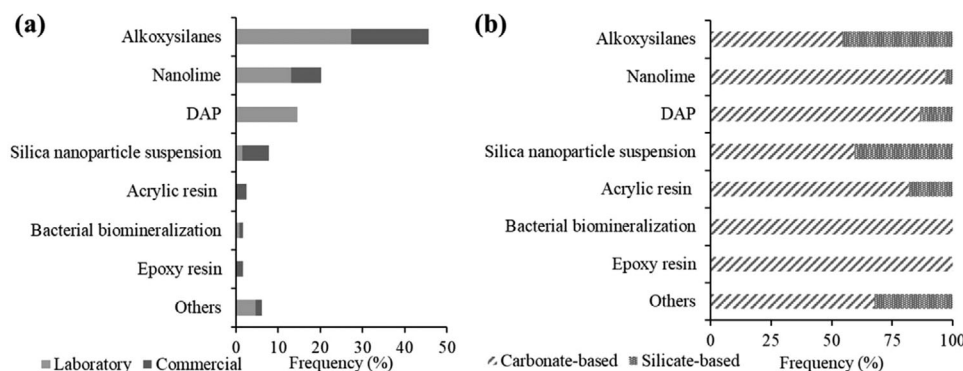


Figure 9. Distribution of the most used families of consolidants in stone consolidation research a) and percentages according to the stone's chemical nature b). Data refer to the latest 10 years. Reproduced under terms of the CC-BY license.^[34] Copyright 2023, the Authors. Published by MDPI.

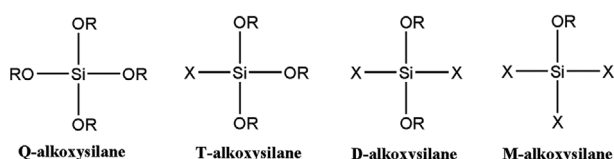


Figure 10. Different types of reactive silanes. R is an alkyl and R' is any organic group. Regardless of the attached organic groups, Q, T, D, and M refer to four, three, two, and one attached oxygen atoms on each silicon atom, respectively.

and Tegovakon V 100 are based on tetraethyl orthosilicate (TEOS) and methyltriethoxysilane (MTEOS).^[2]

4.1.1. Alkoxysilanes

Silicone polymers (i.e., polysiloxanes) and other siloxane materials derived from AS and organoalkoxysilanes (OAS, **Figure 10**) through polymerization reactions including polyhydrolysis, transesterification, and polycondensation.

Alkoxysilane polymerization is a complex reaction comprising three main steps:

- 1) hydrolysis: the hydroxyl group replaces the alkoxy groups; it may occur in a neutral, acidic, or alkaline environment;
- 2) condensation: siloxane (Si–O–Si) bridges are formed by removing one molecule of water or alcohol from two molecules of alkoxysilane;
- 3) phase separation: the reaction medium becomes inhomogeneous because of the simultaneous presence of a solid and a liquid, commonly called gel and sol, respectively.

The reaction rate of these steps is a function of different parameters, namely: i) the nature of the silane; ii) the H_2O/Si ratio; the type of solvent; iii) the silane/solvent ratio; iv) the employed catalyst; v) the pH; vi) the ionic strength; and vii) the temperature.

Thus, a variety of conditions can be used in sol-gel processes, leading to different properties of the obtained products.^[37]

The first step of silane polymerization is hydrolysis, which is followed by a condensation reaction that results in the formation of a sol and a gel.

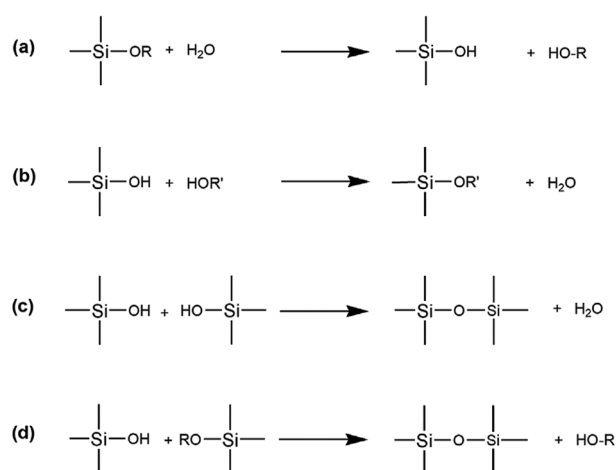


Figure 11. Polymerization of organo-alkoxysilanes: a) hydrolysis; b) re-esterification; c) condensation with water formation; d) condensation with alcohol formation.

In its general form, organo-alkoxysilane polymerization takes place through the reaction sequence depicted in **Figure 11**, which comprises the replacement of the alkoxy- with the OH-groups (hydrolysis) and the subsequent condensation reactions to give the polysiloxane.

Figure 12 shows the first hydrolysis step—which is also the rate-determining one—occurring at different pH ranges.

At high pH values, OH^- or deprotonated silanol attack the Si atoms in alkoxysilane and/or neutral silanol in both hydrolysis and condensation steps.

At variance, when the reaction is carried out at low pH, alcoholate and silanol are first protonated in one rapid step, thus making the Si atom more electrophilic and susceptible to being attacked by water or neutral silanol. As in a base-catalyzed reaction, the reaction rate is influenced by steric and inductive factors.

These reactions occur simultaneously with re-esterification and depolymerization reactions, respectively. Since alkoxysilane polymerization takes place by proton transfer, it is catalyzed by an acid-base reaction. The hydrolysis kinetics have been studied extensively, especially the first hydrolysis step where the

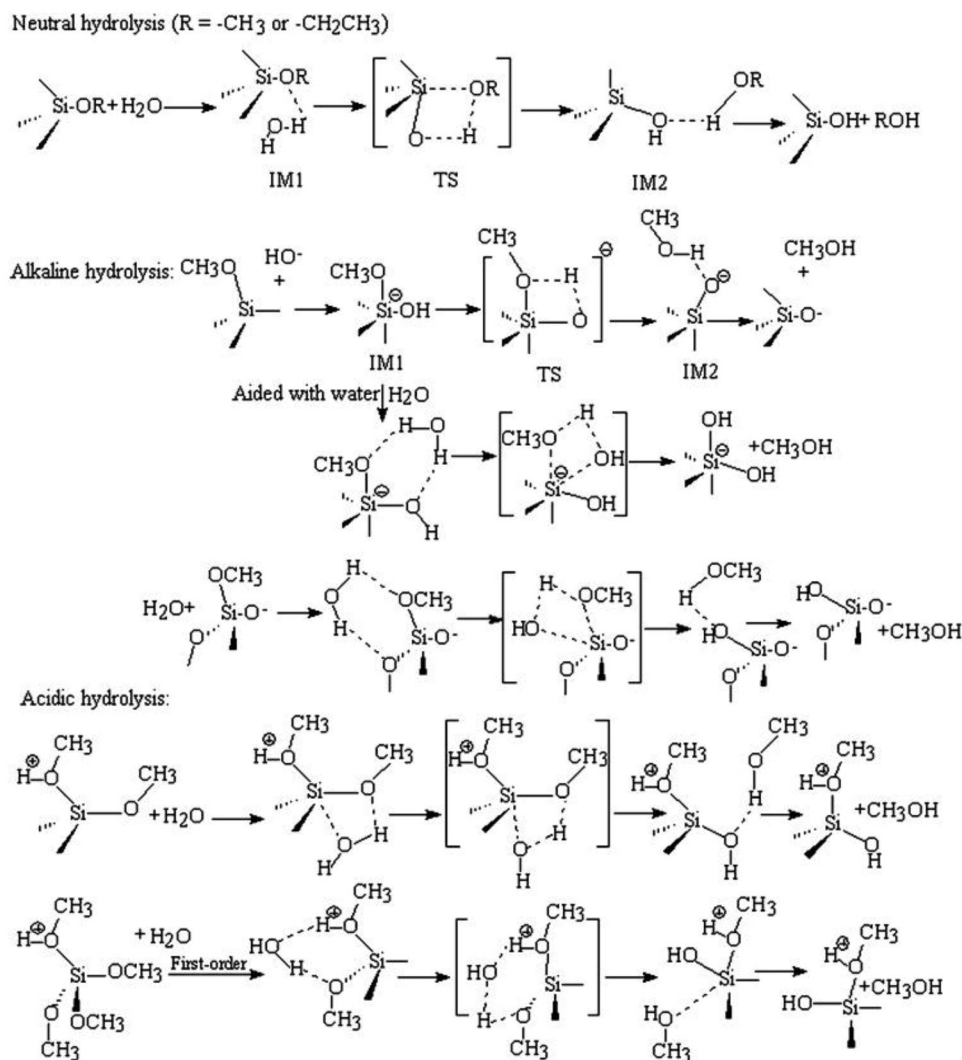


Figure 12. Hydrolysis mechanisms in different pH media. TS = transition state, IM = intermediate. Reproduced with permission.^[38] Copyright 2012, the Royal Society of Chemistry.

consumption of alkoxy silanes is usually easy to monitor since it is believed to be an elementary reaction.

Depending on the reaction conditions, silane reactions can produce different polymerized products. Indeed, some parameters may result in an increase or decrease in the reaction rate as a function of the temperature, while others, such as pH variation, strongly influence the reaction kinetics.

If a proper catalyst is not used, the polymerization reaction is very slow. That is why many catalysts have been proposed, namely, ammonia, mineral acids, phosphoric acid, and organic acids, such as acetic acid, and chloroacetic acid.^[39] Other compounds, such as the alkyl esters of tin,^[40] potassium carbonate,^[41] sodium hydroxide,^[42] and trimethylamine^[43] were also used.

Other factors that influence the silane polymerization kinetics include the type of silane, its ratio with water, and its total concentration, temperature, type of solvent, ionic strength, and pH.^[3]

As mentioned above, hydrolysis is the first step of the polymerization of silanes. If water is present in excess, the subsequent condensation results in the initial formation of soluble

oligomers, mostly dimers and trimers, which polymerize further. As the conversion increases, the solubility of the species decreases, thus making the reaction medium heterogeneous. This results in different types of phase separation; indeed, it may be a colloidal suspension of particles in a liquid (sol), a continuous solid in a continuous liquid (gel), or immiscible oligomers in a liquid (silsesquioxanes). Many parameters are responsible for the type of phase separation: they include the functionality of the silane (Figure 10), the pH, and the catalyst. More specifically, monofunctional silanes can dimerize; bifunctional silanes produce linear polymers or cyclic structures; trifunctional silanes give rise to oligomers and cross-linked polymers (i.e., silsesquioxanes); tetrafunctional silanes form highly cross-linked sol- or gel-polymers.

As already pointed out, alkoxy silanes are currently the class of compounds most used for the consolidation of stone materials by polymers. The replacement of hydrogen atoms in the Si-H bond in silane with alkoxy groups, leads to the formation of various alkoxy silanes, including methoxy silanes, ethoxy silanes,

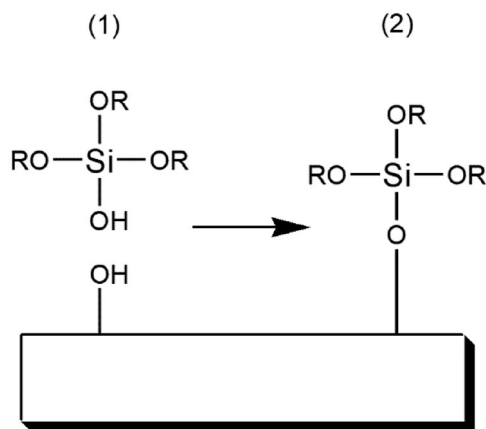


Figure 13. The reaction of organo-alkylsilanes with OH groups on a stone surface.

propoxysilanes, butoxysilanes, etc., which are able to polymerize to form the corresponding polysiloxanes. However, not all the new-formed Si–O–C bonds are equal: the larger the organic group, the greater the steric hindrance that resists hydrolytic cleavage of the bond, necessary to link to an OH-containing stone surface (Figure 13).^[44]

TEOS reacts with the OH groups present on a stone surface. After condensation, the surface is protected by a polysiloxane layer.

One of the most common approaches to consolidate stone materials bearing OH groups on the surface is to use alkoxysilanes that have hydrolyzable alkoxy groups attached to the central silicon atom. This may result in: i) the simple functionalization of the surface by nonhydrolyzable OR groups attached to the Si; ii) the exploitation of the R group as an initiator or linker for appropriate polymeric compounds (for example, epoxy resins); iii) the alkoxysilane polymerization to give the relative polysiloxane compounds.

Thanks to the use of polyalkylsiloxanes, significant improvements have been observed in the rupture modulus of the treated stone material compared to its starting characteristics.

In addition, the same silicone macromolecular chains, often cross-linked, show improved characteristics compared to short-chain alkoxysilanes, which instead tend to be more brittle and break more easily.^[36]

Figure 14 shows the schematic mechanisms of stone consolidation, which includes the infiltration and the gluing processes, and the resulting silica network.

Two generally recognized drawbacks of alkoxysilane consolidants are the inability to bind to calcite and the tendency of the gels to break down upon shrinkage and drying because of their brittleness. Weiss, et al.^[45] have addressed the problem of adhesion to calcite by chemically altering the mineral surface. Given that calcite contains few hydroxyl groups, with which alkoxysilanes can condense, it was proposed that a hydroxyl-rich surface is created by reacting calcite with ammonium hydrogen tartrate. The calcium tartrate formed can condense with the alkoxysilanes to create Si–O–C bonds that bind the gel to calcite. However, the hydrolytic stability of these Si–O–C bonds is highly dependent on the nature and steric hindrance of the organic carbon-bonded

group. Specifically, the tartrate group is large and is in turn hindered by its binding to the calcite substrate.

Alternatively, to improve the stability of the bonds between the calcite interface and the alkoxysilanes, alkoxysilane coupling agents are used, which contain hydrolyzable OH groups (usually three) attached to the central silicon atom and a fourth group attached to the silicon with a nonhydrolyzable Si–C bond. The use of coupling agents has been shown to be critical in significantly improving the modulus of rupture of the resulting materials.

The second major problem associated with alkoxysilane consolidants is their brittleness and relative tendency to crack with drying and shrinkage. This issue has been addressed by various approaches. In particular, Wendler^[46] proposed to lower the brittleness of the consolidating material by using long linear chain siloxane segments, the volume of which is essentially independent of the occurrence of the condensation reaction of the siloxane group. An additional effect of this approach was to make the transition between treated and untreated stone less abrupt, resulting in it being less susceptible to fouling. Both the consolidant and the consolidated stone were found to be less brittle. In addition, the transition between the deteriorated stone that has been consolidated and the nondeteriorated or unconsolidated stone laying below the surface was less abrupt. This smoother transition makes the treated stone less prone to contour scaling.

An effective alternative approach to decrease shrinkage was the use of micrometric silica as an additive. Stone materials treated in this way showed an increase in Young's moduli (up to 153%), while shrinkage-related pore sizes were greatly reduced.^[47]

From a coloration point of view, the application of alkoxysilane consolidants on various types of stone has proven to be effective in maintaining the initial characteristics of untreated stone even decades later.

However, it should be emphasized that the only acceptable condition is that the treated and untreated stones be identical. Clearly, a change in color due to treatment is undesirable. However, for some stones, it has occurred that the treated stone maintains the same color as the untreated stone at the time of treatment but over time becomes darker than the untreated substrate. In some cases, however, the treated stone may appear darker because it is more resistant to erosion: in other words, sometimes it is the continued erosion of the untreated stone that causes the latter to change its color.

4.1.2. Epoxy Resins

Although to a lesser extent than alkoxysilanes, epoxy resins have also been used for the consolidation of stone materials.

In general, epoxy resins, often in the form of oligomers dissolved in a suitable solvent, are infiltrated into the stones to be consolidated. The use of solvent is necessary to decrease the high viscosity of epoxy resins, which limits their infiltration in-depth, especially if the substrate is not made up of sufficiently large pores. Moreover, the size of the pores is a critical parameter also in relation to the size of the consolidant itself. This means that the use of preformed polymers makes the infiltration process even more difficult, if not impossible. From this point of view, it is certainly preferable to infiltrate the precursor of the consolidating

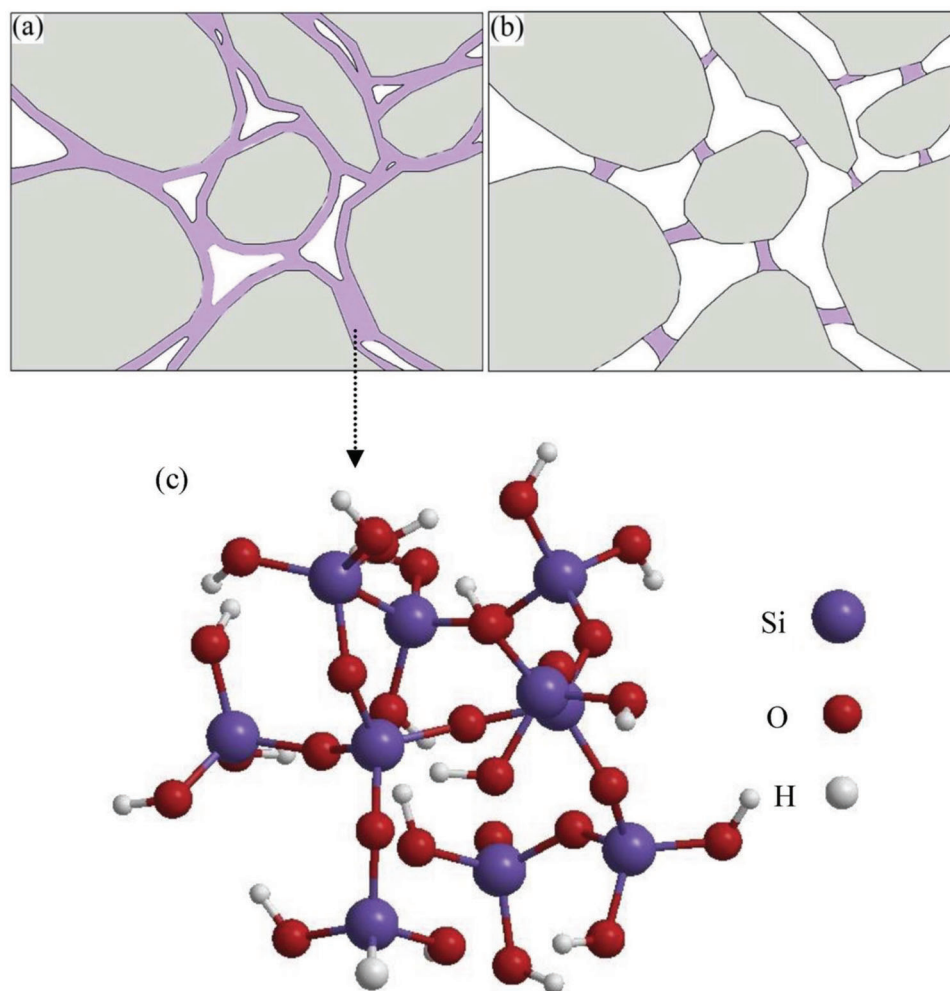


Figure 14. Mechanisms of stone consolidation: cohesion by filling process a), gluing process b). Schematic diagram of a silica network from alkoxy silane consolidants c). Reproduced with permission.^[2] Copyright 2019, Elsevier.

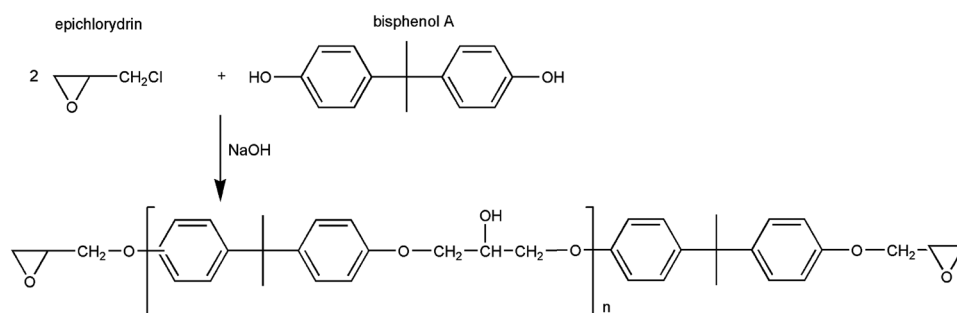


Figure 15. Typical step-growth polymerization mechanism of an epoxy resin.

material (in this case, monomers or oligomers) and carry out in-situ polymerization.^[48–51]

The basic chemistry of epoxy polymers is shown in **Figure 15**. Although a wide variety of epoxy resins are available on the market, among the most used in practice, those based on glycidyl esters of bisphenol-A obtained from the reaction of epichlorohydrin and bisphenol-A stand out. Commercial resins are mixtures

of oligomers of various degrees of polymerization, although, in general, values below 2 are preferred, to guarantee a product in a liquid state.

Since R is polyfunctional and R' contains additional amino groups, the final product can be expected to be extensively cross-linked and have all the properties of a thermosetting polymer. On the other hand, methylene groups, which are doubly

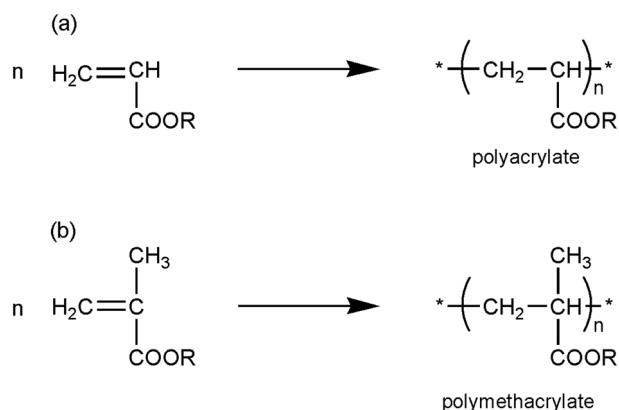


Figure 16. Polyacrylates a), and polymethacrylates b) obtained from the corresponding monomers.

activated between aryl oxygens and hydroxymethylene groups, are susceptible to light-catalyzed autoxidation. This explains the chalking and poor oxidative behavior of the epoxy resins employed as external coatings.

Moreover, regarding the tendency to staining, it has been shown that there are large differences between the various glycidyl ethers of bisphenol A available on the market. Therefore, in addition to the choice of the most appropriate consolidant, the problems are often attributable to the skills and abilities of the operators who leave the resin concentrated as a surface layer rather than favoring a deep homogeneous distribution.^[52]

In addition, notwithstanding the above, polyepoxy compounds are available in a wide range of viscosities. Considering that the introduction of solvents is often a source of practical and environmental issues, there is the possibility of using a combination of epoxy resins, and hardeners, replacing the solvent with a reactive diluent.

The obvious advantage is to allow a better penetrability inside the stone to be consolidated and a more complete and homogeneous filling of the pores, at the same time ensuring a lower environmental impact and better safety for the operator.

4.1.3. Acrylic Polymers

For stone consolidation, acrylic polymers typically belong to two subclasses, namely polyacrylates and polymethacrylates (**Figure 16**), which can polymerize according to the scheme presented in **Figure 17**.

Both the corresponding homopolymers and their copolymers have been studied and used in stone consolidation. Obviously, variations in composition and microstructure do significantly affect their final properties.

In general, these polymers are thermoplastics and can be dissolved in suitable solvents such as aromatic hydrocarbons, halogenated hydrocarbons, acetone, and methyl ethyl ketone.

Generally, acrylic polymers are transparent, and many of them find or have found use in various fields due to their optical properties. Although they are generally believed to be very stable to UV radiation, under these conditions some of them are prone to cross-link.

The glass transition temperature of acrylic polymers, T_g , is a very important parameter to consider in view of their applications. Specifically, the T_g will tend to increase both with the molar mass, and because of the R groups (**Figure 16**). Bulky groups will tend to stiffen the chain and increase the glass transition temperature. In addition, polar groups have a stronger effect than non-polar ones, because polar interactions limit free rotations and, consequently, the T_g is higher. In general, polymethacrylates have much higher T_g values than polyacrylates.^[53]

Due to the side polar groups, acrylic polymers are good adhesives. They can be used for such porous inorganic materials as stones. However, acrylic resins are not structural adhesives, and they are not suitable for joining heavy, bulky pieces. In fact, because of the viscous sliding of macromolecules (i.e., creep), the resulting adhesion is time-dependent: under a constant load, the corresponding deformation first increases rapidly and then slows down over time up to possible failure.

Among acrylic polymers, Paraloid B72 (a copolymer of ethyl methacrylate and methyl acrylate in a ratio of 70:30)^[54] is probably the most successful to produce stone materials since the 1960s.

However, being a preformed polymer, its practical use clashes with the already exposed problems related to the application of a material that, although applied in solution, is characterized by high viscosity and whose molecular dimensions can exceed those of the pores, in which it should infiltrate.

In addition, a change in coloration and surface gloss has often been found in some objects treated with this consolidant.^[55]

As already mentioned for epoxy resins, even in the case of this class of polymeric consolidants, one of the main practical problems is related to the poor ability of the polymer solution to penetrate deep inside the stone substrate, due to both the viscosity and the size of the macromolecules compared to those of the pores of the stone.

To overcome this problem, it has been proposed to carry out *in situ* polymerization of monomers, which have molecular dimensions much smaller than those of the corresponding polymers. In addition, if liquids, they can be applied without dissolving them in any solvent or, if this is necessary, their solutions have a lower viscosity and therefore higher concentrations of consolidant can be applied.

However, in these systems, common polymerization techniques cannot always be applied. In particular, due to the opacity of the stone, classical photopolymerization cannot be used. Thermal polymerization, which involves the heating of the monomer-initiator mixture, is applicable only to small objects, which can be placed in suitable ovens.

To overcome this drawback, our group proposed the frontal polymerization (FP) technique, a method for converting monomers into polymers, in which polymerization is triggered at one point, generally by heating or by radiation. In the case of sufficiently exothermic polymerization reactions, such as those of acrylic and methacrylic monomers, a hot polymerization front is generated, which propagates within the monomer medium transforming the monomer into the polymer (**Figure 18**). Considering that this is achieved without the need to heat the entire substrate, the technique is potentially also useful for the consolidation of large stone materials.^[48–50]

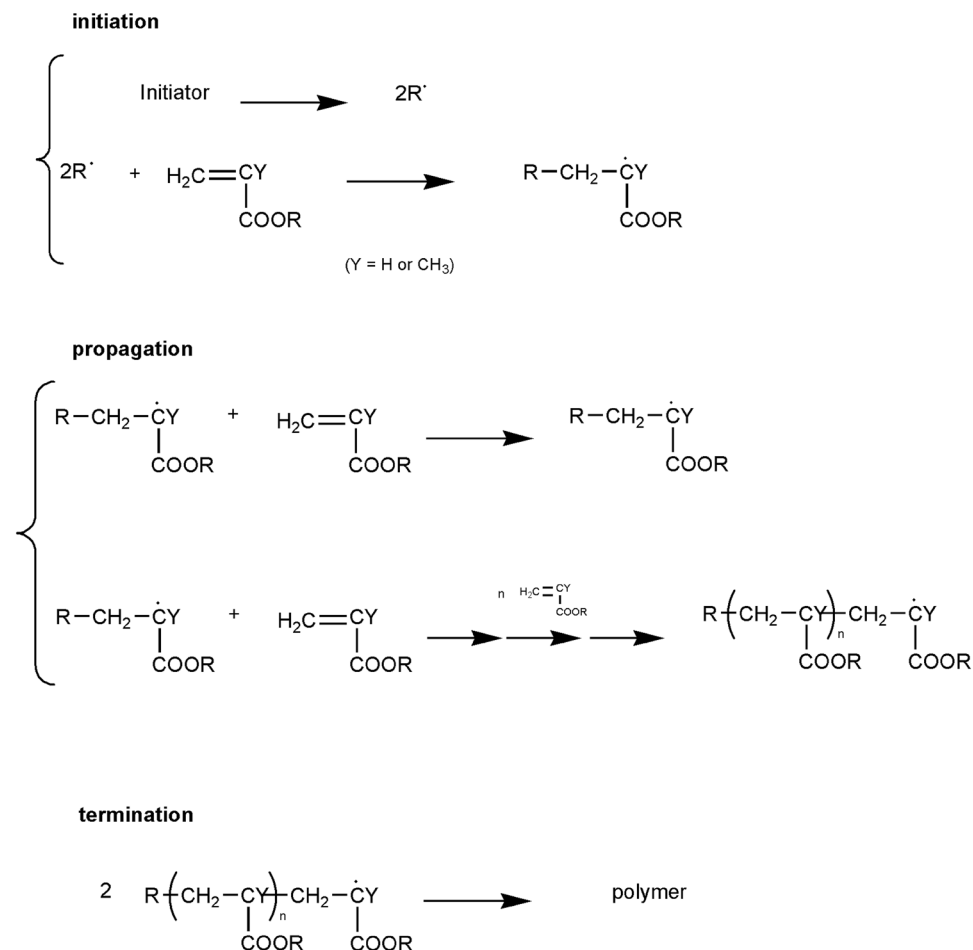


Figure 17. Kinetic scheme of poly(meth-)acrylate polymerization.

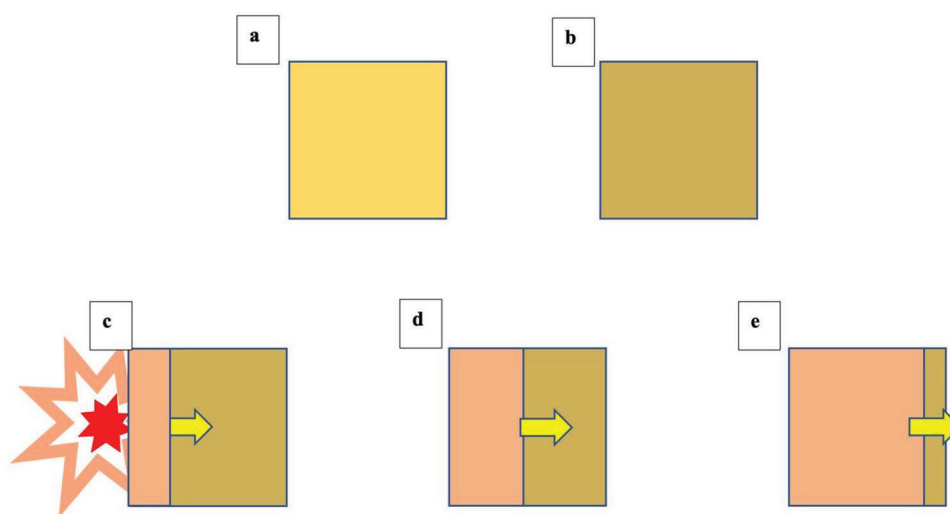


Figure 18. In situ frontal polymerization (FP): a) stone substrate before treatment; b) stone substrate soaked with a proper monomer; c) external polymerization ignition (generally, application of heat in a spot) and front formation; d,e) polymerization front propagation: the monomer is converted into the polymer in depth.

4.2. Viscosity Issues of Organic and Hybrid Consolidants

Although it is not advisable to define viscosity threshold values since stones have even very different absorption capacities, Sena da Fonseca et al. suggested operating under conditions not too far from those of commercial products. In this view, BSOH100 and TV100 (two alkoxy silane-based products) are characterized by viscosity values of 2.5 and 5.3 cP, respectively. However, this is something that needs to be evaluated on a case-by-case basis and therefore should only be considered as a useful starting point.^[56]

Specifically referring to epoxy resins, their viscosity is generally characterized by relatively too high values to ensure effective penetration within the stone substrate. For example, in its low molecular weight form, bisphenol A diglycidyl ether (DGEBA, one of the most used) has a viscosity between 11 000 and 16 000 cP at room temperature. It is therefore necessary to reduce it by adding reactive or nonreactive diluents. The former contain epoxy groups and have viscosities between 1 and 70 cP and can be mixed up to 20 wt% loading. However, as the concentration of DGEBA is reduced, there occurs some loss of mechanical and chemical properties. On the other hand, nonreactive diluents (e.g., benzyl alcohol) tend to increase flexibility and decrease mechanical and chemical strength much more than reactive diluents, since they do not participate in the bonding process but impart properties that change over time due to their evaporation. In general, once fully evaporated, they leave the epoxy much harder, but, at the same time, less tough (i.e., resistant to impact).^[36]

As for acrylic consolidants, Paraloid B-72 (an ethylmethacrylate-methylacrylate copolymer) is among the most widely used. However, its solutions in various organic solvents show too high viscosity values (2500–5500 cP), which are unsuitable for effective deep applications. From this point of view, the two components of Paraloid B-72, which instead have viscosity values of 0.6 cP (ethyl methacrylate) and 0.4 cP (methyl methacrylate), are certainly to be preferred.

4.3. Mechanical Properties of the Consolidated Stones

Summarizing the effects of different organic and hybrid consolidants on the mechanical behavior of the treated stones is very difficult, as it is affected by several parameters, such as the type (structure and chemical composition) of consolidant, the type of treated stone substrate, the consolidation process, and consolidant penetration depth, among others. The scientific literature reports a few examples that are related to specific consolidant-stone pairs, but that can provide some quantitative indications about the mechanical features of the resulting final materials. In particular, Delgado Rodrigues and Costa^[57] compared the mechanical properties of granite after treatments with various consolidants belonging to different classes, namely: ethylsilicate (W); styrene—acrylic—silicone copolymer in aqueous solution (M); poly(vinylidene fluoride co-hexafluoro-propylene) in delifrene AC (AK); cycloaliphatic epoxy resin plus aliphatic polyamine (EP). They first noticed a large difference in the penetration depth: in fact, as one may expect based on viscosity and molecular size issues, polymeric consolidants (i.e., M and AK) exhibited a poorer penetration.

Regarding mechanical properties, the use of EP proved to be the most effective (achieving a Young modulus of 21.4 GPa), followed by R (16.8 GPa) and W (13.8 GPa) with respect to untreated granite (15.5 GPa). Besides, the poor penetration of M did not allow for performing reliable tests after the treatment with this consolidant.

Remzova et al.^[58] observed an improved mechanical behavior achieved by using various ethylsilicate consolidants on different sandstones. A very wide spectrum of performances was found, depending on the consolidants used: actually, the increase in mechanical strength ranged from 0 up to about 230%. Although the use of Dynasylan 40 (a low-viscosity ethyl polysilicate containing 40% silica) has been shown on average to be among the most effective, it is difficult to draw general conclusions about the use of a specific consolidant; conversely, it is necessary to evaluate on a case-by-case basis the best intervention to be applied under the specific conditions encountered.

4.4. Sustainable Polymers for Consolidation of Stone Materials

Quite recently, the so-called “intrinsically reversibility/re-treatability” of biopolymer coatings suitable for the consolidation of stone materials has been successfully assessed: this peculiarity is very important, especially within a circular economy approach, as the consolidating biopolymer coating is expected to either disappear from the surface of the consolidated stone once the consolidating action comes to an end or give rise to the formation of unaggressive residual products, hence avoiding any possible problem when successive consolidation/conservation actions will be required.^[59]

In this view, in their pioneering work, Ocak and co-workers^[60] designed biodegradable coatings for marble stone, made of four different biodegradable polymers, namely, zein, chitosan, poly(3-hydroxybutyrate), and poly-L-lactide. Despite their acceptable barrier features toward SO₂, zein and chitosan polymers promoted the reaction between the stone and the SO₂ gas: this finding was attributed to the higher propensity of the zein- or chitosan-coated marble to entrap water vapor with respect to the uncoated stone. Among the tested biodegradable polymers, poly-L-lactide was the most performing in decreasing the gypsum formation on the stone surface.

Then, Giuntoli and co-workers^[61] tested the performance of 16 fluoro-functionalized poly-L-lactides, synthesized on purpose utilizing 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol and 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyl alcohol as co-initiators in the ring-opening polymerization of L-lactide and rac-lactide (i.e., the racemic mixture of L- and D-lactide), on white dolomitic Shivec marble. Water protection effectiveness, photostability of the coatings, and color changes of the treated marbles were thoroughly assessed: the modification of poly-L-lactide with fluorine accounted for an increased water repellency of the treated stones, as well as enhanced photostability. In a further research effort, the same group^[62] replaced the fluorinated alcohols with Fluorolink D-10H, a commercially available perfluoropolyether bearing two hydroxy telechelic functionalities, and synthesized poly-L-lactide-perfluoropolyether-poly-L-lactide block copolymers, which were coated onto white dolomitic Shivec marble. The coated stones exhibited increased water repellency, as

well as enhanced photostability with respect to poly-L-lactide homopolymer, thanks to the segregation effect of the fluorinated blocks on the outermost layers of the deposited coatings.

Andreotti and co-workers^[63] developed coating formulations based on two polyhydroxyalkanoates (namely, poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-4-hydroxyvalerate)), and assessed their performance on marble, sandstone, and limestone substrates. In particular, 3 wt/vol% solutions in CHCl_3 of each polyhydroxyalkanoate were applied to the selected stones by means of spraying, dip coating, or poultice. The effect of the coating method, also considering the different microstructures of the selected stones, on the overall coating performance was thoroughly evaluated. The coatings based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-4-hydroxyvalerate) turned out to be very effective in decreasing water sorption, regardless of the coating method. Finally, accelerated aging tests demonstrated that spontaneously reversible surface treatments for stones can be profitably achieved using the proposed biopolymers.

Very recently, Caruso and co-workers^[64] dispersed halloysite nanotubes into hydroxypropylcellulose, in the presence of wax microparticles, and assessed the suitability of the resulting biofilm as a stone protective coating, using a hydraulic mortar as a stone prototype. The biofilm was applied either by spraying or brushing: the former application method allowed for attaining very uniform coatings showing a strong adhesion to the stone substrate, hence higher performance with respect to those obtained by brushing.

To prevent salt crystallization in porous limestone (i.e., Lecce stone and globigerina limestone) Bassi and co-workers^[65] proposed the use of a hydroxyapatite-based consolidant (to reinforce the stone), a chitosan solution (to prevent salt crystallization and favor the formation of efflorescence rather than harmful subflorescence) and a combination of the two.

All the treatments, because of the very low amount of deposited material, did not affect the porosity of the stones, revealing outstanding compatibility with them and leading to (i) enhanced resistance to salt crystallization (evaluated as sample weight loss), (ii) the formation of efflorescence rather than subflorescence, and (iii) increased tensile strength, hence showing a good potential for consolidating porous limestone substrates.

From a general point of view, despite the significant research efforts (as witnessed by the nice examples here reported) performed so far in employing biodegradable polymers for the consolidation of stone, further investigation in real cases is undoubtedly needed to better assess their overall performance.

5. Conclusion

From an overall point of view, the current research on the assessment degradation of stones, their preservation, and consolidation, has undoubtedly shown significant efforts, especially by the academic community, leading to the design and application of effective consolidating systems. So far, the main polymer systems used in consolidation belong to three polymer classes, namely: fully organic acrylic and epoxy resins, and hybrid organic-inorganic alkoxysilane derivatives. These systems have known various degrees of success in the recent decades. At present, alkoxysilanes are the most preferred consolidants also

because of their versatility toward different types of stone materials.

Despite these research efforts, the number of polymeric consolidating agents is still quite limited, thus indicating that further research should be dedicated to this issue, also including intrinsically reversible/re-treatable biopolymer coatings. Closer interactions between polymer chemists and scientists having other expertise, such as geologists, archaeologists, architects, engineers, and restorers should be improved.

Moreover, the use of alternative methods of polymerization (e.g., in-situ and frontal techniques) should also be implemented, thus exploiting their high potential.

Besides, consolidation measures are often late and therefore undermine effective stone preservation. The authorities in charge are not always sufficiently aware and updated on the progress of research, and often—perhaps also due to lack of funding—do not intervene to avoid, or at least, limit degradation. Often, the lack of appropriate surveillance, especially regarding artifacts of historical and artistic interest, does not prevent random graffiti and vandalic actions.

Nevertheless, innovative research approaches in stone consolidation are expected to be proposed and applied in the future to significantly improve the durability and state of conservation of stone artifacts, thus resulting in both economic and historical advantages.

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Conflict of Interest

The authors declare no conflict of interest.

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consolidation, curing reactions, monomers and oligomers, stone degradation, stone materials

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