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CHARACTERIZATION OF DETERIORATED PROTECTIVES AND CONSOLIDANTS APPLIED ON STONE MATERIALS AND THEIR EVENTUAL BIO-REMOVAL

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Summary

Today, there is great awareness of the conservation of monuments. Development of techniques and research on plastic materials led to the advancement of new technologies and application methods, which were adapted for the restoration and conservation of stone materials.

Restorers and Conservators contributed to the diffusion of these treatments and application methodologies, though no preliminary experimental tests had been undertaken to ensure their efficacy. This entailed the development of degradation mechanisms, such as the generation of secondary products, due to the chemical interaction between the product applied and the substrate or the environment, and compromised the stability and the aesthetical aspect of the artefact.

For this purpose, a laboratory operating methodology was developed to evaluate the efficacy of commercial products which have been widely used for the restoration of stone materials, and to characterize any associated degradation mechanisms.

The commercial products were carefully selected and applied on stone specimens.

The results obtained were compared with those obtained from a spread sampling of Venetian surfaces treated in the past.

Thus, it was possible to characterize, compare and contrast polymeric groups and commercial products widely used in conservation.

Chemical FTIR and μFTIR analysis, microscopic observations, SEM-EDS studies, sponge tests, natural and artificial ageing in a Solar Box, evaluation of the resistance to growth of mould, were carried out in the laboratory and allowed the complete evaluation of the selected products.

The laboratory operating methodologies experimented have already been applied to the industry, in order to evaluate the applicability of experimental products of the firm Tenax spa, and promote the related commercial growth. A positive feedback was recorded.

Moreover, preliminary reports of the results obtained from the sampling of Venetian surfaces treated in the past, were considered useful for the monitoring of historic-artistic surfaces of interest, by the Venetian Superintendent.

Sommario

Oggi come in passato vi è una grande sensibilità e attenzione verso la conservazione dei monumenti, i quali posso considerarsi chiave di facile lettura della storia di una città.

Lo sviluppo della tecnica e la ricerca nel settore delle materie plastiche hanno portato allo sviluppo di nuove tecnologie e metodi applicativi sempre più all'avanguardia, applicabili al settore della conservazione della pietra. Restauratori e conservatori hanno contribuito alla diffusione e all'impiego di tali trattamenti e metodologie applicative, talvolta senza alcuna garanzia di efficacia data da test preliminari di laboratorio. Ciò ha comportato meccanismi di degrado come lo sviluppo di prodotti secondari di alterazione per interazione del trattamento con il substrato e l'ambiente, che hanno compromesso l'estetica e la stabilità del manufatto stesso. In tale contesto si inserisce il presente lavoro di ricerca, il quale si è proposto di mettere a punto una metodologia operativa di laboratorio per la valutazione dell'efficacia di prodotti commerciali, ampiamente utilizzati nel settore del restauro lapideo, e di caratterizzarne il relativo degrado. Mediante l'applicazione su provini di prodotti accuratamente selezionati ed i risultati ottenuti da campionamenti avvenuti nella città di Venezia su monumenti trattati nel passato, è stato possibile confrontare fra loro classi polimeriche e prodotti commerciali in genere ampiamente utilizzati in conservazione. Indagini chimiche FTIR e μFTIR, osservazioni microscopiche, studi al SEM-EDS, sponge test, invecchiamenti naturali e accelerati in Solar box, valutazioni della resistenza alla crescita biologica, sono stati condotti in laboratorio e hanno permesso la completa valutazione dei prodotti testati. L'applicazione di tale lavoro di ricerca in ambito industriale ha già avuto i primi riscontri positivi per lo studio dell'applicabilità di prodotti di nuova formulazione della ditta Tenax spa e il relativo sviluppo commerciale nel settore del restauro, così come relazioni preliminari sui risultati ottenuti dalle indagini su monumenti veneziani studiati, sono state considerate utili dalla Soprintendenza di Venezia per il monitoraggio delle superfici di rilevanza storico-artistica.

Contents

Chapter 1

Introduction and aim

1.1 The restoration of stone materials: a short review

Stone has been used since prehistory for building and decorative purposes. However, stone also deteriorates with exposure, especially within certain aggressive environments. Many stones such as marble can lose cohesion and break up to a depth where the decorated surface or sometimes the stone itself is imperiled. In the past, as today, though often limited by lack of knowledge, attention and sensibility, people have attempted to protect architectural and decorative stone from their inevitable deterioration.

In ancient times, though restoration meant the remake and reuse of an artefact, there was also a tradition of the maintenance of stone materials. The techniques that could be applied were limited by available materials. Moreover, in order to avoid deterioration and in particular the deleterious effects of water on sculpted surfaces, it was common to apply natural hydrophobic substances such as beeswax, oils, and natural resins either alone or in a mixture [1]. These natural products were the only materials available for the restoration of artifacts until the late XIX century.

The outbreak of the industrial civilization during the XIX century and the rapid development of the chemical industry and industrial complexes which used coal as fuel led to increased air pollution and consequent soiling and decay of building façades. Therefore, the necessity to conserve and restore stone materials became more frequent.

In the last decades of the XIX century and the first part of the XX, many recipes and patents prospered, with the intent to clean and enhance the intrinsic properties of stone materials, and so a wider range of resins became available. Alkaline silicates and fluoro-silicates were suggested as consolidants due to the possibility to hydrolyze after their application, with consequent precipitation of silica in the pores of stone, so strengthening it.

Hydroxides, such as barite and lime, phosphates and phosphoric acid, aluminate and mixtures of organic products such as paraffin, bitumen etc., were also widely experimented.

The advance of the chemical industry and the birth of the petrochemical industry produced a diverse variety of useful products with the potential to slow down the stone deterioration of many monuments.

At the end of the 1940s architectural and sculptural conservators initially accepted the arrival and diffusion of polymeric materials with great enthusiasm. There is hardly a polymer that was not suggested and used for a conservation application. However, the first attempts made in the 1960s were in some cases counter-productive due to the users' ignorance of the characteristics either of the products, or of the substrate-treatment behaviour.

Consequently, the initial great enthusiasm changed to a deep aversion towards organic stone treatment.

Nevertheless, thanks to the increasing research into plastic materials and improvements in application techniques, acrylic and epoxy resins, silicon-based products, fluorinated compounds and polyester polymers have been widely used in restoration, though in many cases without knowing exactly the effects of the treatments on the stone surface. Indeed, there is little record of works in which experimental resins were tested in the laboratory before being applied on monumental buildings [2]. Rehabilitation and restoration undertaken with any products without appropriate control measures can accelerate degradation [3].

Inappropriate use of commercial resins can produce irreversible damage to stone surfaces, leading to modification of several petro-physical parameters of the material (such as porosity) and to its decay by speeding up specific degradation processes such as colour change, formation of crusts and powdering. In addition, most of the organic products used were not specifically developed for use in conservation and restoration but for other industrial applications, and their datasheets are often incomplete as many of them are subject to patents.

Thus, it would be necessary to analytically characterize every material that is going to be used in conservation and restoration. Recently, several laboratory examinations were performed in order to evaluate the possible weak points of products applied on stones. For instance, Ginell and Coffman developed a methodology to reduce the yellowing of stone surfaces treated with aromatic and aliphatic epoxy resins [4], whereas Ferreira Pinto and Delgado Rodrigues used micro-drilling, ultrasonic velocity and flexural resistance as performance indicators to assess the influence of application procedures of three consolidants on four lythotypes and on the amount of product applied [5]. The knowledge of the mechanisms of alteration allows for better understanding of the needs, purposes, and limits of the different conservation treatments.

In the last 10 years, nano-compounds, a new class of products, have been developed and experimented with in conservation and restoration. The use of different products based on nano-particles, such as nano-lime, nano-silica, nano-titania, scattered in a polymeric or inorganic matrix, has been proposed in order to ensure better performances of the treated inorganic substrates. Nonetheless, the use of nano-compounds in restoration remains controversial. There are many concerns regarding their effectiveness, such as the small number of nano-particles currently spread in the binder matrix, the dangerous amount of water introduced into the substrate during the treatment, the corrosive effect produced on carbonate rocks by the acidity of the products, etc. However, they are widely spreading through professional practice and/or research, sometimes poorly, considering their congruence with the mineral nature of the substrate and its state of conservation, sometimes giving good conservation effects [6].

In general, if observing and studying treated surfaces, the application of all the products slowed down stone degradation although, over time, they continued to suffer decay.

Changing materials or interaction with time is inevitable. Aesthetic alterations caused by a treatment are the first to receive condemnation. There are cases where the polymer shows chemical changes, involving the formation of oxidized species, sometimes resulting in a chromatic variation of the surfaces, and physical modification, such as craquelure and powdering of aged products, leading to the de-cohesion of the stone substrate. Aesthetic alteration can also appear as a consequence of cleaning action on monuments treated in the past. This is, for example, the case of the main façade of the Royal Palace of Madrid, where dark stains appeared after cleaning of the surface, due to the previous superimposed protective treatment: a wax-based protection and an organosilic-based treatment [7].

Some products may also support or actually encourage microbe growth and cause unintentional problems. Historical stone monuments exposed to the open air, are generally likely to be covered and infiltrated with dust and organic matter. Rain, groundwater and airborne sources such as pigeon excrement are a rich source of nutrients which encourage biological deterioration of marble statues. The application of organic resins increases the carbon contribution and can support biological colonization. Synthetic polymers may also act as a food source and promote the growth of microorganisms, which leads to deterioration of that object. A wide variety of microorganisms can cause deep and severe degradation effects on stone surfaces, such as changes in their mineralogical composition and irreversible alterations in their aesthetic and artistic appearance [8].

Fungi, in particular, are generally assumed to attack stone by excretion of organic acids, such as oxalic, citric, and fumaric acid [9].

Assessing the resistance of a protective or strengthening agent to natural weathering or to microbiological attack, is typically a lengthy process necessitating long-term field trials.

For these reasons, in the last few years, international scientific research has focused on the study of the chemical stability and solubility of commercial products used in the past, in order to monitor the state of conservation of treated surfaces, and to make informed assessments of where a new treatment is necessary.

For these reasons, today, before any conservation treatments, conservators draw their data about materials from the scientific community, suppliers, fellow practitioners and many other sources.

Each one provides limited information regarding their own field of interest. The scientific community will focus on a narrow range of properties, usually reporting results which extend current experimental techniques. Suppliers will concentrate on the principal properties of the material used, usually reporting in terms of an industry standard test. A conservator will focus on the treatment and the object, frequently thinking less clearly about the material itself. Because the data sources may be incompatible and probably do not directly address the important aspect to the application in hand, it takes considerable experience and care to extrapolate and evaluate the data.

However, the experiences of the last years have clarified that an ideal product suitable for any problem cannot exist. According to the lithotypes, the state of conservation, the kind of artefact and the environmental conditions, it is possible to choose a treatment from those already experimented in the past, or recently produced.

1.2 The sensitivity towards conservation in Venice

In Venice, the sensitivity towards conservation and restoration of monumental buildings increased on the 4th November 1966 when a flood threatened the city. On that occasion, the Italian government asked UNESCO to promote studies of the monuments in order to safeguard one of the biggest and most untouched historical centres of the world, which has been preserved for centuries. Since that moment, several private committees have been set up all around the world, and free enterprise has taken place to make people aware of the necessity to protect the city. Scientific researchers were encouraged, and exhaustive reports were published regarding the general problems of the inner centre and the lagoon and more specifically of stone conservation [10].

The first test treatments in Venice, using synthetic polymers, happened during that period. It was an experimental time. Different typologies of products were tested on stone surfaces and appropriate application methods were developed in order to reach a good penetration depth and to avoid continuous solutions in the distribution. Unfortunately, especially in the case of interventions prior to the 1970s, very few well-documented treatments can be traced.

Often, the archives of Superintendents lack detailed reports of restoration treatments, and the study of the state of conservation of a stone artefact directly in situ could require the use of challenging mechanical instruments, such as movable arms or scaffolding, which are not easy to recruit.

On the other hand, several reports were published describing restoration and conservative treatments on Venetian stone monuments in detail, such as the granitic columns of S. Marco in San Marco square or the Vereri column on Murano island [11]. Detailed observation of the surface, in different areas of the artefact, is particularly important when scarce information regarding the applied treatment is available [12].

1.3 Elements of general principles and procedures of restoration of stone materials

The principles and practice of stone conservation are driven by restoration, economical and professional criteria, as well as correctness, respect for the significance of the object or building, and minimal intervention, and they forbid beginning any intervention without choosing the most suitable materials and methodology for their application. A preliminary study of an artefact is required, to focus on micro and macro-morphologies of the degradation.

Before any intervention, technical and scientific examinations allow an understanding of the petro-graphic nature of the stone or lithoid substrate of which the monumental building or statue is made, covered or decorated in, to define its mineralogical and chemical composition, and those of alteration products which may cover the stone surface such as black crusts, yellow patinas etc. Thus, at the beginning of a restoration process, a complete photographic and chemical documentation, and a detailed archive research have to be made, in order to verify the presence of past treatments on the surface. On the other hand, micro-fragments of stone may be sampled from the surfaces of interest, in order to be analysed in the laboratory. The fragments collected using a scalpel or a small chisel from already damages area or hidden surface have to be characterized either chemically or mineralogically. Plants or biological colonization also have to be identified. The results of the observation in situ, and of laboratory analysis may indicate the morphologies of stone deterioration and allow the choice of the most suitable intervention for the restoration.

The general aim of stone conservation in a monument is to clean/desalinate surfaces and structures, to consolidate (when necessary) the stone, to avoid any loss of materials, to increase its durability and coherence, to protect and to maintain the restored areas in good condition. Stone conservation should also provide a certain protection in order to improve the stone resistance to the environment. Therefore, restorers have to adopt a certain methodology to conserve stone artefacts, which in general can be summarised as: pre-consolidation process, desalination and cleaning, consolidation, protection of the stone surfaces and maintenance.

Every phase will be described more in detail hereinafter.

1.3.1 Preconsolidation

After a complete study of the state of conservation of a monument, if the surface is strongly altered and if scaling, exfoliation and powdering phenomena are present, the monument has to be pre-consolidated before cleaning. Spray or other forms of reversible consolidants can be used in order to fix raised scales onto the substrate.

1.3.2 Desalination and cleaning

Prior to cleaning, in order to remove soluble salts which can cause damage to the artefact, such as loss of materials or cracks due to the development of subflorescence, or the appearance of superficial patina due to the presence of efflorescence, the surface can be treated with a particular poultice (sepiolite for example).

The cleaning process is really delicate and irreversible, as it is possible to definitely compromise the aspect of an artefact if the wrong products or methodology is used.

For this reason, every phase of the cleaning process must be gradual, selective and checkable. Dangerous secondary products, such as soluble salts must not be produced, nor any modification, micro-fractures or strong abrasion of the cleaned surface. The most common methodologies for stone cleaning are water spray, micro sandblasting, chemical mixture of solvents applied with tixotropic media, laser ablation, clay poultices etc.

When the stone surface is completely clean, desalinated and all biological colonization is removed, it is possible to proceed with the consolidation process.

1.3.3 Consolidation

"Consolidation" means a particular treatment oriented to reconstitute those physical-mechanical properties lost through deterioration. In general, consolidation should improve the cohesion between the components of a stone material. As a consequence, the product applied should enhance the mechanical resistance of the substrate and diminish its internal porosity in order to reduce the penetration of water, saline or acid solutions, etc., without altering the breathability of the stone.

The treatment should improve resistance to alteration mechanisms, especially those related to porosity, by volume changes in the pores without increasing the amount of critical micro-pores ($\leq 1\mu$), which increase freezing and thawing processes or favour salt crystallization damage [1].

A good consolidating agent should penetrate to a sufficient depth of the stone and anchor the deteriorated part to the sound one. Moreover, it should be tough and adhesive to stone, chemically stable and should not change the colour or the overall appearance of the material [13].

Where the chemical composition of the product has hydrophobic properties, the strengthening agent can also provide a protective effect. By limiting the penetration of liquid water and vapour, all chemical and physical processes linked to them will be largely reduced.

Even though a single product could work as both consolidant and protective agent, it is important to remember that consolidation purposes are different from those of protection and, in general, a good strengthening agent may not also guarantee the protection of the stone, which is usually the final step of a restoration intervention.

1.3.4 Protection

The “protection” of stone surfaces aims to slow down the alteration processes linked to the exposure of the artefact to the external environment. These treatments should focus on causes of deterioration and related transformations. Consequently, in order to protect surfaces from the inevitable aging, the protective interventions could address either the environment or the stone material. However, since intervention on the environment is not always feasible, chemical products are applied on the stone surfaces to act as a sacrificial protective layer, which needs to be periodically removed and renovated. Chemical products used as protective films should have hydrophobic properties in order to reduce the hydrophilicity of the capillary walls and of the external surface of stone materials.

Either way, consolidating agents or water repellents should not “seal” the stone surface and prevent future treatment.Reversibility is important: in this regard Plenderleith wrote *“in conservation work, there is a dictum that nothing should be done that cannot, if necessary, be undone easily in the future”* [14]. In fact, as it is mentioned by the 1972 Italian Carta del Restauro; any product applied to an art material should not interfere with future restoration treatments.

If reversibility is one of the most desirable features of treatment materials and methods, it needs also to be remembered that “total reversibility” is only a theoretical concept [15]. In general, the products applied in restoration usually undergo physical and chemical transformations under the influence of time, air, light and heat. Cross-linking or oxidation of the chains may cause a polymer to become insoluble in its solvent. Moreover, when it is applied to a porous material, or one with which the polymer reacts, it may be impossible to totally remove the polymer.

Even if the polymer chosen is the most stable on the market, after a certain period, it will necessarily be removed and renovated.

1.3.5 Maintenance

Maintenance, which is the last but the longest process in restoration, is based on the controls and the care of the conservation of monumental surfaces, as it is unacceptable to abandon and neglect a historical monument after its restoration.

1.4 Consolidation and protective agents: application methods and durability

In recent decades, art conservators have constantly required new products for coatings and consolidants to be applied on outdoor monuments. Inorganic products have been widely used in the conservation of stone materials and, since the second decades of the last century, different classes of synthetic polymers have been widely used for the conservation and the stone protection of monuments. While there is a widespread opinion that inorganic products should give better results, due to their closer similarity to the composition of the substrate, their greater longevity, their lattice structure and physical properties [16], synthetic polymers, if correctly chosen, ensure a better water repellent effect and an increase in the mechanical properties of the stone.

In general, the consolidation mechanism of inorganic products entails the precipitation of a new compound in the stone capillaries as a consequence of the chemical reaction between the product and carbon dioxide in the air, the water or some component of the stone. As an example, barium and calcium hydroxides have been commonly used for the consolidation of carbonate rocks due to the transformation into barium and calcium carbonates during the chemical reaction with the carbon dioxide of the atmosphere. The improvement of the mechanical properties of the treated material, using inorganic consolidants, depends on the nature and the abundance of chemical bonds, which take place between the product and the substrate. In general this improvement is less effective than using organic products, as inorganic consolidants are more fragile and less elastic. Using inorganic products it is possible to weld fractures whose walls distance less than 50-100 μm.

Both natural (drying oils) and synthetic film-forming materials are based on polymers, which are large molecules built up of many small identical units, named monomers [17]. In order to form a polymer, every monomer molecule has to be able to join up with two other molecules. Continued reaction of monomers produces a straight or branched chain.

Commercially, there are two main mechanisms used to build up polymers: vinyl polymerization and condensation polymerization. Vinyl polymerization is the result of the ability of a carbon-carbon double bond to open under the influence of an initiator (usually free radicals) and it is used to make by far the largest bulk of polymers. During condensation polymerization, which is the most used, two molecules react together to eliminate a small molecule, usually water, and to form the polymers chains by isolated reactions.

If there are no formal chemical bonds attaching one polymer molecule to another, the molecules will flow past one another. They can be dissolved in solvents and will melt when heated. For this reason, they are named thermoplastics. Examples of thermoplastics resins are polymethyl methacrylate (PMMA), polyvinyl acetate (PVAC) and organic compounds based on silicon. On the other hand, as the chains join with one another because of the presence of sufficient trifunctional monomers, it will be impossible to separate the chains from each other without breaking a chemical bond. The molecules will not melt with heating, but will only soften, due to a cross-linked structure. These are, for example, epoxy resins and polyester casting resins.

The two main properties that distinguish polymers from materials made up of smaller molecules are the variability of molecular weight and the fact that they have a glass transition temperature. In conservation, changes in the molecular weight distribution provide early evidence of significant reactions and changes in properties, while the glass transition temperature (T_g) is important in choosing a consolidant, adhesive or coating because of the softness of the polymer [18].

The main reasons for the popularity of organic resins are the great variety of polymers available and the possibility to add other components to their formulation to improve their characteristics. The chemical formulation, as well as the molecular size distribution, the degree of crystallinity, the nature and the proportion of additives, fillers and reinforcements, are responsible for their properties [19].

In conservation, polymers have to be applied to an object in a fluid state, in order to achieve coverage of the interstices of the object. If used as consolidants, adhesives or coatings, adhesion must be ensured between the polymer and the object.

Methods for applying the polymer vary. Some materials, such as epoxy resins, are applied as liquid prepolymers, which set by chemical reaction to form a polymer, others as a solution of polymer, which sets by evaporation of the solvents, or others again in emulsion or dispersion. However, diluted solutions of organic strengthening agents penetrate inside the pores of altered materials, and remain there after polymerization. The polymeric film sticks to the internal surfaces of the pores, and partially fill the cavities, soldering fractures whose walls have a distance of about 50-100 µm. Due to their macromolecular nature and the small diameter of the stone pores, in some cases deep penetration of the products in the stone substrate is avoided [20].

The success of a consolidation treatment is based on the penetration depth and the distribution of a product into the stone material. The concentration of the solution, the solvent, the contact period time, the pressure and the temperature may affect the distribution and the amount of the product, which can penetrate the stone material. The application method has to be chosen in order to optimize all the conditions, and it has also to take into account the dimensions of the artefact and its state of conservation. Two methods can be used both for small (i.e. a statue) and big (i.e. building façade) objects: the application of the product by brushing until complete saturation, and by spray. Unfortunately, these two methods cannot ensure good penetration depth. In the case of the object which might be treated in the laboratory, other application methods are preferable, such as treatment by capillary absorption of the product, complete immersion of the artefact in the consolidant solution and under-vacuum impregnation in an autoclave. These methods may also be used in situ with proper precautions. For example, the statues of the Porta della Carta of Palazzo Ducale in Venice were treated in situ by capillary absorption method by K. Hempel [21].

Polymers used in conservation must not change or cause harm to the objects. Most polymers are applied to objects in the hope that the process will not need to be repeated for 20 years minimum. For this reason, the useful life of a polymer has to be defined for conservation [22]. Chemical reactions due to light, heat, oxygen, water and pollutants cause change which make polymers unfit for their use in this context. Polymer films may undergo many alterations, such as yellowing, or may become brittle, weaker or insoluble, shrink, flow and dirty. The major chemical changes are cross-linking between chains, chain scissoring and oxidation of the main chains or side groups. These chemical changes reveal themselves as increasing insolubility, reduction in strength, increasing polarity and change in colour.

At room temperature or under direct sunlight, purely thermal degradation is probably unknown, whereas photolytic deterioration is found more frequently. Visible light causes slow changes in polymer properties as it provides the minimum amount of energy sufficient to activate the breaking of many chemical bonds in the polymer. Although heat and light provide the activation energy, reaction with oxygen usually causes the greatest damage. Oxidation occurs with all organic materials but the resistance of different materials varies greatly. It is essentially the reaction of oxygen with radicals formed in the polymer. Those polymers, which were originally prepared by condensation reactions, may undergo hydrolysis. One reason for the insolubility in a solvent is cross-linking between the polymer chains to form an intractable three-dimensional network, which occurs over a long period.

Finally, physical deterioration, due to the inherent properties of the polymer, from change in polymer properties or from outside influences, may cause shrinkage, expansion, cracks or absorb dirt.

Probably the ideal way to test a polymer for conservation purposes does not exist. However, the best way to test a resin would be to apply it to a likely range of objects, using several application methods, leave it there for many years, then reverse the treatment and assess the results. Therefore, this is not a realistic approach. The first step of any test procedure is to decide on the role of the polymer, and the general characteristics that it needs to possess. Evaluation methods of polymer properties may be divided into two groups: those designed by research into polymer properties, and those examining the interaction between the object and the added material. Most companies have introduced a battery of tests to validate the properties of the starting materials, the intermediate products, through to the final output. These tests have been increasingly standardized at both national and international levels, e.g. American ASTM International, British Standards Institute and the International Organization for Standardization. These industrial standard tests are usually carried out for reasons unconnected with conservation and their results should not be applied uncritically to restoration. Conservators need instead to understand the interaction between the objects and the polymers, and their variability. Tests carried out by the working conservator necessarily require simpler equipment than that available in a research laboratory. The conservator should carry out simple investigations on every batch of material to be used on objects. The results will become a valuable resource when the treatment must later be assessed and reversed [12].

It is advantageous that samples and tests are prepared consistently over years in order to ensure the repeatability of tests in different laboratories and comparison of the results obtained. Usually, a conservator must evaluate the solubility of a polymer, the amount of dust adhering to a treated surface, the effect of a polymer on mechanical properties, the effect of light, heat, water and impurities.

1.5 References

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Chapter 2

Experimental

2.1 Materials and methods

After detailed research to understand the restoration treatments employed in the last 50 years in Venice, the most commonly used consolidants and water-repellents were selected and, when still available in the market, applied on *venato* Carrara marble and Vicenza white limestone specimens, by brushing until complete saturation. When the chosen products were no longer available, the current commercial substitutes were tested.

Carrara marble (*venato*) and Vicenza white limestone, respectively metamorphic and sedimentary carbonate rocks, were selected as stone substrates because of their similar mineralogical composition but different texture and porosity. The Pietra di Vicenza is a workable soft limestone extracted from the Oligocene horizons in Colli Berici (Vicenza, Italy). It is totally uniform, white, porous (P_{TOT} % 27.8 [23]) and with small cavities covered by an ochre patina. The grain is heterogeneous due to the presence of remains of bioclasts made of calcareous algae and several groups of foraminifera, which constitute rather abundant skeleton rather abundant in the finer matrix carbonate. It is a very pure calcareous rock, principally made up of calcite and a lesser fraction of dolomite. The insoluble residue is a minor constituent (~1%) and is constituted of quartz (SiO_2), k-feldspar ($KAlSi_3O_8$), iron oxide (Fe_2O_3), goethite ($Fe^{3+}O(OH)$) and white mica ($XY_{2-3}Z_4O_{10}$ (PH, F)$_2$) [24].

Carrara marble is a general name indicating a variety of different marble types with varying colors, from pure white (*statuario*) to dark grey (*bardiglio*), passing through the most common greyish (*ordinario*), sometimes yellowish and pinkish (*pavonazzetto*). The texture of Carrara marble is normally massive and isotropic, sometimes foliated, with foliation marked by grey vein patches (*venato*), or brecciated (*calacatta* and *arabescato*). Carrara marble mostly shows a crystalloblastic-homeoblastic fabric formed by a mosaic of calcite crystals with straight-to-curved boundaries. Other common fabrics are slightly heteroblastic, sometimes weakly lineated, with more interlocked crystals showing embayed, more rarely sutured boundaries. Common accessory minerals are quartz, albitic plagioclase, K-micas, pyrite, magnetite. Tiny, dusty, black particles of carbonaceous matter/graphite are normally present. However, if these black particles are scarce, dispersed and abundant, they impart the dark grey of the *bardiglio*, whereas if concentrated in stains and veins they generate the *venato*. The total porosity (P_{TOT}) is about 0.7% (experimental data), whereas the water absorption at standard conditions (1 bar, 25°C) is 0.19% (EN 13755-08) [25].

Prior to treatment, the supports were carefully washed and brushed in order to remove soluble salts. After that, they were dried in a ventilated oven and kept in a desiccator until the application of the products. Specimen dimensions were 5 x 5 x 1 cm (fig. 2.1).

Figure 2.1: *Carrara marble and Vicenza white limestone specimens*

All the products tested were subjected to three different typologies of degradation: natural weathering, artificial ageing and resistance to growth of mould.

Natural weathering was carried out by exposing the treated specimens to Venetian outdoor conditions, precisely in a balcony of Palazzo Badoer (S. Polo). The balcony is located in a garden, far from channels and water-bus pollution. The specimens were placed on a plastic support, which was inclined by 60°, and totally exposed for 12 months. The aging was monitored monthly for the first three months, then every three months.

With the cooperation of Dr. Susanna Bracci, chemist at ICVBC-CNR Institute in Florence, photo-oxidative weathering was carried out using a SolarBox 3000 UV chamber, equipped with a xenon light source, with constant irradiation of 500 W/m^2, and filters 305 outdoor and IR in order to avoid the heating of the specimens. The samples were aged totally for 1200 h and monitored, for the first 600 h every 200 h, then every 600 h.

The resistance of coatings to growth of mould was tested exposing the treated specimens to outdoor condition for a month and, subsequently, keeping them for three months in a box with high humidity (about 95%) and temperature between 24-26 °C. The environmental chamber was built taking into account the ASTM D 3273 – 76 recommendation [26]. The bottom of a small plastic box, suitable for 30 specimens, was covered with wet absorbent paper. Some bars, made of polyester, were used in order to hold a grating panel inside the box and to separate it from the wet papers. The specimens were located on the panel, in a horizontal position, and the box was closed. A thermometer inside the box allowed checking of the internal temperature of the chamber.

2.2 Commercial products tested

The commercial products chosen for this research belong to different chemical groups of consolidants and water repellents commonly used in the restoration and conservation of stone materials. All the examined categories have been applied in Venice since 1960 in order to improve the cohesion between the components of a stone material or to protect the stone surfaces.The examined commercial products are detailed in Sections 2.2.1-2.2.7 below:

2.2.1 *Inorganic compounds*

BARIUM HYDROXIDE: a saturated solution of barium hydroxide was prepared in laboratory using distilled water and powder of barium hydroxide ($Ba(OH)_2 \cdot 8\ H_2O$) produced and sold by Carlo Erba.

2.2.2 *Silicon based products*

EAS 40 - CONSOLIDANTE: ethylic ester of silicic acid (ethyl silicate, TEOS). The product is commercialized by Sinopia Restauro and the solution is provided ready-to-use.

RHODORSIL CONSOLIDANTE RC90: tetraethylorthosilicate (TEOS) combined with a tin-siloxane catalyst and a water repellent component, which is a methyl-phenyl resin. The solvent is white spirit with the addition of xylenes, presumably to improve dissolution of the methyl-phenyl resin. The solution was prepared at 50% in the laboratory mixing the commercial product with non-aromatic white spirit.It is a strengthening and water-repellent agent.

<u>RHODORSIL CONSOLIDANTE RC80</u>: tetraethylorthosilicate (TEOS) combined with a tin-siloxane catalyst and a water repellent component, which is a methyl resin. The solvent is white spirit and the solution was prepared in laboratory at 50%, mixing the commercial product with non-aromatic white spirit. It is a strengthening and water-repellent agent.

<u>RHODORSIL H 224</u>: alkyl polysiloxane polymer. The solvent is a mixture of aliphatic hydrocarbons and the solution to be used for its application on stone materials has to be diluted by 10% using white spirit. It is a water-repellent transpiring agent.

<u>HYDROPHASE</u>: alkyl-alkoxy silane with molecular dimensions similar to those of water (5-10 Å). The commercial product, produced by Phase Restauro, was provided ready-to-use. It is a water-repellent agent.

2.2.3 *Nano-particles products*

<u>PF3</u>: water dispersion of photo-catalytic titanium dioxide modified with organic derivative of silicon.The commercial product has pH 4.5 ± 0.2 and is provided ready-to-use. It has a water-repellent and self-cleaning effect.

2.2.4 *Acrylic polymers*

<u>PARALOID B72</u>: ethyl methacrylate – methyl acrylate copolymer, PEMA-PMA, produced by Rohm and Haas. Thermoplastic resin with good resistance to light and aging. It was prepared in the laboratory and used for the tests in solution of 4% in acetone.

<u>ACRYLIC 33</u>: (ex PRIMAL AC 33) acrylic emulsion. Water dispersion of pure acrylic resin with excellent resistance to alkalis and weathering. pH 9. A solution of 8% was prepared in the laboratory and applied on the specimens.

2.2.5 *Epoxy resins*

<u>EUROSTAC EP2101</u>: cyclo-alyphatic epoxy resin dissolved in organic solvents and catalyzed with the hardener K2102, aliphatic ammine, mixed in ratio 5:1 in weight or 4,5:1 in volume, sold in Italy by Bresciani and produced by STAC industry. It polymerizes at room temperature and has an excellent resistance to light and UV radiation.

2.2.6 *Fluorinate products*

FLUOROPHASE: vinildene–fluoroesafluoropropene copolymer dissolved in acetone and produced by Phase Restauro. The product is oil and water repellent and is provided ready-to-use. It is stable to chemical agents and UV radiation.

2.2.7 *Traditional and modern hydrophobic treatments*

LINSEED OIL: a drying oil commonly used in restoration in the past due to its hydrophobic properties. A portion of linseed oil was applied by brushing on the stone surfaces.

R21 MICROCRYSTALLINE WAX: mixture of saturated aliphatic hydrocarbons having a high average molecular weight. White scales of microcrystalline wax with a melting point of 105°C, were melted and applied hot in liquid form on stone surfaces. It is commercialized by Phase Restauro.

LINSEED OIL AND MICROCRYSTALLINE WAX: the linseed oil cited above was applied on the stone surfaces by brushing. After the complete impregnation of the stones, when the surfaces were completely dried, a solution of hot R21 microcrystalline wax was brushed on the samples.

After a preliminary characterization, all the tested products were applied on Carrara marble and Vicenza white limestone specimens by brushing until complete saturation imbibition of the substrates. The samples were initialed as is showed in table 2.1.

COATINGS	*NATURAL AGEING*		*PHOTO-OXIDATIVE AGEING*		*BIOLOGICAL DEGRADATION*	
	Carrara marble	*Vicenza limestone*	*Carrara marble*	*Vicenza limestone*	*Carrara marble*	*Vicenza limestone*
Ba(OH)$_2$	*C6*	*V6*	*C-F*	*V-F*	*Bio C6*	*Bio V6*
EAS 40	*C5*	*V5*	*C-E*	*V-E*	*Bio C5*	*Bio V5*
Rhodorsil RC90	*C3*	*V3*	*C-C*	*V-C*	*Bio C3*	*Bio V3*
Rhodorsil RC80	*C4*	*V4*	*C-D*	*V-D*	*Bio C4*	*Bio V4*
Rhodorsil H 224	*C8*	*V8*	*C-H*	*V-H*	*Bio C8*	*Bio V8*
HYDROPHASE	*C11*	*V11*	*C-K*	*V-K*	*Bio C11*	*Bio V11*
PF3	*C7*	*V7*	*C-G*	*V-G*	*Bio C7*	*Bio V7*
Paraloid B72	*C1*	*V1*	*C-A*	*V-A*	*Bio C1*	*Bio V1*
Acryl 33	*C13*	*V13*	*C-M*	*V-M*	*Bio C13*	*Bio V13*
EP2101	*C2*	*V2*	*C-B*	*V-B*	*Bio C2*	*Bio V2*
FLUOROPHASE	*C12*	*V12*	*C-L*	*V-L*	*Bio C12*	*Bio V12*
Linseed oil	*C9*	*V9*	*C-I*	*V-I*	*Bio C9*	*Bio V9*
Microcrystalline wax	*C10*	*V10*	*C-J*	*V-J*	*Bio C10*	*Bio V10*
Oil + Wax	*C14*	*V14*	*C-N*	*V-N*	*Bio C14*	*Bio V14*
Untreated	*C0*	*V0*	*C-O*	*V-O*	*Bio C0*	*Bio V0*

Table 2.1: *Classification of specimens*

2.3 Investigation Methods

The selected products were preliminary characterized in sol (by GC/MS only in few cases) and gel form by FTIR analysis. The polymerization processes were enhanced and the morphology of the films cured on a slide were carefully observed using optical and scanning electron microscopes (OM and SEM).

Thanks to the cooperation with the scientific laboratory of Prof. Noni-Pagona Maravelaki of Polytechnic of Chania, some products were also analyzed by TG and EDXRF analysis and the films, polymerized on a slide, aged by photo and thermo oxidation. The UV chamber used for the photo oxidation was equipped with four 8 W black light blue lamps, emitting in the near-UV range (315-400 nm; 3 mW cm^{-2}), whereas the thermo oxidation was carried out in a ventilated oven set at 60°C. These experiments are designed to simulate the ongoing degradation of resins exposed to outdoor conditions.

All the products were applied by brushing on stone surfaces until complete saturation of the samples. The specimens were characterized by observing and describing the treated surface with the stereomicroscope, measuring the superficial hydrophobicity by Sponge Test, checking the polymerization reaction using μFTIR analysis, and assessing the chromatic variation of the surface by spectrophotometer.

The same methodology was repeated periodically on the surfaces of those specimens subjected to natural weathering and artificial ageing in order to monitor the degradation processes of the coatings.

At the end of the ageing processes, the samples were cut and the cross-sections were observed by SEM in order to measure the penetration depth of the treatments.

2.3.1 GC/MS measurements

The GC/MS analysis performed in this research was carried out using a TRACE GC 2000 Gas Chromatograph interfaced with the quadrupole Mass Spectrometer TRACE MS (Thermo Finnigan). The gas chromatograph was equipped with an HP5-MS column (length: 30 m, I.D.: 0.25 mm, film: 0.25 μm). The samples were injected in the split flow mode and the oven was set from 80°C to 300°C.

The identifications were supported by NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library, 2.0.

2.3.2 FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize both the sols and the xerogels, using a Perkin-Elmer 1000 spectrometer and a Jasco-Europe model FT/IR 4200 instrument in the spectral range of 400-4000 cm^{-1}. The sol samples were initially placed inside an AgBr cell with a Teflon spacer (0.05 mm thick) between the windows. In the case of the xerogels, they were homogenized with KBr and pressed to obtain a pellet using a vacuum hydraulic press. Sols and xerogels were recorded in the absorbance mode with a spectral resolution of 4 cm^{-1} and 75 consecutive scans were summed and averaged before applying the Fourier transform, in order to obtain a good signal-to-noise ratio.

After the application of the products on the specimens and during the ageing process, μFTIR analysis were carried out, in order to evaluate the polymerization and the degradation of the products. The instrument used was a Jasco IRT-5000 Irtron Infrared Microscope.

A micro scale of the polymeric films was sampled from the stone surface, using a needle, laid and pressed on a standard KBr pellet, then analyzed in transmittance mode.

2.3.3 Thermal analysis

The thermal decomposition of some of the coatings was assessed by means of differential thermal analysis (DTA) and thermogravimetric (TG) analysis with a Setaram LabSysEvo 1600. The TG analysis was performed under air atmosphere at a heating rate of 10 °C/min from 27 °C to 1000 °C, on samples dried at 60 °C for one day.

2.3.4 EDXRF technique

An EDXRF unit with ^{55}Fe, ^{109}Cd and ^{241}Am radioactive sources, and Si(Li) semiconductor detector (resolution 150 eV at 5.9 keV) was employed for the identification of the catalyst included in siloxane resins. The EDXRF analysis was performed in powder originating from cured films of the resins.

2.3.5 Optical microscope (OM)

The films cured on a slide were observed using a Leitz LABORLUX 12 POL S optical microscope, with magnifications of 40x, 100x, 300x. The films morphology was photographed by Leica CLS150E camera.

2.3.6 Stereomicroscope

The surface of the treated samples were periodically observed during the ageing processes using a Leica WILD M3Z stereomicroscope with increasing magnification (6,5x, 10x, 16x, 25x, 40x) in order to describe the physical and morphological characteristics of the samples.

A mask with 5 holes, as shown in figure 2.2, was built using a polyethylene slide, in order to take repeated pictures in a specific area of the sample’s surface to be able to compare the results obtained throughout the ageing process. The camera used was a Leica CLS150E model.

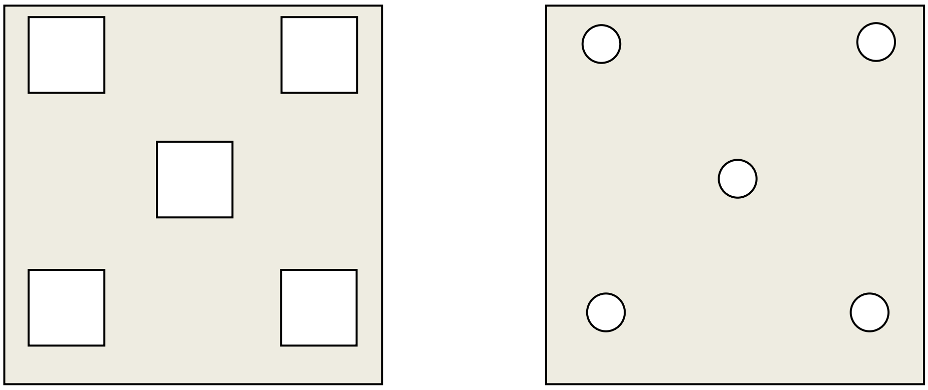

Figure 2.2: *Polyethylene slides projected for microscopic observations (on the left) and colorimetric measurements (on the right).*

2.3.7 Scanning Electron Microscopy (SEM)

Morphological observations and detailed chemical microanalyses of dried films polymerized on a slide and coated with a thin gold layer were carried out by Philips XL 30 SERIES SEM instrument. The semi-quantitative elemental composition was measured using an EDS coupled with EDAX X-ray dispersive spectrometer, equipped with a thin beryllium window. The accelerating voltage was 25 keV. The observations were carried out with respect to Normal 8/81 recommendation [27]. The same instrument was also used to measure the penetration depth of the products in the specimens, observing the cross-section of the cut samples.

2.3.8 XRD analysis

XRD analyses were carried out on both powder of cured films and powder of treated stones at the end of the aging processes, in order to study the crystallinity degree of the products used, the mineralogical forms which take place from the polymerization of the products, and the eventual mineralogical transformations of the stone material. The samples were analyzed using a PANalytical Empyrean, Series 2, difractometer (CuK/Ni, 40mA, 40KV).

The difractrograms were studied using X'Pert HighScore software.

2.3.9 Colorimetric measurements

Colour changes induced by degradation of polymers were evaluated by colorimetric measurements on treated specimens using a Konica Minolta CM-2600d. A mask with 5 holes, as shown in figure 2.2, was built using a polyethylene slide, in order to repeat the analysis always in the same area of the sample. Each datum is the mean value of these 5 measurements. The results were reported in the CIE-L*a*b* system and used to calculate the colour variation ΔE, as shown in the mathematic formula in equation 2.1. The analysis were carried out with respect to NORMAL 43/93 recommendation [28].

$$\Delta E^{*}\text{ab} = \sqrt{(L1 - L2)^2 + (a1 - a2)^2 + (b1 - b2)^2}$$

***Equation 2.1:** mathematic formula to calculate the colour variation ΔE*

2.3.10 Contact Sponge Method

The Sponge test was applied to check the maintenance of hydrophobic features of the treated stone surfaces.It consists of a 1034 Rodac_contact-plate, with a 5.6 cm diameter, containing a humid sponge Calypso natural make-up Spontex, with approximately 5 ml of water, which is thicker than the height of the borders of the contact-plate. During the test, the contact-plate is pressed against the treated surface of the specimens in a vertical position, applying the maximum amount of pressure, which is determined by the contact of the borders of the contact-plate with the examined surface. The period of time of contact-plate application was 3 minutes for Carrara marble and 1 minute for Vicenza white limestone samples. The difference in application time is due to the higher porosity of Vicenza limestone than Carrara marble.

The initial and final weight of the contact-plate containing the humid sponge, before and after contact with a surface, was measured using an analytical balance. The mean value of the difference in weight, corresponding to the amount of water which has been absorbed by the material surface under test, was expressed by the mass difference as a function of area and time, using the mathematic formula in equation 2.2, where Wa is the water absorption per square meter and unit time, m_i is the initial weight of the sponge inside the contact-plate, m_f is the final weight of the sponge inside the contact-plate after the test, A is the sponge area and t is time:

$$Wa(g/m^2 s) = \frac{\Delta m}{A \cdot t} = \frac{(m_i - m_f)}{A \cdot t}$$

Equation 2.2: *mathematic formula to calculate the water absorption per square meter and unit time (Wa)*

The sponge test was repeated 3 times for every specimen. The test was carried out with respect to UNI 11432 recommendation [29].

2.4 Resistance of coatings to growth of mould

In order to evaluate the resistance of coatings to the growth of mould, the specimens introduced into the environmental chamber were examined after three months of exposure, and the biological colonizations developed were characterized in detail. All the specimens were observed using the optical microscope Leitz LABORLUX 12 POL S (paragraph 2.3.5) and, thanks to a frame, all the different typologies of fungi were mapped in every specimen.

Then, using a Leitz Orthoplan optical microscope, on increasing magnifications (50x, 81x, 138x e 275x), the fungi were studied in detail and photographed by a Leica DC300 camera. In order to allow their identification, the fungi were laid on a carbon bi-adhesive disk using a needle and observed using the Scanning Electron Microscope (Philips XL 30 SERIES SEM, paragraph 2.3.7).

Due to the difficulties which emerged during the identification of the fungi, two different culture media were prepared in the laboratory with the same procedure: Difco^{TM} Mycological agar and Gelose Rose Bengale chloramphenical agar, in order to obtain more information about their nature from the aspect and the morphology of the fungal colonies.

To prepare 0.5 l of *medium*, using a flask, 14.85 g of agar was dissolved in 0.5 l of distilled water, heated by the bain-marie method, and located in a sterilizer at 120 °C for 20 minutes. The liquid culture *medium* was poured into Petri dishes and allowed to cool.

The treated and colonized faces of the specimens touched the media for almost 2 seconds, which became gelled and cooled. Then Petri dishes were kept for almost three days in a stove at 28°C. The developed colonies were observed and studied using a Wild Leitz M3 stereomicroscope with 6,5x, 16x, 40x magnifications. Some biological slides were set up in order to examine the morphology of the fungi in detail.

2.5 Evaluation of past treatments

In order to evaluate the behaviour of the main chemical groups of water-repellents (protectives) and consolidants after several decades of their exposure in Venice, chemical investigation of the alteration morphologies of the conservative treatments applied on stone surfaces were undertaken.

As a consequence of thorough research in the Venetian Superintendent archive, several monumental surfaces, which have been consolidated or protected since 1960 as part of well-documented restoration projects, were chosen as surfaces of interest. In order to enhance the degradation forms suffered by the resins and caused by the Venetian environment, a formal request was submitted to the Venetian Superintendent to sample the artefacts of interest. Following Normal 3/80 recommendations [30], some micro-fragments were sampled from the selected surfaces using a scalpel or a little chisel, with the support of the director conservator and restorer Lucia Bassotto of *Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna*, to be later studied in the laboratory. The samples were observed as such at the stereomicroscope (see paragraph 2.3.6) and their cross-sections were studied using the optical microscope (see paragraph 2.3.5). FTIR and μFTIR (see paragraph 2.3.2) were adopted in order to understand the chemical nature of the products applied, to investigate their state of conservation and the presence of eventual secondary products. SEM observations and EDS analysis (see paragraph 2.3.7) were carried out to understand the morphology and cross-section of the sample, focusing on the elementary composition of the treatments and mapping the penetration of the products in the stone substrate.

The surfaces of interest are summarized in table 2.2.

Chemical groups	***Surface of interest***	***Product used***	***Year of restoration***	***Treatment***
ACRYLIC RESINS	*ALTAR OF SACRISTY IN S. STAE CHURCH Author: probably Giuseppe Torretto*	*Raccanello ARD E0057 Raccanello ARD E0023*	*1978*	*Cleaning of surfaces using pure water and sepiolite poultice. The marble was consolidated using ARD E0057, whereas the stone was protected with ARD E0023. Responsible: Ing. Todeschini (Venice) with the supervision of S. Magnani and S. Longega.*
	MAIN PORTAL OF ARSENAL	*Paraloid B72*	*1973-1976*	*Cleaning of surfaces with tap water and AB57. The stone was treated using Paraloid B72. Responsible: Istituto centrale del Restauro of Rome, Supervisor: P. Mora.*
EPOXY RESINS	*VERERI COLUMN IN VERERI FOUNDATIONS - MURANO ISLAND*	*EUROSTAC EP2101*	*1985*	*Cleaning of surfaces using micro-sandblasting method in order to remove black crusts, washing and drying. For consolidation, cyclo-alyphatic epoxy resin EP2101 by capillary method was used (with gauzes and polyethylene sack) [31, 32]. Responsible: RWS Padova. Ing. Cavaletti*
	FRAGMENT COMING FROM THE S. MARCO BASILICA	*EUROSTAC EP2101*	*1984*	*Consolidation by brushing until complete impregnation of the surface. Responsible: prof. Lorenzo Lazzarini*
SILICONE RESINS	*S. ALVISE STATUE, located on the main façade of S. Alvise church. Author: Tino da Camaino/Agostino di Duccio or Tuscan author (XV c.)*	*SOGESIL XR-893 phenyl-methyl siloxane (50% benzene)*	*September-December 1967. It was the first treatment with synthetic polymers in Venice*	*Desalination, cleaning and consolidation by under-vacuum impregnation. [33-34] Responsible: LARES Diagnostica e conservazione di opere d'arte. Supervisor: prof. L. Marchesini.*
	4 ANGELS HOLDING THE ALTAR OF HOLY SEPULCHER IN S. MARTINO CHURCH. Author: Tullio Lombardo (second half of XV c.- first half of XVI c.)	*SOGESIL XR-893 phenyl-methyl siloxane (50% xilene) and MICROCRYSTALLINE WAX*	*1968: consolidation with SOGESIL XR-893 1991: protection with microcrystalline wax*	*Consolidation by under-vacuum impregnation with Sogesil XR-893. [34] Responsible: LARES Diagnostica e conservazione di opere d'arte. Laboratorio di San Gregorio. Supervisor: prof. L. Marchesini Protection with microcrystalline wax by brushing. Responsible: Ch. Vasco Fassina*

	FRAGMENT OF A LITTLE COLUMN OF CA' D'ORO PALACE.	*SOGESIL XR-893 phenyl-methyl siloxane*	*1967*	*(Venetian Superintendence) Consolidation by under-vacuum impregnation with Sogesil XR-893.* *Responsible: prof. Lorenzo Lazzarini*
	LUNETTE OF THE ANGLE CHAPEL OF S. MARIA GLORIOSA DEI FRARI CHURCH. Author: Maestro della cappella dei Mascoli	*X54-802 in propan-2-ol, distilled water, 2-ethoxy ethanol 1:0.1:0.04:1*	*1973-1974*	*Cleaning using sepiolite poultice and micro-sandblasting. Consolidation of marble by brushing [9].* *Responsible: K. Hempel and his assistant G. Musumeci*
INORGANIC COMPOUNDS	*HOLY WATER STOUP IN S. FANTIN CHURCH*	*Cold water solution of barium hydroxides, urea and glycerine.*	*1970*	*Impregnation by capillary absorption.* *Responsible: S. Z. Lewin (New York)*
	A COLUMN UPON THE GRAIT SCALE IN SCUOLA S. GIOVANNI EVANGELISTA	*Cold water solution of barium hydroxides, urea and glycerine.*	*1970*	*Capillary absorption method* *Responsible: S. Z. Lewin (New York)*
	LABORATORY SAMPLES	*1. Cold water solution of barium hydroxides* *2. Cold water solution of barium hydroxides and protection with a siloxane resin.*		*1. Total immersion in a cold solution of barium hydroxides* *2. Total immersion in a cold solution of barium hydroxides. Application of siloxane resin by brushing* *Responsible: prof. Lorenzo Lazzarini*
TRADITIONAL HYDROPHOBIC PRODUCTS	*MAIN ALTAR OF S.GIORGIO CHURCH*	*No information is available*	*No information is available*	*No information is available*

Table 2.2: *Venetian surface of interest to evaluate the state of conservation of past treatments.*

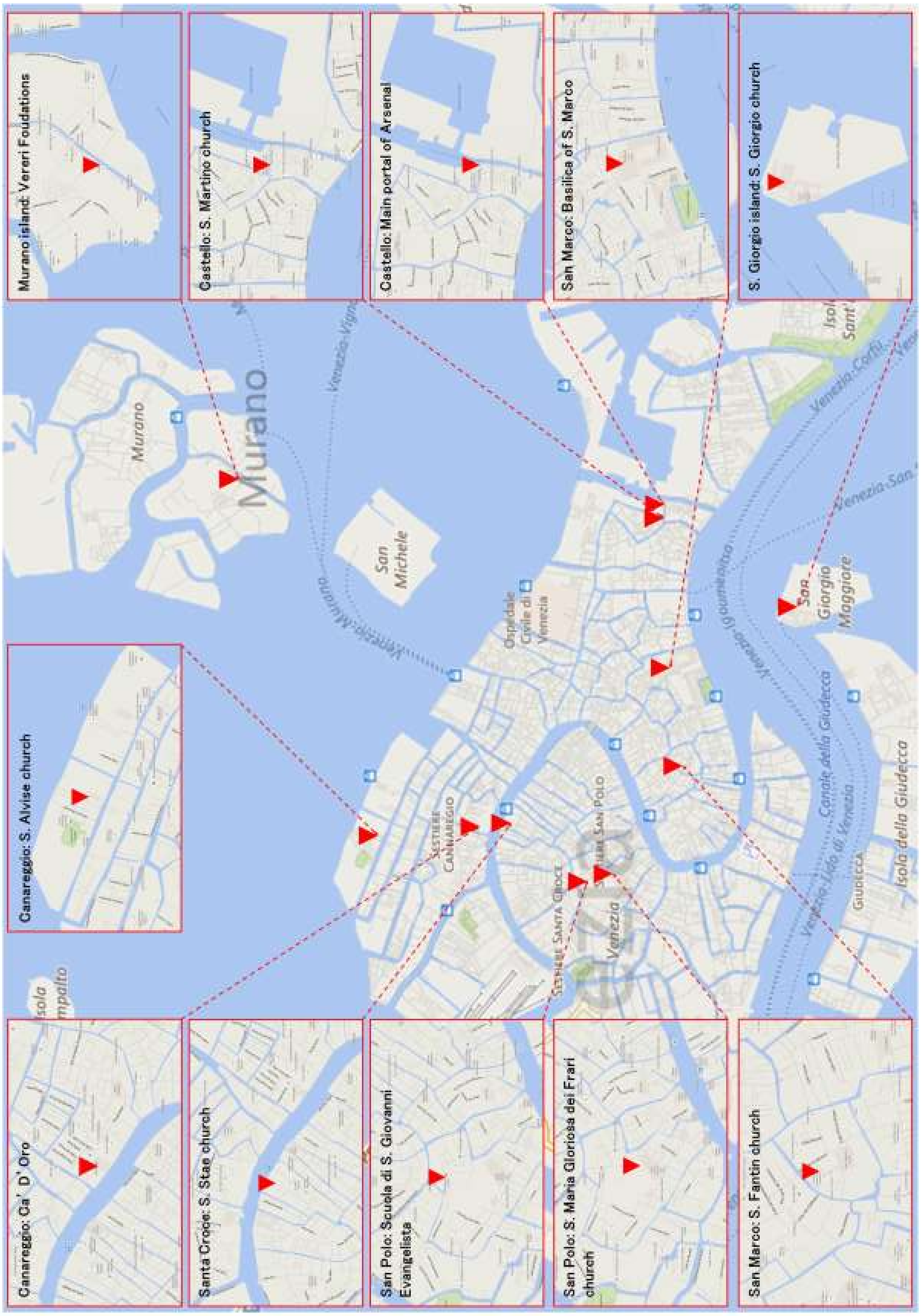

Figure 2.3: *Venice map with the location of the monuments chosen.*

2.6 References

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Chapter 3

Inorganic compounds

3.1 Inorganic compounds

Inorganic compounds are the oldest known strengthening agents used for the consolidation of stone materials. Due to their nature they are the most similar to stone materials and, for this reason, they are usually considered the most suitable for stone conservation. In general, they are inorganic reagents, such as hydroxides or bicarbonates, which are able to react with water, environmental humidity or atmospheric carbon dioxide to produce insoluble salts mineralogically similar to the mineralogical nature of those found in stone materials.

During the last century, water solutions of lime and calcium bicarbonate were widely used for the conservation of carbonate rocks. Both give rise to the formation of calcium carbonate, as shown in scheme 3.1, which precipitates into the stone pores and should bridge the cracks. Unfortunately the calcium carbonate of natural stones is quite different to that of the chemical reactions showed in scheme 3.1 and, consequently, they will have different mechanical properties. Due to the unsatisfactory results obtained, they were rarely used.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

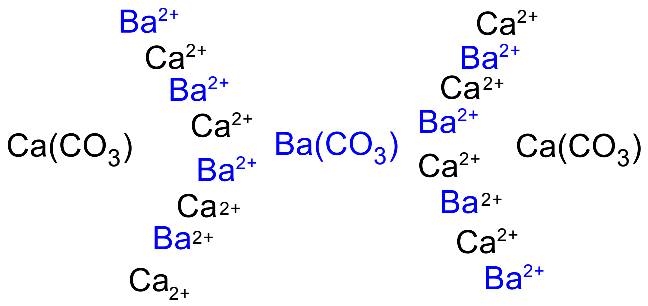
Scheme 3.1: *Formation of calcium carbonate from calcium hydroxide and calcium bicarbonate.*

Barium hydroxide is the most diffuse inorganic consolidant in restoration and it is still in current use. Barite reacts with atmospheric carbon dioxide producing barium carbonate (scheme 3.2) which is a salt almost insoluble in water.

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$$

Scheme 3.2: *Chemical reaction between barium hydroxide and carbon dioxide and consequent formation of barium carbonate.*

Prof. S.Z. Lewin examined this process in detail [35] and developed a theory regarding the possibility for barium ions to partially substitute calcium ions of the external layers of the crystalline network when two calcite grains, which are 50 μm apart, are in the presence of a barium hydroxide solution (scheme 3.3). The greater the distance between the grains, the greater the amount of pure barium carbonate which precipitates in the pores.



Scheme 3.3: *Schematic representation of calcium ions exchange with barium ions*

To increase the precipitation of barium carbonate, prof. S.Z. Lewin proposed adding 10% of urea to the concentrated solution of barium hydroxide (≈ 20%), which developed carbon dioxide and ammonia (scheme 3.4). In order to prevent an excessively rapid reaction, a certain amount of glycerine was added at the alkaline solution. This method was patented in 1971 in the USA.

$$NH_2{-}CO{-}NH_2 + H_2O \longrightarrow NH_3 + CO_2$$

Scheme 3.4: *Chemical reaction of urea decomposition*

This treatment gives many advantages such as not changing the chemical nature of the substrate, the insolubility in water of barium carbonate, and the possibility to form barium sulphate (a salt more insoluble in water than barite) for the alteration of barium carbonate.

Unfortunately, an excess of barium hydroxide solution can cause a whitening of the surface due to the precipitation of barium carbonate on the stone surface. Moreover, it is necessary to remove all soluble salts from the stone surface before treating the stone, in order to avoid the formation of dangerous soluble salts (scheme 3.5).

$$Na_2SO_4 + Ba(OH)_2 \longrightarrow BaSO_4 + 2NaOH$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Scheme 3.5: *Chemical reactions which produce soluble salts*

Another inorganic product used in restoration, especially by the Laboratorio di Restauro del Vaticano, was potassium aluminate. The consolidation process is based on the hydrolysis of potassium aluminate and the formation of aluminium oxide, which precipitates in stone pores and links electrostatically with the polar mineral surfaces. Hypothetically, calcium aluminate or silicon-aluminate and ferrite are also formed in the substrate [36]. A side effect is the formation of potassium hydroxide, which can react and form potassium carbonate or potassium sulphate (dangerous soluble salts).

An example of the application of Barium Hydroxide for the consolidation of stones is, for instance, in the treatment of the main relief of the lunette of San Giovanni Evangelista in Venice [37]. Lewin applied a solution of Barium Hydroxide with urea and glycerine by brushing and then covered the surface with polyethylene sheets for three weeks. Moreover Barium hydroxide was used for the consolidation of fire-damaged stucco and marmorino decoration of the Foyer and Apollinee rooms in "La Fenice" Theatre, in combination with ion-exchange resins [38].

3.2 Laboratory test

A saturated solution of $Ba(OH)_2$ was prepared in the laboratory using distilled water and powder of barium hydroxide ($Ba(OH)_2 \cdot 8\ H_2O$) supplied by the Carlo Erba company.

The solution was brushed on Carrara marble and Vicenza white limestone specimens until the complete saturation of the surface, taking care not to cause whitening of the treated plane. Three samples of each substrate were prepared. After application of the product, the specimens were maintained at room temperature until they were completely dry (15 days).

Although there was no surplus product on the treated specimens, the surface of the samples appeared whitened to the naked-eye. Study of the surfaces using an optical microscope showed the presence of acicular white crystals in the pores of the stone (fig. 3.1).

The aspect of the specimens did not change during exposure to outdoor conditions, but a diffuse microbiological growth was observed.

Figure 3.1: *Micrographs of the same area of Vicenza white limestone untreated, treated with* $Ba(OH)_2$ *at zero time and after 12 months of outdoor exposure. Long side images 6.78 mm.*

Studying the cross-section of the samples with SEM, the high atomic weight of barium is recognizable as white particles, and it was possible to measure the penetration depth of the treatment into the stone.

Carrara marble showed a thin white superficial layer and no penetration was observed, whereas on Vicenza limestone the presence of barium was ascertained to a depth of 13 mm.

In particular, high concentration of barium was observable for the first centimetre, while barium concentrations gradually decreased with greater depth.

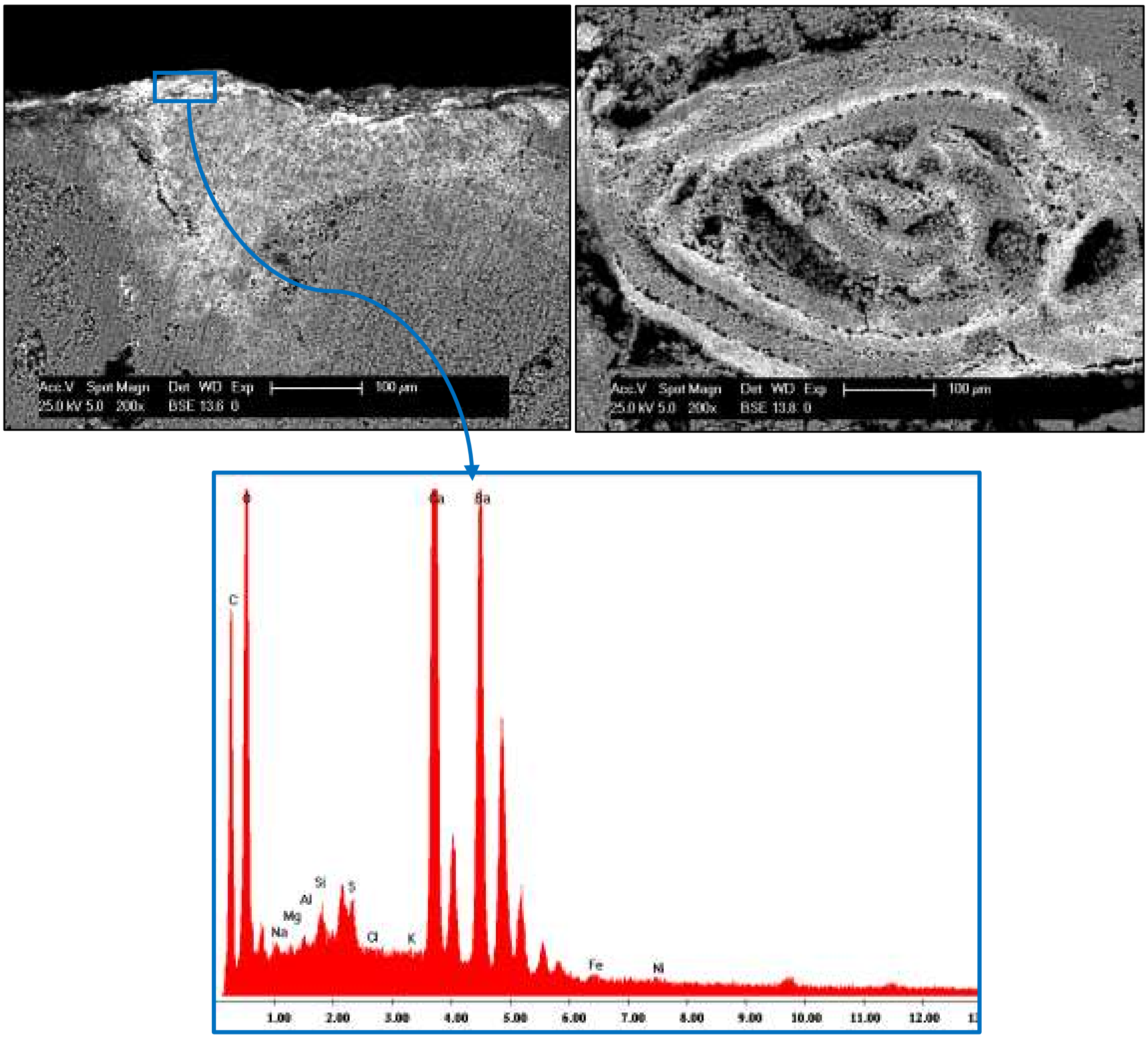


Figure 3.2: *SEM micrographs of the cross-section of V-6 specimen showing the penetration of the product into the stone, and related EDS spectrum. Detail at the top right showing the distribution of barium in a section of a micro-foraminifero in a specimen of Vicenza limestone.*

SEM observations confirmed the morphological aspect of the treatment as thin white crystals having an acicular shape. EDS analysis of the superficial layer of V6 sample showed calcium and barium peaks together, but also those of sulphur, the commonest degradation agent of carbonates (figure 3.2). Sulphurous anhydride from the atmosphere reacts with rain water and humidity to produce sulphuric acid, which attacks the carbonate of the substrate and produces sulphate following scheme 3.6.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$H_2SO_3 + 1/2\ O_2 \longrightarrow H_2SO_4$$

$$SO_2 + 1/2\ O_2 \longrightarrow SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$H_2SO_4 + CaCO_3 \longrightarrow CaSO_4 + H_2O + CO_2$$

Scheme 3.6: *Chemical reactions of the sulphation process of calcium carbonate*

This chemical reaction between barium carbonate and sulphuric acid on the surface of specimens exposed to outdoor conditions was also confirmed from the results obtained with μFTIR analysis, and shown in figure 3.3 and figure 3.4. In the spectra collected, it is possible to study the progressive carbonation and sulphation of barium hydroxide. At zero time, it is possible to simultaneously observe the presence of barium carbonate formed by the chemical reaction between barium hydroxide and atmospheric carbon dioxide (scheme 3.2), and calcium carbonate of the substrate.The peaks characteristics for calcium carbonate at 1795, 1412, 878 cm^{-1} disappeared from the third month, whereas those related to barium carbonate at 1751, 1448, 858, 712, 694 cm^{-1} became more evident. Moreover, after the third month, the characteristic triplet of barium sulphate at 1180, 1132 and 1080 cm^{-1} appeared in the spectra and increased in intensity in subsequent months.

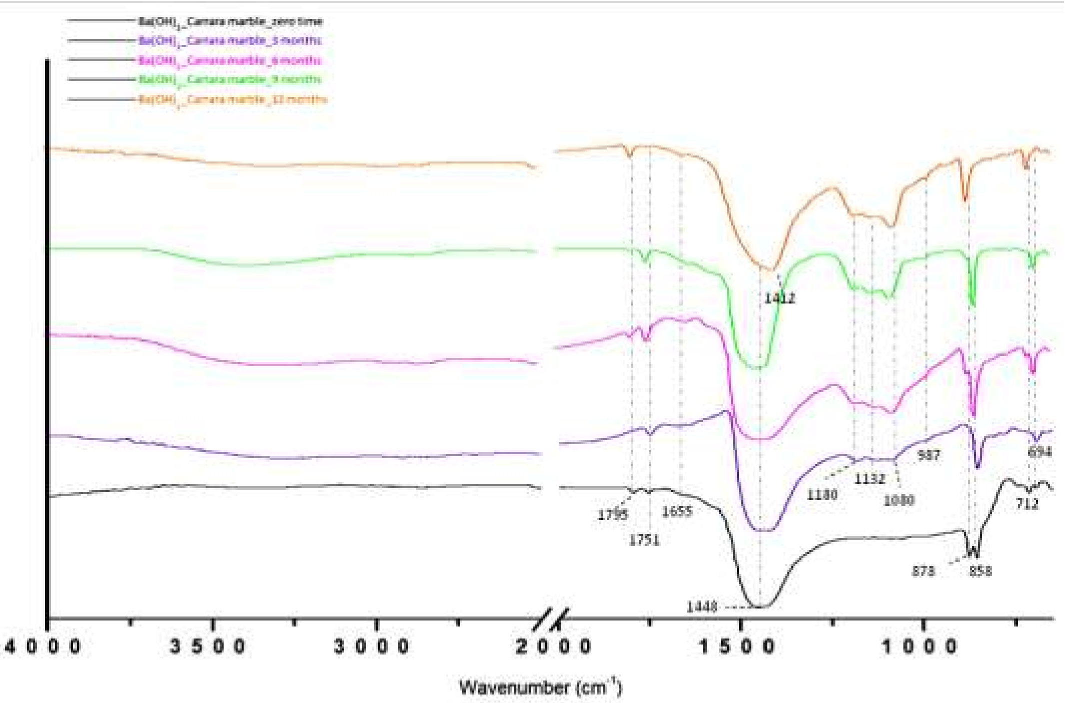


Figure 3.3: *µFTIR of Ba(OH)$_2$ applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

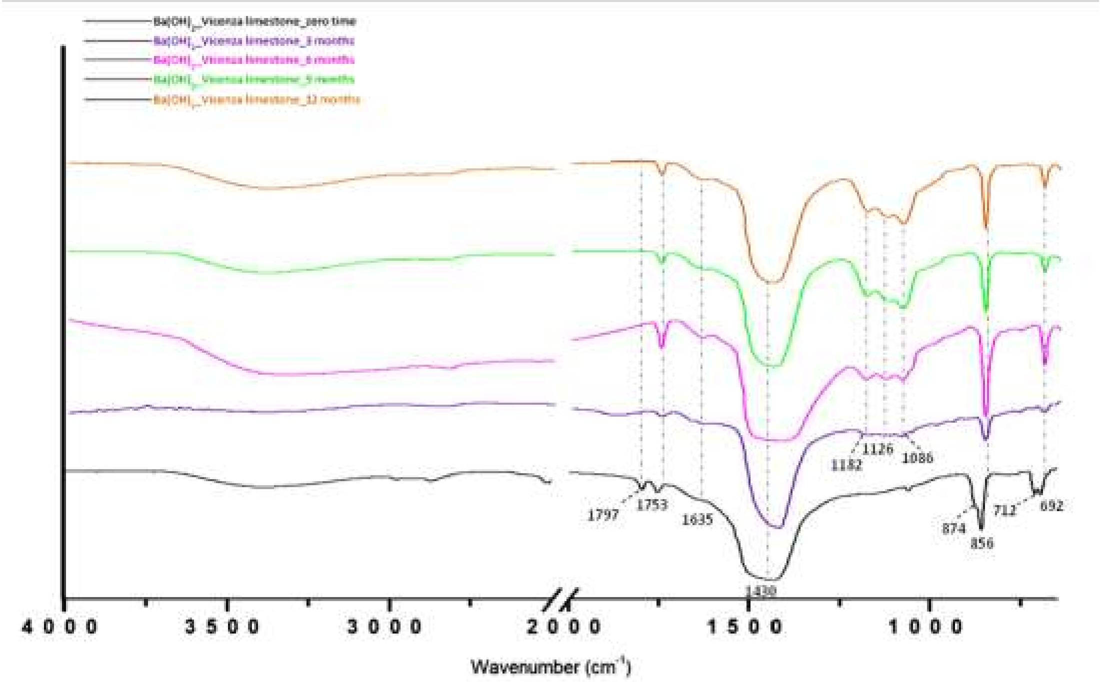
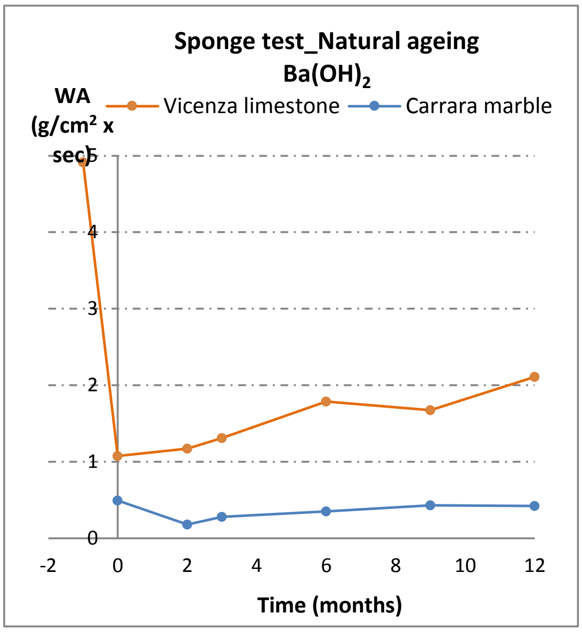
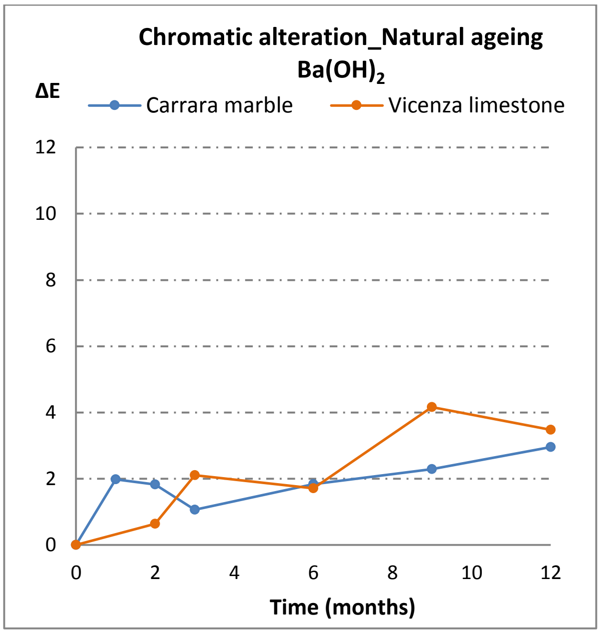


Figure 3.4: *µFTIR of Ba(OH)$_2$ applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was carried out at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

The formation of barium sulphate did not determine any variation in the properties of the treated surfaces such as hydrophobicity or chromatic changes, as demonstrated in graphs 3.1 and 3.2 . Barium sulphate (T = 298 K, $K_{ps} = 1.07 \cdot 10^{-10}$) salt is more insoluble than barium carbonate (T = 298 K, $K_{ps} = 1.17 \cdot 10^{-9}$), calcium carbonate (T = 298 K, $K_{ps} = 1.07 \cdot 10^{-10}$) or sulphate (T = 298 K, $K_{ps} = 7.10 \cdot 10^{-5}$). However, this characteristic does not have any peculiar impact on the superficial hydrophobicity of the treated specimens. In graph 3.1, the trend of water absorption of the surfaces from the untreated value to 12 months of outdoor exposure after the treatment is illustrated. Both Carrara marble and Vicenza limestone showed an interesting difference between the values of the untreated and treated samples, which can be related to filling of the stone pores by the treatment applied, and the consequent crystallization of the salt in the pores and on the surface. In addition, the initial value of water absorption increased during natural ageing. This may be related to the natural removal of the superficial powder of the treatment by wind or by the gradual development of biological growth which colonizes the surfaces and is able to create cavities in the stone surface due to hyphae penetration.

No chromatic differences between barium carbonate or sulphate are normally present as both are white salts. Consequently, there was no expectation of a possible chromatic change of the treated surface due to the sulphatation of the barium carbonate after the third month of outdoor exposure. This was confirmed by study of the results of the colorimetric test (graph 3.2). The line showed a slightly progressive increase of the chromatic alteration value, probably due to deposition of dust and atmospheric particles on the exposed specimens.

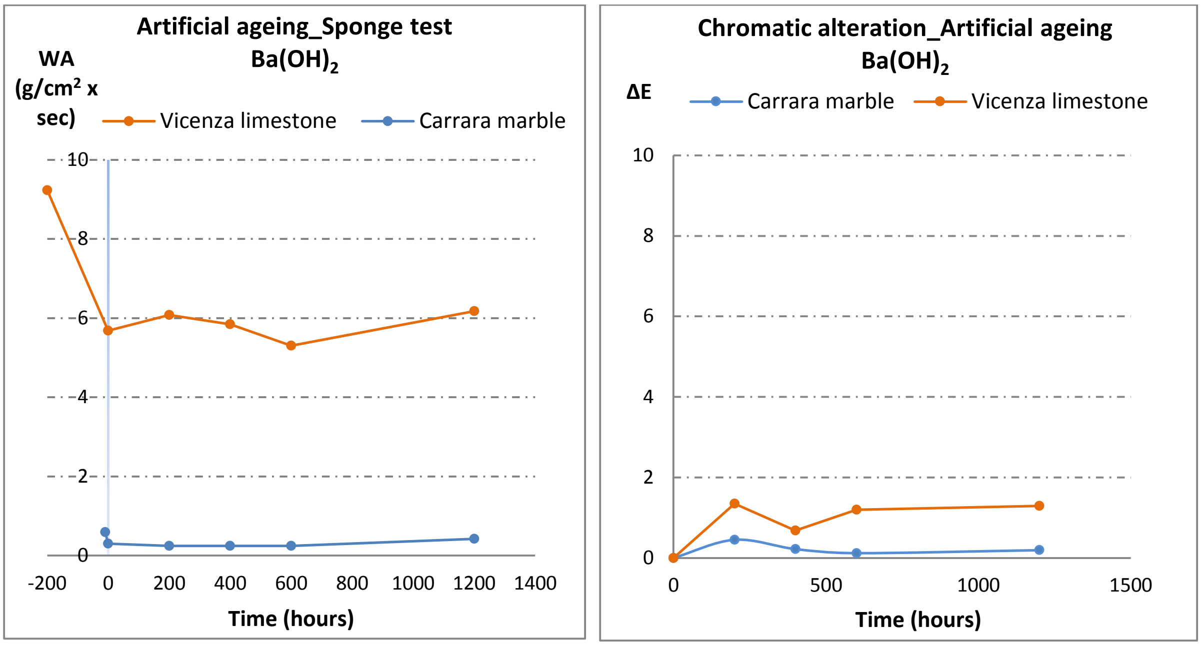




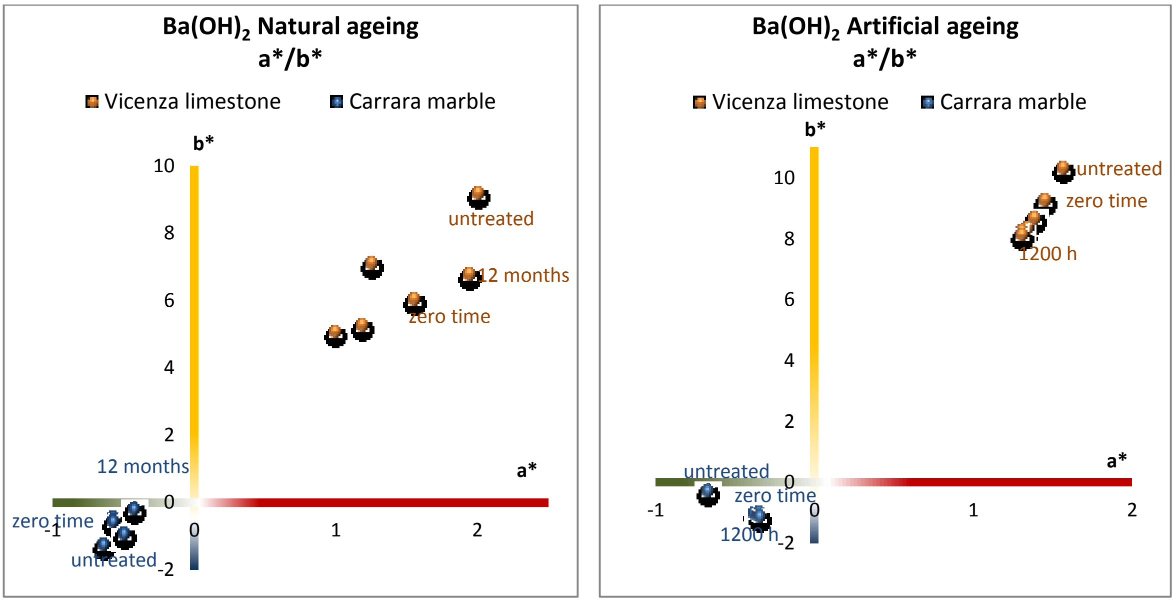
Graph 3.1: *Water absorption variation during outdoor exposure.*

Graph 3.2: *Trend of colour change of surfaces treated with* $Ba(OH)_2$ *during exposure to outdoor conditions*

UV radiation seems not to confer any particular effect on the treatment. The samples showed no particular changes in their morphology, with no yellowing, craquelure or micro-fractures observed. The specimens showed no change from their untreated state after 1200 hours in the Solar box. No peculiar differences in water absorption or colour changing were found (graphs 3.3 and 3.4), or any significant change in µFTIR spectra observed (fig. 3.5).



Graph 3.3: *Water absorption variation (on the left) and trend of colour change (on the right) of surfaces treated with Ba(OH)$_2$ during UV exposure.*



Graph 3.4: *Colour graph of the chromatic alteration suffered by specimens treated with Ba(OH)$_2$ during exposure to outdoor conditions (on the left) and exposure to UV radiation (on the right).*

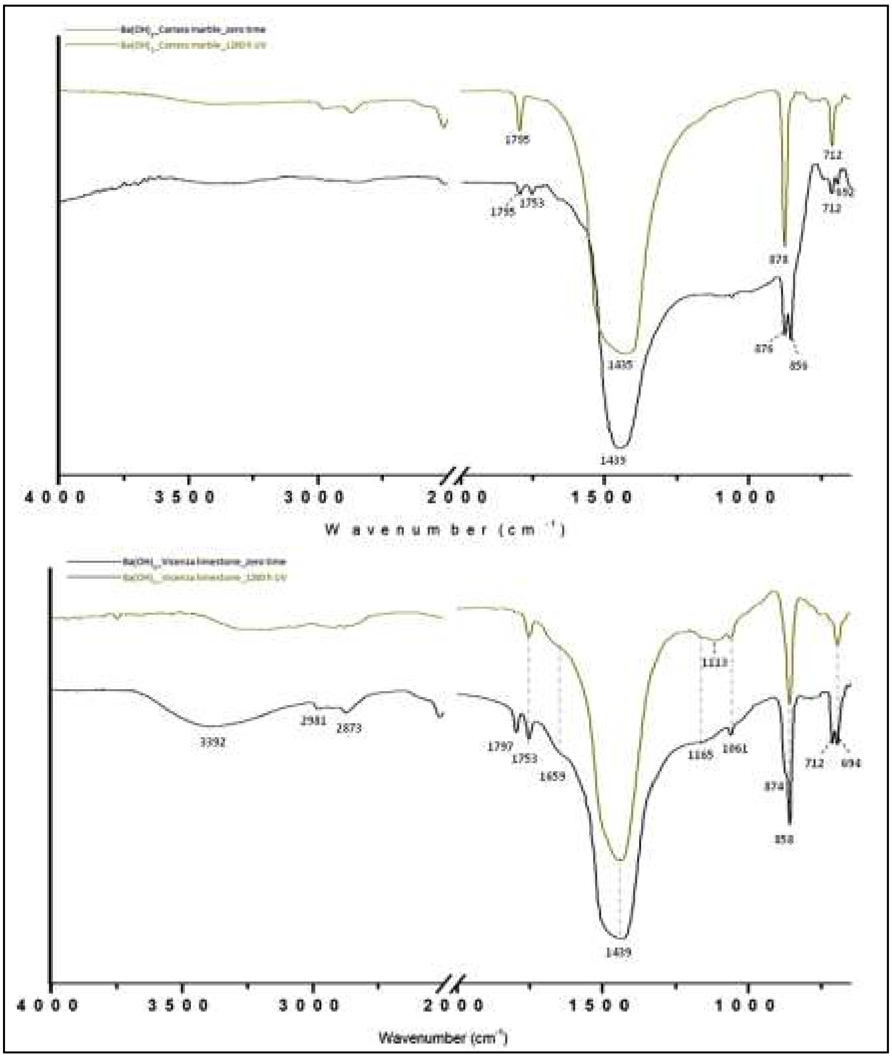


Figure 3.5: *μFTIR of Ba(OH)$_2$ applied to Carrara marble (on the left) and Vicenza limestone (on the right) exposed to UV rays for 1200 hours. Monitoring was carried out at zero time (black line) and after 1200 h of exposure (dark yellow line).*

3.3 Monitoring of past treatments performed in Venice

In the archive of the Venetian Superintendence there are many archived documents concerning the application of $Ba(OH)_2$ on stone surfaces during significant restoration including some also published in the scientific literature.

In this section the results obtained from the sampling of two different surfaces of Venice interest will be presented, including two laboratory samples formerly treated by Prof. Lorenzo Lazzarini on Vicenza limestone which have particular scientific importance.

- **S. Fantin church (1507-64) (*Sestiere S. Marco*): Font**

  Substrate: Carrara marble

PAST RESTORATIONS:
1968 S. Z. Lewin, N.Y. University
Cold solution of barium hydroxide, urea and glycerine by capillary absorption.

SAMPLING:
07.05.2013
Operators: restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna).
Number of micro-fragments sampled: 1 sample from the upper part of the font, adjacent to a spalled area.
The sampling was carried out with a small chisel.

Figure3.6: *Font, S. Fantin church. Venice*

Figure 3.7: *Area of the sampling of the micro-fragment.*

MACROSCOPIC OBSERVATIONS:

The surface appeared compact and no new fractures were observed, but some areas of the treated surface had whitened.

ANALYTICAL RESULTS:

Figure 3.8: *micrography of sample cross-section.*

- MICROSCOPIC OBSERVATIONS:

The fragment sampled was homogeneous and compact, with slight light brown layer of deposited dust on the surface. No characteristic aspect due to the presence of a superficial treatment was observed.

- FTIR AND SEM-EDS ANALYSIS:

  Both analytical methods used confirmed the absence of barium (carbonate or sulphate) on the stone surface and in its pores.

- ***Scuola di S. Giovanni Evangelista* (*Sestiere S. Polo*): Column**

  Substrate: Lumachella del Tasso

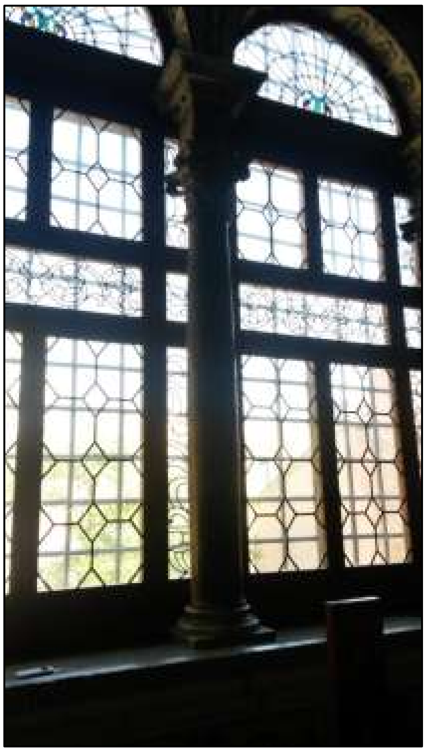


Figure 3.9: *Column, Scuola di S. Giovanni Evangelista, Venice*

PAST RESTORATIONS:
1968 S. Z. Lewin, N.Y. University
Cold solution of barium hydroxide, urea and glycerine by capillary absorption.

SAMPLING:
07.05.2013
Operators: Prof. Lorenzo Lazzarini (Iuav University).
Number of micro-fragments sampled: 1 sample from the lower part of the column, in front of the window, from an inhomogeneous area.
The sampling was carried out using a small chisel.

Figure 3.10: *Area of sampling of the micro-fragment.*

MACROSCOPIC OBSERVATION:

The column appeared well-conserved, compact with no fractures or fissures. However, the part adjacent to the window was completely eroded and fragile. Some scales were lifted from the substrate, but no whitened effect was observed.

ANALYTICAL RESULTS:

- FTIR ANALYSIS:

  A small amount of the fragment sampled was ground with KBr powder. The FTIR analysis of the pellet prepared can confirm the permanence of the treatment on the sample. The spectrum collected showed the characteristic triplet at 1180, 1126 and 1082 cm^{-1} of barium sulphate. The spectrum also showed the main band at 1437 cm^{-1} related to a carbonate compound. However, it is not possible to distinguish calcium carbonate from barium carbonate due to the broadening of the band [39].

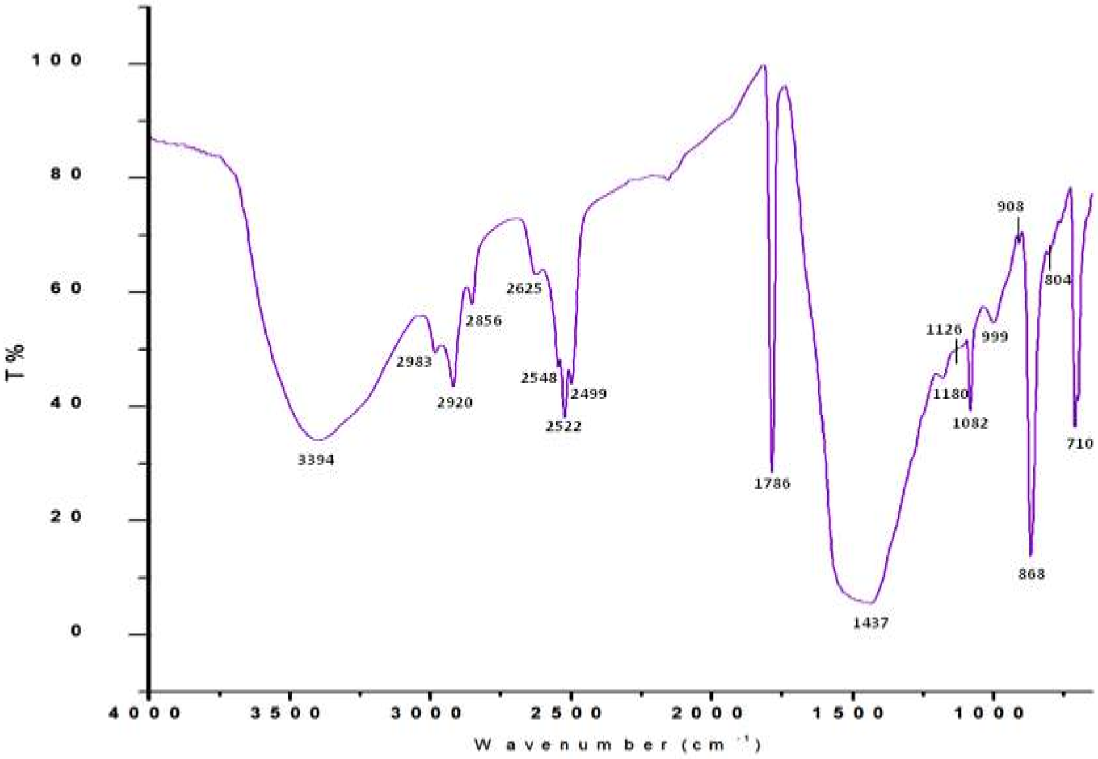


Figure 3.11: *FTIR spectrum of the powder of the fragment sampled.*

- SEM-EDS ANALYSIS:

Macroscopic observation by SEM allowed the penetration and distribution of the treatment based on barium in the stone sample to be understood. EDS analysis showed a penetration depth of 250 µm but the treatment was not well distributed across the surface (fig. 3.12). Some areas showed the presence of a superficial layer of stone alteration. The EDS spectrum in figure 3.13 shows the presence of sulphur, barium and calcite, which appears to derive from the sulphation of carbonatic compounds from the superficial layer of the stone.

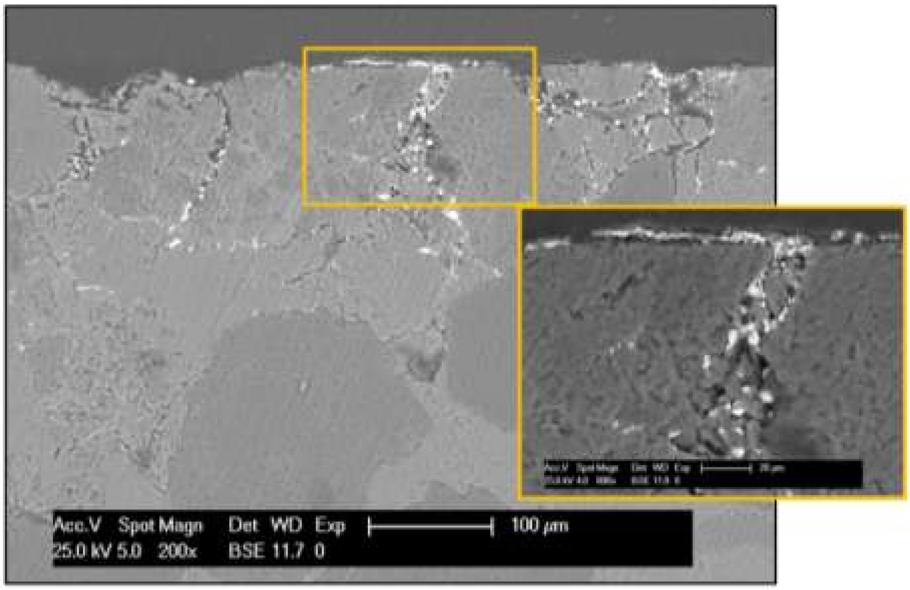


Figure 3.12: *SEM micrograph showing the penetration of the treatment in the stone substrate.*

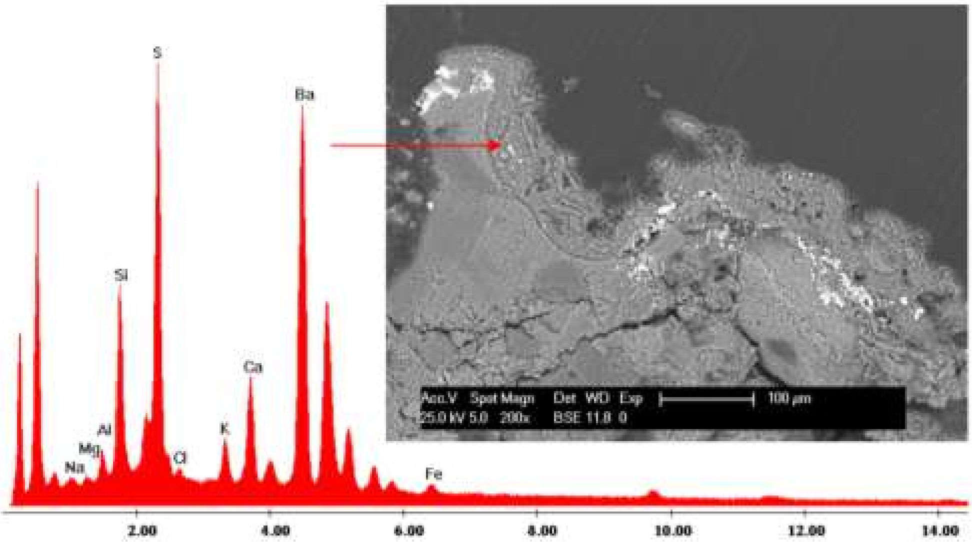


Figure 3.13: *EDS spectrum and SEM micrograph of the altered superficial layer of the stone.*

- **Laboratory samples**

  Substrate: Vicenza limestone

Figure 3.14: *Specimens of Vicenza limestone treated with barium hydroxide (on the right) and barium hydroxide and a siloxane resin (on the left).*

TREATMENT:
1977: prof. L. Lazzarini (IUAV university)

Two specimens of Vicenza white limestone, with rectangular shape x = 10 cm, x = 10 and z = 1.7 cm, were treated with a warm solution of $Ba(OH)_2$ by immersion and, in the same way, $Ba(OH)_2$ with an unknown silicone resin.

ANALYTICAL RESULTS:

The study of the sample was particularly interesting due to the results obtained from SEM observations and EDS analysis. Examination of the treated surface confirmed the epitaxial growth of barium carbonate (fig. 3.15). Moreover, analyzing it using EDS microprobe revealed a mixed composition of Ca and Ba in these minerals.

Consequently, the Lewin's theory of a partial substitution of Ca^{2+} ions of calcite with Ba^{2+} ions of barium hydroxide during the consolidation mechanism, cited in section 3.1, was confirmed (fig. 3.16).

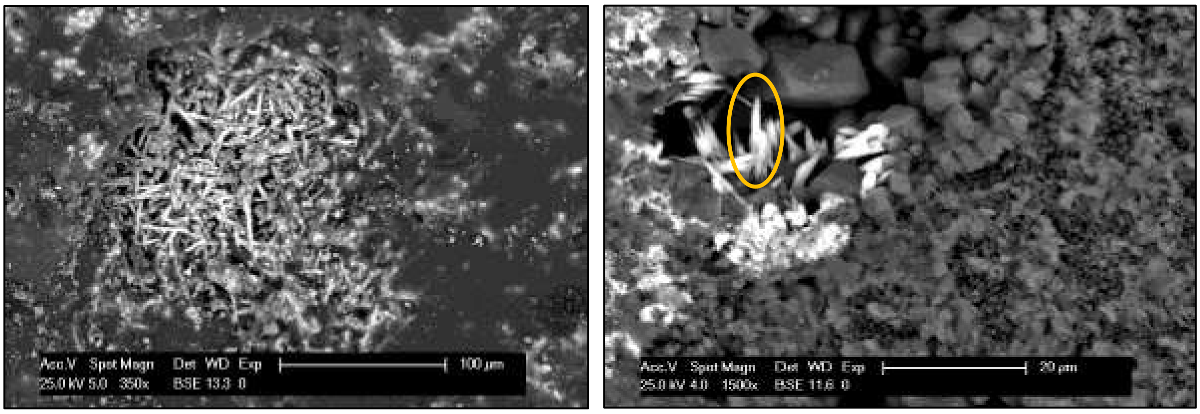


Figure 3.15: *SEM micrograph of epitaxial growth of barium – calcium carbonate.*

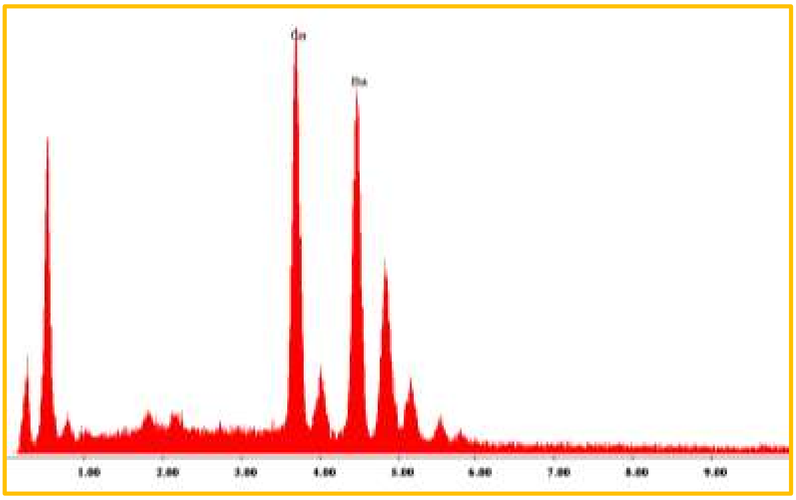


Figure 3.16: *EDS analysis of barium-calcium carbonate.*

The elementary map in figure 3.17 showed the major concentration of barium in the interface spaces between calcite and silico aluminates areas, and in the more porous zones.

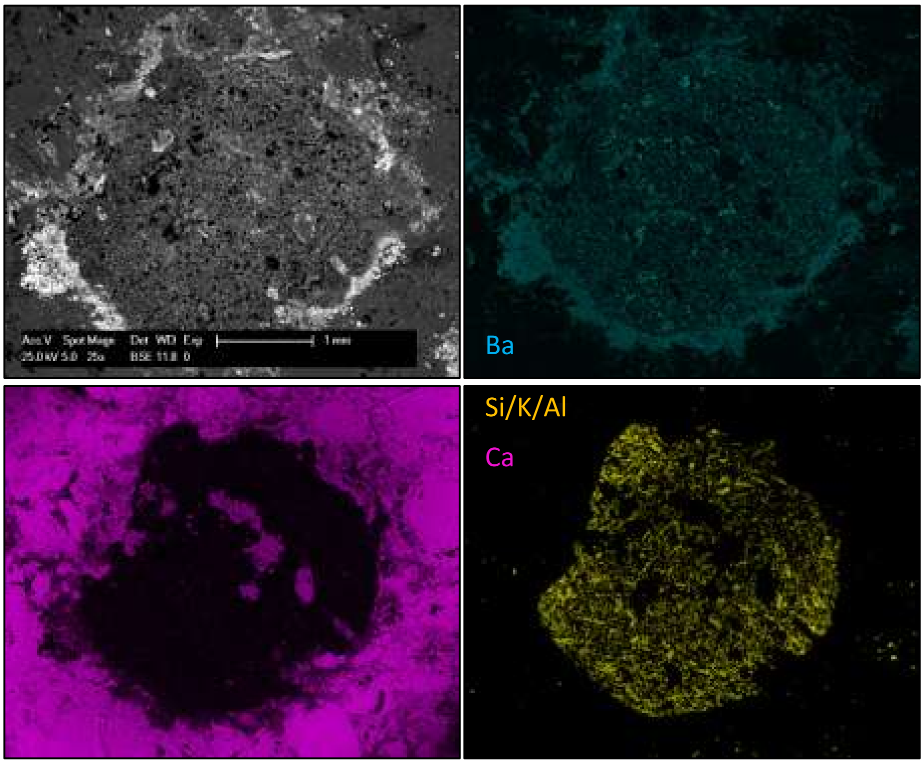


Figure 3.17: Elementary map by EDS microprobe of an area of a fragment of the samples.

FINAL OBSERVATIONS:

The analyzed surfaces showed three different situations. In particular, it is possible to surmise that barium hydroxide penetration of the stone depends on both porosity and the application method. The fragments sampled from the Carrara marble font of S. Fantin and from the Lumachella del Tasso column of S. Giovanni Evangelista showed either no or scarce penetration. On the contrary, Vicenza limestone specimens treated by total immersion showed penetration depth greater than 3 mm (figure 3.18).

FTIR analysis of the fragment sampled from the column from S. Giovanni Evangelista confirmed the tendency to sulphation of barium carbonate, which is faster than that of calcium carbonate. This result confirmed what was already described in the experimental section (3.1).

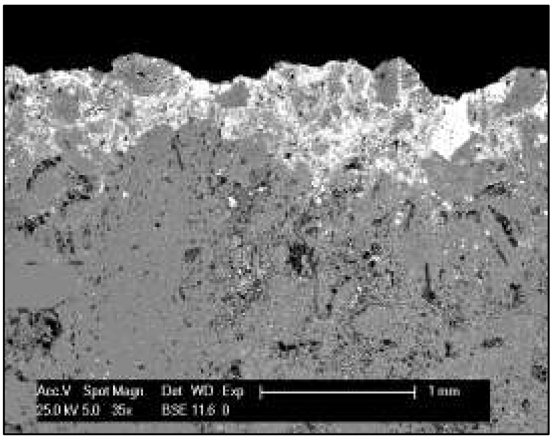


Figure 3.18: *SEM micrograph of the cross-section of a fragment sampled from the experimental specimens.*

3.4 References

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Chapter 4

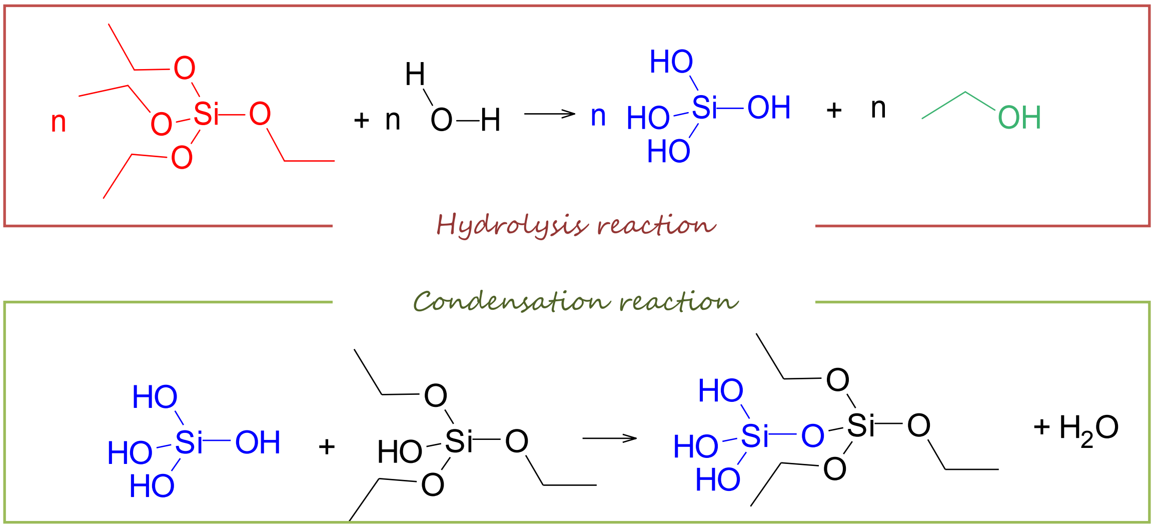
Silicone resins

4.1 Silicone resins

Organosilicone compounds, such as silanes, alkyl-alkoxy-silanes and alkyl-aryl-polysiloxane, have been widely used as protective and consolidating agents to preserve stone materials from the inevitable weathering associated with environmental exposure. Good chemical stability resulting from the high strength of the silicon-oxygen bond, together with low surface tension, good elasticity and resistance to thermal stress encouraged their application on different stone substrates [40].

The chemistry of silicone is close to that of carbon-based organic compounds.

Monomeric silane derivatives used in conservation are tri or tetrafunctional silanes, such as tetraethoxysilane (ethyl silicate, TEOS). The polymerization process is by hydrolysis giving off ethanol, and condensation of the silanol groups giving rise to the formation of cross-linked siloxane chains Si-O-Si (Scheme 4.1). The curing process depends on environmental humidity conditions.



Scheme 4.1: *Hydrolysis and condensation reaction of TEOS.*

High atmospheric RH permits a rapid and near-complete hydrolysis reaction, but the condensation of silanol groups will be poor and the polymeric film will develop cracks. With decreasing RH, hydrolysis slows down, but the number of residual silanol groups is less than before and, consequently, polymerization will be extended, and the film will form without cracks [41].

Not all silanol groups, Si-OH, will react at the same time, and not all of them will effectively condense to form cross-linking, but they will be able to react with –OH groups on a surface to create chemical links. For this reason, silanes are considered good consolidant agents. Tetrafunctional monomers form polymers similar to silica gel, whereas trifunctional monomers such as methyltrimethoxysilane react in the same way but retain the Si-C bond.

The presence of the Si-C bond and consequently apolar alkyl groups, makes the product hydrophobic, thus it also has a water-repellent effect. The strength developed on a stone surface by organosilicone compounds is due to the possibility to create secondary chemical bonds between the capillary walls of the stone and the polar side of siloxane chain or, in the case of alkoxy-silane, hydrolyzed groups which have not yet polymerized. In both cases, the polar part of the molecule will link directly to the stone material, whereas the organic apolar side will be oriented towards the centre of the capillary and will create a hydrophobic obstacle for water penetration.

The commonest organic substituents are methyl, phenyl, fluorinated groups etc., and they are chosen to impart special characteristics to the silicones. In particular, aromatic groups give greater flexibility to the polymer than aliphatic ones, however they are less resistant to UV radiation than aromatics.

There are also particular commercial formulations which improve the consolidation and efficacy of a product in which silane and siloxane are mixed together. With such an example, in order to increase cross-linking, methyl or phenyl-polysiloxane can be mixed with a cross-linking agent (commonly TEOS) and a dialkyl tin catalyst.

Analytical tests have demonstrated that the most significant problem with silicone resin is related to the cracking of the derived gel due to the evaporation of the solvent during the gelification process, or in case of products based on TEOS, to the TEOS/organometallic catalyst ratio [42]. In order to solve this drawback, alternative mixtures of acrylic and silicone polymers [43] or, more recently, mixed systems of epoxy-silicone resins have been synthesized in an organic-inorganic formulation with acid catalysts [44].

In general, silanes can be supplied and applied in several formulations. TEOS for example was applied in restoration up to the 1960s and now is usually applied as a slightly pre-polymerized solution in order to improve the initial rate of cross-linking and gelling. This reduces evaporation of the silane and the viscosity of the solution, and improves its penetration into the stone.

As mentioned before, silanes applied on stone surfaces reduce water absorption and have strengthening effects. The consolidation can cause colour alteration of the surfaces, which in many cases returns near to the original colour of the stone as the silane degrades.

The first commercial products based on TEOS were Sansteinverfestiger OH by Wacker Chemie, Tegovakon V by Th. Goldschmidt A.G., the Motema 28 commercialized in Switzerland and AC70 by Rhône Poulenc [41].

Polysiloxanes, polymerized products dissolved in suitable solvents and unable to chemically react to develop further chemical bonds, were widely used in the past for consolidation treatments. In Venice, their first application took place in 1967 when a particular commercial product was applied to the marble statue of St. Alvise located on the main façade of the church dedicated to that saint. The statue was treated by vacuum impregnation in an autoclave using the silicone resin Sogesil XR893 [45]. As far as could be ascertained the resin, which was produced by Rhône Poulenc and is no longer available on the market, was a methyl-phenyl-polysiloxane dissolved in benzene with a solid content of 50%. Right away, it was considered very promising and began to be used elsewhere in the city. In the following year it was employed for the consolidation of the four angels supporting the Holy Sepulchre altar in the Church of San Martino; it was also used during the restoration of the Ca’ D’Oro in 1969; and again in 1977-78 for the consolidation of the statues located on the gable-end of the façade of the Basilica of San Marco [46]. No datasheet is available to indicate the chemical composition of the resin currently used.

Moreover, no studies have been carried out to illustrate the characteristics of the resin or the mechanisms of the polymerisation process. However, several years after the applications cited above, authoptic observations were carried out to evaluate the effectiveness of these past treatments: all the stone surfaces showed a good state of conservation and no new fracture planes were observed [47].

Alkyl-alkoxy-silane and aryl-alkoxy-silanes have been generally considered good protective agents for stone surfaces but they have also been used as a strengthening agent.

The low molecular weight of alkyl-alkoxy-silane monomer and the low viscosity of the polymeric solutions allows good penetration depth in all stone materials. In addition to alkyl-alkoxy-silane monomers, it is possible to use semi-polymerized products which, having a good percentage of Si-O-C bonds, will hydrolyze and polymerize in stone material.

The first commercial product used as consolidants and based on alkyl-alkoxy-silane formulation was Rhodorsil X54-802 by Rhône Poulenc. It was applied by K. Hempel for the consolidation of the Lunetta Corner of S. Maria Gloriosa dei Frari church, and the Loggetta del Sansovino in Venice. Other important products still available on the market are Dri-Film 104 by General Electric and Tegosivin HL100 by Th. Goldschmidt A.G. .

4.2 Laboratory tests

For the purposes of this study 3 consolidant and 2 protective products based on silicone were tested.

The commercial consolidants tested were EAS 40 Consolidante, an ethylic silicate (TEOS) commercialized by Sinopia Restauro; and Rhodorsil Consolidante RC90 and Rhodorsil Consolidante RC80, supplied by the Italian company Siliconi Padova. Both Rhodorsil commercial products were composed of tetraethylorthosilicate (TEOS) combined with a tin-siloxane catalyst and a water repellent component: a methyl resin in the case of RC80 and a methyl-phenyl resin in the case of RC90.

The tested water repellent commercial products were Rhodorsil H 224, an alkyl polysiloxane polymer dissolved in a mixture of aliphatic hydrocarbons and supplied by the Italian company Siliconi Padova, and Hydrophase, an alkyl-alkoxy silane commercialized by Phase Restauro.

Due to the different effects on stone surfaces, the results obtained from this group of resins, are described separately below.

4.2.1. Silicone based consolidants

Prior to any laboratory tests, RC90 and RC80 were chemically characterized in sol and gel form, following UV radiation and thermal treatment under laboratory conditions to ascertain their chemical composition, microstructure and stability. The polymers were chemically characterized in liquid and dried form. After the complete sol-gel changeover, films were subjected to UV radiation in a UV chamber equipped with four 8 W black light blue lamps, emitting in the near-UV range (315-400 nm; 3 mW cm^{-2}). The volume of the photoreactor was 25 ml. The films were also subjected to thermal-oxidation in a ventilated oven fixed at 60°C [48]. These experiments simulate to a high degree the ongoing degradation of resins exposed to outdoor conditions.

The results obtained were published in a scientific paper reported in the appendix A of this thesis and summed up as follow [49].

Monitoring of curing processes on slides and the consequent polymerization mechanism couple with the existing literature allowed critical observations of RC90 and RC80 resins. Due to the development of branched siloxane structures during the polymerization process and the hydrophobic feature of methyl groups in their formulation (confirmed by GC/MS and FTIR techniques), the resins provide both strengthening and waterproofing properties. Both are durable with respect to UV and thermo oxidation. In particular RC80 does not suffer any chemical transformation, whereas UV rays and oxidation cause cross-linking in RC90, probably limiting the removability of the polymers from treated surfaces should this become necessary. These modifications in RC90 result in a gradual shifting towards lower wavenumber values of the main peak, related to the Si-O-Si stretching bond in a cycle structure (from 1080 cm^{-1} to 1068 cm^{-1}) and to the appearance of Si-OH bonds at 3440 cm^{-1} (fig. 4.1).

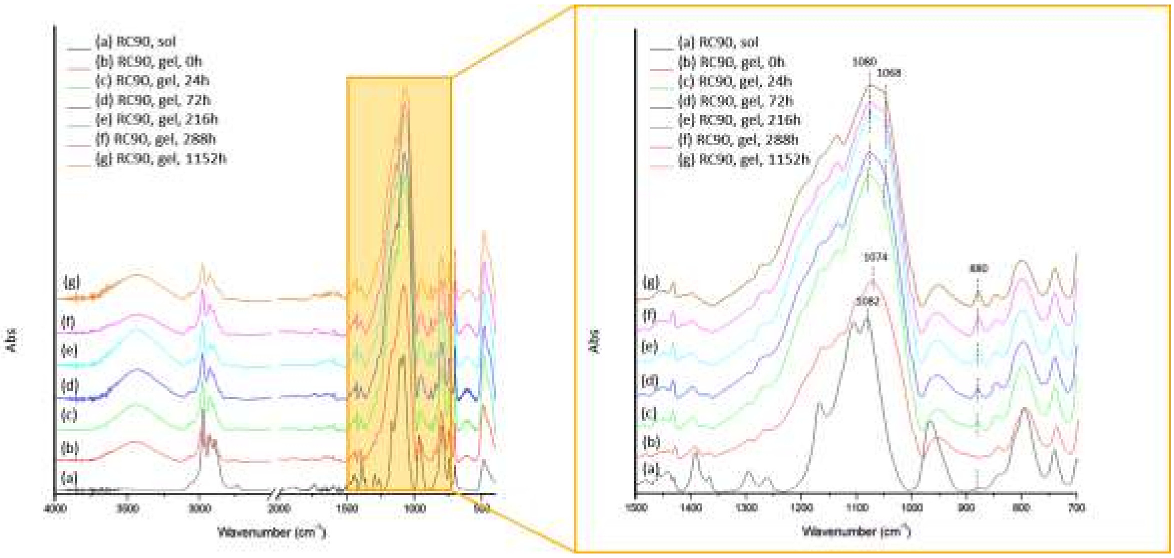


Figure 4.1: *Comparison between RC90 sol and gel at different time intervals of UV-oxidation.*

However, the limited deterioration process on polymers, ascribed to the low permeability to oxygen, reduced photo-oxidative reactions [50].

RC80 film applied on a slide is characterized by cracks, which were microscopically observed, and an irregular distribution of the organometallic catalyst, as was proved by SEM-EDS and EDXRF analysis (fig. 4.2). This peculiarity could not preserve carbonate rocks from sulphatation. In addition, this also determines macroscopic opacity and whitening of the RC80 polymeric film.

RC90, which macroscopically is characterized by a transparent film, can undergo less chromatic alteration than RC80. Nevertheless, the phenyl groups in RC90 can impart a colorimetric change of the treated surface with natural ageing. Moreover, at low temperatures, the phenyl groups guarantee better thermo stability than that assured by RC80.

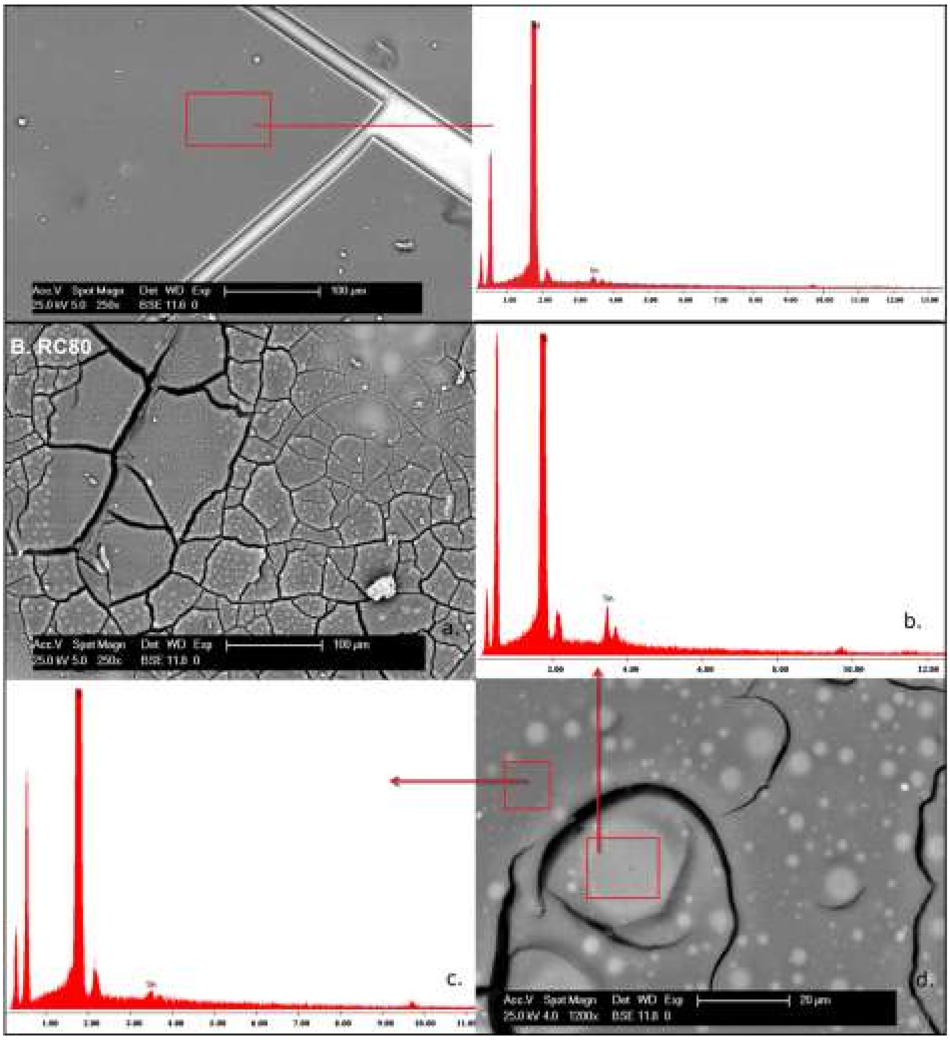


Figure 4.2: *SEM micrographs of RC90 (A) and RC80 (B) xerogels showing micro-cracks and white spots in RC80. EDS study of RC80 revealed an inhomogeneous distribution of tin with localization in the white spots.*

A research decision was made not to characterize EAS 40 as it is a common formulation based on pure TEOS with a large number of studies available on it [51-52].

Rhodorsil RC80 and RC90, and EAS 40 were deposited on Carrara marble and Vicenza limestone specimens by brushing until complete impregnation of the substrate. Three samples were prepared for each product. After the application of the consolidants, the samples were maintained at room temperature until cured polymers were achieved (15 days).

All the treated samples showed the formation of a thin superficial layer on the stone surface, which was transparent in the case of EAS40 and RC90, and opaque in the case of RC80. All films were characterized by a diffuse craquelure after the first month of outdoor exposure. By the sixth month all stone surfaces showed the presence of biological microorganisms with different growth rates, which were most pronounced on a Carrara sample treated with EAS40.

After 12 months the aspect of the samples seemed untreated and only by observing the surfaces using the stereomicroscope with high magnifications it was possible to observe the presence of white or light-yellow powder in the inter-grain spaces in case of RC80, as shown in fig. 4.3 , or micro-scales of transparent resin in the case of RC90.

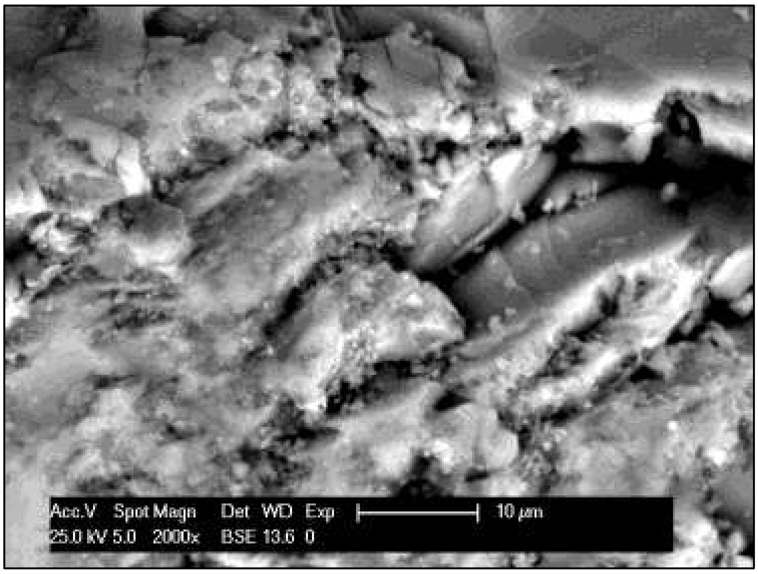


Figure 4.3: *SEM micrograph of RC80 applied on Carrara marble.*

Studying cross-sections of samples with the SEM microscope after 12 months of outdoor exposure, the absence of a superficial film was confirmed on both Carrara marble and Vicenza limestone. The presence of silicon in all tested products allowed the measurement of the penetration depth of the resin in the section of the samples. From the measures recorded by EDS analysis, all products showed scarce/no penetration in Carrara marble, whereas in Vicenza limestone the penetration of the resin seems dependent on the dimension of the macromolecules. EAS 40 showed the most homogeneous distribution of the resin in the sample section, while RC80 penetrated until 7500 µm and RC90 until 4500 µm (fig. 4.4).

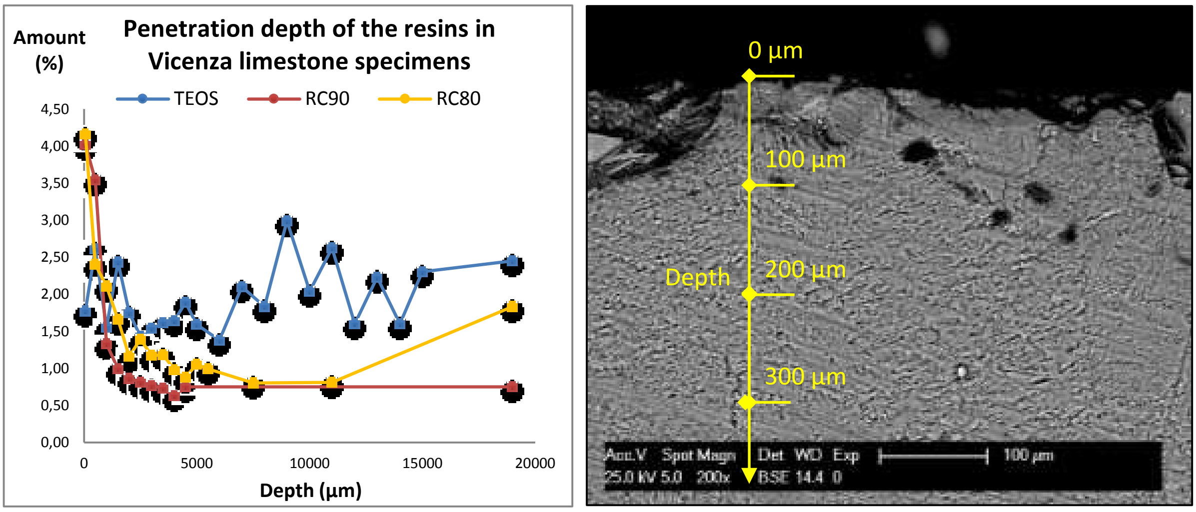


Figure 4.4: *Penetration depths of consolidant agents measured in Vicenza limestone using EDS microprobe (graph on the left) and exemplification of the measuring modality in a SEM micrograph.*

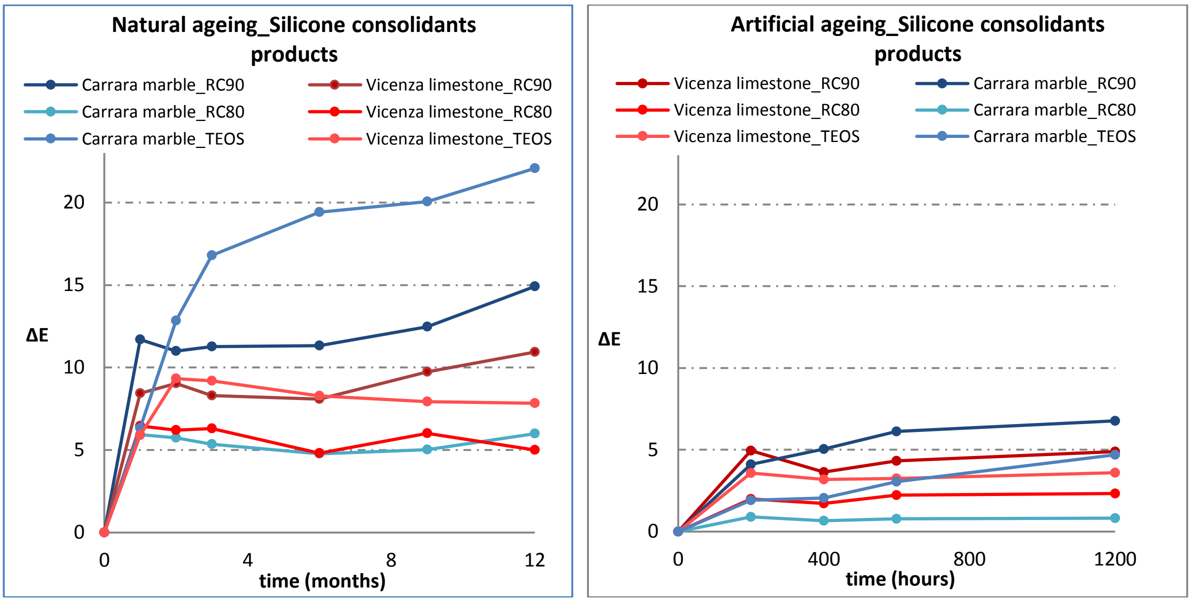
The surfaces of all the treated samples seemed slightly altered. All specimens exposed to outdoor conditions and the climatic chamber showed darkening of the surfaces visible to the naked-eye, especially those treated by Rhodorsil RC90 consolidant.

Measuring the colour variations with a spectrophotometer demonstrated that specimens exposed to outdoor condition suffered major chromatic alteration, probably due to the deposition of atmospheric particles and biological growth (graph 4.1). In particular, the specimens treated by EAS 40 (TEOS), which exhibited the most relevant biological colonization both in Vicenza limestone and Carrara marble, changed most in their chromatic data.

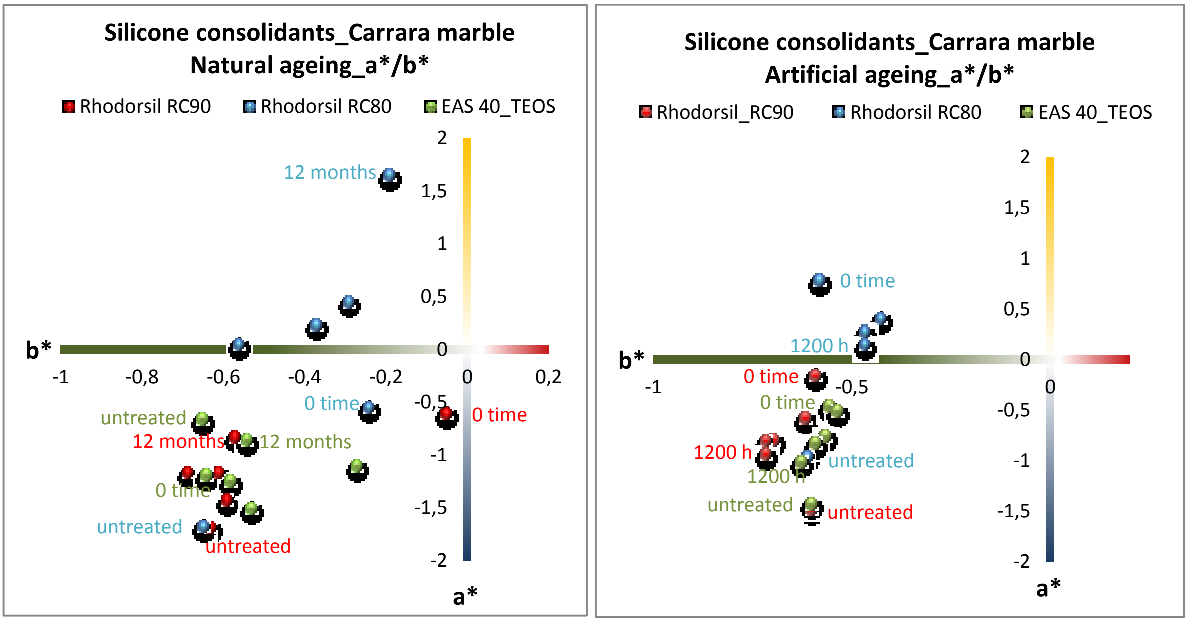
Despite superficial deposition, Rhodorsil RC90 showed the most sensitivity to UV radiation due to the presence of phenyl groups in its macromolecules chemically linked to the siloxane chain. This colour alteration revealed a darkening of the polymeric film, whereas no significant variation in the colour graph (graph 4.2) are observable.

Rhodorsil RC80 showed the smallest colour variation but when exposed to outdoor conditions it tends to yellow.

From the colour graph (graph 4.2) it is also possible to observe the general behavior of the chromatic data to return to its untreated value, probably due to the natural loss of the cracked film by wind erosion, rainfall, simply moving the specimens from their exposure location, or during the analysis of the periodic monitoring.



Graph 4.1: *Trend of colour changes of surfaces treated with silicone consolidants during exposure to outdoor conditions (on the left) and exposure to UV radiation (on the right).*

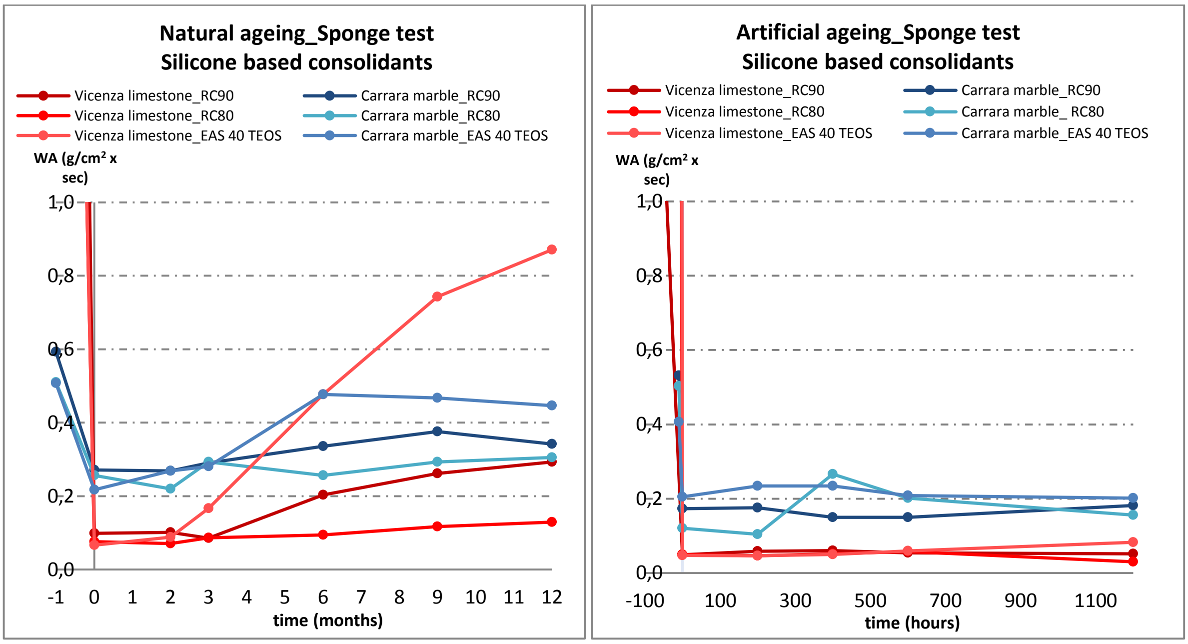


Graph 4.2: *Trend of colour changes of surfaces treated with the three different consolidant agents during exposure to outdoor conditions (on the left) and to UV radiation (on the right).*

The superficial cracking of the polymeric film and the loss of detached scales during outdoor exposure also permitted increases of the hydrophilicity of the surfaces. The loss of part of the sacrificial protective layer left the stone exposed to natural weathering.

In graph 4.3 it is possible to observe that surfaces treated by EAS 40 absorbed water and how this amount increased over time, especially in the case of Vicenza limestone. The reason for this is probably the general tendency to crack of TEOS, but also the absence of hydrophobic chemical groups such as methyl and phenyl groups which characterize Rhodorsil resins, as well as the presence of fungi which metabolize and degrade the organic matter of the applied product.

Samples exposed to UV rays showed a constant hydrophobic feature for the entire exposure time.



Graph 4.3: *Water absorption variation during outdoor (left) and UV exposure (right).*

The tested consolidants appear to be chemically stable. The μFTIR collected by the outdoor exposure did not show any peculiar changes in the form of the appearance or disappearance of particular peaks or bands, of which assignments were summarized in table 4.1. In general, during natural ageing there was a shift towards higher wavenumbers for all peaks related to the C-H chemical bond. According to the literature this trend suggests a shortening of the chemical bond due to the minor degree of liberty of the molecules during the polymerization process [50-53-54].

Regarding the Si-O-Si chemical bond a different behaviour for the consolidants tested was observed. In particular, in the spectra of RC90 applied on a Carrara marble specimen, as shown in fig. 4.5, the doublet at 1070-1051 cm^{-1}, related to the symmetrical stretching of the Si-O-Si chemical bond in a branched structure, shifted gradually towards lower values of wavenumber becoming definitely a singlet at 1053 cm^{-1}. Further evidence of the cross-linked siloxane chain, upon the polymerization process, derives from the broadening of this peak and the appearance of a shoulder at 1134 cm^{-1}, which is probably due to the presence of the phenyl group. These results are in accordance with what was studied and published about the polymerization process of RC90 resin on a slide [50]. In contrast, in the spectra of RC90 applied on Vicenza limestone, higher intensity for those peaks related to C-H chemical bond (1431, 1450, 1471 cm^{-1}) were observed, with a shift of the peak related to the Si-O-Si chemical bond towards higher value of wavenumbers, from 1053 to 1078 cm^{-1} (fig. 4.6).This may be related to a different interaction between the product and the substrate. This could form an interesting topic for more detailed research in the future.

Wavenumber (cm^{-1})			*Functional groups*	*Assignments*
RC90	*RC80*	*EAS 40*		
3600	*3630*	---	*v O-H*	*Hydroxyl groups*
3440	*3400*	*3344*	v_s *Si-OH*	*Silanol (hydrolysis reaction)*
3097, *3074,* *3052*	---	---	v_{s-as} *C-H aromatic*	*Phenil groups*
2974, *2928,* *2904*	*2962,* *2935,* *2904,* *2862*	*2981,* *2899,* *2872*	*v C-H*	*Aliphatic bonds in cyclic structures or hydrocarbon chains*
1624	*1635*	*1628*	*v C-C aromatic; v O-H*	*Phenyl groups and hydroxyl groups*
1595			*v Si-Ph; v C-C aromatic*	*Phenyl groups*
1485			*v Si-Ph*	*Phenyl groups*
1444			*v Si-Ph*	
1450	*1452*	*1454*	*v C-H*	*Aliphatic bonds*
---	---	*1429*		
1392		*1383*	*δs C-H*	*Methyl groups*
1264	*1254*		*v Si-(CH_3)*	
1161	*1170*	*1159*	*ρ C-H*	*Methyl groups*

1106		*1111*	ν_s *Si-O-Si*	*Siloxane chain in linear structure*
1040	*1068*	*1061,1034*	ν_s *Si-O-Si*	*Siloxane chain in cyclic structure*
962			ν_s *Si-O-Si*	*Siloxane chain*
951	*947*	*916*		
880		*876*		
793	*793*		δ_s *Si-O-Si*	*Siloxane chain*
698			δ_s *Si-Ph*	*Phenyl groups*

Table 4.1: *FTIR assignments of the main peaks observed for Rhodorsil RC90, Rhodorsil RC80 and EAS 40 resins, according to the literature [12-13].*

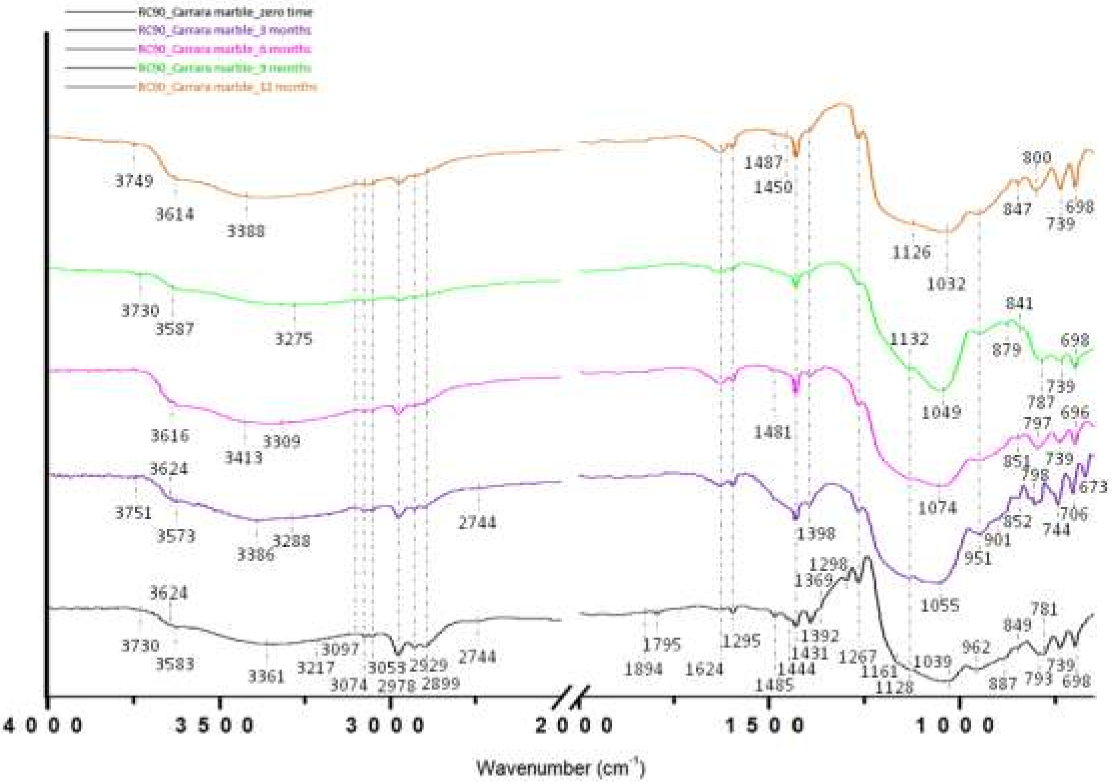


Figure 4.5: *µFTIR of Rhodorsil RC90 resin, applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

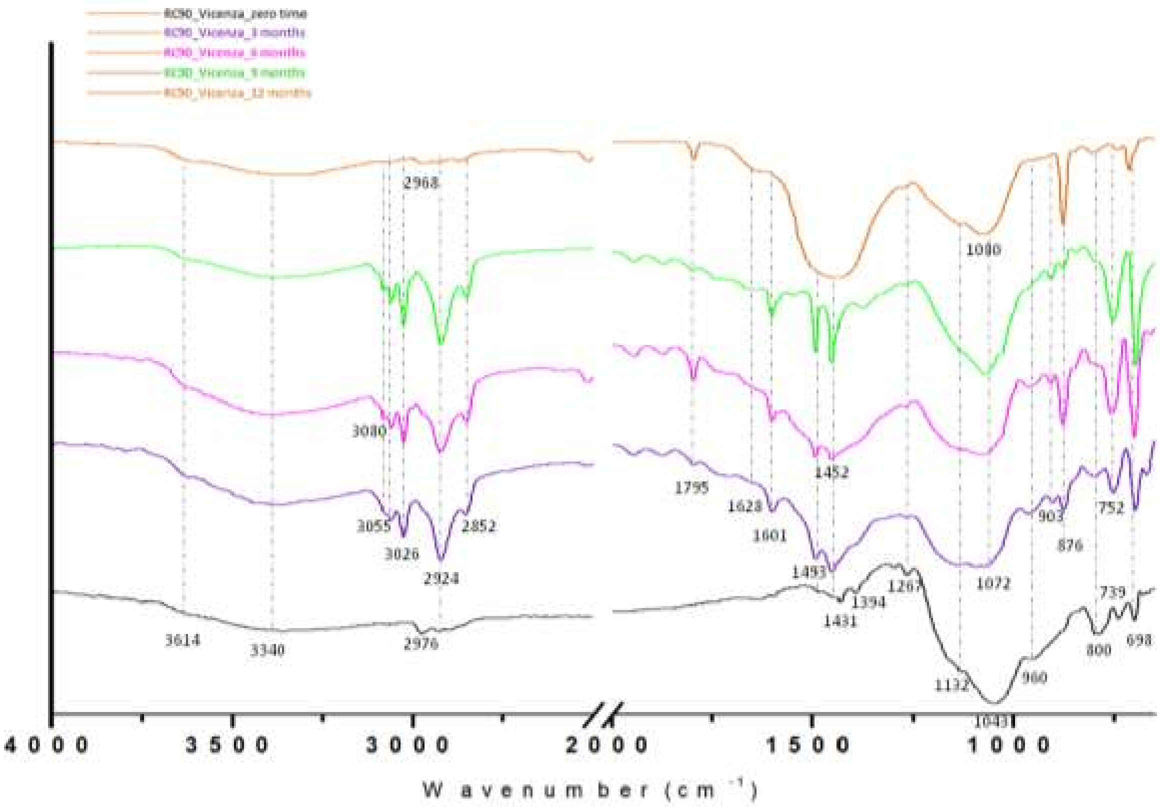


Figure 4.6: *μFTIR of Rhodorsil RC90 resin, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was udnertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

Rhodorsil RC80 applied to Carrara marble as well as on Vicenza limestone, confirmed what is explained above for RC90 applied to Carrara marble. In fact, also in this case, a gradual shift of the peak related to the Si-O-Si chemical bond was observed, towards lower values of wavenumbers from 1082 to 1049 cm^{-1}, as it is shown in figure 4.7 and 4.8.

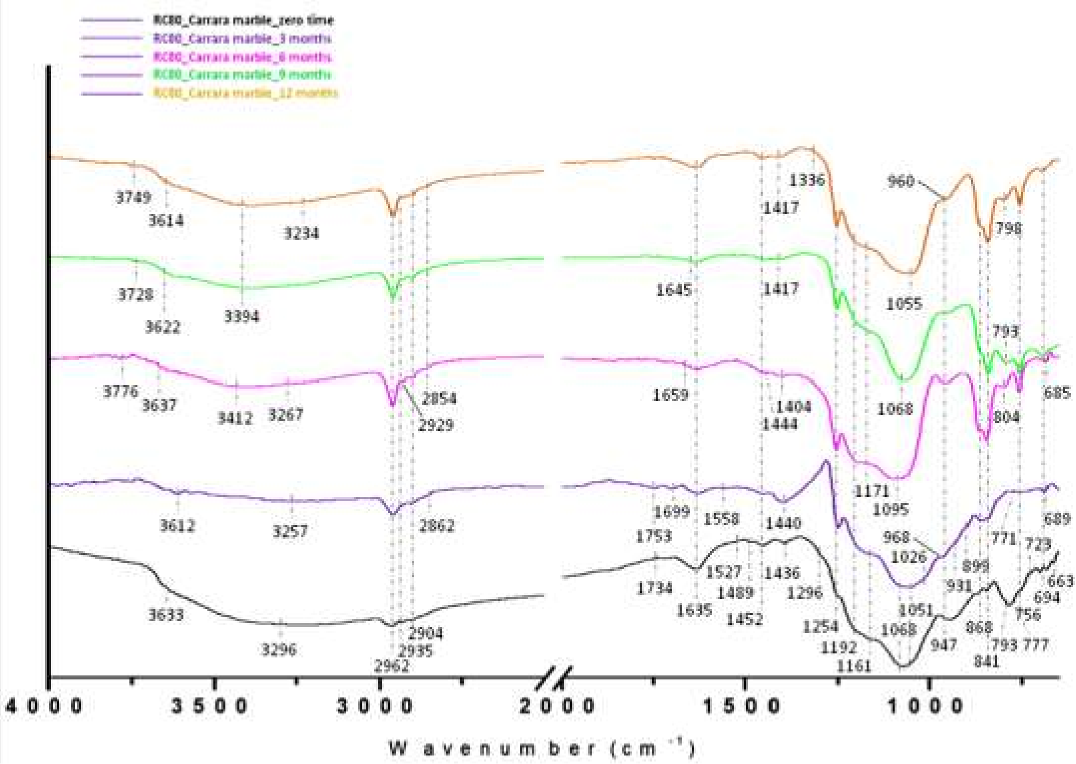


Figure 4.7: *µFTIR of Rhodorsil RC80 resin, applied to Carrara marble and exposed to outdoor conditions. Monitoring was carried out at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

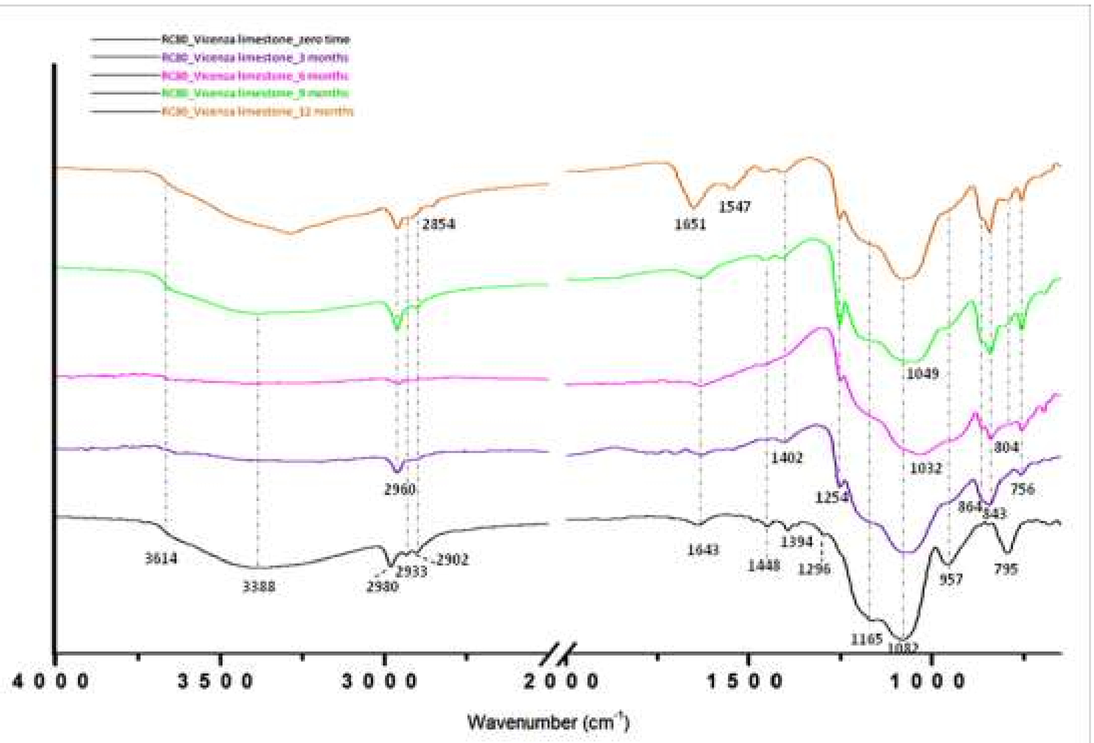


Figure 4.8: *µFTIR of Rhodorsil RC80 resin, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring carried out done at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

In EAS 40 spectra collected from specimens exposed to outdoor conditions, an arrangement of linear siloxane chain at 1093 cm^{-1} was found because of a gradual shift of peaks at 1059-1034 cm^{-1} towards a higher wavenumber (fig. 4.9). Moreover, after the sixth month, it was possible to observe on the spectra collected the appearance of all the peaks related to calcite (calcium carbonate $CaCO_3$) at 1795, 1450, 876 and 712 cm^{-1} (fig. 4.9 and 4.10). The clear presence of calcite attested to the loss of several cracked polymeric film fragments and the absence of a homogeneous protective layer.

However, even if the surfaces were not completely covered by the protective layers, not all the treated surfaces suffered from the sulphatation of calcite.

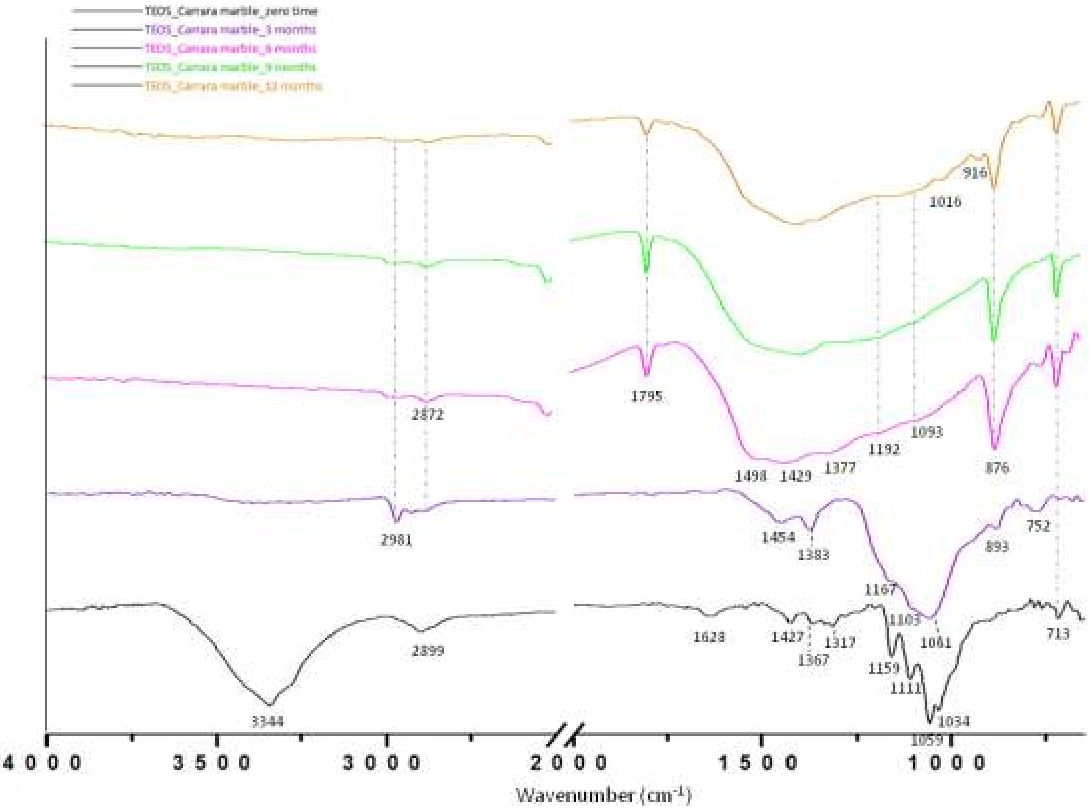


Figure 4.9: *µFTIR of EAS 40 commercial product, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

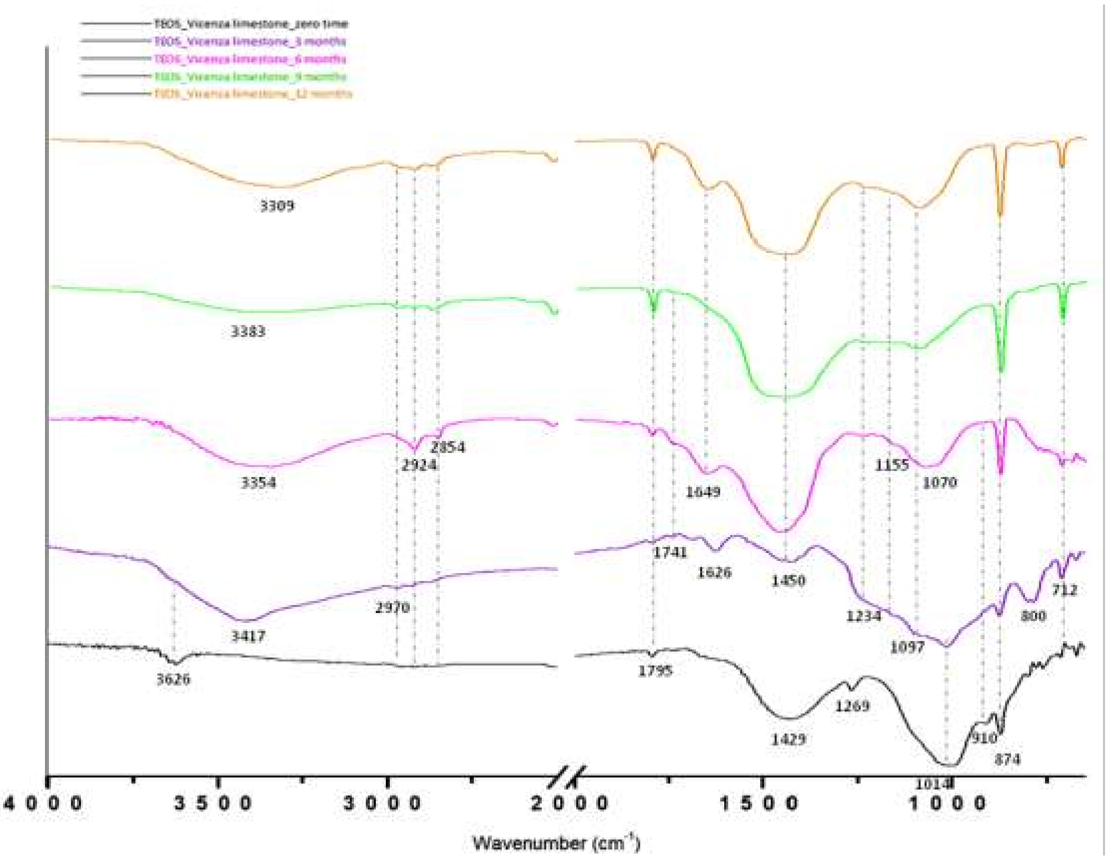


Figure 4.10: *μFTIR of EAS 40 commercial product, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

The spectra of all the silicone based consolidants examined and exposed to UV radiation showed the same trend. In general, the peaks related to C-H chemical bond at about 1431, 1390 cm^{-1} shifted towards higher values of wavenumber (1450, 1416 cm^{-1}) and an increasing of the bonds at 3440 and 1633 cm^{-1}, related respectively to Si-OH and O-H chemical bonds is observable. In addition, all the collected spectra showed a variation of the main band related to the Si-O-Si chemical bond. In fact, it was observed that the peak at 1030-1050 cm^{-1}, related to branched siloxane chains in a cycled structure, became a doublet at about 1110 cm^{-1} and 1050 cm^{-1}. This confirmed cross-linking, but also the breakage of the siloxane chain induced by UV light with consequent formation of a linear chain (1110 cm^{-1}) and terminal groups Si-OH (3440 cm^{-1}). No differences were observed between Carrara marble and Vicenza limestone. For these reasons and for convenience, it was chosen to present in this work only the spectra of the products applied on Carrara marble, as shown in figure 4.11, 4.12 and 4.13 below.

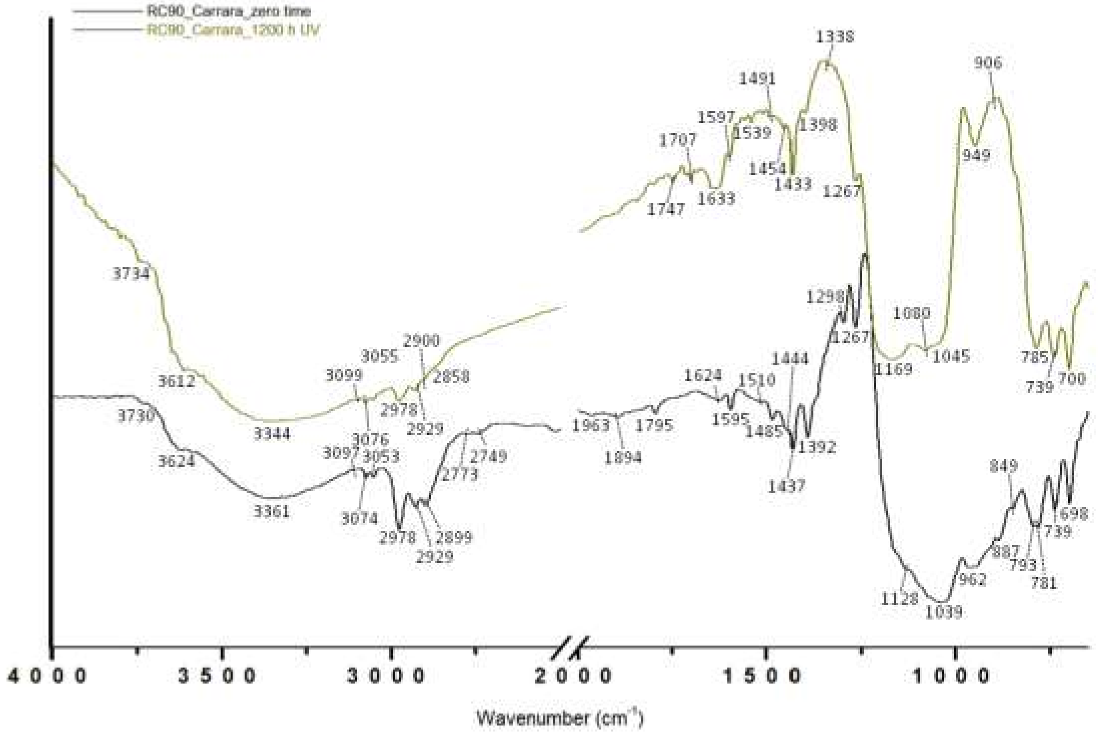


Figure 4.11: *μFTIR of Rhodorsil RC90 resin, applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

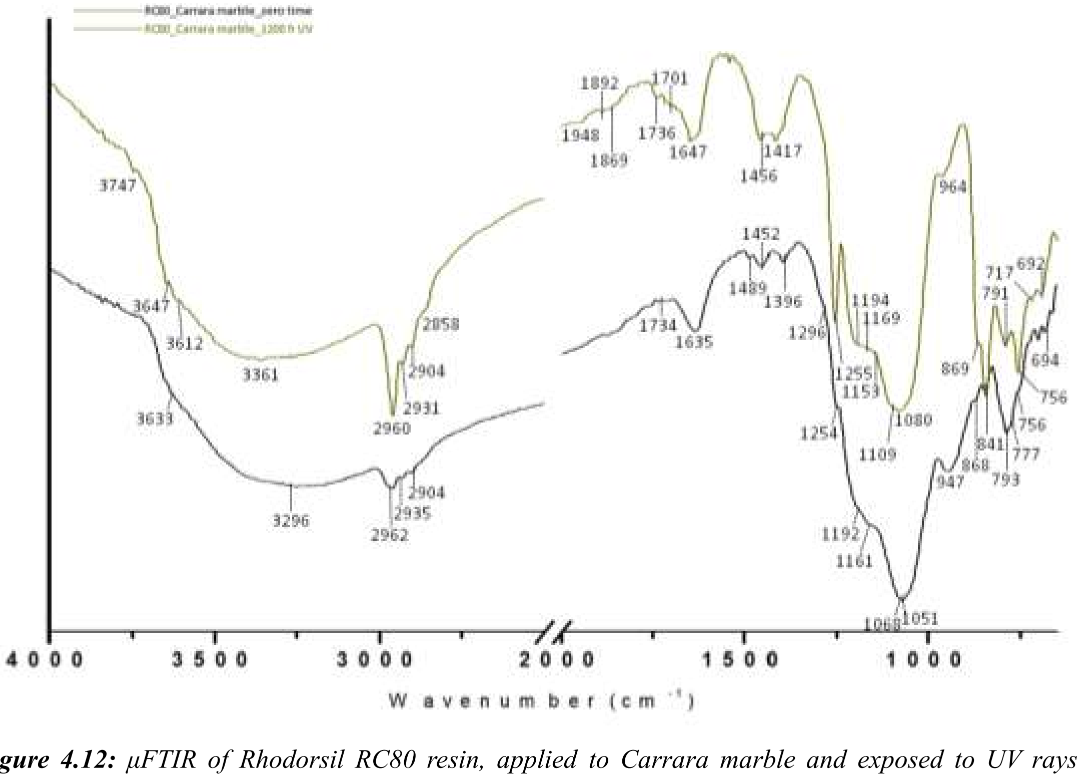


Figure 4.12: *μFTIR of Rhodorsil RC80 resin, applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

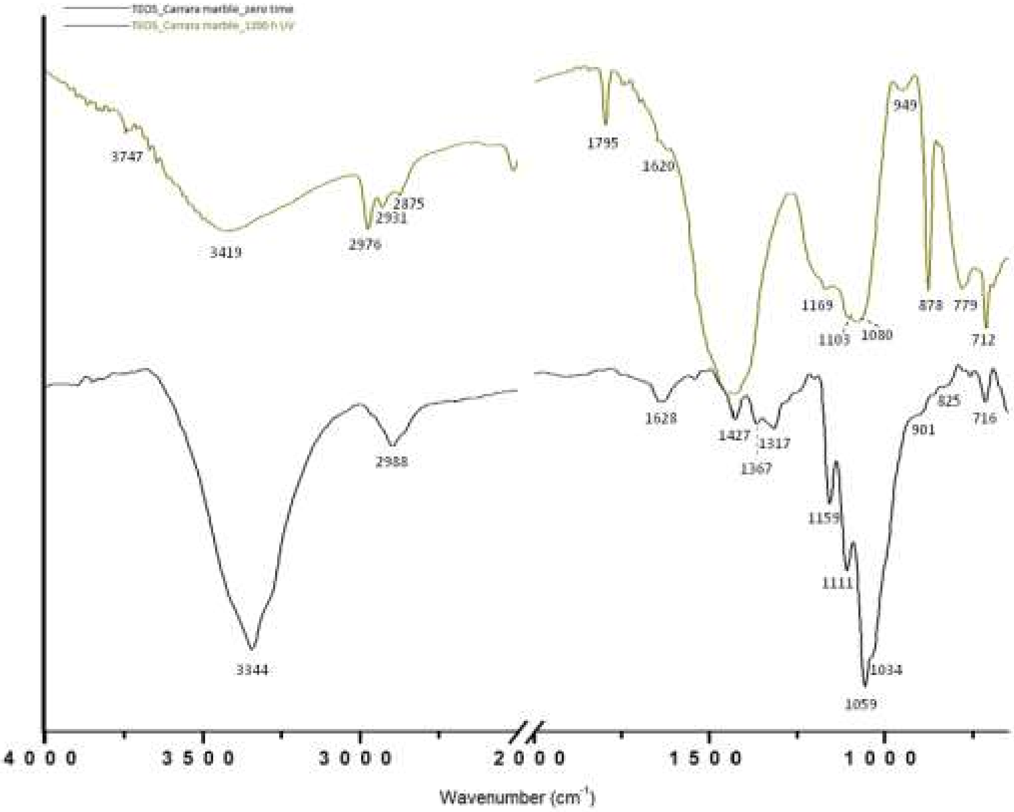


Figure 4.13: *µFTIR of EAS 40 commercial product, applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

4.2.2 Silicone based protectives

Hydrophase and Rhodorsil H 224 were applied to Carrara marble and Vicenza limestone specimens by brushing until complete impregnation of the substrate. Three samples were prepared for each product. After the application of the consolidants, the samples were maintained at room temperature until cured polymers were achieved (15 days).

Rhodorsil H 224 applied to Carrara marble polymerized in a homogeneous and transparent film, though during outdoor exposure many particles adhered and the surface soon became soiled. No craquelure due to natural ageing was observed and the film remained bright and transparent for the entire exposure time. On Vicenza limestone, H 224 did not form a continuous film but the resin showed transparent crystals in the pores of the stone. The entire surface appeared to be covered by a superficial white patina, probably due to the interaction between the product and the stone substrate. During 12 months of exposure the superficial patina turned yellow and cracked. Both samples showed the presence of biological microorganisms, predominantly fungi, after the third month of exposure and growth was observed in the following months.

Hydrophase applied to Carrara marble and Vicenza limestone showed the formation of a bright, thin polymeric film in both cases, which covered the entire stone surface. With natural ageing of the stone, white particles developed and wore thin. A diffuse fungal growth was observed on the surfaces.

Studying cross-sections of the samples after exposure to natural ageing for 12 months (fig. 4.14 and 4.15), the formation of a polymeric layer on the treated surfaces was confirmed, which was generally very thin, except H 224 on Vicenza limestone which showed a thick superficial layer with a low amount of silicone (1.9%) in comparison with the percentage of the resin calculated to have penetrated the porous network of the stone (2.35%). For this reason, it was considered that the superficial layer was composed not only of the resin, but also of an incoherent material made up of an aggregation of calcite and resin, probably due to alteration of the surface after application and curing of the resin.

From the measurements collected by EDS analysis, using silicon as a tracer, Rhodorsil H 224 resin is able to penetrate stone surfaces, as shown in graph 4.4. A decision was made to distinguish between the results obtained from the penetration of the resins in Carrara marble samples with those obtained in Vicenza limestone, due to the different percentages of carbon in the two different substrates.

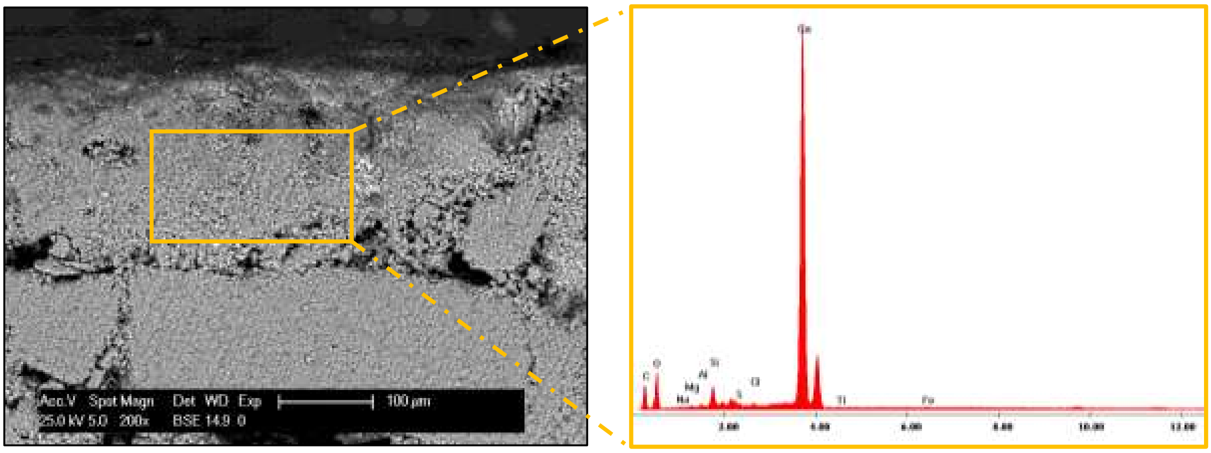


***Figure 4.14**: SEM micrograph of the cross-section of V-8 specimen and EDS analysis of the superficial layer.*

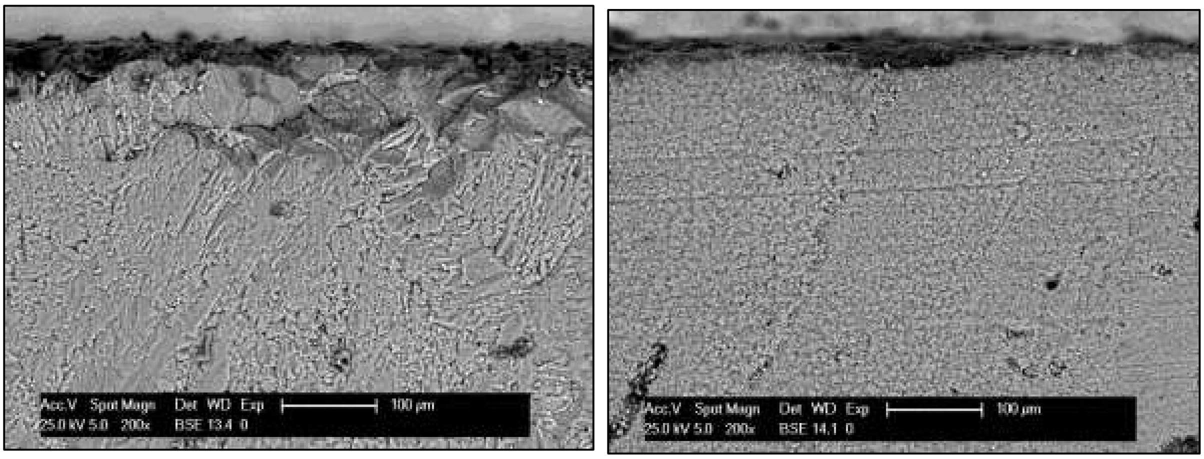
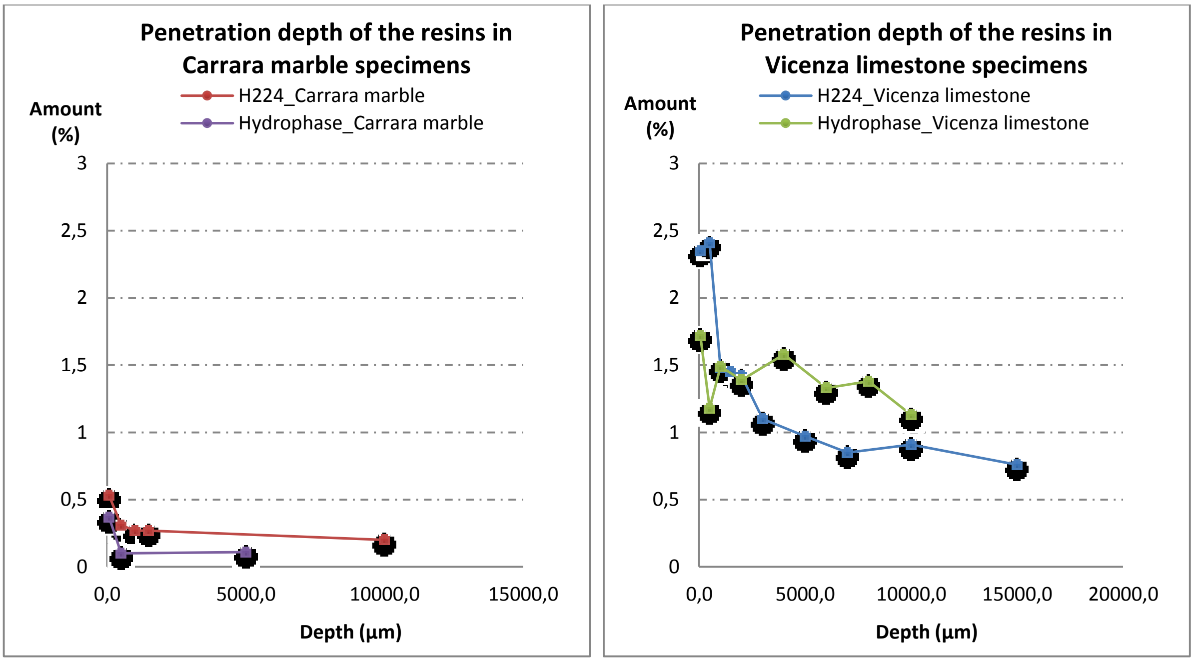
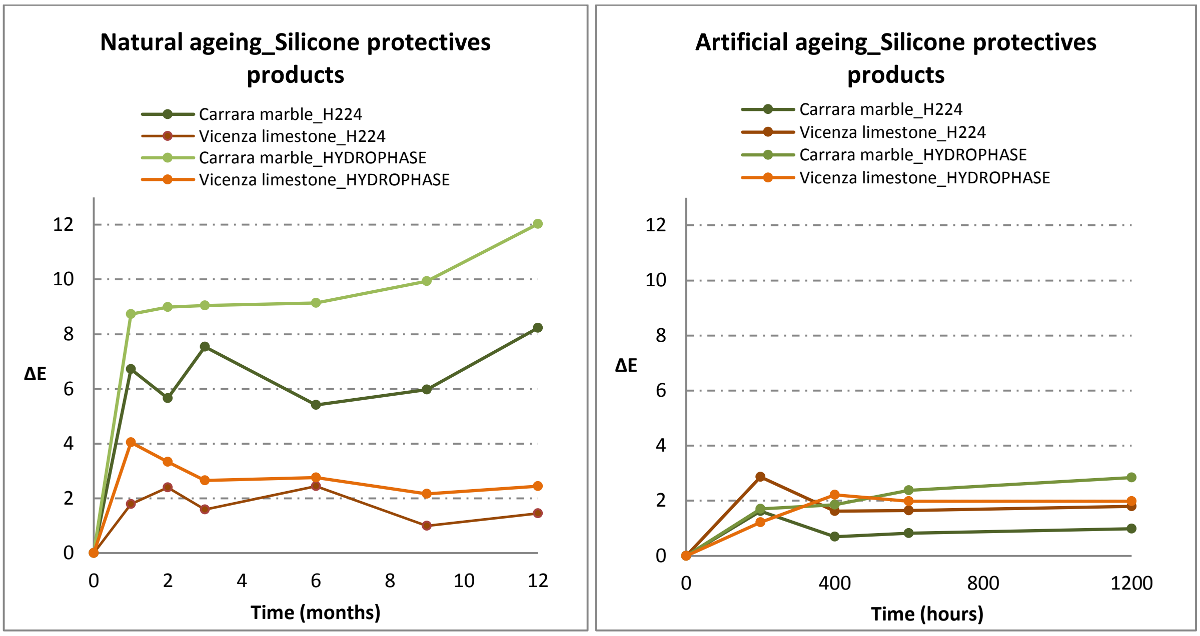


Figure 4.15: *SEM micrographs of the cross-section of C-11 (on the left) and V-11(on the right) specimens.*

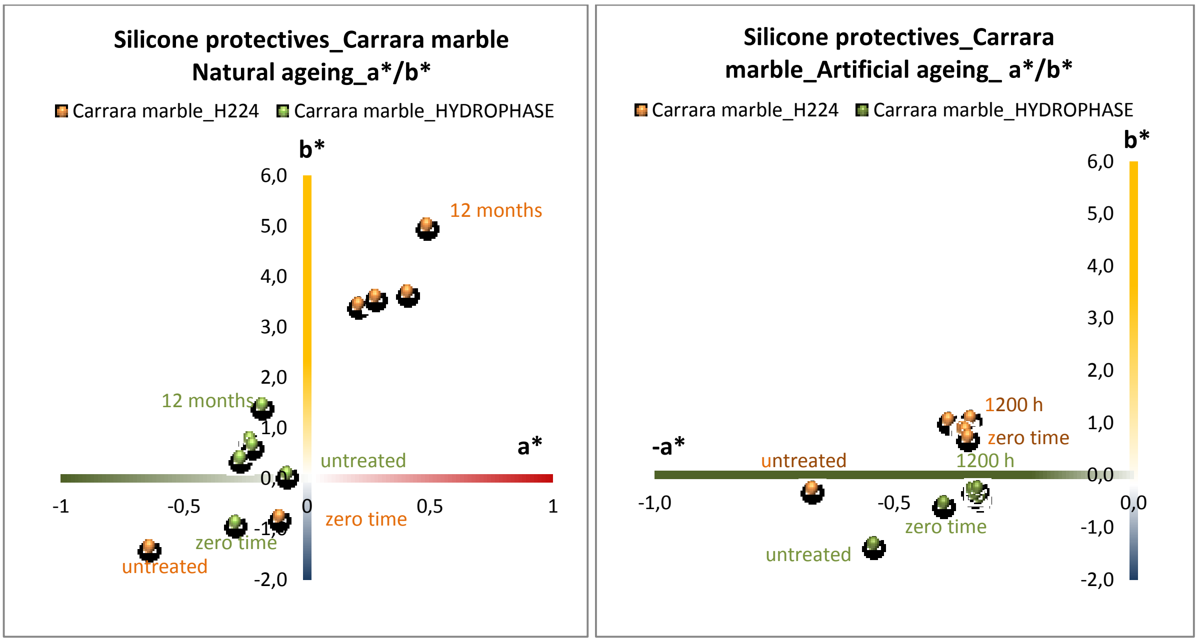


Graph 4.4: *penetration depths of consolidant agents measured in Carrara marble (on the left) and Vicenza limestone(on the right) using EDS microprobe.*

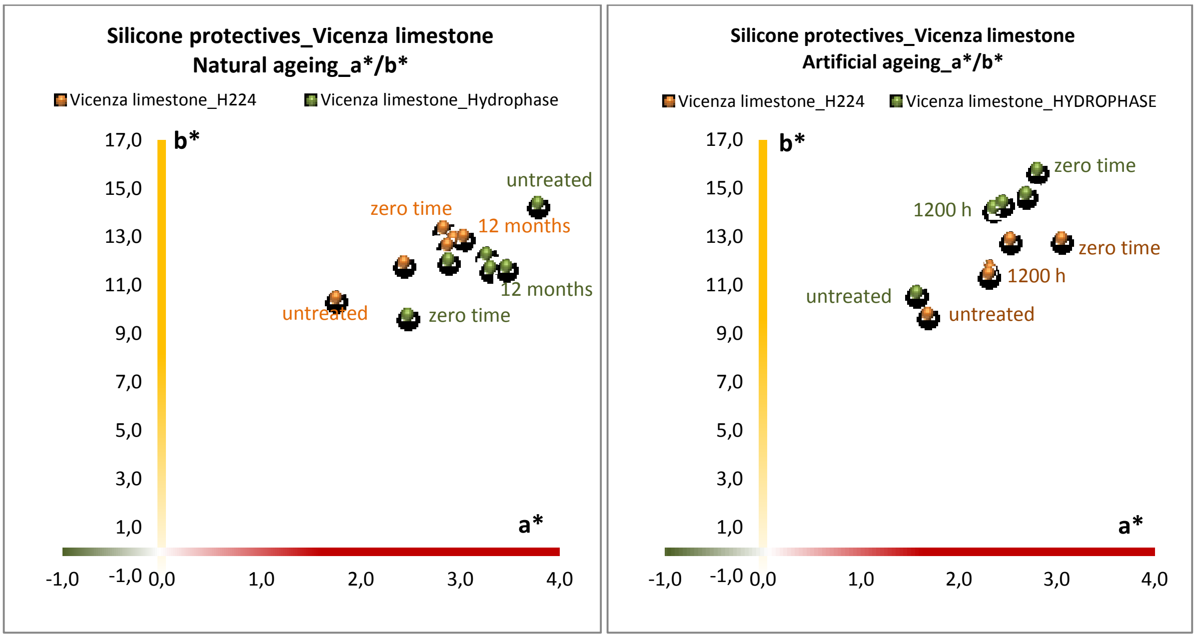
Outdoor exposure of the specimens caused significant colorimetric variation of the superficial resin, which is greater than those caused by UV rays (graph 4.5). In particular treated marble, on which many particles had adhered, showed the greatest chromatic alteration. Comparing Hydrophase with Rhodorsil H224, the former appears be more susceptible to UV radiation. Both resins applied to Carrara marble showed a peculiar tendency to yellowing, more substantial in the case of Rhodorsil H 224 (graph 4.6), whereas on Vicenza limestone the colour data tend to return to the untreated or zero value (graph 4.7).



Graph 4.5: *Trend of colour change of surfaces treated with Rhodorsil H224 and Hydrophase during exposure to outdoor conditions (left) and UV radiation (right).*

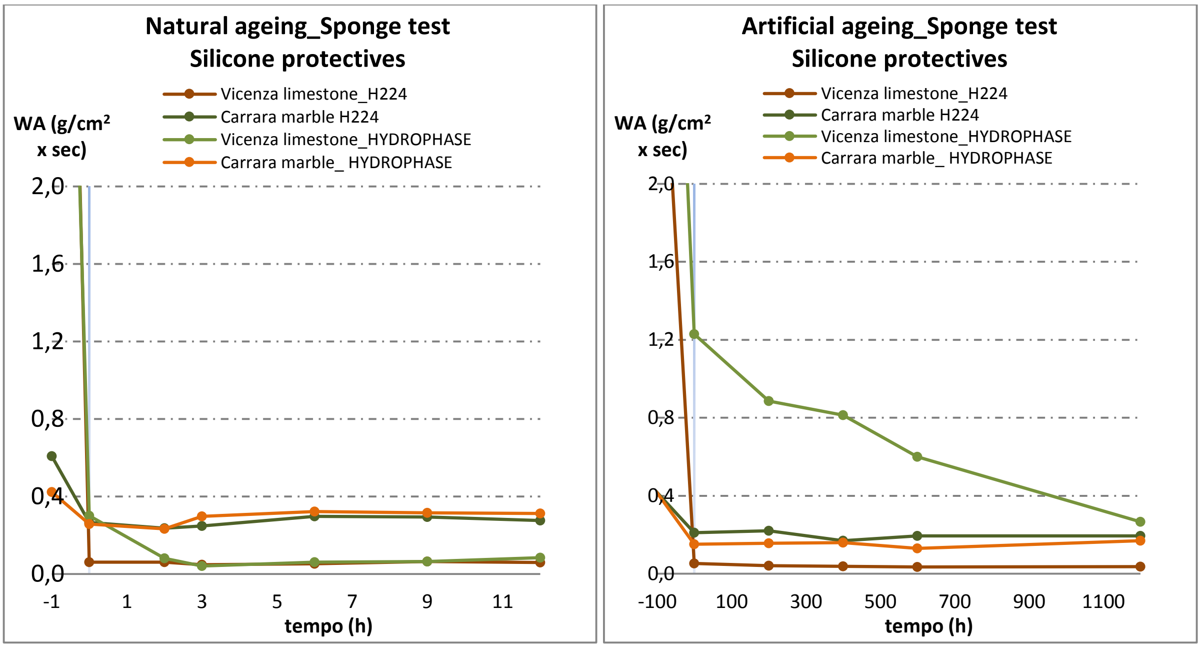


Graph 4.6: *Trend of colour change of surfaces treated with Rhodorsil H224 and Hydrophase, applied on Carrara marble, during exposure to outdoor conditions (left) and UV radiation (right).*



Graph 4.7: *Trend of colour change of surfaces treated with Rhodorsil H224 and Hydrophase, applied on Vicenza limestone, during exposure to outdoor conditions (left) and UV radiation (right).*

Moreover, both resins maintained their hydrophobicity during ageing processes assuring good protection effect (graph 4.8). In particular, the behaviour of Hydrophase applied on Vicenza limestone is distinct, as the value of superficial hydrophobicity of the stone increased with time.



Graph 4.8: *Water absorption variation during outdoor (on the left) and UV exposure (on the right).*

The chemical stability of Hydrophase and Rhodorsil H224 was ascertained by µFTIR analysis. The spectra collected during the natural ageing of the resins exposed to outdoor conditions showed stability of the main peaks on both Carrara marble and Vicenza limestone.

The spectra of samples exposed to UV radiation showed decreasing and broadening of the main band at 1130-1020 cm^{-1} related to symmetrical stretching of Si-O-Si chemical bond in the siloxane chain. The assignments of all peaks were summarized in table 4.2.

For convenience, only spectra related to the aging of protectives on Vicenza limestone are shown below.

Wavenumber (cm^{-1})		*Functional groups*	*Assignments*
H224	*HYDROPHASE*		
3425	*---*	v_s *Si-OH*	*Silanol*
2981, 2953	*2956, 2931, 2873*	*v C-H*	*Aliphatic bonds*
---	*1795*	$(CO_3)^{2-}$	*Calcium carbonate*
1725	*---*	*v C=O*	*Carbonyl group*
1471, 1448	*1448*	*v C-H*	*Aliphatic bonds*
1387	*---*	*δs C-H*	*Methyl groups*
1232, 1267	*1219*	*v Si-*(CH_3)	
1144	*1144*	*ρ C-H*	*Methyl groups*
1028	*1068*	v_s *Si-O-Si*	*Siloxane chain in cyclic structure*
874	*876*	$(CO_3)^{2-}$	*Calcium carbonate*
797	*---*	δ_s *Si-O-Si*	*Siloxane chain*
710	*712*	$(CO_3)^{2-}$	*Calcium carbonate*

Table 4.2: *FTIR assignments of the main peaks observed for Rhodorsil H224 and Hydrophase resin, according to the literature [12-13].*

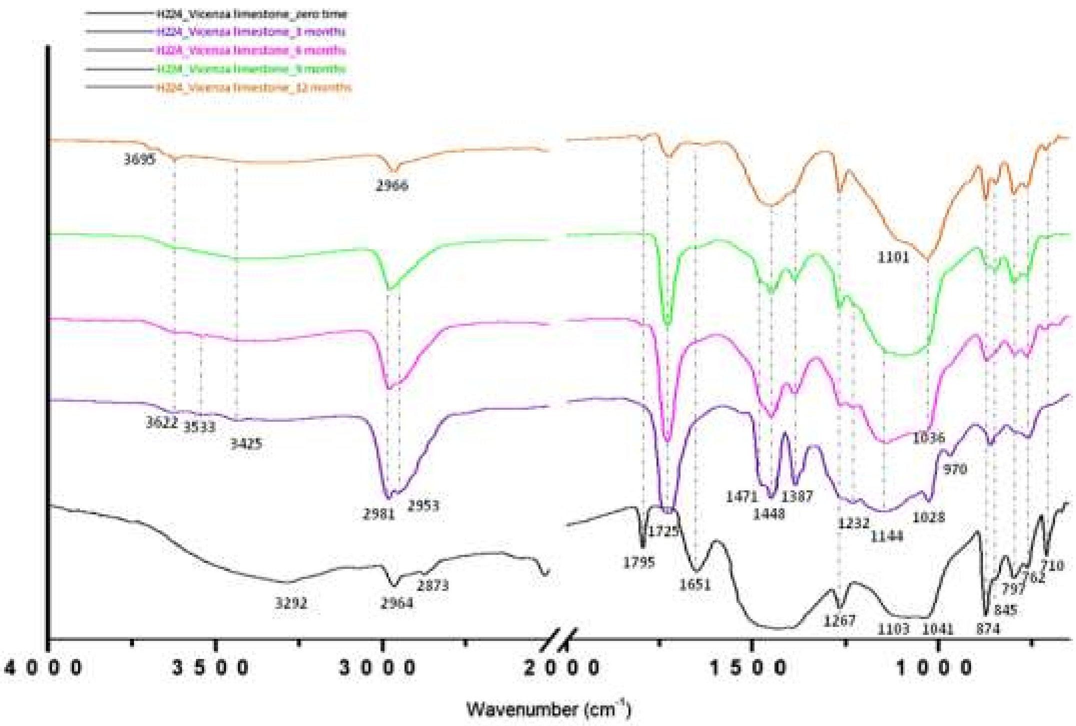


Figure 4.16: *µFTIR of Rhodorsil H224, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

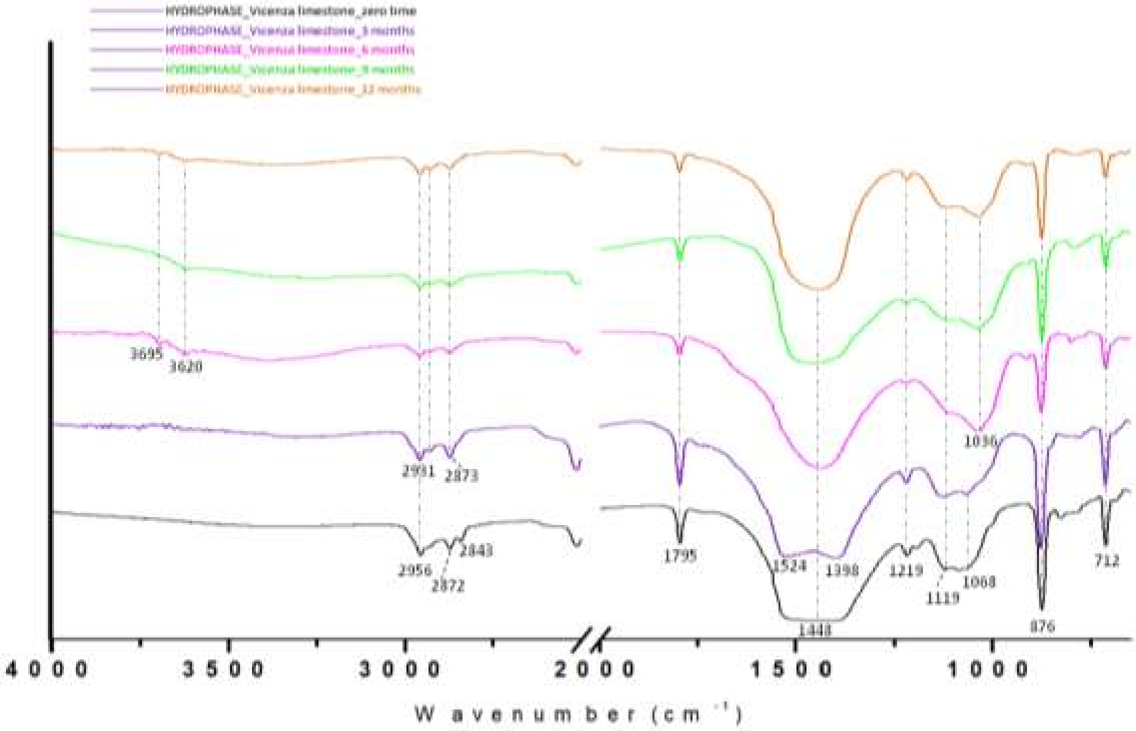


Figure 4.17: *µFTIR of Hydrophase, applied to Vicenza limestone and exposed to outdoor conditions.Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

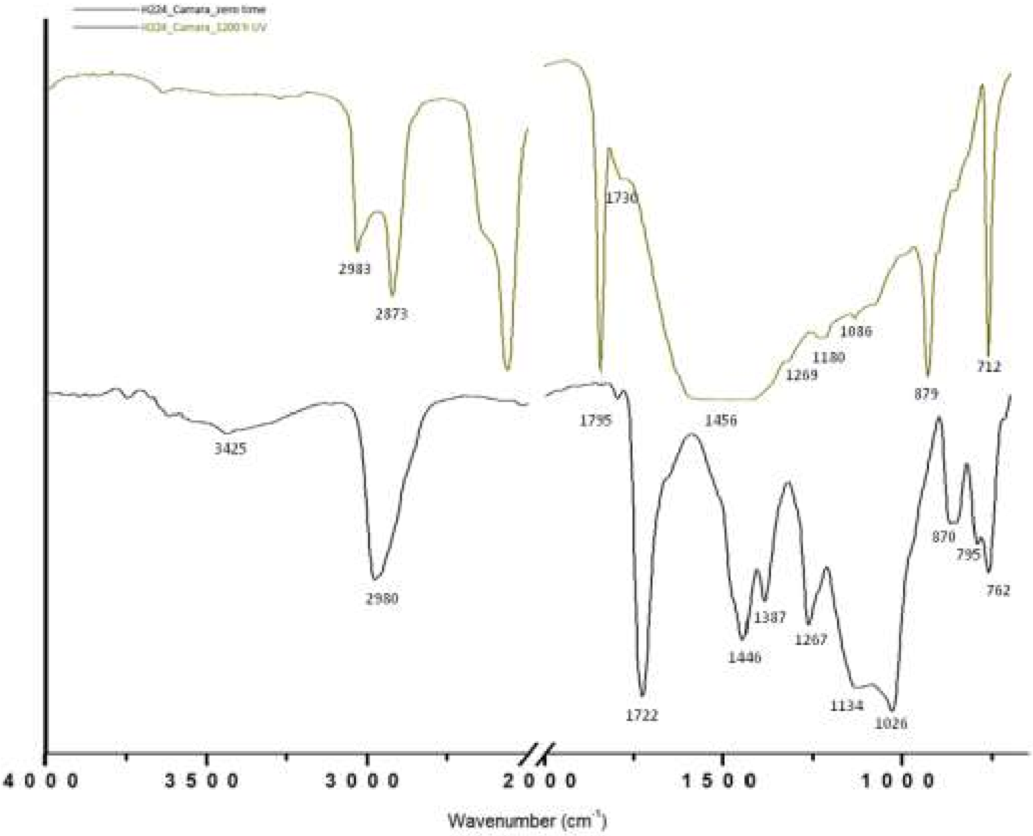


Figure 4.18: *μFTIR of Rhodorsil H224, applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

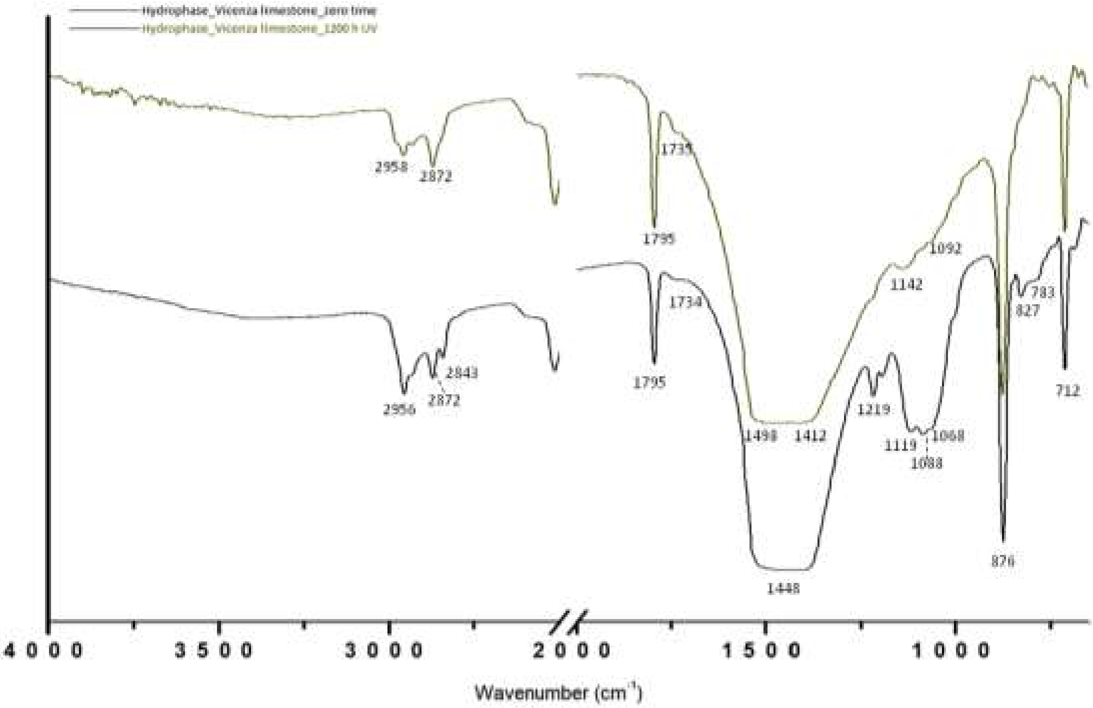


Figure 4.19: *μFTIR of Hydrophase, applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was carried out at zero time (black line), and after 1200 h of exposure (dark yellow line).*

4.3 Monitoring of past treatments performed in Venice

In this section, the most significant analyses undertaken on some fragments sampled from surfaces of interest treated in the past with silicon based resins are reported, and these can confirm or refute the observations made in the previous sections.

First, the results obtained from two different consolidation treatments in Venice will be presented, in which a single consolidant resin, Sogesil XR893[1] was used.

In 1985, prior to use, the experimental resin was tested in the scientific laboratory of the Venetian Superintendent by Prof. Lorenzo Lazzarini on a Proconnesian marble fragment available in the laboratory due to a stone substitution during a restoration intervention in Ca' D'Oro palace. The fragment was treated by under-vacuum impregnation in autoclave and conserved in the laboratory.

- **Laboratory experimentation**

A small chip sampled from a column of the Ca' D'Oro façade in Venice carved from Proconnesian marble and treated in 1963 by Profs. L. Marchesini and L. Lazzarini using Sogesil XR893, by vacuum impregnation has been chemically analysed. The cross-section of a micro-fragment showed homogeneous distribution of the resin which is still present in the inter- and intra-grain spaces, confirmed by microscopic observations and SEM-EDS analysis (Fig. 4.21 and 4.22).

Figure 4.20:*Fragment of a column of Ca D'Oro façade, Venice.*

However, SEM-EDS elementary map allowed the recognition of a chemical alteration of calcite for the presence of sulphur linked to calcium sulphate ($Ca(SO_4)$), between calcite grain and the resin (fig. 4.23). The sulphatation of calcite in the stone probably took place prior to the treatment with the siloxane grain.

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[1] *Sogesil XR893:* methyl-phenyl-polysiloxane dissolved in benzene with a solid content of 50%. It was produced by Rhône Poulenc and it is no longer available on the market.

Figure 4.21: *Micrographs of the sample under the optical microscope. Long side images 1.03 mm.*

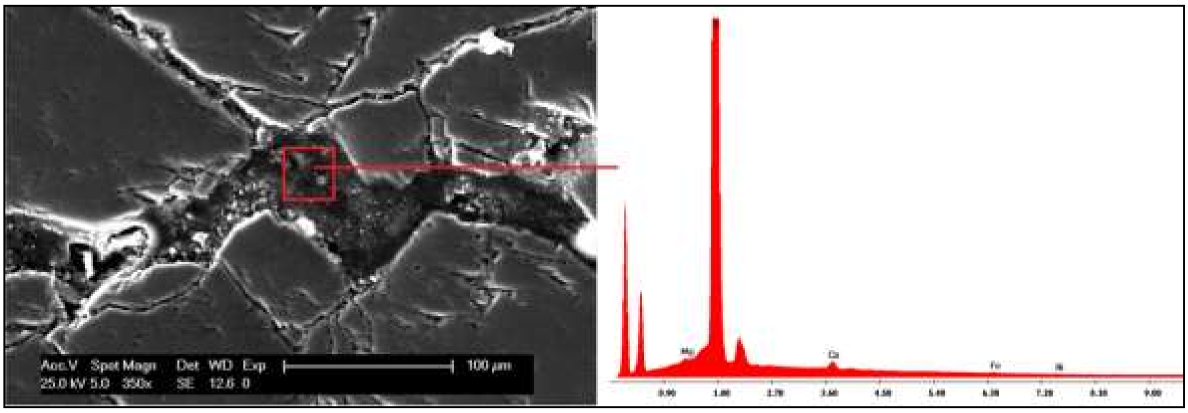

Figure 4.22*: Detail of a cross-section of the fragment sampled from a portion of a column at Ca' D'Oro. SEM observations and EDS analysis showed the presence of the resin in the inter- and intra-grain spaces.*

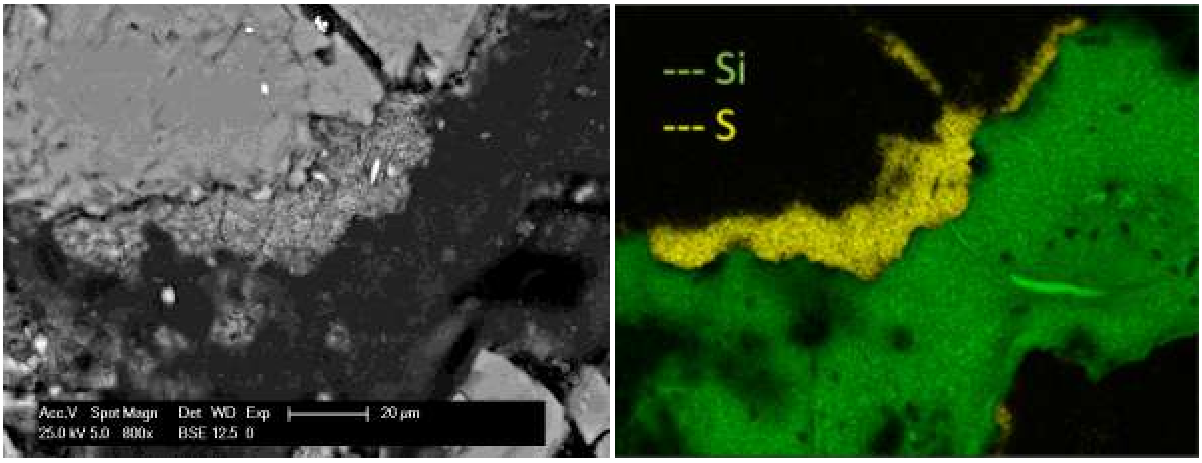

Figure 4.23: *Detail of a cross-section of the fragment sampled from a portion of a column at Ca' D'Oro. SEM observations and EDS map showed the presence of the resin and sulphur in the inter- and intra-grain spaces.*

Study of the wavenumbers of each µFTIR peak of the spectra collected confirmed the chemical nature of methyl (1267 cm^{-1}) – phenyl (3068, 1464-1429, 706 cm^{-1}) - polysiloxane (1082, 1030 cm^{-1}) and its cross-linked structure (fig.4.24).

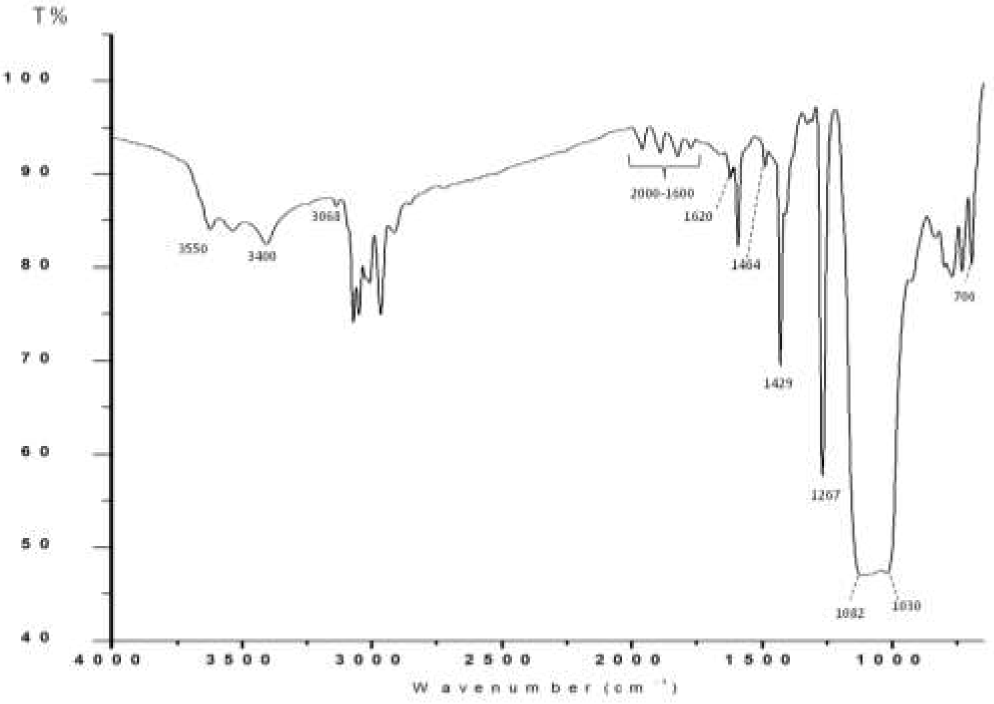

Figure 4.24: *μFTIR analysis of a micro-scale of the sample.*

- **<u>S. Martino Church - (*Sestiere Castello*): 4 angels supporting the S. Sepulcher altar (Tullio Lombardo)</u>**

  Substrate: Carrara marble

Figure 4.25: *S. Sepulcher altar in S. Martino church (sestiere Castello), Venice.*

PAST RESTORATIONS:

1968-1969: Prof. L. Marchesini, Prof. L. Lazzarini, Prof. O. Nonfarmale (LARES and O. Nonfarmale company).

In situ: Cleaning of the angel statues surfaces from dust deposits. Pre-consolidation using a very dilute solution of siloxane resin in order to protect the statues during transport to the laboratory.

In the laboratory: Washing of the statue with pure water, drying and consolidation under vacuum in an autoclave using Sogesil XR893 resin. Polymerization by heating at 60°C [55].

1991: dr. Vasco Fassina
Evaluation of the past treatment by micro-probing (2 cm depth). Protection of the marble substrate with microcrystalline wax.

SAMPLING:
Date: 22.01.2012
Operators: Restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna)
Number of micro-fragments sampled: 1 sample from the right-heel of the forward angel on the left, where there was a previous spall.
Sampling was undertaken using a small chisel and the area of the sampling was finally covered by brushing with Rhodorsil RC90 resin.

Figure 4.26: *sampling of micro-fragment from the right-heel of the forward angel on the left.*

MACROSCOPIC OBSERVATIONS:

The statue appeared in a good state of conservation. The surface was visually compact and cohesive. No new fractures, micro-cracks or powdering were observed.

ANALYTICAL RESULTS:

- MICROSCOPIC OBSERVATIONS:

The sampled micro-fragment was observed and studied with the stereomicroscope both at the surface and in cross-section. The consolidant resin Sogesil XR893 was observed in the inter and intra grain spaces. It appeared as a transparent and bright substance, which linked the calcite crystals to each other. The calcite was strongly degraded. A thin layer of white homogenous matter (microcrystalline wax) covered the surface of the sample, having heterogeneous substances within it.

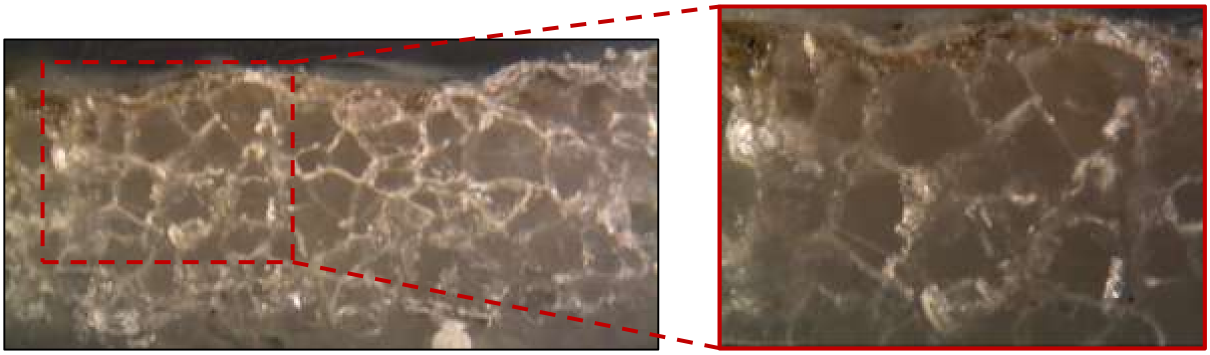

Figure 4.27: *Micrographs of the sample under the optical microscope. Long side images 2.5 mm and 1.03 mm.*

- FTIR ANALYSIS:

Spectroscopic analysis FTIR by KBr pellets, µATR with Ge crystal on cross-section, and µFTIR of micro-scales sampled from the fragment, revealed the distribution of resin in the inter and intra grain spaces of calcite, confirming the nature of the protective film and showing the presence of gypsum on the stone surface, as a product of the chemical alteration of calcite.

In particular, looking at figure 4.28, the blue line indicates the spectrum collected from the superficial layer of the sample, in which the peaks at 2954, 2918, 2850, 1738, 1466 and 1377 cm^{-1} are attributable to microcrystalline wax. The green spectrum is representative of the dark patina on the surface, in which gypsum, calcite and the siloxane resin are contained. Finally, the black spectrum, collected from the intra grains space of the sample, confirmed the chemical nature of methyl (1269 cm^{-1}) – phenyl (3070-3051, 1429, 1136, 714 cm^{-1}) - polysiloxane (1082, 1028 cm^{-1}) of the resin.

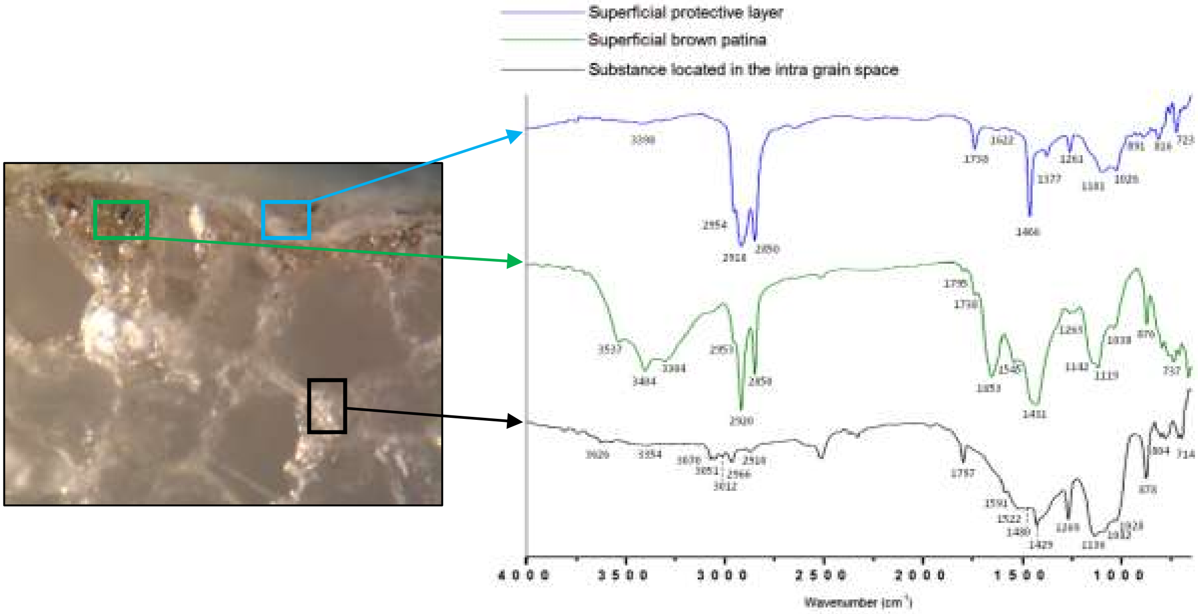

Figure 4.28: *µFTIR analysis of different areas of the sample cross-section: the siloxane resin in the intra grain spaces (black line), the superficial layer (green line) and the protective film (blue line).*

- **S. Alvise Church - (*Sestiere Canareggio*): S. Alvise statue (Tuscan nameless of the XV c.)**

Substrate: Greek marble (probably Pario)

PAST RESTORATIONS:

1967: Prof. L. Marchesini, Prof. L. Lazzarini (LARES company).

The statue was moved from its location to the laboratory of Superintendence for restoration.

In the laboratory: The statue was washed with pure water, checking the salts content in the water after cleaning. The statue was then dried using hot air and consolidated under vacuum in an autoclave using Sogesil XR893 resin. Polymerization by heating at 60°C [46-56].

Figure 4.29: *S. Alvise statue located on the main façade of S. Alvise church (sestiere Canareggio), Venice.*

1997: G.R.C. snc company (Dr. Adriana Spagnol); Venetian Superintendence (Dr. Basso e Spadavecchia); UNESCO (Dr. Millerchip).
Superficial cleaning by brushing and pure water poultice. Evaluation of the past treatment.

SAMPLING:
data: 15.05.2013
Operators: restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna)
Number of micro-fragments taken: 1 sample from the right side of the statue, close to the base, where there was a previous spall.
The sampling was carried out using a small chisel and the area of the sampling was finally covered by brushing Rhodorsil RC90 resin.

Figure 4.30: *Sampling of a micro-fragment from the right side of the statue, close to the base.*

MACROSCOPIC OBSERVATIONS:
The statue appeared in a good state of conservation. The surface was visually compact and cohesive. No new fractures, micro-cracks or powdering were observed.

ANALYTICAL RESULTS:

- MICROSCOPIC OBSERVATIONS:

  The sampled micro-fragment was observed and studied under the stereomicroscope both as found and in cross-section. Black crusts covered the greater portion of the sample (fig. 4.31), probably adhering on the surface due to ineffective cleaning of the statue. It was possible to verify the presence of a light-ocher powder, presumably ancient polychromy of the statue.

Figure 4.31: *Micrographs of the sample under the optical microscope. Long side images 2.5 mm and 1.03 mm.*

- SEM-EDS ANALYSIS:

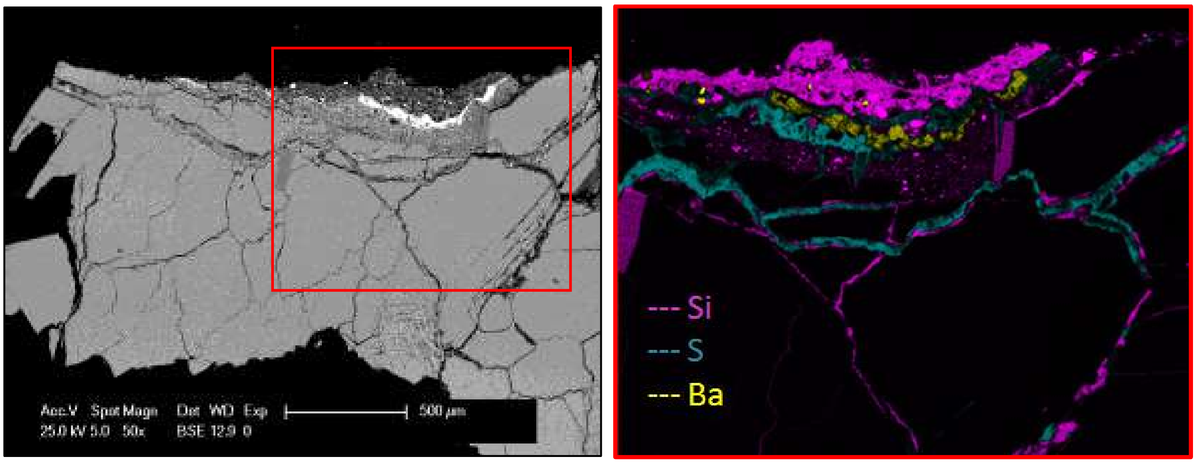

Figure 4.32: *SEM micrograph (on the left) and elementary map (on the right) of a fraction of the fragment sampled.*

Observing the cross-section of the sample, the area of black crust was examined in order to ensure the supposed composition based on gypsum. Analysis of this area revealed the presence of another previous conservative treatment based on barium hydroxide.

In fact it is assumed that, in order to conserve the altered marble, the statue was treated with barium hydroxide ($Ba(OH)_2$) without cleaning the surface. Consequently, the presence of gypsum due to the sulphatation of calcium carbonate of the substrate determined the transformation of barium hydroxide directly into barium sulphate (Ba_2SO_4) and not into barium carbonate ($BaCO_3$) (fig. 4.32). However, the presence of Barium on the surface did not prevent complete penetration of the siloxane resin into inter and intra grain spaces of the substrate, as shown in the map in figure 4.33.

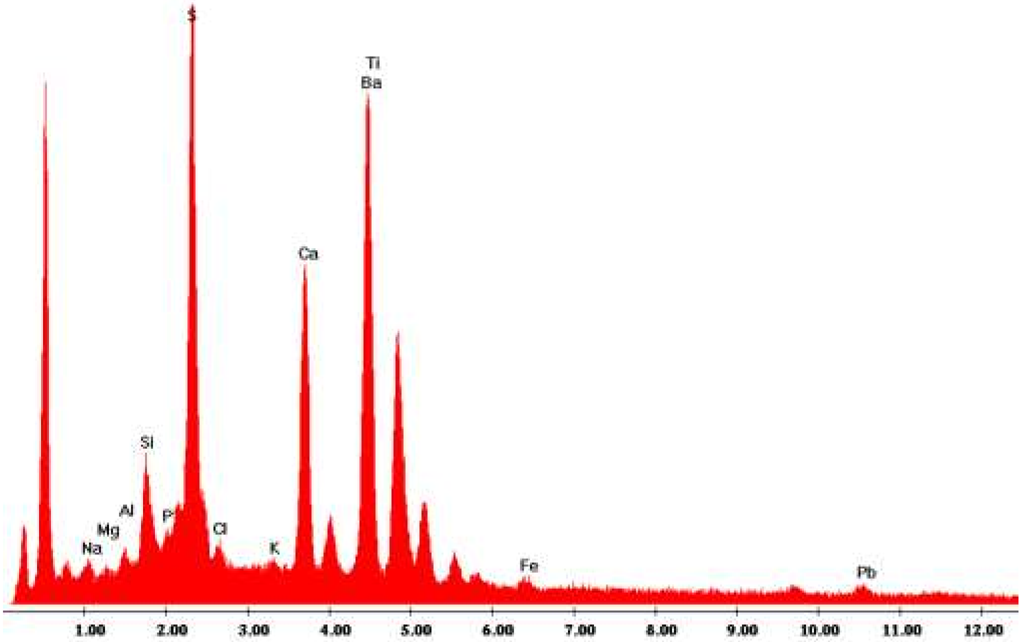

Figure 4.33: *EDS spectrum of a small area of the fragment considered*

- FTIR ANALYSIS:

Spectroscopic analysis FTIR by KBr pellets, µATR with Ge crystal on cross-section, and µFTIR of micro-scales sampled from the fragment confirmed the formulation of methyl phenyl polysiloxane of the resin and proved the sulphatation of calcite due to the presence of gypsum. Studying the spectrum in figure 4.34, it is possible to note the peaks at 3095-3072-3053-3028 cm^{-1} related to C-H symmetrical stretching in aromatic structure, those at 1429 cm^{-1} linked to ν_s C-H and at 1269 due to the ν_s $Si\text{-}CH_3$ and finally the peak at 1038 cm^{-1} related to Si-O-Si symmetrical stretching, which could be all related to the durability of the methyl- phenyl-polysiloxane resin in the sample. Moreover the peaks at 3533-3406-3246 cm^{-1} related to ν_s O-H, and those at 1680, 1622, 1138, 878, 675 cm^{-1} are typical of calcium sulphate.

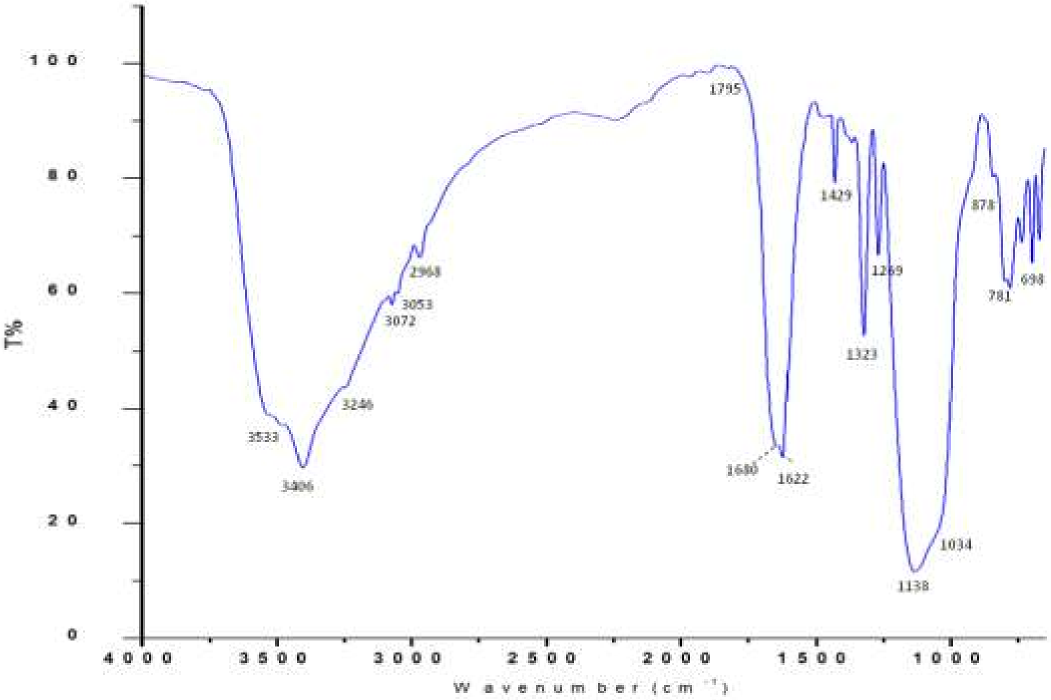

Figure 4.34: *µFTIR analysis of the backside of the fragment sampled.*

FINAL OBSERVATION:

The assumed chemical nature and cross-linking tendency of Sogesil XR893 have been confirmed by examining the 50/40-year-old polymerised resins from different marble artefacts. The value of wavenumber related to ν_S Si-O-Si in a cross-linked structure is low at about 1030 cm^{-1}. Since the resin Sogesil XR893 is no longer available on the market, it was not possible to evaluate an eventual shift towards lower wavenumbers during the ageing time, as was studied in the case of Rhodorsil RC90, RC80 and EAS 40.

However the resin was extracted with xylene from three different samples and the spectra were compared each other. As shown in fig. 4.35 a different intensity of the band related to the siloxane chain at about 1100-1000 cm^{-1} was observed, and confirmed by measurement of the area of the peaks (table 4.3). In particular, greater decrease in the case of the S. Alvise statue was compared with the S. Martino angel and the fragment of column of Ca' D'Oro, the oldest treatment exposed to outdoor conditions. Consequently, it is possible to surmise that the resin suffered a breakage of the siloxane chain proportionally to the period of exposure to outdoor conditions.

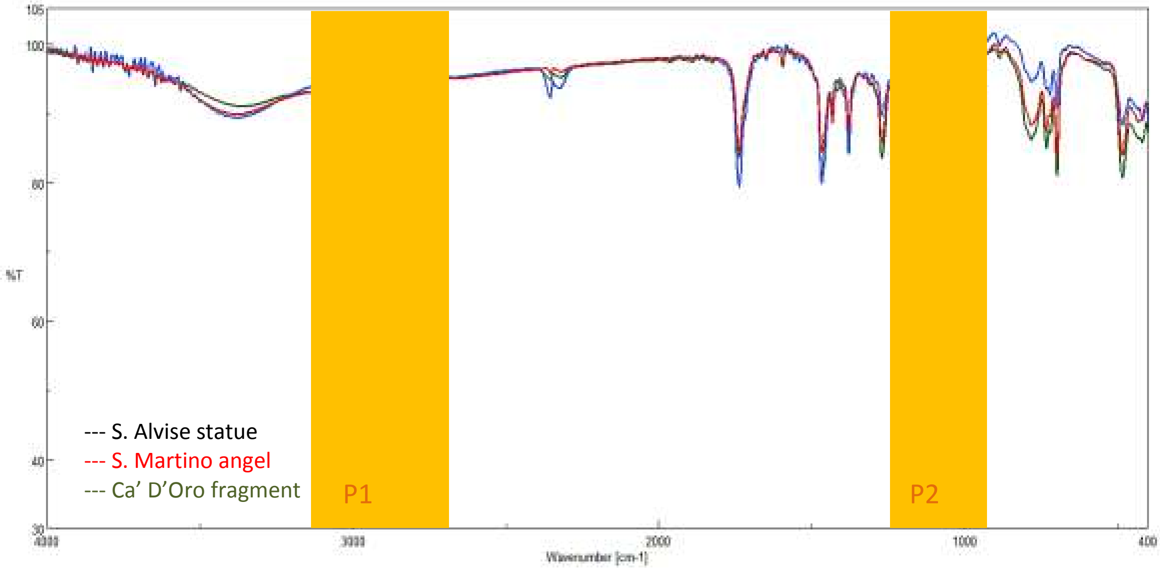

Figure 4.35: *Comparison between FTIR spectra of the resin XR893 extracted with xylene from Ca' D'Oro, S. Martino and A. Alvise samples.*

Campione	P1	P2	P1/P2	P2/P1
Ca' D'Oro	20.99	23.10	0.91	1.10
S. Martino	29,14	26,95	1.08	0.92
S. Alvise	29,73	15,16	1.96	0.51

Table 4.3: *Values of the area P1 and P2 of every FTIR spectrum and measurement of the relative ratio.*

The use of benzene as a solvent and its high volatility could, in all probability, generate cracked polymeric films, allowing penetration of water and pollutants into the cured layer and consequent sulphatation of the carbonatic surface. However, in all samples examined, the presence of gypsum in the inter and intra grains spaces which could pre-date all the conservative treatments.

The under-vacuum technique ensured good penetration of the resin in the porous network of the stone.

On end, the results obtained from a past treatment based on an alkyl-alkoxy-silane resin and used as consolidant.

- **<u>S. Maria Gloriosa dei Frari Church - (*Sestiere S. Polo*): Lunette above the portal of Corner chapel “Madonna con bambino e angeli” (Lamberti, Maestro dei Mascoli, Bartolomeo Bon)</u>**

  Substrate: Candogia marble

PAST RESTORATIONS:
1973-1974: K. Hempel, G. Musumeci
The surface was cleaned with pure water, sepiolite poultice and micro-sandblasting.
The marble was lightly heated, treated with the solvent and consolidated using X54-802 (Rhone Poulenc) 1:0.1:0.04:1 in propan-2-ol and pure water.

Figure 4.36: *Lunette “Madonna con bambino e angeli”above the portal of Corner chapel. S. Maria Gloriosa dei Frari Church, Venice.*

SAMPLING:
Date: 16.05.2013
Operators: dr. Fabrizio Antonelli (researcher at Iuav University), restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna) and Prof. Lorenzo Lazzarini.
Number of micro-fragments sampled: 1 sample from the lowest left part of the mantle of the Virgin Mary, adjacent to a previous broken area.
The sampling was undertaken using a small chisel and the area of the sampling was finally covered by brushing with Rhodorsil RC90 resin.

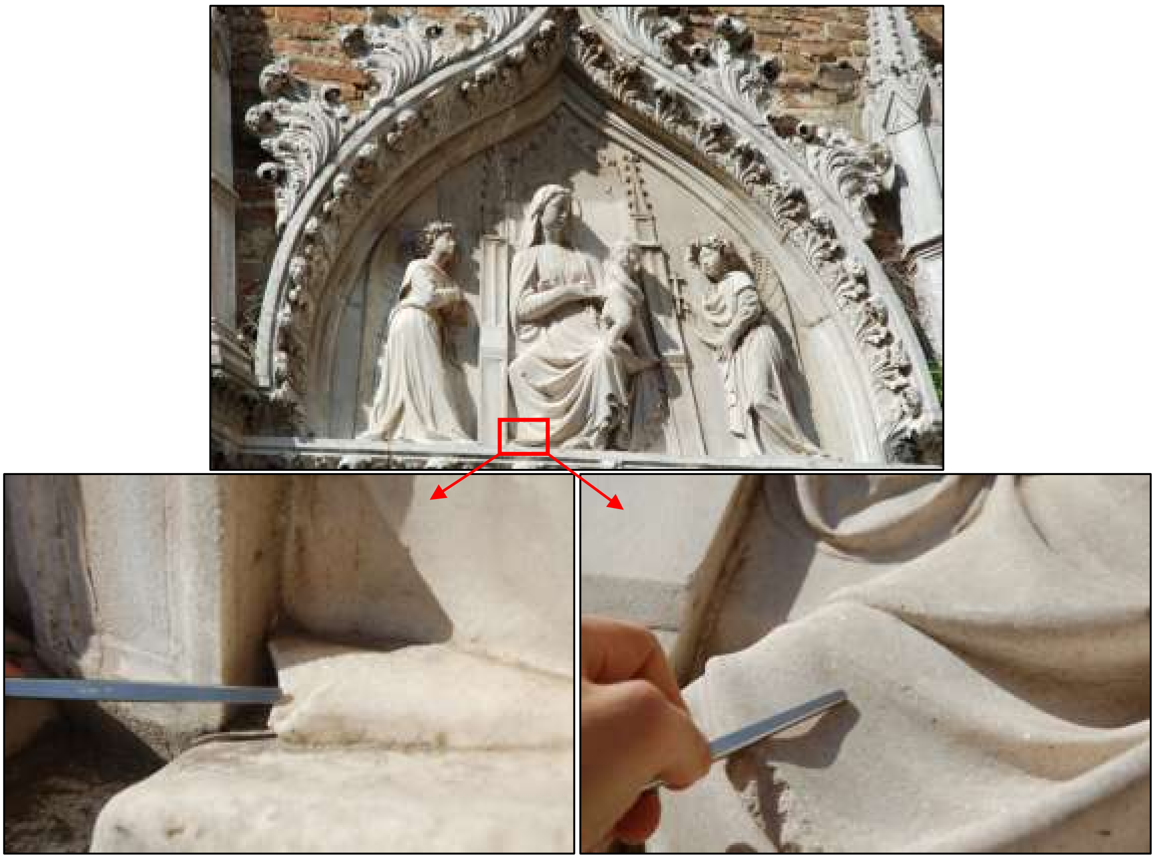

Figure 4.37: *Sampling of a micro-fragment from lowest left part of the mantle of the Virgin Mary, adjacent to a previous broken area*

MACROSCOPIC OBSERVATION:

The statue appeared in a good state of conservation. The surface was visually compact and cohesive. No new fractures, micro-cracks or powdering were observed. The grain size of the marble is from 2 to 3 mm.

ANALYTICAL RESULTS:

- MICROSCOPIC OBSERVATIONS:

  The micro-fragment sampled was observed and studied as found and in cross-section using stereo and optical microscopy.Dark superficial particles covered the sample surface, on which a superficial polymeric layer, deemed a protective feature, was observable by study of the cross-section.

Figure 4.38: *Micrograph of the cross-section of the sample under the optical microscope. Long side image 1.03 mm.*

- SEM-EDS ANALYSIS

Microscopic observations by SEM and elementary analysis of the cross-section of the examined sample showed the presence of a superficial layer based on silicon (protective superficial film), and good penetration of the resin in the inter and intra grain spaces. Alumina grains were distributed on the superficial layer, probably due to the use of micro-sandblasting for the cleaning process.

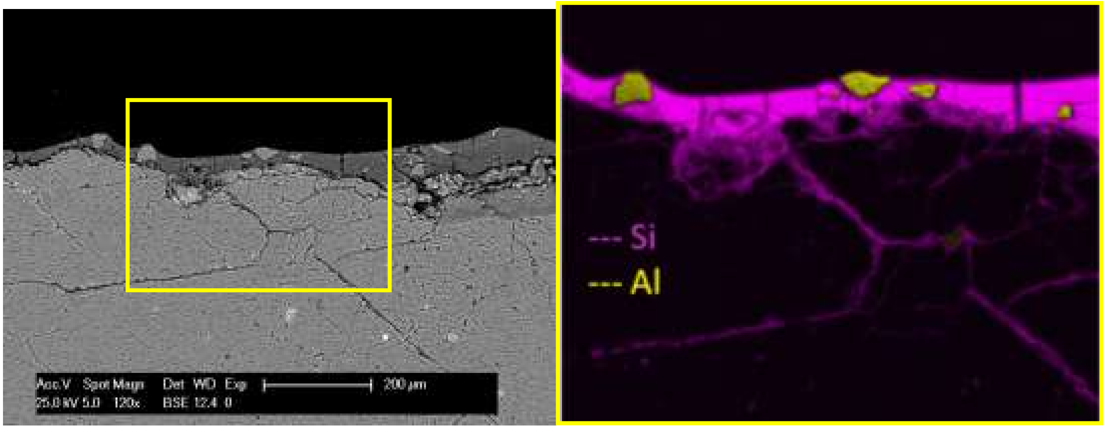

Figure 4.39: *SEM micrograph (on the left) and elementary map (on the right) of a fraction of the fragment sampled*

- FTIR ANALYSIS:

Spectroscopic analysis FTIR by KBr pellets, µATR with Ge crystal on cross-section, and µFTIR of micro-scales sampled from the fragment, confirmed the good state of conservation of the resin and its siloxane nature. In particular, the peak at 2970, 2916 cm^{-1} related to ν_s C-H, those at 1410-1437 and 1323 cm^{-1} respectively linked to ν_s C-H and δ C-H, the peak at 1273 cm^{-1} due to the symmetrical stretching of

Si-CH_3 chemical bond, and finally those at 1034-1043 cm^{-1} and 779-781 cm^{-1} referring respectively to ν_s and δ of Si-O-Si in a siloxane chain, ensured the alkyl-alkoxy-silane formulation of the protective. Moreover, FTIR analysis also allowed detection of the presence of gypsum (3541, 1408, 3246, 1684, 1622, 1124, 675 cm^{-1}) on the reverse of the sample where cleaning of the statue could not remove it.

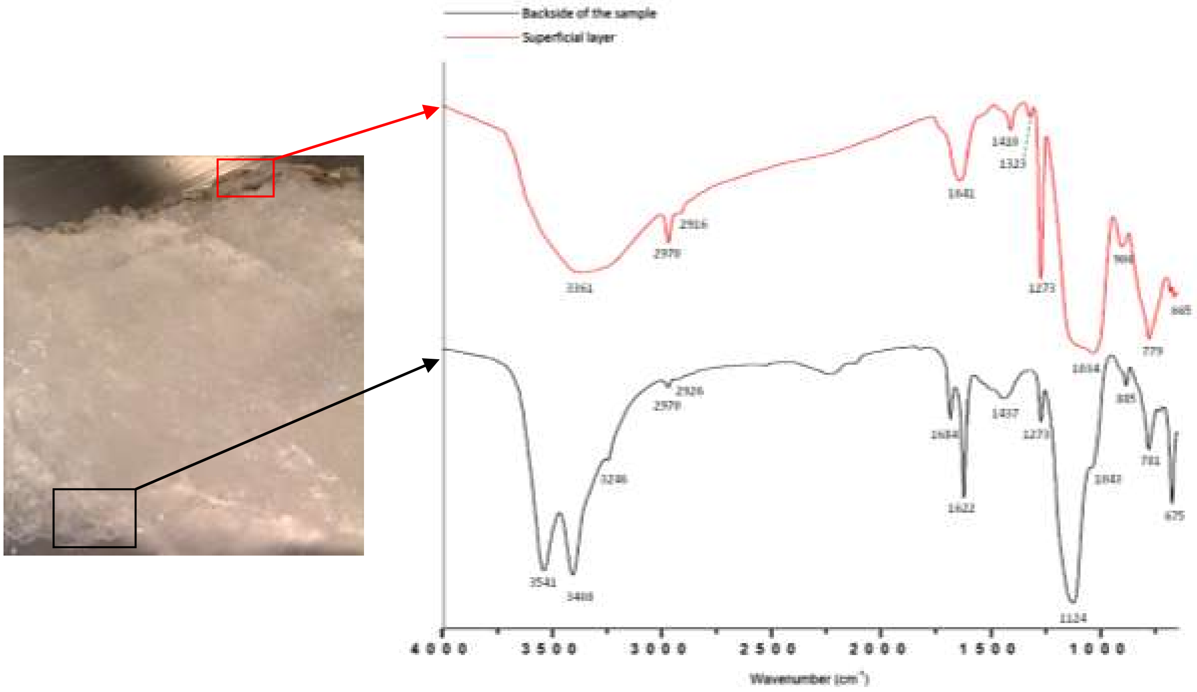

Figure 4.40: *μFTIR analysis of the reverse of the sampled fragment and of the superficial polymeric layer.*

FINAL OBSERVATION:

Macroscopic examinations and the results obtained from analysis of the sampled fragment confirmed the good state of conservation of the artefact and the effectiveness of the resin 40 years after treatment. The resin still protects the stone surface and seems unaltered. However in this case it was not possible to compare the aged resin with a fresh one because of its unavailability on the market.

4.4 References

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Chapter 5

Nano-particle products

5.1 Nano-particles products

During the last 10 years, several research projects carried out within the conservation and restoration field have proposed the use of different products based on nanoparticles scattered in polymeric or inorganic matrix, in order to ensure better performances in the treated inorganic substrates. In fact, it has been verified that nanoparticles, due to their specific physical-chemical characteristics, improve the penetration depth of the treatment, promote hydro-repellency of the treated surfaces, avoid the biological colonization and, consequently, guarantee the conservation of the substrates over time.

However, the use of nano-compounds in the restoration field is still really controversial. Many are the objections concerning their effectiveness: the insufficient amount of nano-particles currently spread in the binder matrix; the dangerous amount of water introduced into the substrate during the treatment; the real no-germicide action carried out by some commercial products based on titanium dioxide; the corrosive effect produced on carbonate rocks by the acidity of the titanium dioxide products.

Nevertheless they are spreading widely, sometimes poorly considering the congruence with the mineral nature of the substrate and its state of conservation, sometimes giving good preservation effects.

During the last decades, there has been a strong impulse to develop innovative building materials that can offer extra value in addition to outstanding mechanical properties and workability.

In this way, the building industry, inspired by nature, has recently shown a great interest in developing easy-to-clean and de-pollution surfaces which can be cleaned simply by rainfall, using nanotechnology [56]. The use of photo-induced catalysis and super-hydrophilicity permits the transfer of self-cleaning and de-pollution properties of the "Lotus effect" [57] to man-made surfaces.

Photocatalysis, that is the acceleration of chemical redox reactions, thanks to the synergy of particular materials (usually semiconductor) and solar light, is one of the most promising tools for the handling of different problems in several areas of applied chemistry, including environmental science.

In fact, it allows the photo-decomposition of both organic and inorganic polluting substances adsorbed or deposited on photoactive surfaces, by a redox reaction induced by solar light [58].

In practice, when a semi-conductor is hit by photons with hν energy higher than its E_g (E_g is the lowest energy that the light must have to give energy to a conductive material), an electron (e^-) is able to move from the valence level to the conduction level, and form an electronic gap, or lacuna (h^+), on the upper borderline of the valence level. The component of the photo-generated couple (e^- and h^+) can respectively reduce and oxidize an absorbed substance on the photo-catalytic surface.

The synergy of photo-induced redox reaction of adsorbed substances and photo-induced super hydrophilicity is the foundation of self-cleaning applications in building and construction materials [59].

Titanium dioxide (TiO_2) nanostructered coatings have been widely investigated for self-cleaning and antipolluting properties [60-61]. Because of its $E_g \approx 3eV$, which corresponds to an activation by radiation in the UV sector, it can be a semi-conductor in presence of water, sun/UV light and an organic matter. Nano-sized TiO_2 crystals acquire new characteristics in their nanometric form based on particle size [62]: transparency, superhydrophilicity [63-64] and photocatalysis [58-65].

Since the early discovery of the self-cleaning properties of titanium dioxides [58], it has been considered to be the most efficient, stable and cheap photocatalytic material available [66]. In fact, the extensive use of TiO_2 is due to its characteristics: relatively inexpensive, safe, chemically stable, high photocatalytic activity compared with other metal oxide photocatalysts, and effective under weak solar irradiation in an outdoor environment.

In general, TiO_2 shows three different crystal structures: anatase, rutile and brookite.

Its photocatalytic efficiency is greatly influenced by its structrure: amorphous titania shows very little photoactivity while this property is much more evident in crystal form, especially for anatase nanocrystals. However, among the interesting properties of anatase nanoparticles, they are characterized by a mean diameter below the wavelength of light and thus they are transparent if applied on a substrate or dispersed in a matrix [59].

When a self-cleaning product needs to be applied on the external surface of existing buildings or on previously formed materials, such as stone, tiles or plasters, there are serious restrictions to the synthesis process, because the product is applied, in situ under outdoor conditions [67-68]. In the literature there are only a few references to TiO_2-based products applied to buildings. Specifically, TiO_2 nanoparticles have been previously applied to the external surface of building materials by dispersion in water [69], but the results obtained for these products on stone are not wholly satisfactory because of the cracked coating formed on the surface and the easy removal from the treated stone [70]. Nowadays, most commercial products applied for the protection of stonework and other building materials contain alkoxysilane monomers or oligomers [71]. As explained in paragraph 4.1 of this work, these materials have the tendency to crack during their drying process and it is obvious that a cracked substance cannot protect the treated stone very effectively. An alternative approach for producing a long-term coating is to incorporate TiO_2 nanoparticles in a starting sol containing silica oligomers and n-octylamine [59] or preparing a starting sol by mixing Ti and Si alkoxides to produce a self-cleaning coating on stone [72].

Different TiO_2 nanostructured coatings on stone and their efficiency as self-cleaning treatments were investigated [73] but in many cases the long-term behavior of the system was not investigated [74-75]. According to the literature, the photocatalytic efficiency of TiO_2 varies over time and it is related to the weathering conditions undergone, the duration of ageing and mutual interactions between coating and substrate [76-77].

5.2 Laboratory test

This study refers to a commercial product named PF3, which is a water dispersion of photo-catalytic titanium dioxide modified with an organic derivative of silicon.

The product was applied on Carrara marble and Vicenza white limestone by brushing, three coats, until complete imbibition of the substrate.

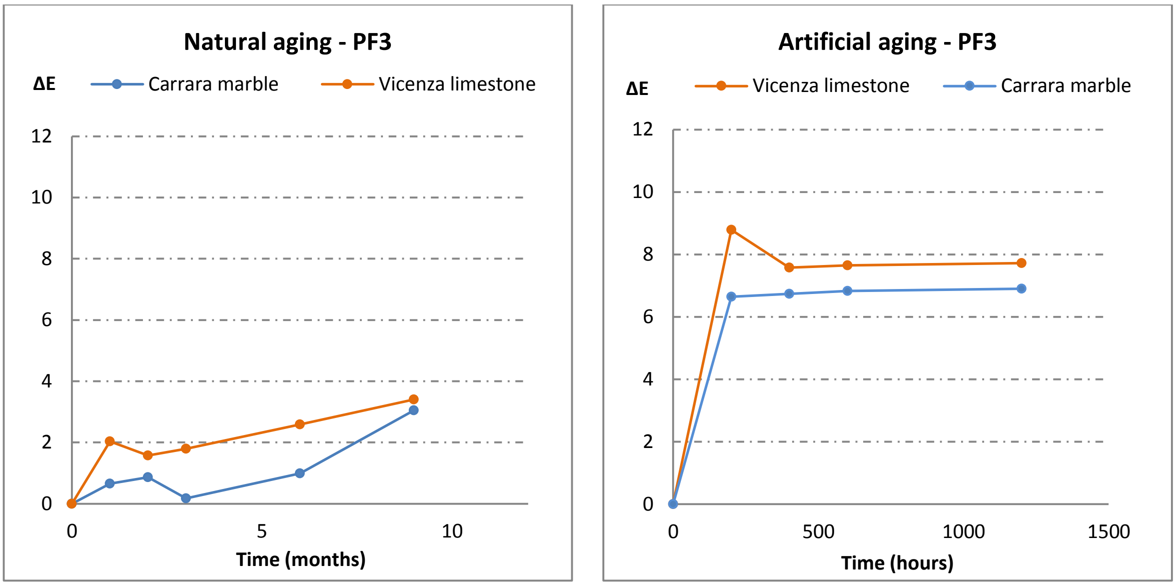
After the application of the consolidants, the samples were maintained at room temperature until cured polymer was achieved (15 days).

Observing the specimens microscopically after the treatment, it was observed in both Carrara marble and Vicenza limestone, with the naked eye, that there was a chromatic alteration of the treated surfaces and a yellowing effect (fig. 5.1 and 5.2). Initially, the treatment covered homogeneously the stone substrate in a bright film but, during the ageing process it lost its brightness and it remained only in the inter and intra grain spaces as light-yellow crystals.

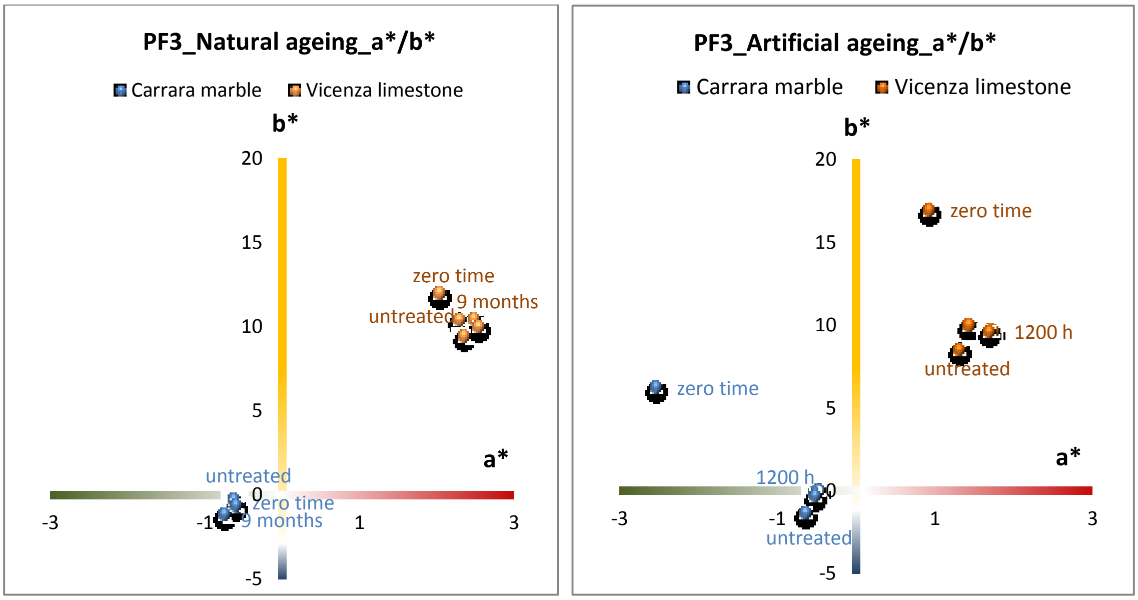
Figure 5.1: *superficial aspect of untreated Carrara marble specimen, treated with PF3 at zero time and after 12 months of outdoor exposure. Long side images: 6.78 mm.*

Figure 5.2: *superficial aspect of untreated Vicenza limestone specimen, treated with PF3 at zero time and after 12 months of outdoor exposure. Long side images: 6.78 mm.*

The chromatic alteration suffered by the stone due to the application of the treatment was confirmed by colour test. As it is possible to observe in graph 5.1, from zero time, the specimens exposed to outdoor conditions did not suffer chromatic variation noticeable to the naked-eye. The colour variation values increased gradually during time, probably due to the loss of film brightness and compactness. The treated specimens exposed to UV radiation changed significantly in the value of colour change during the first 200 hours and then it remained stable. The graph 5.2, especially in the case of artificial ageing, shows well the yellowing of the surfaces due to the application of the protective product. However the colour values tend to come back to the untreated values.



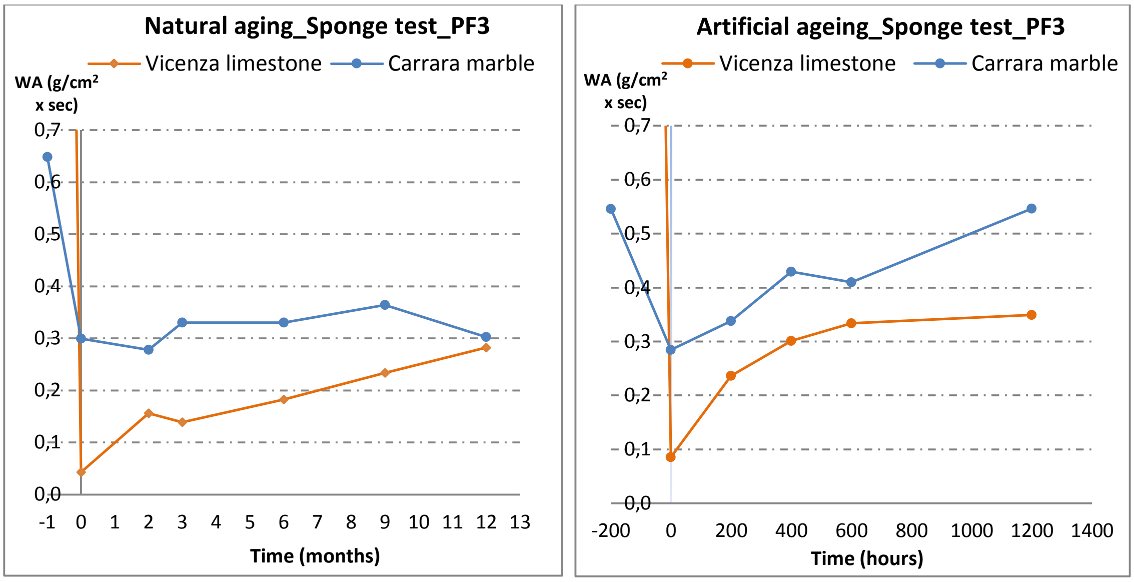
Graph 5.1: *Trend of colour change of surfaces treated with PF3during outdoor exposure (right) and UV radiation (left).*



Graph 5.2: *Chroma and tone variation calculated by a* and b* experimental value*

The organic derivative of silicon in the formulation of PF3 guaranteed a water-repellent effect. During the outdoor exposure, as is shown in graph 5.3, Carrara marble maintained through time the hydrophobicity conferred by the treatment, whereas Vicenza limestone gradually lost its initial value becoming more hydrophilic.

Observing the water absorption variation during UV radiation, both Carrara marble and Vicenza limestone increased their superficial hydrophilicity. In particular Carrara marble came back to its untreated value.



Graph 5.3: *Water absorption variation during outdoor exposure (left) and UV radiation (right).*

PF3 commercial product proved to have a high stability with respect to UV oxidation, since no macroscopic differences were observed after UV ageing of the xerogel polymerized on a slide. Xerogels spectra were recorded at various time intervals during the ageing of resins subjected to UV radiation. The time intervals were of 0, 22, 72, 216, 288 and 1154 h (fig. 5.3).

The only modification was the progressive disappearing of the peak at 1600 cm^{-1}, which could be related to the carbonyl groups in ketones. However, because of the lack of information about the chemical structure of the product, it is not permitted to make any supposition about the chemical decay of the polymer.

In table 5.1 are summarized FTIR assignments of the main peaks of PF3.

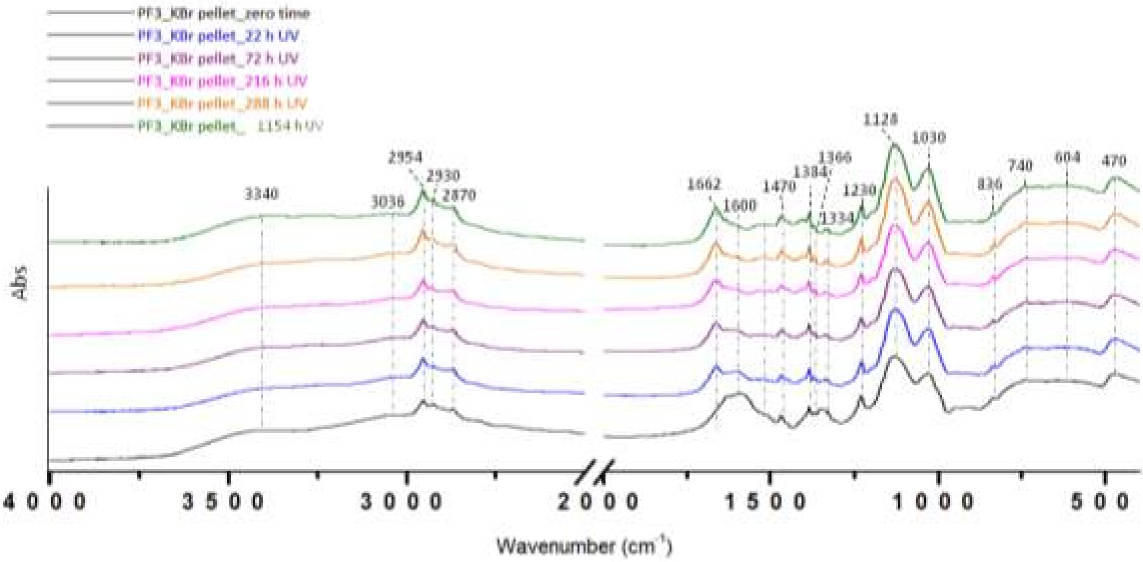


Figure 5.3: *Comparison between PF3 gel at different time intervals of UV-oxidation.*

Monitoring of the polymer applied on stone surface and exposed to outdoor condition for 12 months shows clearly the chemical instability of the resin. In fact, studying the spectra in figure 5.4 and 5.5, the peaks related to the siloxane component at about 1100 and 1020 cm^{-1}, and indicative for the polymer, disappeared from the sixth month in the case of Carrara marble and in the twelveth month in the case of Vicenza limestone. Anyway, in both cases, the peaks at 1580-1600 cm^{-1} disappeared from zero time and the third month. Consequently, it is possible to suppose that this peak is related to the polymerization of the product and not to the degradation of the resin.

Wavenumber (cm^{-1})	Functional groups	Assignments
3340	ν O-H	Hydroxyl groups
3036		
2954, 2930, 2870	ν C-H	Aliphatic bonds in EMA and MA
1662	ν C=O	Carbonyl groups in EMA and MA
1595-1600	ν C=O	Carbonyl groups in ketones
1470	ν C-H, ν C-C	Aliphatic bonds
1384	δs C-H	Methyl groups
1334	δs C-H	
1230	ν C-O	
1128	ρ C-O	
1105-1090	ν_s Si-O-Si	Siloxane chain in linear structure
1030	ν_s Si-O-Si	Siloxane chain in cyclic structure
955	Ti-O, ν_s Si-O-Si	
740	ν C-C	

Table 5.1: *FTIR assignments of the main peaks observed for PF3 commercial product, according to the literature [19].*

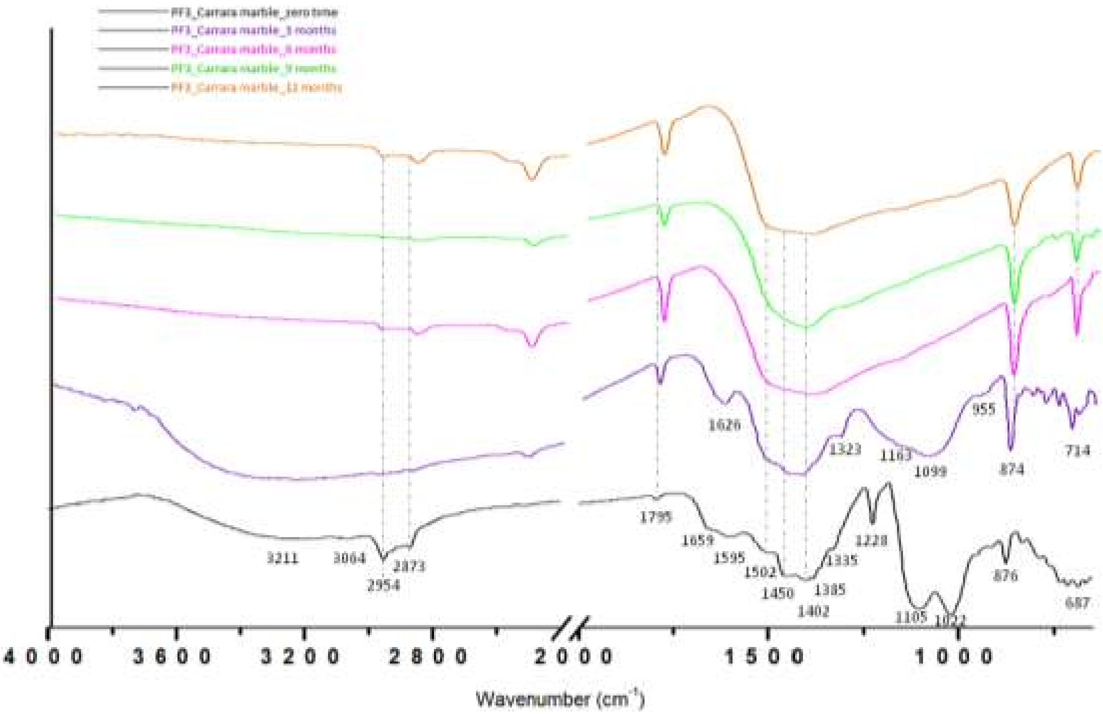


Figure 5.4: *µFTIR of PF3 applied toCarrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

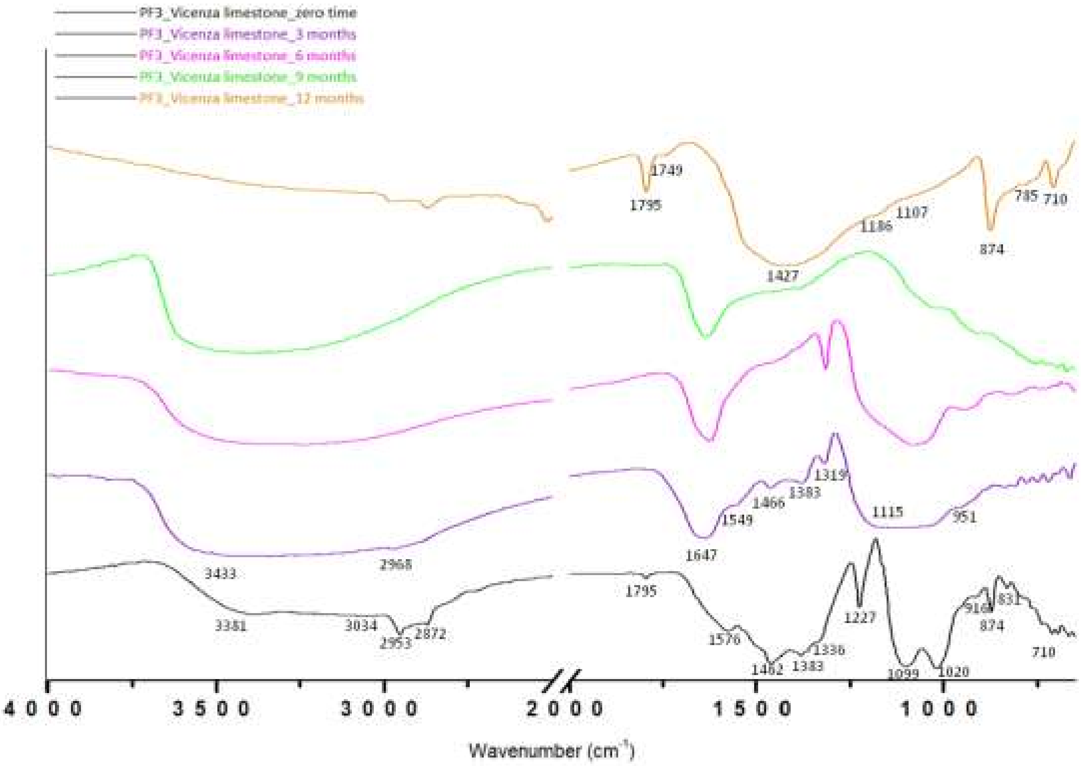


Figure 5.5: *µFTIR of PF3 applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was carried out at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

UV ageing of polymer applied to a stone substrate shows the same behaviour in Carrara marble and Vicenza limestone. The spectra after 1200 hours of UV radiations are perfectly comparable. Also in this case was observed the disappearing of the peak at 1590-1600 cm^{-1} but also the presence of the peaks at 1078-1080 cm^{-1} and 960 cm^{-1}, which can explain the newly created Si-O-Si bonds in a siloxane chain. Moreover, the peak at 1227-1228 cm^{-1} related to the symmetrical stretching of C-O disappeared after the first 200 hours of UV exposure, as well as from zero time and the third months of outdoor exposure. Consequently, it is possible to connect this transformation to the polymerization reaction as well.

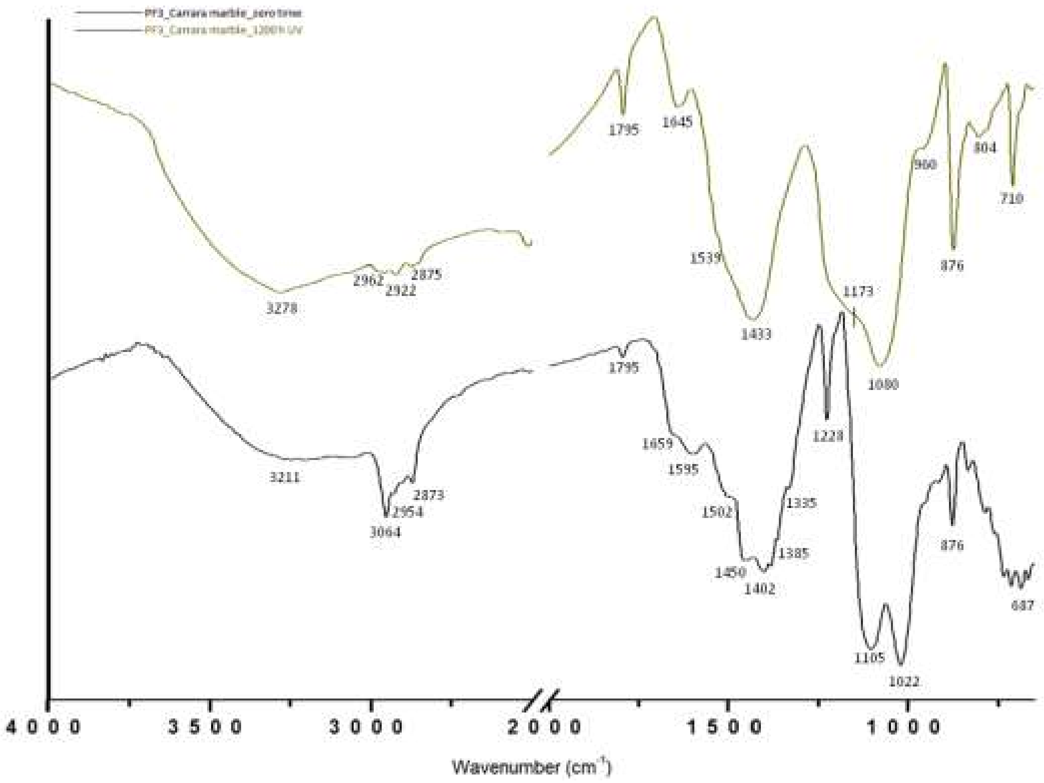


Figure 5.6: *µFTIR of PF3 applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was carried out at zero time (black line), and after 1200 h of exposure (dark yellow line).*

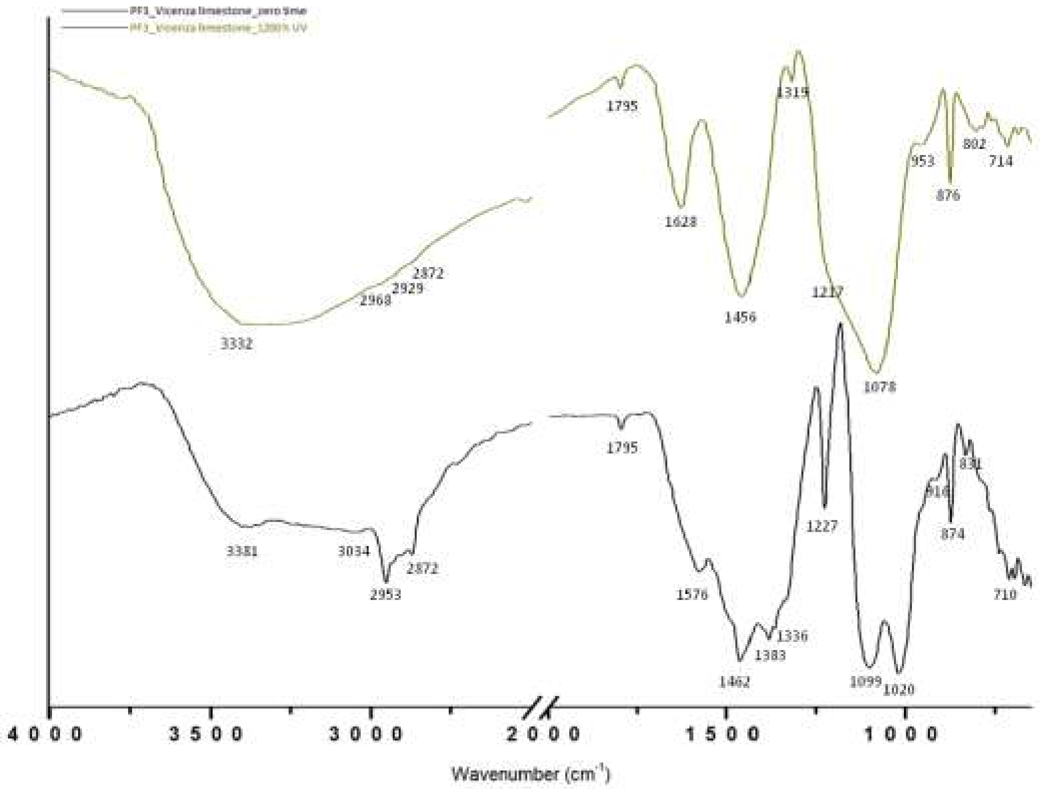


Figure 5.7: *µFTIR of PF3 applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was carried out at zero time (black line), and after 1200 h of exposure (dark yellow line).*

5.4 References

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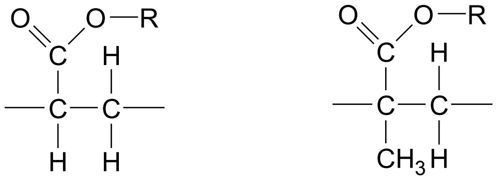
Chapter 6

Acrylic resins

6.1 Acrylic resins

In conservation, the majority of acrylic resins in use are thermoplastic compounds based on two families of monomers: the acrylates, derived from acrylic acid, and the methacrylates derived from methacrylic acid. Other monomer groups used are acrylonitrile and cyanoacrylates or, occasionally, styrene [78].



Poly-alkyl-acrylate Poly-alkyl-methacrylate

Figure 6.1: *Monomer units of acrylic polymers. The alkyl group (-R) affects the characteristics of the polymer.*

In copolymers of acrylates with methacrylates, gel formation, by a radical mechanism, depends on the proportion of the monomer groups and the temperature of exposure.

Depending on this ratio, it is possible to construct a resin with the desired chemical and physical characteristics, such as the balance of scissoring and cross-linking behaviour.

The features of acrylic resins change due to the monomer used, as well as their plasticity and the molecular weight of the polymer. In general, commercial acrylic products are soluble in opportune organic solvents and, increasing the oxygen in the polymer, increases the polarity of the solvents suitable for dissolution. These products have good resistance to ageing, particularly to light and chemical agents. They are not structurally adhesive, even though they have good polarity.

Acrylic resins are appreciated for their exceptional clarity and optical properties. They have excellent transparency, translucency, surface gloss, weather resistance, high surface hardness and superior design adaptability.

The most used commercial acrylic product in conservation is Acryloid or Paraloid B-72 (Acryloid is the commercial name used in USA to recognize acrylic polymers by Rohm & Haas). It has been reported as a poly-methyl-methacrylate/ethyl-metacrylate polymer (P-MMA/EA) on the authority of Rohm & Haas. Its chemical structure is shown in figure 6.2. Paraloid B-72, in its formulation, can also contain various matting agents and solvents, whose major components are usually toluene or xylene.

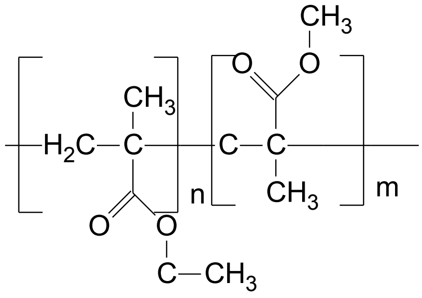


Figure 6.2: *Chemical structure of Paraloid B-72*

Initially, in 1947, Paraloid B-72 was used as a silver lacquer and then also for textile consolidation. Its chemical formulation and properties prompted further uses as hot melt adhesive for paper, consolidant for matt pigments, lacquer work and wood, coating for iron and stone conservation, although studies showed low penetration depth when applied as a stone consolidant [79]. For this reason at high concentration (10%) it is considered as a protective of stone surfaces, and at low concentration (3-5%) it is seen as a consolidant.

Paraloid B-72 is probably the most tested and accepted commercial product for conservation work. It has been also used in combined formulations in order to improve its characteristics. For example, Raccanello produced the ARD E0057 and ARD E0023 commercial products, respectively an acrylic/silane consolidant and an acrylic/wax protective.

Moreover, Paraloid B-72 has been an ingredient, with a poly-methyl-siloxane, of Bologna Cocktail, a consolidant mixture formulated by O. Nonfarmale in the 1970s [80].

A similar commercial product, Paraloid B-67, a poly-isobuthyl-methacrylate polymer (PiBMA), has been also used in conservation, but it is soluble in less polar solvents than B-72 and rapidly becomes insoluble when applied to marble, and it also decays faster [81].

Acrylic 33, ex Primal AC-33, an acrylic dispersion quite similar to Paraloid B-72 has proved more successful for conservation treatments. Acrylic dispersions slowly increased in popularity during the 1950’s due to the film’s greater resistance to yellowing and its higher solubility, especially in case of Acrylic 33.

In general, acrylic polymers and, in particular, Paraloid B-72 have been used in restoration since the 1960s. In Venice, for instance, Paraloid B-72 was used in 1968 for the consolidation of the portal of Venetian Arsenal and in 1972 for the basement of the Bartolomeo Colleoni statue in SS. Giovanni e Paolo square [82]. In Rome, it was used in 1978 for the restoration of “Anime Oranti” statues in S. Maria dell’Anima Church, and in 1980 for the marble architrave in “Tempio di Romolo” in Foro Romano and some Trajan reliefs of the Arco di Costantino. In 1980 it was also used for the conservation of Maitani’s low relief on the main façade of Duomo di Orvieto [83].

6.2 Laboratory test

Paraloid B-72 and Acrylic 33 were tested in this study.

The products were purchased from C.T.S. (Italy) and used without further purification.

The films were obtained by brushing a solution of the polymers (10% and 4% in acetone for Paraloid B-72 and in the original solution of Acrylic 33) on Carrara marble and Vicenza limestone specimens. The impregnations were carried out until the substrate no longer accepted liquid. Three samples were prepared for each product and after the applications, samples were maintained at room temperature until a cured polymer was achieved (15 days).

In the case of Paraloid B-72 a decision was made to expose the specimens, treated with the product at a concentration of 10%, to outdoor conditions, while those with a concentration of 4% were subjected to artificial ageing and biological tests.

With regard to the treated samples, it was considered that the application of Paraloid B-72 at a 10% concentration, completely changed the original aspect of both marble and limestone supports. A thick, homogeneous, bright and transparent film completely covered the surface (fig.6.3) changing the natural morphology.

Figure 6.3: *superficial aspect of untreated (on the left) and treated (Paraloid B72) specimen (on the right) of Carrara marble and Vicenza white limestone. Long side images: 6.78 mm.*

Using SEM, after 12 months of outdoor exposure, when the samples were cut, it was possible to measure the thickness of the cured films in detail, on the surface (200-250 µm) and its penetration in both Carrara marble and Vicenza white limestone. In the case of Vicenza limestone, Paraloid B-72 penetrated the stone to an approximate depth of 400 µm (fig. 6.4).

SEM studies also allowed the observation of the presence of microorganisms, in particular fungi, on the film and their penetration of the sacrificial layer.

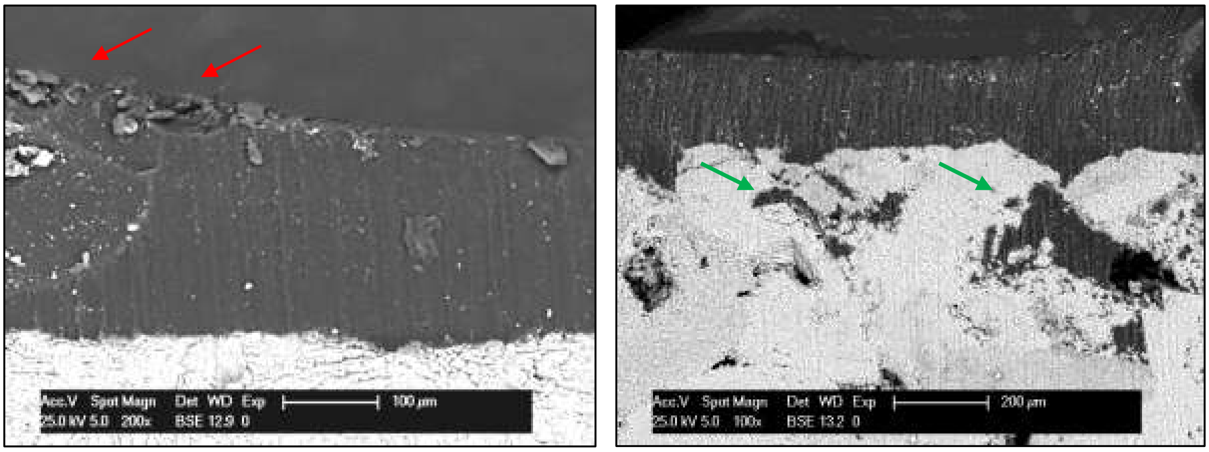


Figure 6.4: *SEM micrography of Paraloid B-72 (10%) superficial layer. The cross-section of both Carrara marble (on the left) and Vicenza limestone (on the right)samples, also show the presence of fungi (red arrows) and the penetration of the resin in the support (green arrows).*

Microscopic observations of the superficial aspect of the cured film after 12 months of outdoor exposure showed no significant changes in film morphology. Neither cracking nor other optical variations were detected on the polymeric films. Biological microorganisms, in particular dark fungi, were observed on the surfaces after the ninth month of exposure and a slow growth on the surfaces was studied. The morphology of the coatings was not greatly altered by accelerated ageing.

Acrylic 33 cured film was really bright, adhesive, homogeneous and transparent, and its application partially changed the superficial aspect of the specimens (fig. 6.5).Studying the cross-section of the samples by SEM after complete natural ageing, it was possible to observe the superficial layer of the film with a thickness of 20 μm in the case of Carrara marble, and less than 20 μm in the case of Vicenza limestone. It was not possible to measure the latter in detail due to the morphology of the sample.

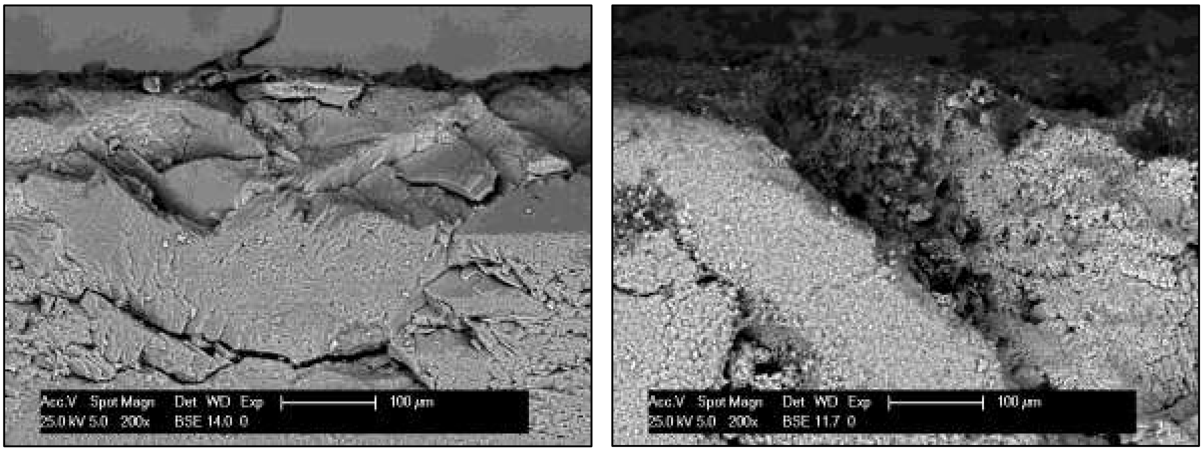


Figure 6.5: SEM micrography of Acryl 33 cured film. The cross-section of both Carrara marble (on the left) and Vicenza limestone (on the right) show the presence of a polymeric superficial layer and partial penetration of the product in the limestone.

During outdoor exposure of the samples, it was observed that the polymeric film rapidly became dirty and many particles remained upon it. No biological growth had developed on the treated surfaces during the exposition time. UV radiation in the Solar box did not influenced the morphological aspect of the cured film.

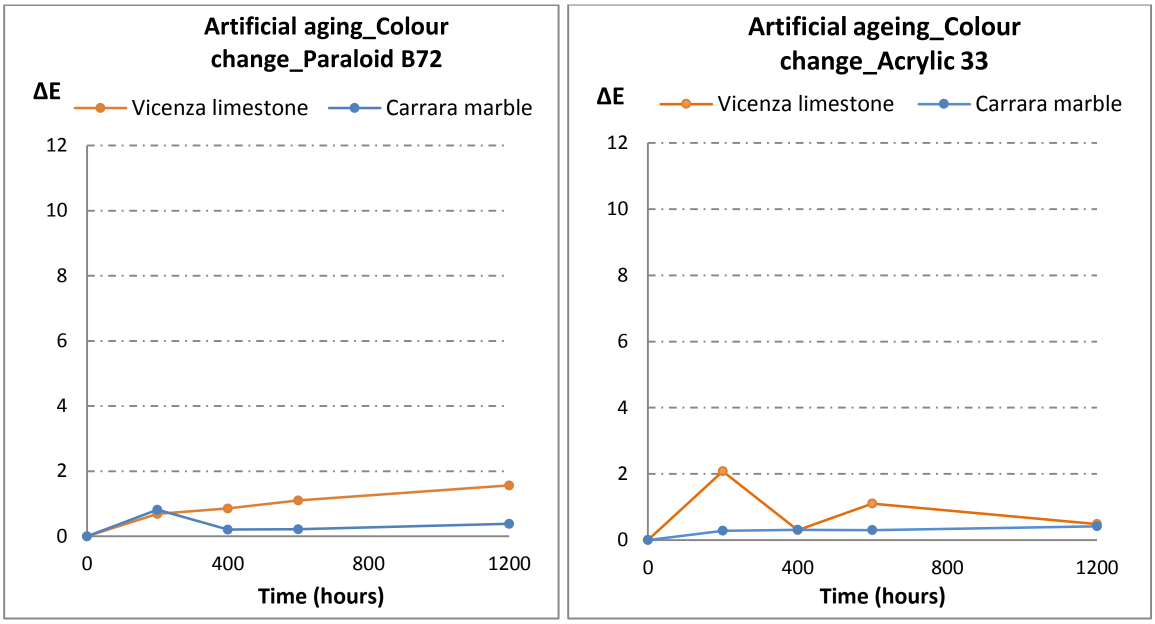
Figure 6.6: *Superficial aspect of untreated (left) and treated (Acrylic 33) specimens (right) of Carrara marble and Vicenza white limestone. Long side images: 6.78 mm.*

As colour changes with ΔE less than 5 are conventionally not visible to the naked eye [84], it is possible to assert that Paraloid B-72 gave higher colour variation than Acrylic 33 and that these variation are visually detectable.

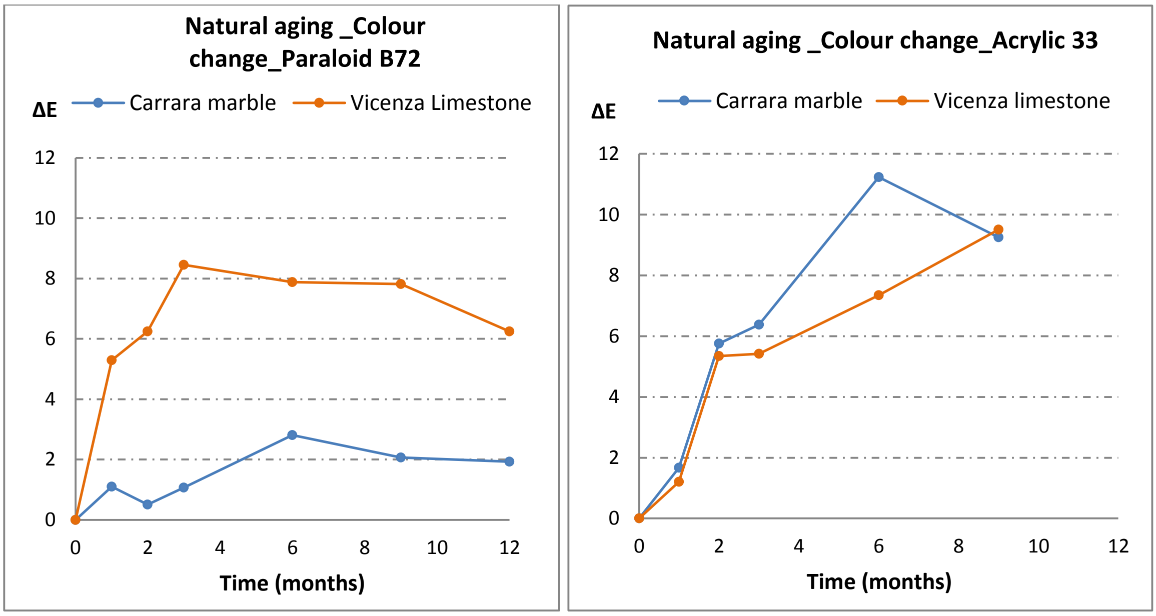
Chromatic changes during long-time exposure to UV rays are negligible for both coatings, undetectable to the naked eye (graph 6.1). Treated surfaces exposed to outdoor conditions showed an interesting chromatic variation (graph 6.2). In particular, focusing on specimens treated by Paraloid B-72, it was possible to observe a significant increase of yellow tone for Vicenza limestone, more than observed on Carrara marble, as shown in graph 6.3.

Acrylic 33 showed the same yellowing effect (graph 6.3) and the total chromatic variation is higher than that caused by the ageing of Paraloid B-72 (graph 6.2).

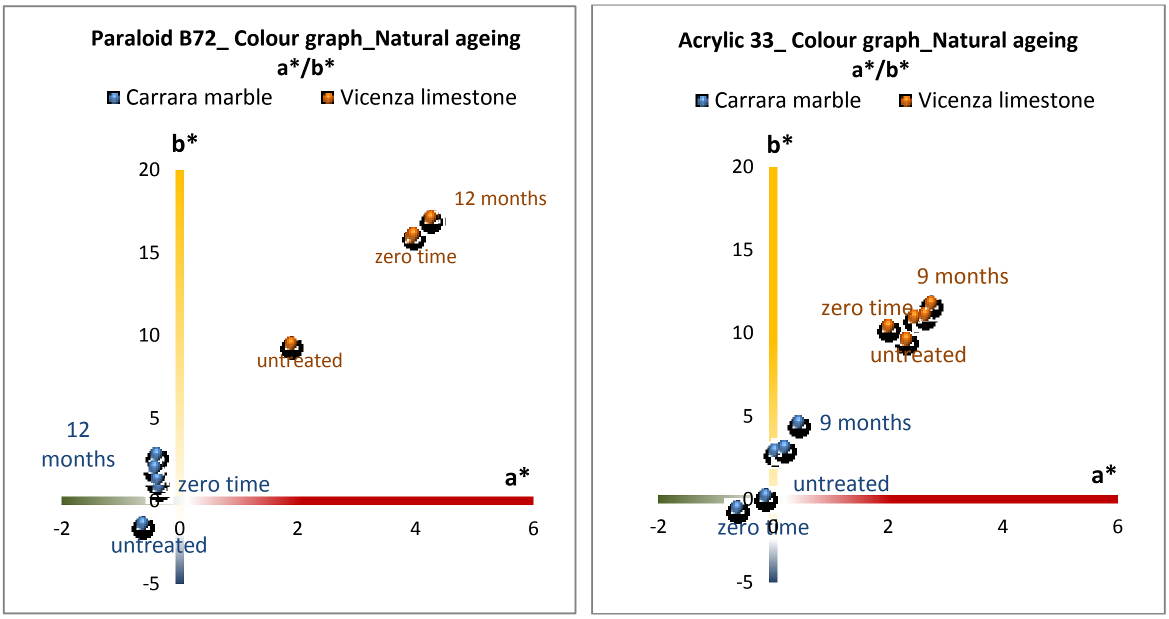
So, the values of colour variations do not seem to depend on UV radiation but probably on oxidation of the polymeric film.



Graph 6.1: *Trend of colour change of surfaces treated with Paraloid B-72 (left) and Acrylic 33 (right) during exposure to UV radiation.*



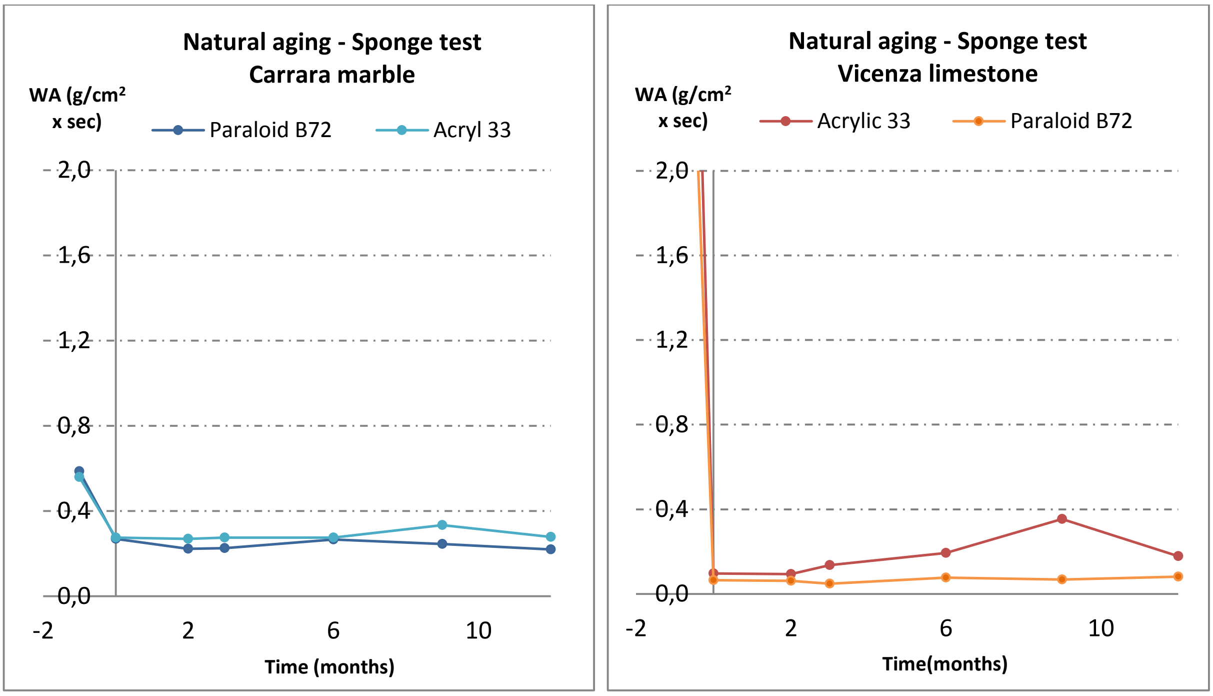
Graph 6.2: *Trend of colour change of surfaces treated with Paraloid B-72 (left) and Acrylic 33 (right) during exposure to outdoor conditions.*



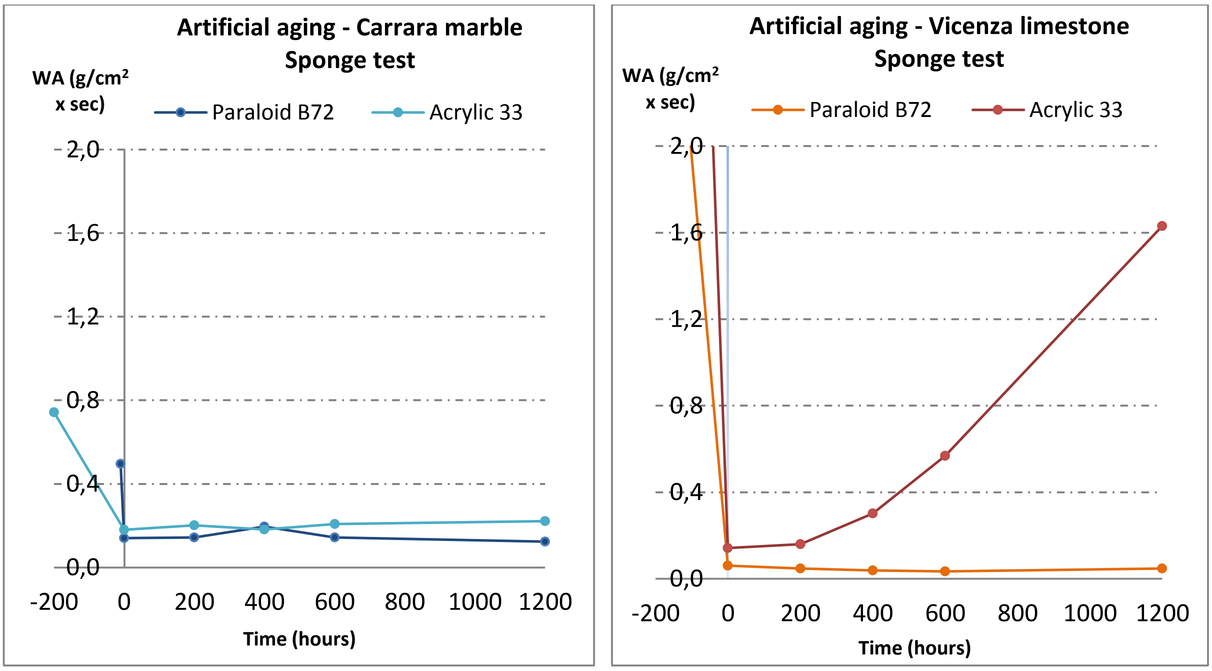
Graph 6.3: *Chroma and tone variation calculated by a* and b* experimental value*

The ageing processes did not seem to significantly alter the hydrophobicity of the treated surfaces during the exposure time. Paraloid B-72 and Acrylic 33 both impart a water-repellent effect, comparable each other, due to the presence of methyl groups (strongly apolar) in their chemical structures. Testing the variations of the hydrophobic feature of the treated surfaces during the exposure to the environment, a general stable trend was observed for Acrylic 33 and Paraloid B-72 applied to the specimens and exposed to outdoor conditions and to UV rays (graph 6.4). A substantial increase in the hydrophilyc feature was observed in the case of Acrylic 33 applied to Vicenza limestone and exposed to UV radiation.

Natural ageing did not influence water absorption and the trend of their values was not very different in comparison with zero time.UV rays influenced hydrophobicity only in the case of Acryl 33 applied to Vicenza limestone, in which a substantial increase in water absorption was observed. Probably this behaviour could be related to a modification of its chemical structure.



Graph 6.4: *Water absorption variation during outdoor exposure*



Graph 6.5: *Water absorption variation during exposure to UV radiations*

Studying the relevant FTIR spectra collected, no differences were observed between Paraloid B-72 and Acrylic 33. They were analysed in sol and gel phase after polymerization on a slide. The characteristic peaks of acrylic resins have been shown in table 6.1.

Wavenumber (cm^{-1})	*Functional groups*	*Assignments*
3626, 3552, 3439	*v O-H*	*Hydroxyl groups*
2983, 2953	*v C-H*	*Aliphatic bonds in EMA and MA*
1720-1730	*v C=O*	*Carbonyl groups in EMA and MA*
1473	*δas α-CH_3*	*EMA*
1448	*δas CH_3*	*COOR in EMA*
1385	*δs CH_3*	*COOR in EMA*
1267	*v C=O*	*MA*
1236	*v C=O*	*MA*
1167	*vas C-C(=O)-O*	*MA*
1146	*vas C-C(=O)-O*	*EMA*
1026	*v O-C-C*	

Table 6.1: *FTIR assignments of the main peaks observed for examined acrylic resins*

No chemical differences were observed from the interaction between the resins and the respective Carrara marble or Vicenza limestone substrates.

Paraloid B-72 applied to Carrara marble and Vicenza white limestone and exposed for 12 months to outdoor conditions showed good chemical stability. During ageing, no appearance of new bands or disappearance of old ones were observed in any spectra. They showed only a slight decrease and very limited broadening of the carbonyl peak. The shifting towards higher value of wavenumber of the peak related to the carbonyl group from 1722 to 1732 cm^{-1} confirmed a cross-linked structure (fig. 6.7). However, the spectra of Paraloid B-72 exposed to UV radiation, especially on Vicenza limestone, showed some other interesting modifications regarding the absorption band assigned to the C=O stretching (1720-1730 cm^{-1}). Increasing the irradiation hours, this band enlarges progressively; a shoulder at higher frequency (1788 cm^{-1}) and a new band at lower frequency value (≈1649-1624 cm^{-1}) can be observed (fig. 6.10).

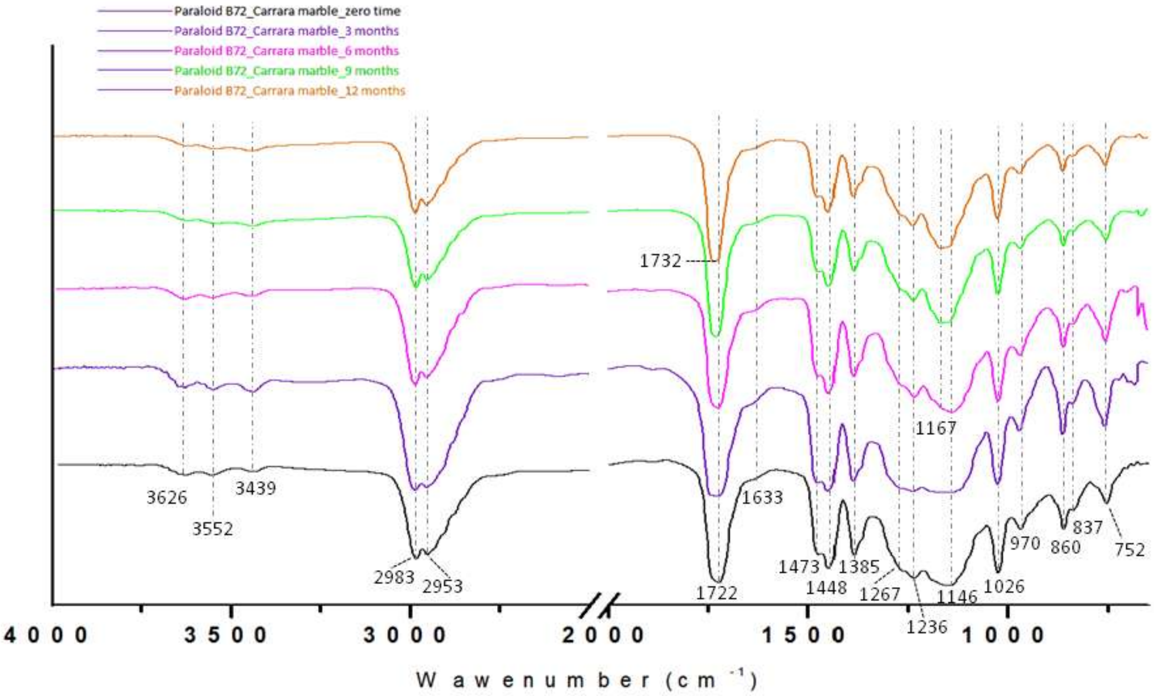


Figure 6.7: *µFTIR of Paraloid B-72, applied to Carrara marble and exposed to outdoor conditions. The monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

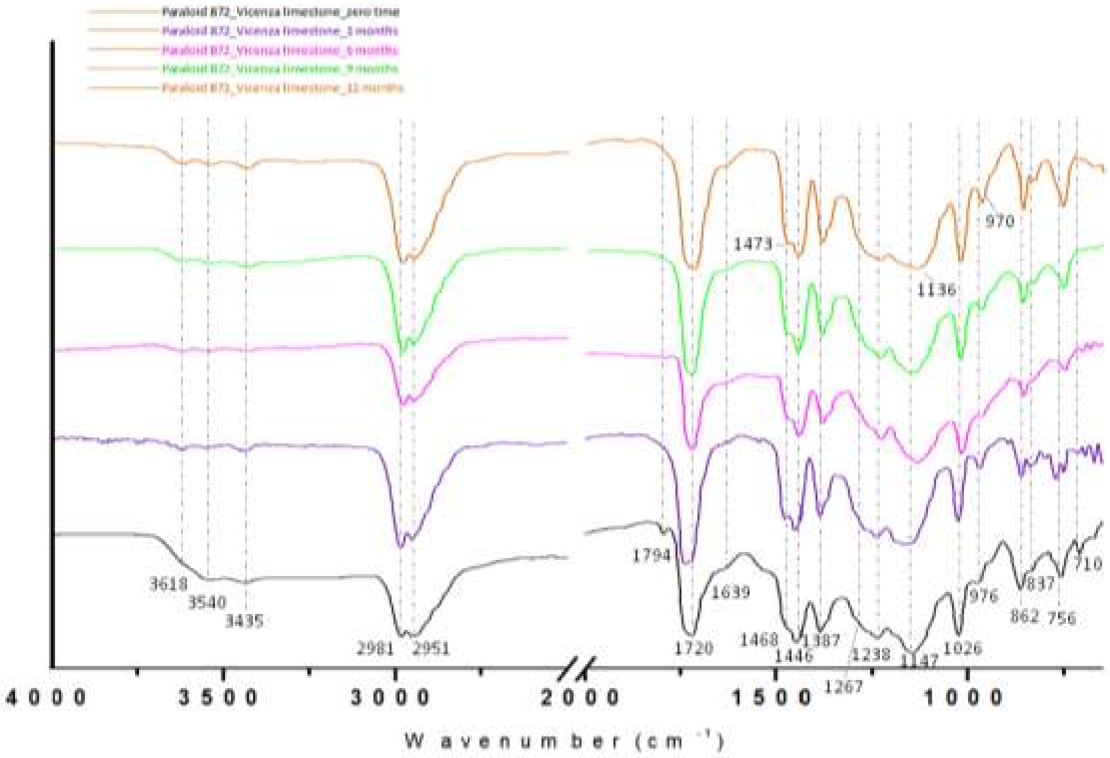


Figure 6.8: *µFTIR of Paraloid B-72, applied to Vicenza limestone and exposed to outdoor conditions. The monitoring was carried out at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

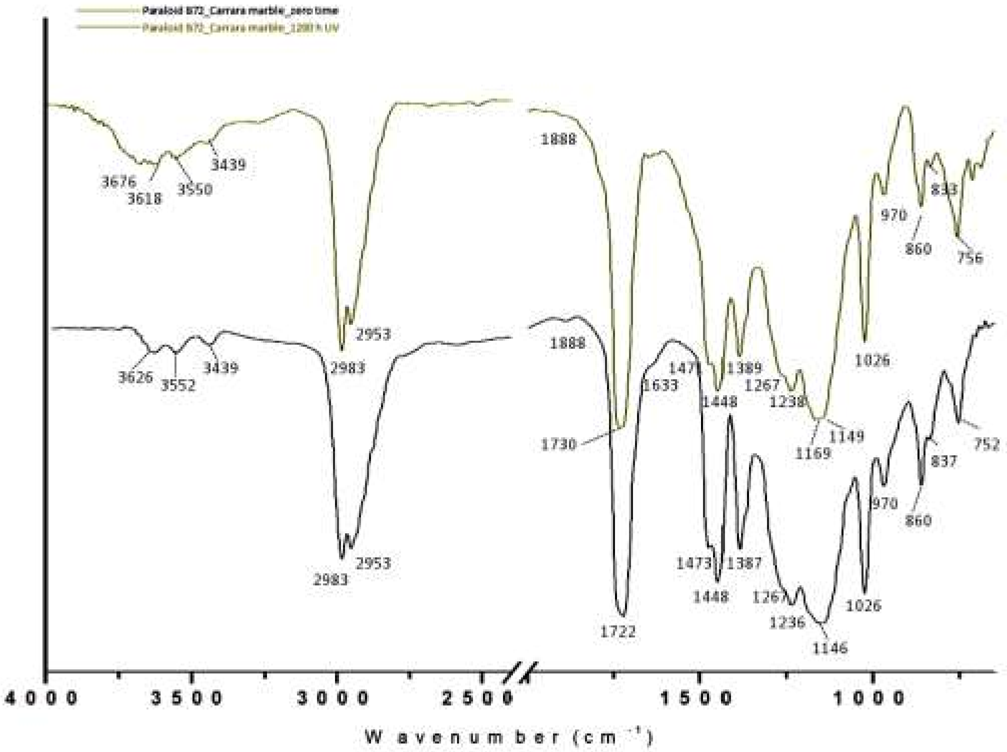


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Figure 6.9: *µFTIR of Paraloid B-72, applied to Carrara marble and exposed to UV rays for 1200 hours. The monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

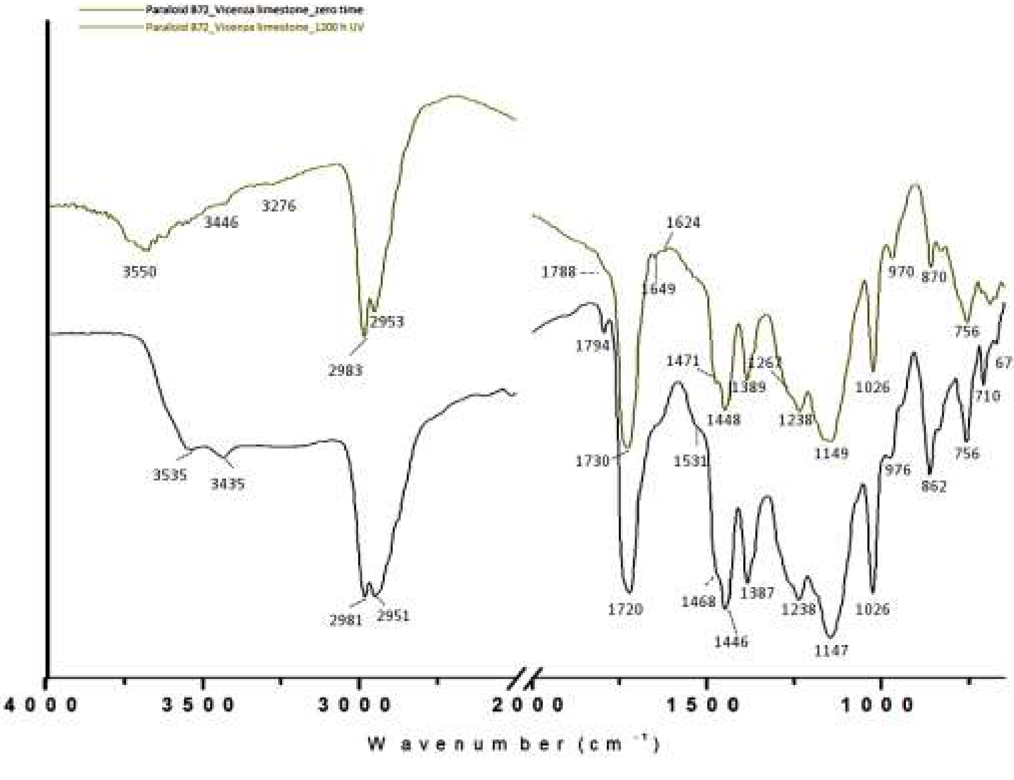
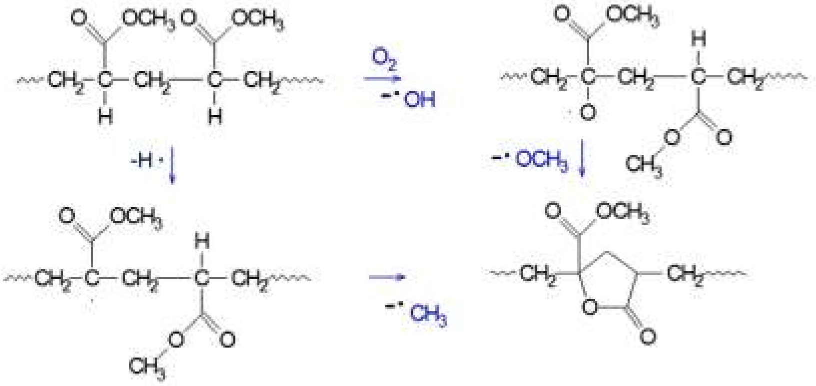


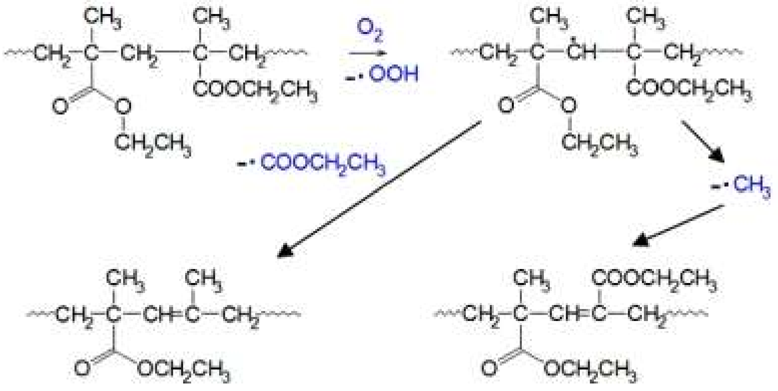
Figure 6.10: *µFTIR of Paraloid B-72, applied to Vicenza limestone and exposed to UV rays for 1200 hours. The monitoring was carried out at zero time (black line), and after 1200 h of exposure (dark yellow line).*

These two new bonds are in agreement with the theory of the degradation mechanism of acrylic resins reported in the literature [85, 79]. In the case of artificial solar light irradiation, the onset of degradation seems to be related to chromophores groups, while oxidation itself is favoured by the presence of labile hydrogen atoms located on the tertiary carbon of acrylic units, or eventually of ester side groups, which may be easily extracted by radicals present in the system [86]. In particular, the shoulder at 1780 cm^{-1} may be attributed to a γ-lactone. The reaction involved has already been reported by various authors [87, 88, 89]. During photo-oxidative ageing, the addition of O_2 to the radicals, formed by the extraction of hydrogen bonded to the tertiary carbons in the methacrylate, or oxidation in the same position, can easily form cyclic esters, as depicted in Scheme 6.1.



Scheme 6.1: gamma-lactone

The band at 1645 cm^{-1} is characteristic of a C=C double bond. In the photodegradation of acrylic and methacrylic polymers terminal carbon-carbon unsaturations are produced as a consequence of chain scission. The concentration of unsaturated molecules increases as the fragmentation of the polymer chains increases, with a likely chemical path suggested in Scheme 6.2 [90].



Scheme 6.2: *Fragmentation of the polymer chains*

Acrilyc 33 seems more sensitive to photo-oxidation than Paraloid B-72. When comparing the spectra of the product exposed to outdoor conditions, it is possible to observe the presence of new bonds at 1780 and 1640 cm^{-1} after 3 months from the beginning of the exposition (fig. 6.11-12). Moreover, from the spectra collected from treated samples exposed to UV radiations, it seems that the polymeric film becomes thinner during the ageing process. It is possible to detect a gradual decreasing of the acrylic bonds and an increase of those related to calcium carbonate (1795, 1430, 870 and 712 cm^{-1}). The product applied to the limestone surface seems more stable than Carrara marble, perhaps due to the greater amount of resin penetrated in the porous stone.

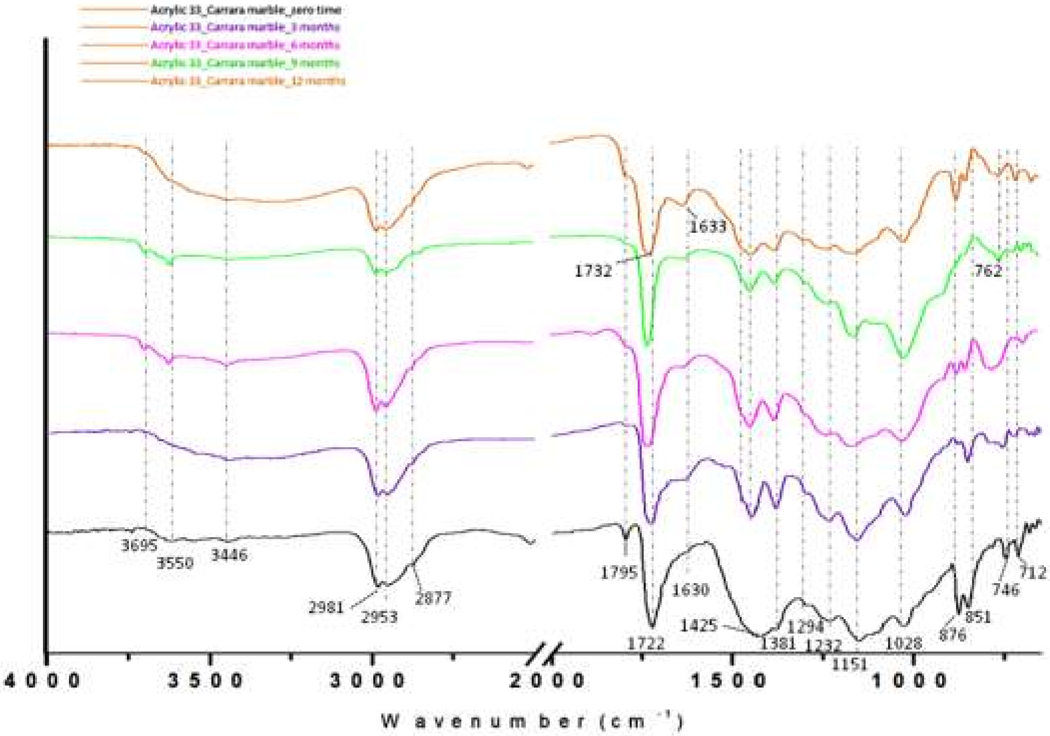


Figure 6.11: *µFTIR of Paraloid B-72, applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

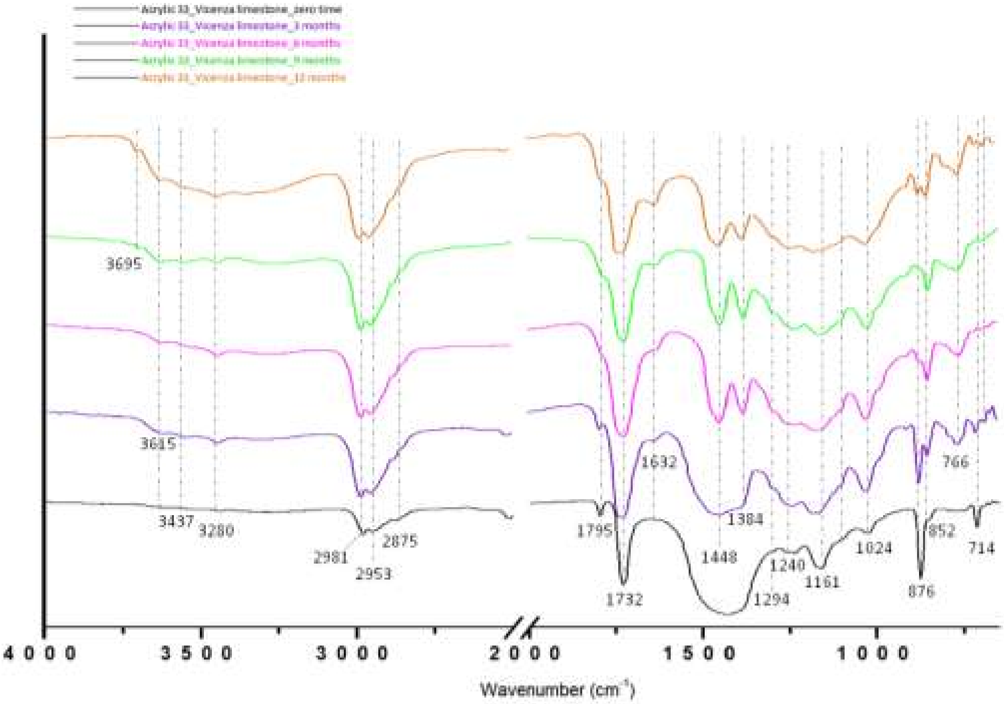


Figure 6.12: *µFTIR of Paraloid B-72, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was carried out at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

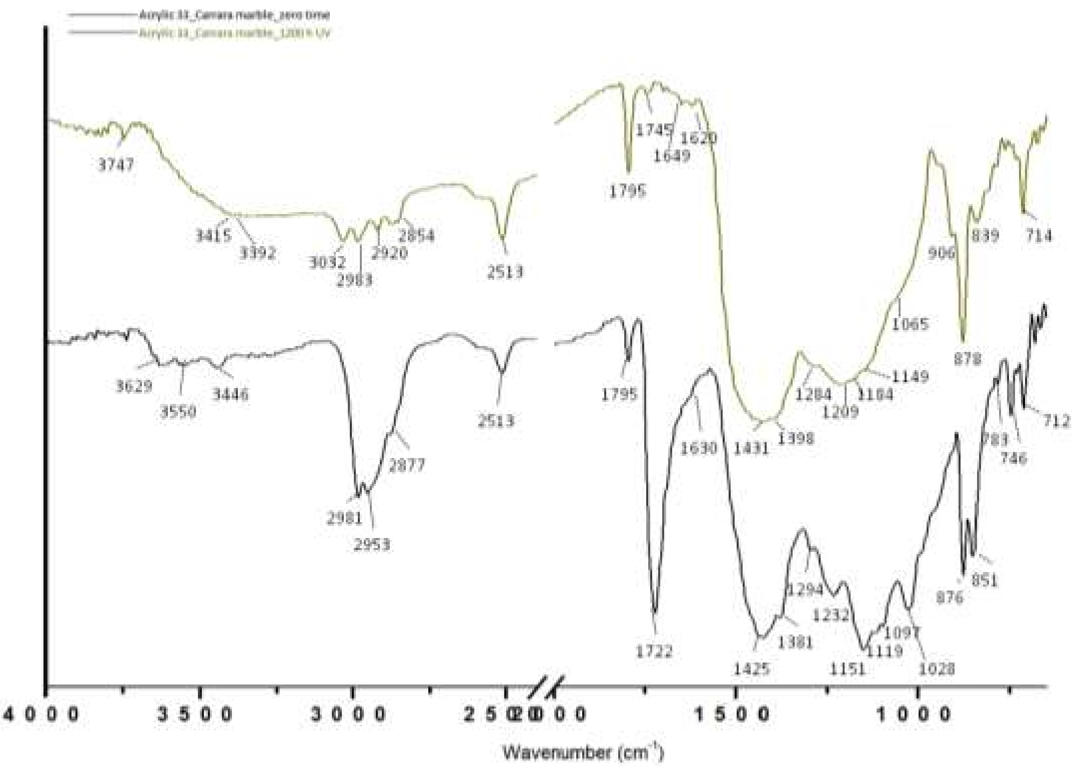


Figure 6.13: *µFTIR of Paraloid B-72, applied to Carrara marble and exposed to UV rays for 1200 hours. The monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

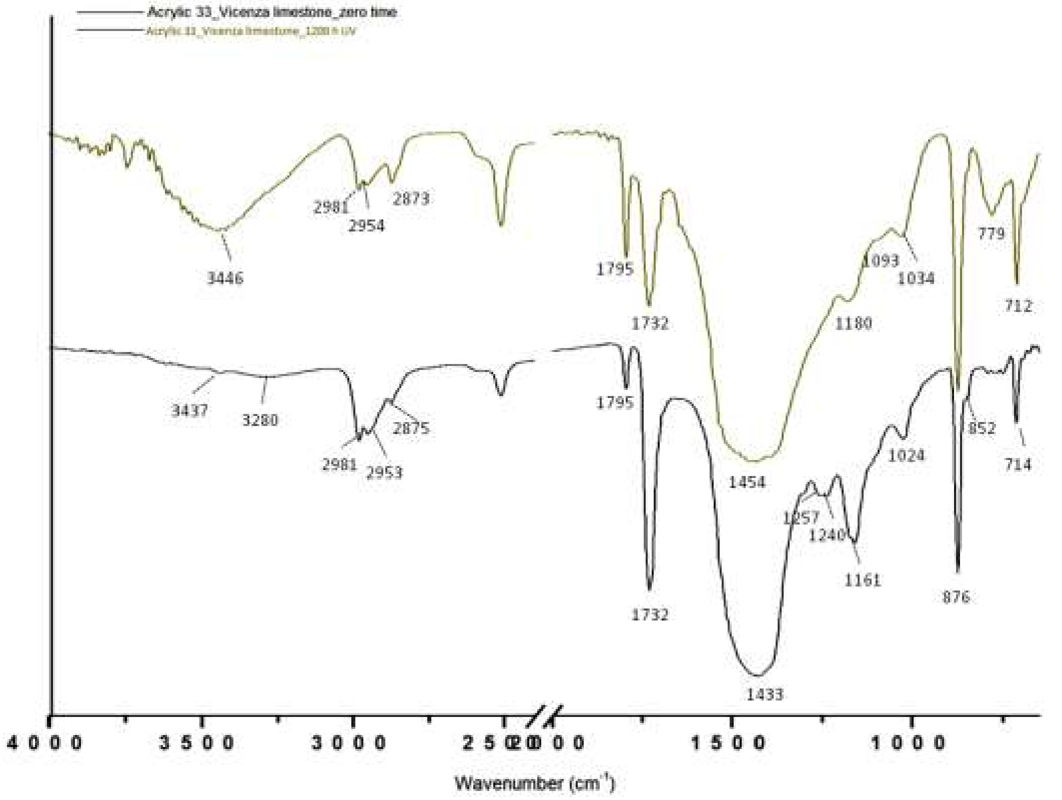


Figure 6.14: *µFTIR of Paraloid B-72, applied to Vicenza limestone and exposed to UV rays for 1200 hours. The monitoring was carried out at zero time (black line), and after 1200 h of exposure (dark yellow line).*

6.3 Monitoring of past treatments performed in Venice

This section reviews the most significant analyses undertaken on some fragments sampled from surfaces of interest treated in the past with acrylic resin and which can confirm or refute the observations made in the previous section.

- **S. Stae Church (1709) - (*Sestiere S. Croce*): Altar of sacristy**
  Substrate: *Lumachella di S. Vitale* and Istrian stone

PAST RESTORATIONS:
1978 : Ing. Todeschini (Venice) and supervisors S. Magnani e S. Longega.
Cleaning of surfaces using sepiolite and pure water.
Consolidation of marbles with Raccanello ARD E0057 (acrylic-siloxane mixture)
Protection of stones with Raccanello ARD E0023 (acrylic-wax mixture)

SAMPLING:
22.01.2013
Operators: restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna).
Number of micro-fragments sampled: 5 samples from different areas of the artifact
2 micro-scales of Istrian stone
3 micro-scales of *Lumachella di S. Vitale*
The sampling was carried out using a scalpel.

Figure 6.15: *Altar of sacristy. S. Stae Church, Venice*

Figure 6.16: *Area of the sampling of micro-fragments.*

MACROSCOPIC OBSERVATIONS:

The stone and marble surfaces are widely disaggregated. It is possible to observe scaling phenomena, loss of material and powdering.

ANALYTICAL RESULTS:

-

Figure 6.17: *Micrography of sample SS04 at the stereomicroscopy. Long side image 4.23 mm.*

- MICROSCOPIC OBSERVATIONS:

Microscopic study of the samples showed a totally disaggregated surface, on which the bright superficial polymeric film was characterized by micro-cracks and swelling (fig. 6.17).

The cross-section of Istrian stone samples showed a white opaque superficial layer which can be related to the wax component of the resin.

- FTIR ANALYSIS

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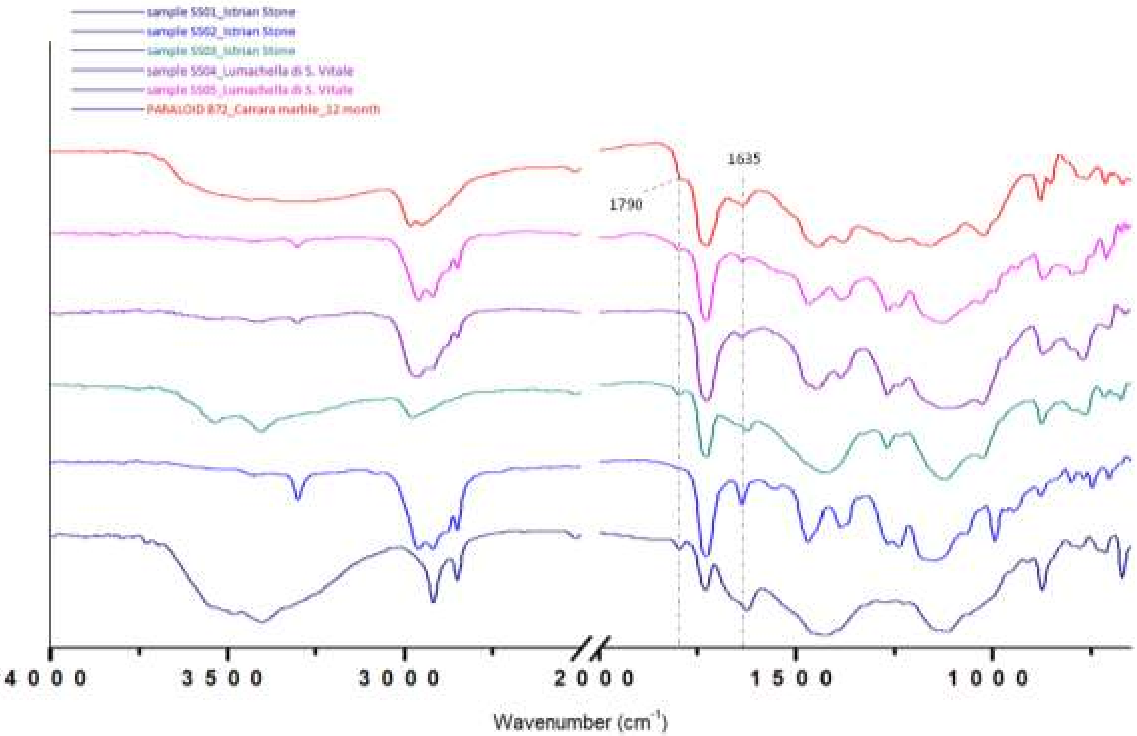

Figure 6.18: *Comparison between µFTIR spectra of polymeric film of the fragments sampled from S. Stae church and the spectrum of Paraloid B72 applied to Carrara marble and exposed to outdoor conditions for 12 months (red line).*

µFTIR analysis confirmed the chemical nature of the products which were applied. Even though the treatments were not pure Paraloid B-72 but a mixture of Paraloid and a siloxane resin or Paraloid and a wax, the spectra showed peaks at 1635 and 1790 cm^{-1}, which cannot be related to wax or siloxane but were indicative of the photo-oxidation of Paraloid B-72 in the µFTIR spectra presented in section 6.2.

- **<u>Arsenal (*Sestiere Castello*): main portal: *Porta da Terra*</u>**

  Substrate: Istrian stone and Greek marble

Figure 6.19: *Main portal of the Arsenal*

PAST RESTORATIONS:

1973-1976: Istituto centrale del Restauro of Rome, supervisor P. Mora.

Cleaning of surfaces with tap water and AB57. The stones were treated using Paraloid B-72.

SAMPLING:

17.06.2014

Operators: restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna).

Number of micro-fragments sampled: 2 samples from different areas of the artifact

2 micro-scales from the relief of the lion to the right of the main portal

Figure 6.20: *Area of the sampling of micro-fragments.*

MACROSCOPIC OBSERVATIONS:

The state of conservation of the lion on the main portal is quite good. The substrate is compact with no fractures, no loss of material, but low powdering and whitening are observable.

ANALYTICAL RESULTS:

- MICROSCOPIC OBSERVATIONS:

Figure 6.21: *Front and rear of sample AS1*

The samples showed a smoothed surface, opaque, with no microbiological growth, no cracks or fissures. The cross-section did not show a superficial layer related to the treatment.

The rear of the samples had the typical crystalline aspect of the stone.

- FTIR ANALYSIS

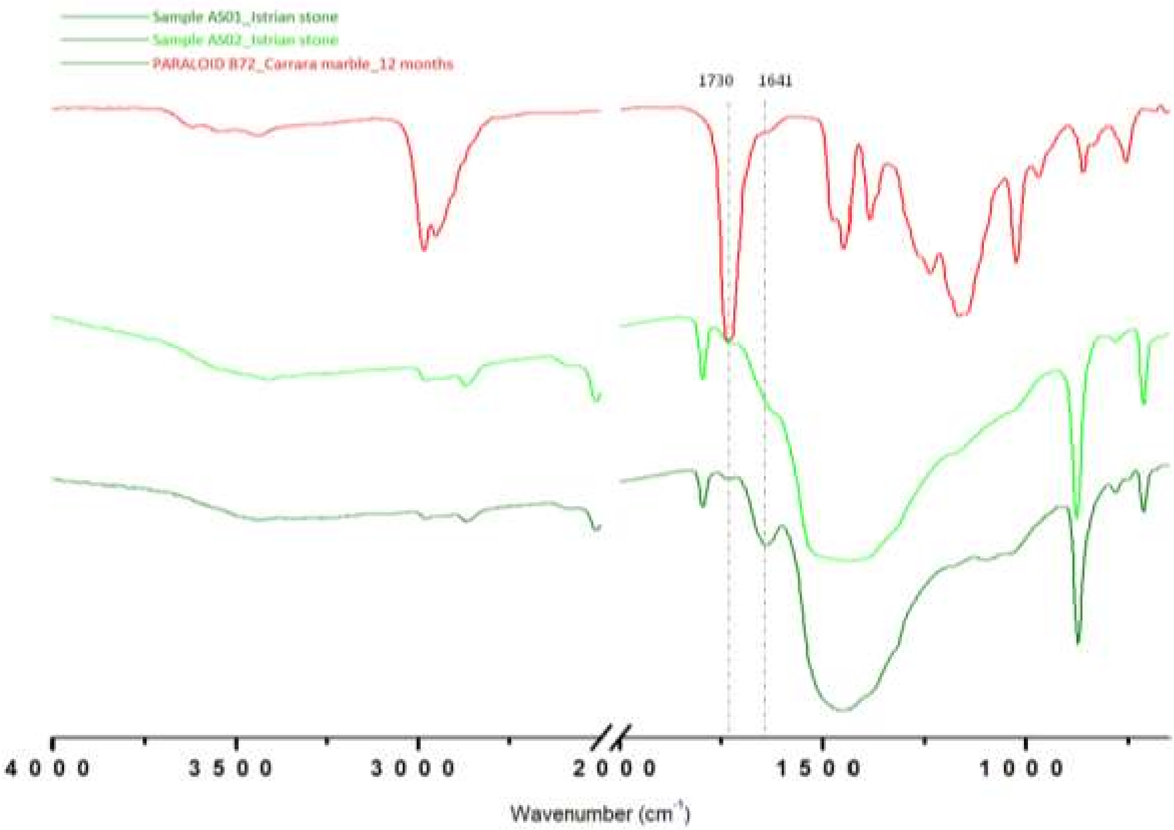

Figure 6.22: *Comparison between μFTIR spectra of polymeric film of the fragments sampled from the main portal of the Arsenal and the spectrum of Paraloid B72 applied to Carrara marble and exposed to outdoor conditions for 12 months (red line).*

μFTIR analysis of the surfaces of the samples confirmed the absence of a superficial treatment, as all the peaks of the spectra can be related to the calcium carbonate of the substrate. However it is still possible to observe a peak at 1730 cm^{-1}, of low intensity, which is related to ν C=O and proves that the past treatment was based on acrylic resin.

The peak at 1641 cm^{-1} could be related to photo-oxidation of the acrylic resin, as explained in 6.2 section.

FINAL OBSERVATIONS

The results obtained generally confirm the experimental results obtained in the laboratory and shown in section 6.2. However it is important to consider that even though the two considered treatments were coeval, in the case of the treated surfaces of S. Stae church, the best state of conservation of the resin was observed, but also the worst condition of the stone substrate. In fact, the altar of the sacristy in S. Stae church is not exposed to outdoor conditions and the product used is not pure Paraloid B-72 but a commercial mixture of Paraloid B-72 and a siloxane resin or a wax, which can confer greater stability to the resin.

Nevertheless the application of the resin did not allow the transpiration of the substrate. Consequently, the water absorbed from the stone by capillary rise cannot evaporate from the substrate, but instead exerts pressure on the surface and causes swelling and micro-cracks.

6.4 References

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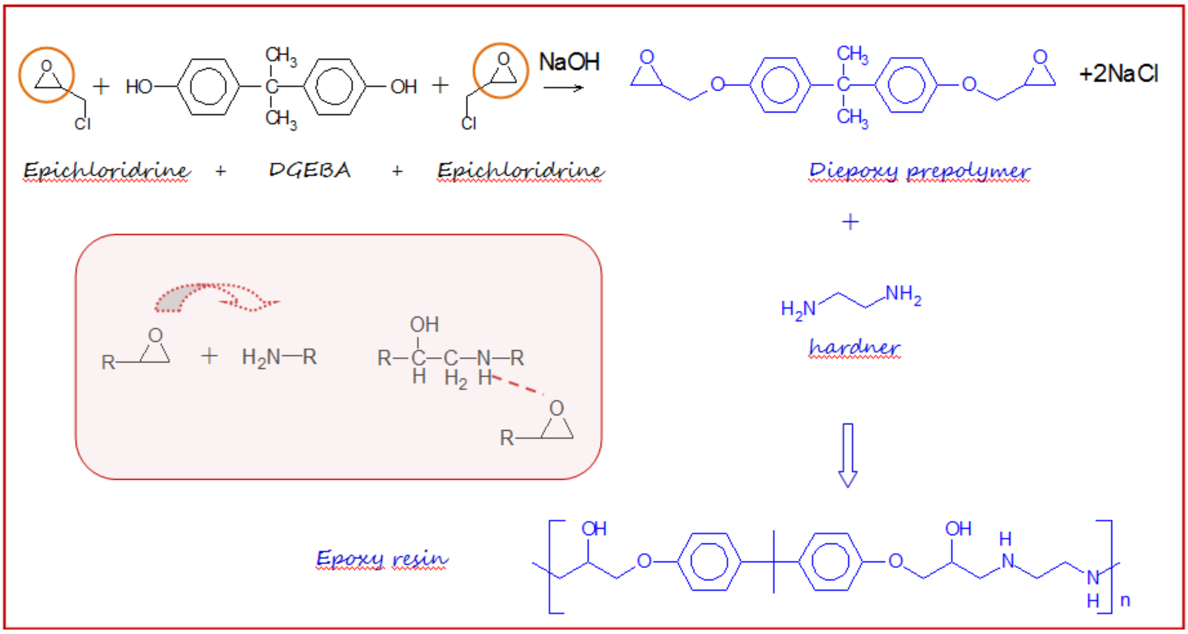
Chapter 7

Epoxy resins

7.1 Epoxy resins

Epoxy resins were produced in the late 1940s and were soon adopted for use in conservation. They are thermosetting polymers made up of two parts: a monomer or prepolymer which incorporates the epoxy group, and the hardener which can have acids or amino groups and reacts with the epoxide and cross-links the molecules (Scheme 7.1). The commonest prepolymers for epoxy resins are produced by diglycidyl ether of bisphenol A (DGEBA) and Epichloridrine and have the general formula shown in scheme 7.1. The benzene ring in the chain ensures that the resin cures to a strong rigid polymer in a short time.



Scheme 7.1: *General polymeriazation mechanism of epoxy resins*

The commonest hardeners used for room temperature polymerization are aliphatic amines and amides, whereas acid anhydrides are used for high-temperature curing. The number of epoxy groups is revealing for the correct proportions of prepolymer and hardener.

The curing process occurs in two stages: in the liquid state, which is generally fast depending on the formulation of the resin, and a second stage when the polymerizing mixture has passed its T_g. This stage can extend to months or years until the unreacted groups diffuse through the glassy mass [91].

In general, epoxy resins have good chemical resistance (especially to alkali), and also have good resistance to water and organic solvents. Aromatic DGEBA are prone to degradation and yellowing by light, ultraviolet absorption and heat [92], whereas aliphatic epoxy resins are more stable to weathering [93]. The yellowing effect can be attributed to the photodegradation of the amine hardner [94], to the degradation of additives [95] or of the resin itself [96]. The main peculiarity of epoxy resins is their excellent resistance to mechanical stress and adhesion to the majority of substrates. Cured epoxy resins, as well as all cross-linked polymers, are insoluble in any solvents though they are swollen by solvents, which enables the gel to be mechanically removed.

In stone conservation, mechanical resistance and good adhesion make epoxy resins good consolidants, but their use is limited by their high viscosity. Good penetration requires a low-viscosity formulation, <2 mPa·s, and the lowest-molecular-weight epoxies and amines have a viscosity equal to ≈10 mPa·s and also tend to be more sensitive to weathering and hydrolysis [92]. In the past, good results were obtained testing a cycloalyphatic epoxy resin which is still available on the market. This resin was the commercial product EP2101, produced by EUROSTAC from Milan, which was catalyzed with a low-molecular-weight polyamine K2101, and was used as a 25% solution in propan-2-ol/toluene. The authors, testing the application and the stability of the resin applied on different stone substrates, reported its stability to UV radiation as comparable to acrylic resins. Moreover it seemed that EP2101 could improve the mechanical resistance of different stone types [97].

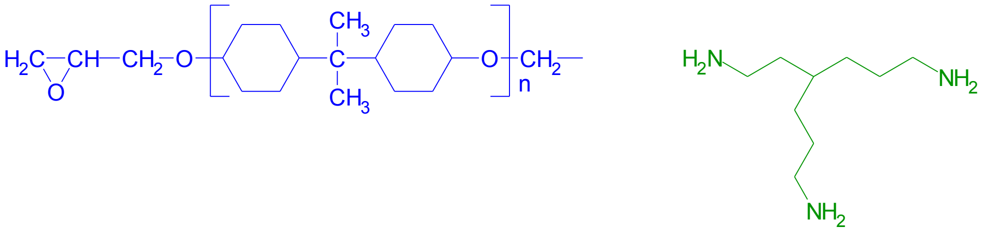
Epoxy resins have been more commonly used in eastern Europe than in Italy.

Several commercial products have been tested and applied on monumental buildings: in 1972 the aromatic epoxy resin Maraset X555 with the hardener H555 by Maraglass Corp was applied for the consolidation of the statue of Madonna con Bambino (G. Lascaris) on the main façade of S. Maria dei Miracoli church in Venice [98]; in 1972-1975 Araldyt AY 103 with the hardner HY 951 by Ciba Geigy S.p.A. was used for the protection of *rosso di Verona* marble of Loggetta del Sansovino, but the results were considered unsatisfactory. EP2101 cycloalyphatic epoxy resin was applied on a Roman aqueduct close to Rome, on a bell-tower in Arzignano (Vi), on a statue of a lion in Padua and a column in Murano (Ve) [99].

Epoxy resins were more widely used as a mortar binder in order to fill cavities or cracks, or as a structural adhesive to join different parts.

7.2 Laboratory test

This study refers to Cycloaliphatic epoxy resin EP2101 purchased from Bresciani (Italy) and used without further purification.According to the literature [98], this resin is a cyclo-aliphatic diglycidyl epoxy with the desirable properties of the aliphatic epoxies, but with much lower hydrophobic qualities. The resin is available commercially as a 25% solution in a mixture of isopropanol and toluene. The hardener, K2102, is an aliphatic polyamine that is mixed with the resin 1:5 by weight or 1:4,5 by volume. From some laboratory notes of an epistolary correspondence with STAC staff, which prof. Lazzarini kindly shared for the sake of research, the chemical nature of EP2101 had to be that described in scheme 7.2.



Scheme 7.2: *hypothesis of the chemical structure of the resin EP2101 (blu) and the hardner K2102 (green) according to the literature [97].*

After the two components were mixed 1:5 by weight, they were brushed on Carrara marble and Vicenza white limestone specimens until the substrate no longer accepted liquid.

Three samples were prepared for each substrate. After application of the consolidants, the samples were maintained at room temperature until cured polymer was achieved (15 days).

In order to enhance the chemical nature of the components, the epoxy prepolymer and the hardener were analytically characterized in the laboratory by GCMS and FTIR analysis in sol phase.

Unfortunately, it was not possible to identify the precise chemical structure of the components from the results collected of the laboratory analysis. However, the cycloaliphatic structure, and the presence of carbonyl and ester groups (figure 7.1) was confirmed.

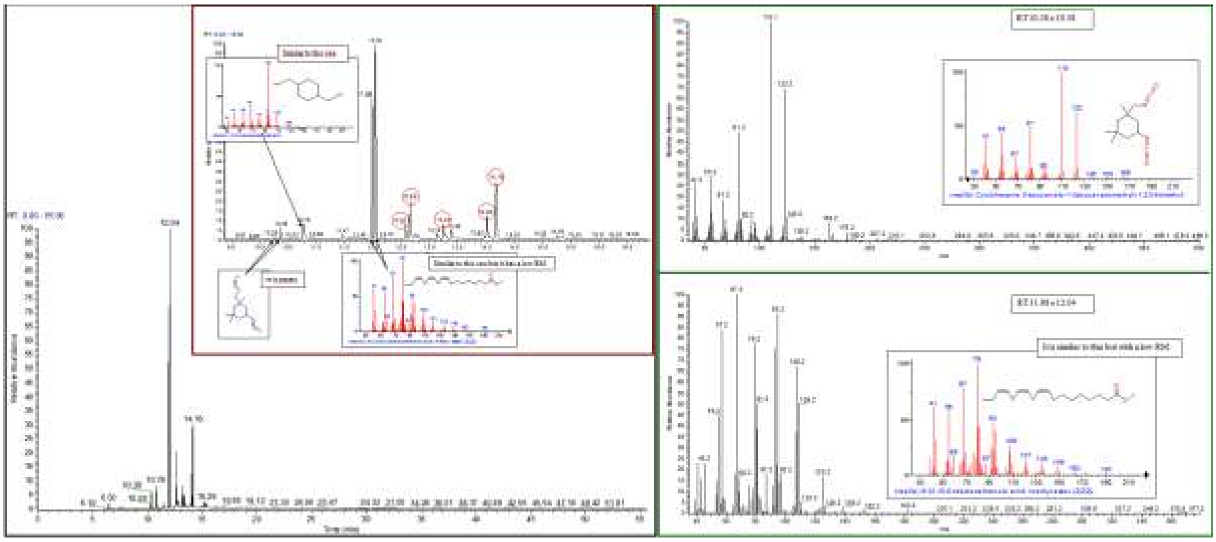
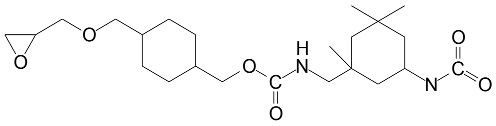


***Figure 7.1:** GCMS results from the analysis of resin EP2101.*

From the fragmentations observed during GCMS analysis it can be surmised there is a uretane linkage between cycloaliphatic diol and cycloaliphatic diisocyanate, resulting in an intermediate of the epoxy prepolymer. The surmised structure is shown in scheme 7.3 below.



***Scheme 7.3:** hypothesis of chemical structure*

FTIR spectra of EP2101 in sol phase confirmes the GCMS results and lends support to the surmised chemical structure. In figure 7.2, the peaks highlighted in light blue represent toluene, which with isopropanol (ν O-H at 3382, 1307, 1099, 1042 cm^{-1}, ν C-H at 2956, 2926, 2872 cm^{-1}, δas and δs C-H 1470 and 1382 cm^{-1}) is the solvents of EP2101 solution. All other peaks are related to the monomer, in particular the peaks at 2926, 1469 and 731 cm^{-1} can be related to CH_2 of the cyclic hydrocarbons and hydrocarbon chains, as well as those at 2956, 2872, 1455, 1373 and 1368 cm^{-1} which could be linked to symmetrical and asymmetrical stretching and bending of methyl groups. The peaks at 1726 and 1240 cm^{-1} could refer to C=O symmetrical stretching of disubstituted carbonyl, whereas the peaks at 1707, 1529, 1235 and 1048 cm^{-1} could show the presence of urethane chemical bonds in the molecule. Finally the peaks at 1244, 896 and 846 cm^{-1} confirm the presence of epoxy rings in the monomer. Probably the prepolymer in the solution is dissociated and, for this reason, not all the chemical bonds assumed in the scheme 7.3 have a related peak in the spectra.

Comparing the IR spectrum of K2102 hardener with the spectra collected in the standard commercial library of Jasco Europe, it was possible to be sure that it is a branched polyamine.

Unfortunately, no datasheet or scientific studies of EP2101 can confirm the chemical structure supposed for the epoxy prepolymer or give more detail in order to better understand its chemical nature.

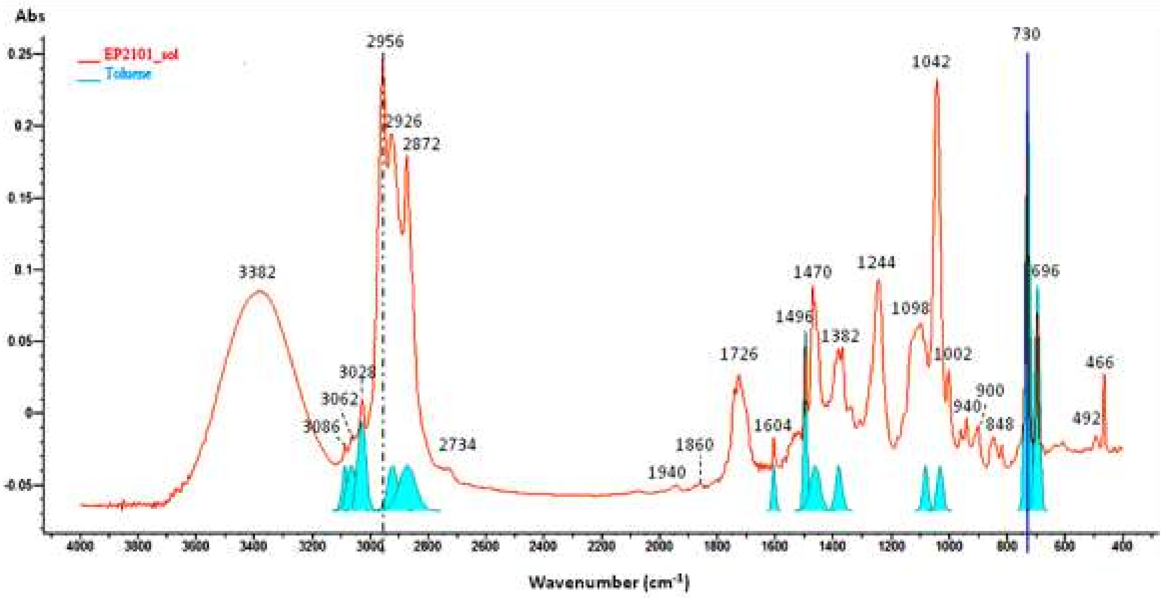


Figure 7.2: *FTIR spectrum of sol EP2101 (red line), in comparison with toluene from the Jasco Europe library (light blue peaks).*

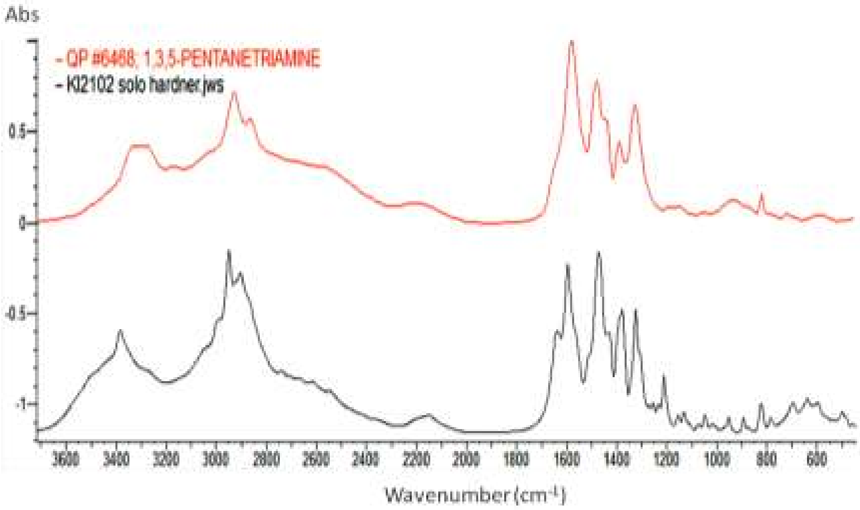


Figure 7.3: *Comparison between FTIR spectrum of K2102 hardener (black line) and a branched polyamine, in particular 1,3,5-pentanetriamine (red line).*

The resin applied on the specimens formed a cured superficial film on the surface, which covered but did not change the original aspect of the stones. The film was transparent, homogeneous and bright.

On the surface of Carrara marble the thickness of the film was 160-200 μm and no penetration of the resin into the stone substrate was observed using SEM (fig. 7.4). On the other hand, EP2101 applied to Vicenza limestone not only formed a cured film of 50 μm upon the surface, but also penetrated the stone to a depth of 25 μm. Analysis of the elemental composition of the resin using EDS microprobe gave a result of 5.36% of Cl. The presence of Cl probably derived from the reaction between epichloridrine and diglycidyl ether, and it was very useful to ensure, using EDS microprobe the penetration depth of the resin.

SEM observation of a cross section of the treated Vicenza limestone sample, after 12 months of outdoor exposure, showed some rising of the polymeric film from the stone surface (yellow arrow in fig. 7.4), which could lead to detachments, loss of material or the development of an environment, where biological species, such as algae and fungi, could flourish.

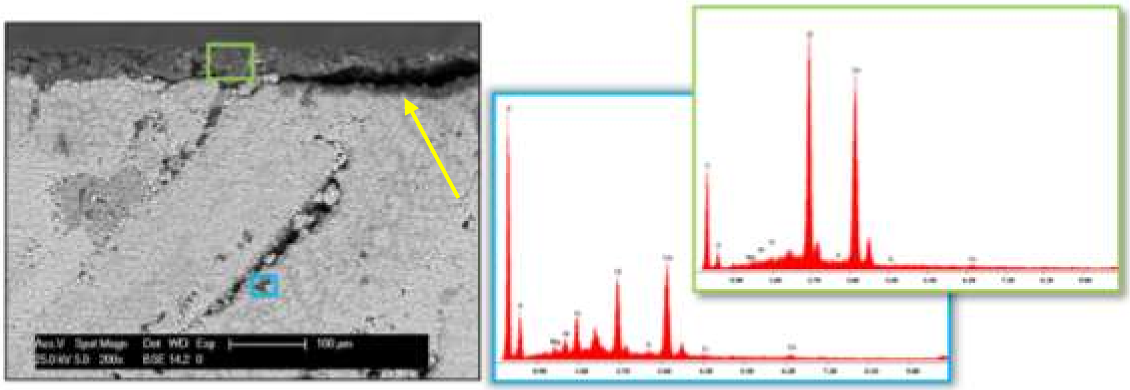


Figure 7.4: *SEM micrograph of the cross-section of V-2 specimen and EDS analysis of the resin.*

Both treated samples exposed to environmental conditions suffered gradual decay.

The polymeric film on the surface of Carrara marble lost its brightness and became quite yellow. Among the border of the specimens some cracks were visible and, after six months, spheroidal microbiological microorganisms, probably fungi, were on the surface. After twelve months, fungi with dark hyphae had colonized the treated surface.

Concerning treated Vicenza white limestone, EP2101 suffered discolouration and cracking effects, and after 12 months it was still not possible to observe the original aspect of the stone. The visible alteration of the surface by the formation of a thin layer similar to a white compact powder distributed throughout the entire superficial area appeared on the stone after the first month, and increased during the following months. Cracking phenomena were observable from the sixth month of exposure, whereas fungal microbiological growth diffused from the third month.

Figure 7.5: *micrographs of the same area of Vicenza white limestone untreated, treated with EP2101 at zero time and after 12 months of outdoor exposure. Long side images 6.78 mm.*

The situation was different for specimens treated with EP2101 resin and exposed to UV radiation. A gradual yellowing increased during the ageing process from 200 hours until 1200 hours, but no cracking or powdering phenomena were observed. The yellowing effect is much more evident to the naked-eye in Carrara marble than in Vicenza limestone because of the more homogeneous and clear texture of the stone (fig. 7.6).

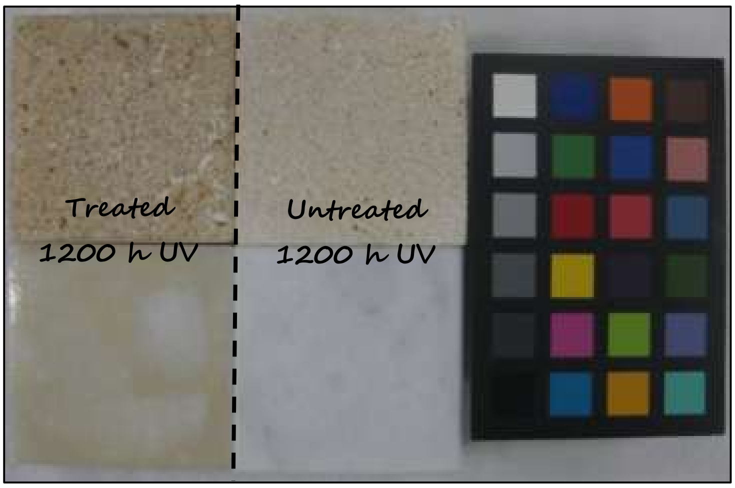
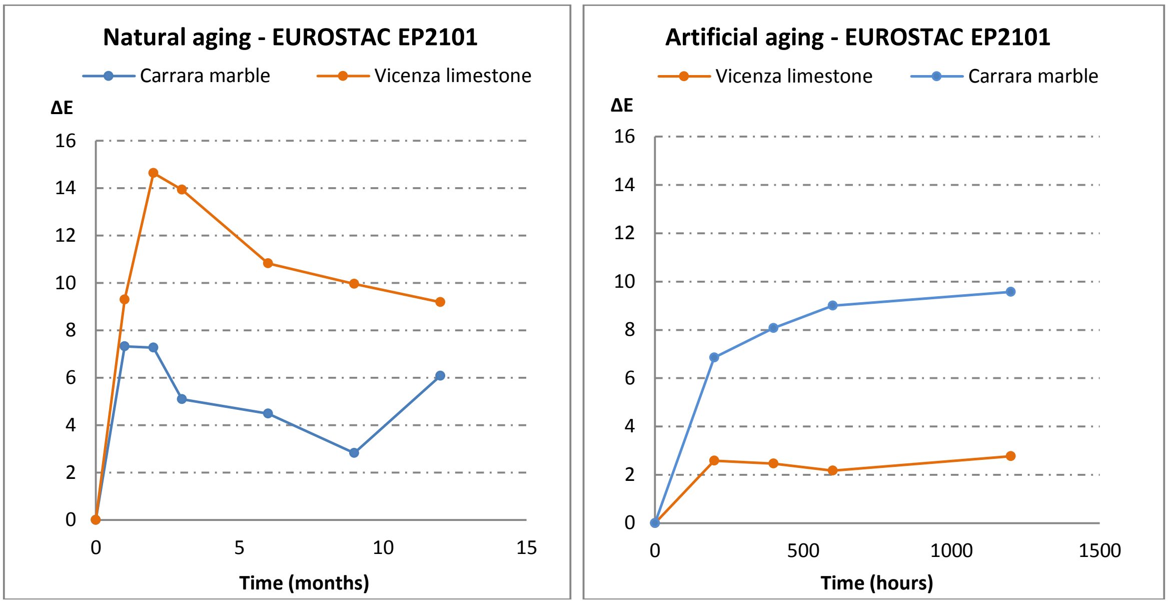
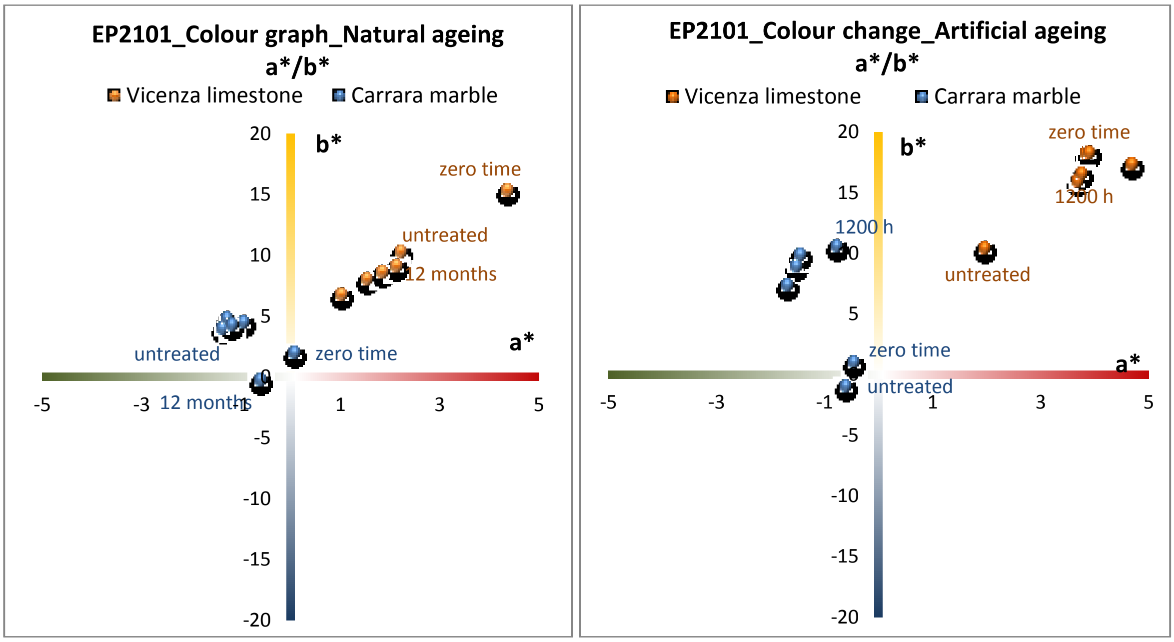


Figure 7.6: *Photograph of treated and untreated samples after 1200 h of UV radiations.*

The colour variation of specimens, exposed to both ageing environments, was measured using a spectrophotometer and the results compared which each other, as shown in graph 7.1.



Graph 7.1: *Trend of colour change of surfaces treated with EP2101 during exposure to outdoor conditions (on the left) and the exposure to UV radiation (on the right).*

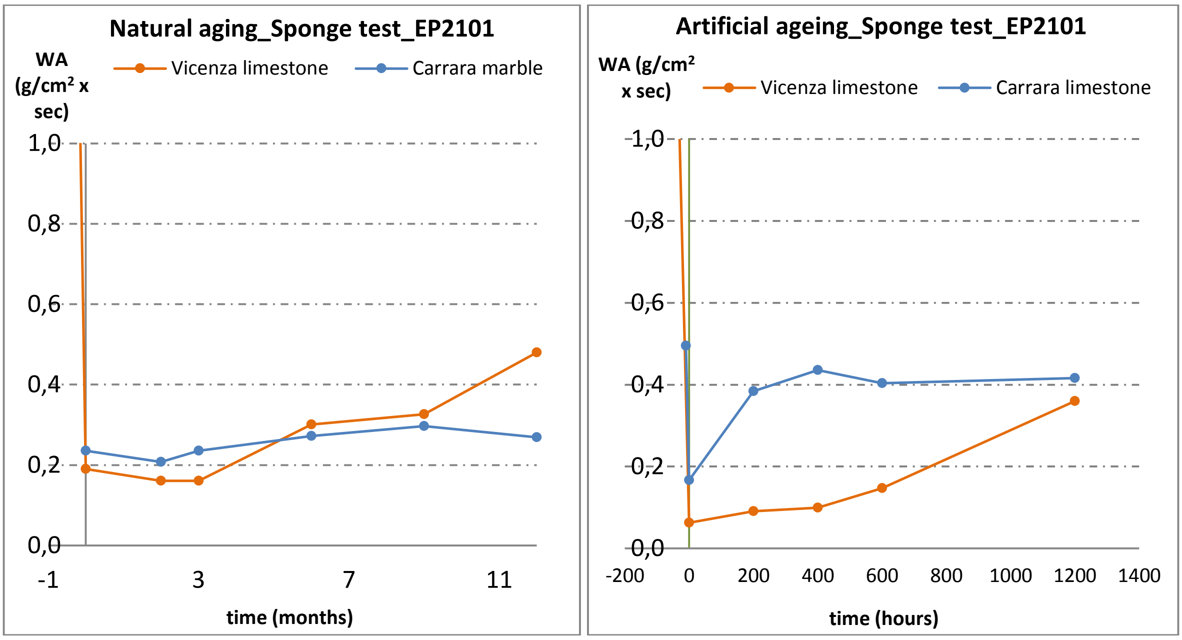


Graph 7.2: *Trend of colour change of surfaces treated with EP2101 during exposure to outdoor conditions (left) and the exposure to UV radiation (right).*

The cured film of EP2101 resin showed a gradual but significant chromatic alteration when exposed to different aggressive environments (graph 7.1-2). In particular, EP2101 applied on Carrara marble exhibited a noticeable colour change when exposed both to outdoor conditions and UV radiation, which tend to yellowing, increasing until reaching stability over time. Treated Vicenza limestone exposed to outdoor conditions showed greater chromatic alterations than when exposed to UV radiation. Increasing exposure time, it seems that the resin lost its yellow tone, moving towards lower b* value (graph 7.2). Comparing these results with those obtained from microscopic observations, it can be surmised that photo-oxidation is not the only factor responsible for alteration of EP2101, but other factors can cause chemical-physical transformation of the resin and related degradation processes, changing its aesthetical aspect. Moreover, after exposure to outdoor conditions, the roughness of Vicenza limestone was more susceptible to superficial dust deposition, which could also have influenced the colour of the stone surfaces. On the other hand, the thickness of the polymeric film on Carrara marble, as well as the smoother and more homogeneous aspect of its surface, allowed better appreciation of the yellowing effect caused by chemical interaction between UV rays and the resin.

Changes in superficial hydrophobicity also varied depending on the ageing process.

In particular, when exposed to outdoor conditions Vicenza white limestone showed a gradual decreasing of superficial hydrophobicity with 3 months of exposure, whereas the trend of Carrara marble was quite stable. On the other hand, if the behaviour of treated Vicenza limestone was quite similar to that one explained above, exposed to UV radiation, Carrara marble lost hydrophobicity especially during the first 200 hours of exposure, stabilizing then during the following hours.



***Graph** 7.3: Water absorption variation during outdoor (on the left) and UV exposure (on the right).*

Figure 7.7:Picture of the imprinting of the sponge, during sponge test, on Carrara marble surface.

Moreover, it was demonstrated that treated Carrara marble, exposed to UV radiation, produced a smell during the sponge test, and the imprint of the sponge remained on the marble treated surface (fig. 7.7).

The µFTIR spectra collected during the monitoring of the ageing process ensured that a degradation mechanism began for all the treated specimens and increased during the ageing time. In table 7.1 all the vibrational modes observed have been reported to assist in reading the spectra and in understanding the chemical groups involved.

The supposed epoxy intermediate, illustrated in scheme 7.3, may help to check the correspondence between the peaks and the macromolecule.

Comparing the FTIR spectra of the cycloaliphatic epoxy resin before polymerization, in figure 7.2, and after, in figure 7.8, the decreasing of characteristic bands at 896 and 846 cm^{-1} from the epoxy ring of the monomer functional groups reflected the conversion reaction.

Polymerization also increased the characteristic band around 1090 cm^{-1} from the polymerized polyether structure, as well as the band at about 3450 cm^{-1} from the stretch of the hydroxyl groups formed during the ring-opening reaction [100]. The band at 3450 cm^{-1}

related to ν_s of O-H chemical bond, could also refer to humidity of the atmosphere or deposits on the film surface.

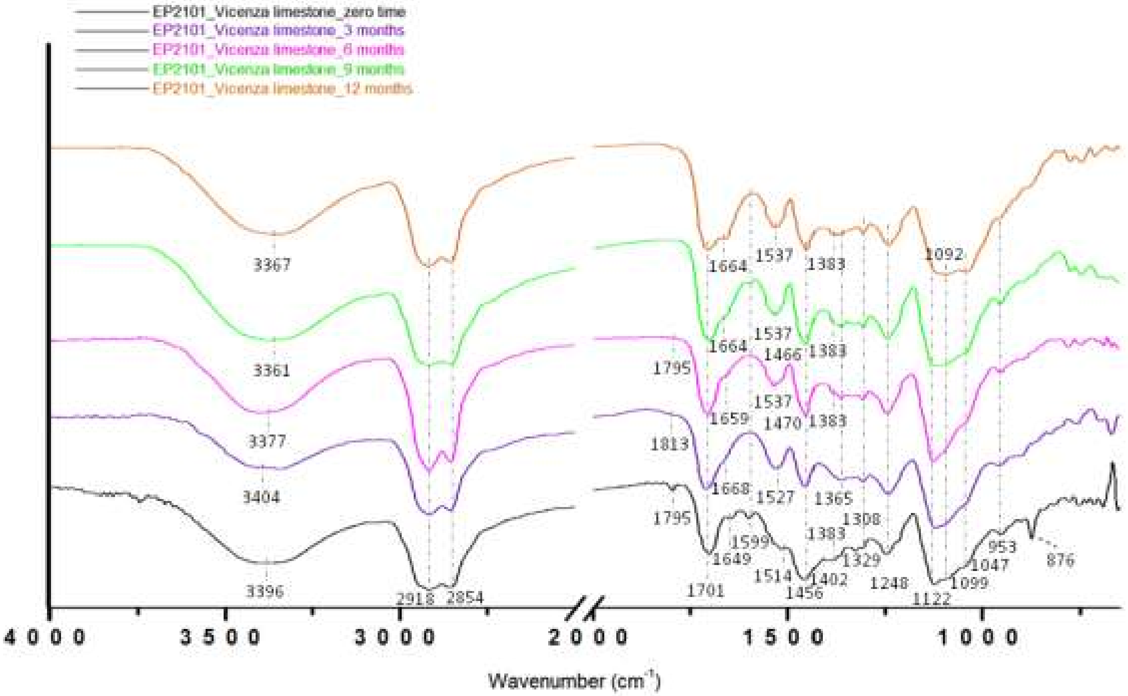


Figure 7.8: *µFTIR of EP2101 resin, applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

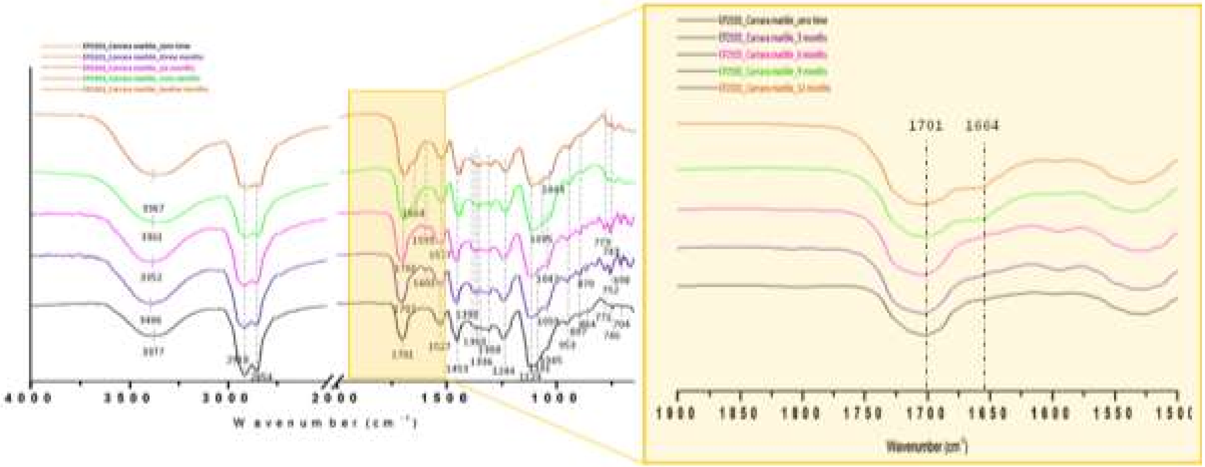


Figure 7.9: *µFTIR of EP2101 resin, applied to Carrara marble and exposed to outdoor conditions. Monitoring was carried out at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

Wavenumber (cm^{-1})	Functional groups	Assignments
3396	v O-H ; v N-H	Hydroxyl groups
2918, 2854	v C-H	Aliphatic bonds in cyclic structures or hydrocarbon chains
1701	v C=O	Associated in urethane (H,R')N-C(O)-O-R''
1664	v C=C	Olefinic groups
1533	v C-N; δ N-H	Associated in urethane (H,R')N-C(O)-O-R''
1456	δas CH	CH_2, CH_3
1383, 1365	δs CH_3	CH_2, CH_3
1308	R-OH	Hydroxyl groups
1248	v N-C-O	Associated in urethane (H,R')N-C(O)-O-R''
1122	v C-O-C	Ether
1090	v C-O-C; v C=O	Ether Associated in urethane (H,R')N-C(O)-O-R''

Table 7.1: *FTIR assignments of the main peaks observed for examined epoxy resins, according to the literature [101].*

The spectra collected from the treated specimens exposed to outdoor conditions and to UV radiations showed a gradual prominent peak revealed at wavenumber of 1664 cm^{-1} (figure 7.9). Moreover, studying the spectra of applied resins exposed to UV rays, the shoulder at 1664 cm^{-1} cited above, tended to be a peak. The carbonyl bond at 1701 cm^{-1} decreased and those related to methyl groups at 1454, 1380 and 1377 cm^{-1} increased.

Examining the white alteration of the polymeric film observed microscopically on Vicenza limestone exposed to outdoor conditions, no significant differences from those already described are noticeable on FTIR spectra. Only larger area of bands related to hydroxyl groups are appreciated. It is likely that the effect differs from that observed on Carrara marble surface due to the different amount of product absorbed by the respective specimens (2.00 g in Vicenza limestone, 0.50 g in Carrara marble).

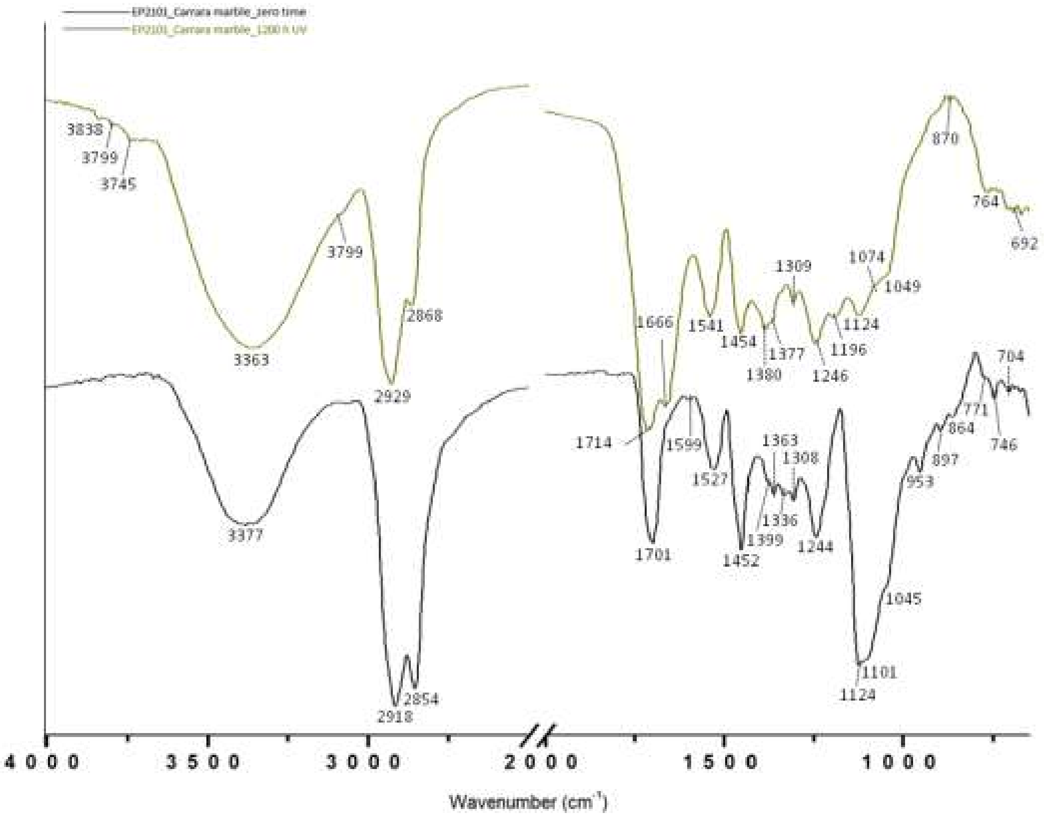


Figure 7.10: *µFTIR of EP2101 resin, applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was carried out at zero time (black line), and after 1200 h of exposure (dark yellow line).*

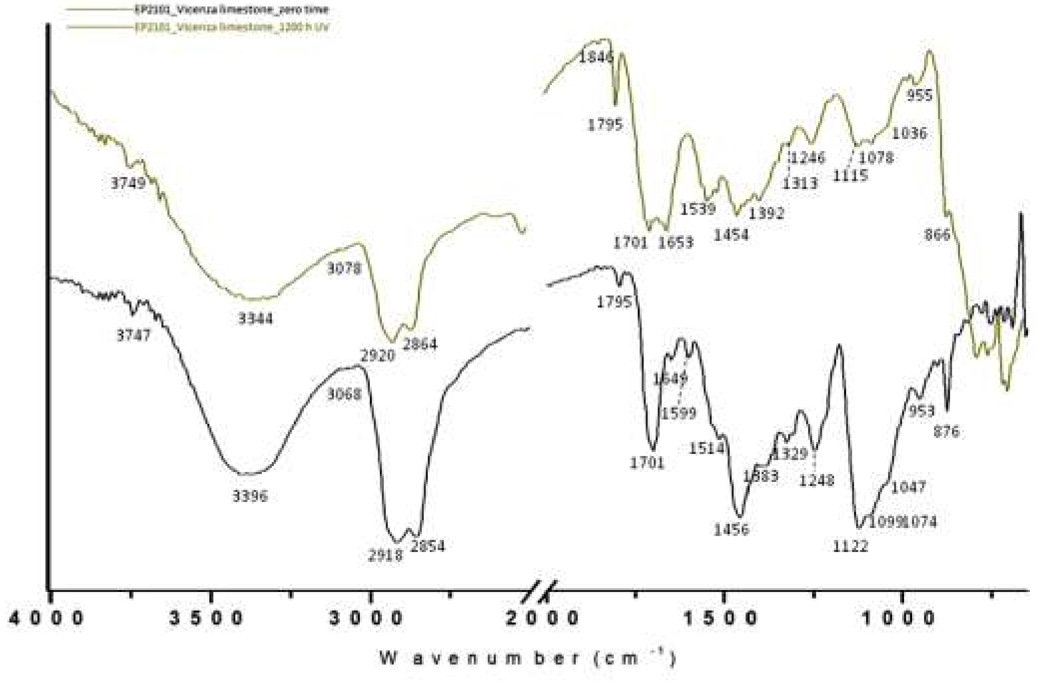


Figure 7.11: *µFTIR of EP2101 resin, applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).*

Ascribing this new peak at 1664 cm^{-1} to olefinic groups (C=C chemical bond), it is possible to argue that EP2101 cycloaliphatic resin decays by the opening of cyclic structure and chain scission. Previous studies suggested that photo-degradation generates polymer carbonyl and hydroxyl groups through chain scission and hydrogen abstraction from the polymer backbone, as shown in figure 7.12 [102, 103, 104, 105].

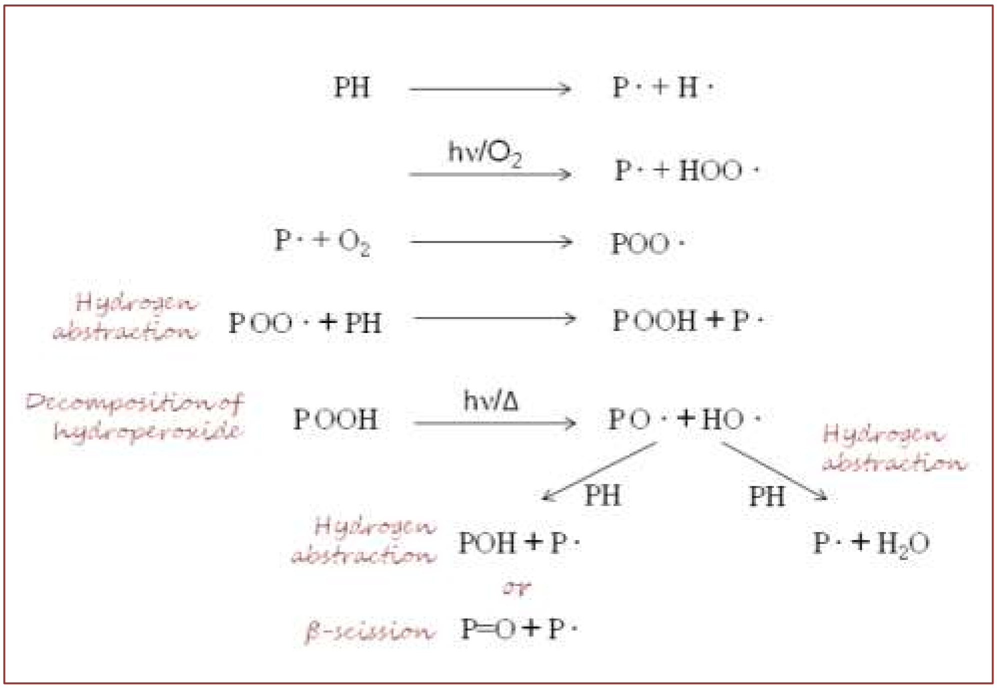


__Figure 7.12:__ Hypothesized photo-degradation mechanisms.

The generation of olefinic species arises from the recombination of alkyl radicals. This process occurs throughout the degradation process, provided that the alkyl radicals are present due to UV rays. However, since the essential propagation step is the formation of hydroperoxides and their subsequent decomposition yielding alkoxy radicals, the carbonyl species are generated as a result of ß-scissoring from the alkoxy radicals [106].

The C=C and C=O groups belong to the chromophoric groups, which occur during the degradation process and tend to absorb light by excited state when exposed to UV radiation.

Once these chemical species absorb certain visible wavelengths and transmit or reflect others, discolouration occurs in the polymer [107].

7.2 Monitoring of past treatments in Venice

EP2101 epoxy resin was applied in Venice during the well-documented restoration of the Vereri column on Murano island [108].

In 1984, prior to the treatment, the experimental resin was tested in the scientific laboratory of the Venetian Superintendent by Prof. Lorenzo Lazzarini on a Proconnesian marble fragment, present in the laboratory due to a stone substitution during a restoration intervention in S. Marco Basilica. The fragment was treated by capillary absorption and conserved in the laboratory.

In this section the results obtained from these two different consolidation treatments will be presented.

- **<u>Murano island (*Fondamenta dei Vereri*): Vereri column</u>**
  Substrate: column of Misio marble (granite)

PAST RESTORATIONS:
1985: R.W.S company from Padua
Cleaning of the surfaces.
Consolidation of marble with EP2101 resin by capillary absorption technique.

SAMPLING:
23.04.2013
Operators: restorer Lucia Bassotto (Soprintendenza per i beni architettonici e paesaggistici di Venezia e laguna)
Number of micro-fragments sampled: 2 samples from different areas and height of the artifact
The sampling was carried out using a scalpel.

Figure 7.13: *Area of the sampling of micro-fragments.*

MACROCOPIC OBSERVATION:

The state of conservation of the artifact was poor. Many scales were lifting from the surface and disaggregation phenomena of the underlying substrate were observed.

ANALYTICAL RESULTS:

- MICROSCOPIC OBSERVATIONS:

Studying cross-sections of the samples with the stereomicroscope, it was possible to observe the presence of a superficial polymeric film on the stone surfaces. The film was dark, disaggregated and raised from the substrate. The raising of the film contributed to the development of biological growth at the interface between the stone and film.

Figure 7.14*: Micrography of CVM01 cross-section. OM. long side immage 1.03 mm.*

- FTIR ANALYSIS:

The µFTIR analysis of resin scales, sampled from the fragments CVM01 and CVM02, confirmed the surmised deterioration mechanism. Comparing the spectra of Murano column with those collected from the laboratory tests reported in section 7.2, the appearance of the peak at 1659 cm^{-1} was confirmed. This peak relates to symmetrical stretching of the C=C chemical bond, and the increasing of the intensity of the peaks relates to symmetrical and asymmetrical bending of methyl groups at 1452 and 1369 cm^{-1}. These strengthen the hypothesis of the opening hydrocarbon rings and the scission of the chain with the consequent formation of olefinic groups

***Figure 7.15**: Specimen of Proconnesian marble from S. Marco Basilica treated in 1984 using EP2101.*

Moreover, the spectra were also compared with the spectrum obtained from the μFTIR analysis of EP2101, sampled from the specimen of Proconnesian marble from S. Marco Basilica (fig. 7.15), which was treated in 1984, in order to previously test the resin before its application *in situ*. The spectrum collected is comparable with those collected from the Vereri column, as shown in figure 7.16.

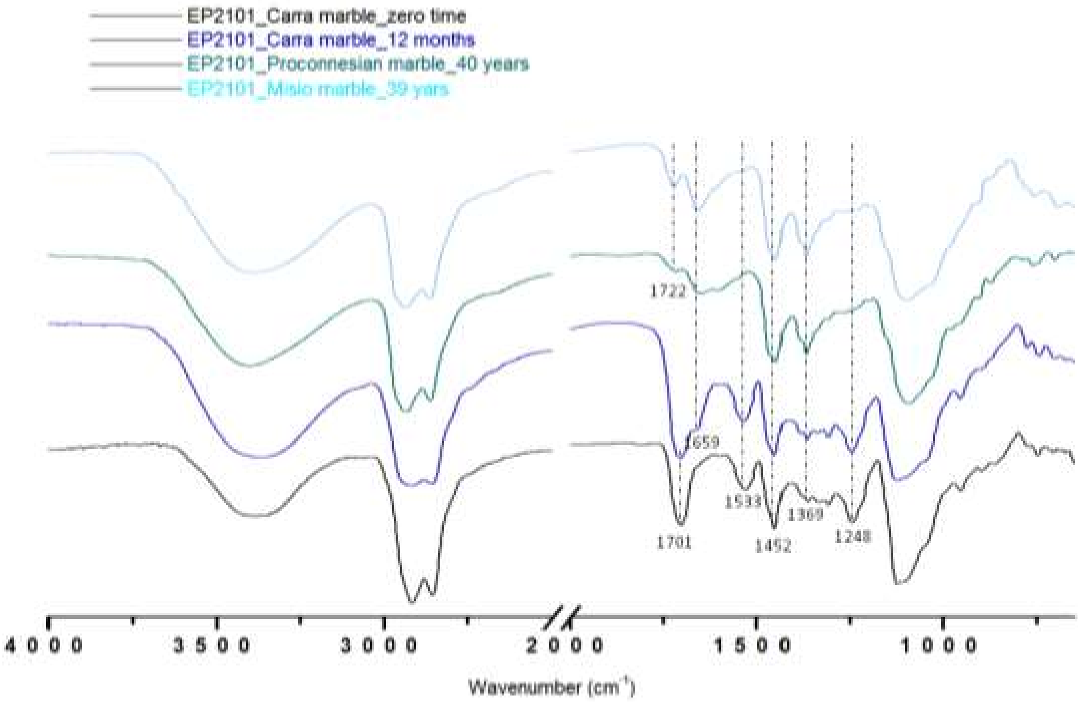


***Figure 7.16**: Comparison between μFTIR spectra of polymeric film of fragments sampled from the Vereri's column (light blue line) and S. Marco basilica (indigo line) with the spectra of EP2101 applied on Carrara marble at zero time (black line) and exposed to outdoor conditions for 12 months (blue line).*

FINAL OBSERVATION:

The results obtained confirm the experimental results obtained in the laboratory and shown in section 7.2.

7.4 References

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Chapter 8

Fluorinate products

8.1 Fluorinate products

Fluorinate resins are linear polymers which are obtained through the curing process of fluorinate monomers. It is possible to optimize the final features of the polymer by altering the C/F proportion and adding other elements such as H, O or Cl. The high percentage of fluorine in the macromolecule, due to the high energy of the C-F chemical bond (116 Kcal/mole), gives the resin high chemical stability, stiffness, compactness and insolubility.

By substituting a part of fluorine in the polymer with hydrogen or chlorine, it is possible to increase the elasticity of the resin. It is possible to improve the solubility of the final polymer by altering it with organic groups based on C-O bond (i.e. esther bond).

Fluorinate products are used in the conservation of stone materials due to the high chemical stability of the macromolecule and its high resistance to UV radiation.

Unfortunately, there are no specific formulations on the market for stone conservation and the products used are often elastomers or lubricant oils, insoluble in organic solvents, and consequently unsuitable for the restoration.

8.2 Laboratory test

This study refers to a vinildene–fluorine esafluoropropene copolymer, marketed under the commercial name Fluorophase and purchased from Phase Restauro (Italy). The resin is available commercially dissolved in acetone and ready-for-use without further purification in order to protect stone materials.

Vinildene-fluorine Esafluoropropene

Sheme 8.1: *monomers hypothised in Fluorophase commercial products*

The product was brushed onto Carrara marble and Vicenza white limestone specimens until the substrate no longer accepted liquid. Three samples for each substrate were prepared. After the application of the protective treatment, the samples were maintained at room temperature until a cured polymer was achieved (15 days).

The cured film applied on stone surfaces showed the formation of an homogeneous, bright and pearly film. The film appeared elastic and dust adhered well to it. On Carrara marble, which has very low porosity, the resin did not penetrate the stone and it remained on the surface as shown in fig. 8.1, such as a sacrificial layer. The high porosity of Vicenza white limestone allowed the product to penetrate 2 mm into the stone. Moreover, SEM-EDS study showed an incoherent film on the surface of the Carrara marble sample, which at some points had lifted up from the surface of the stone.

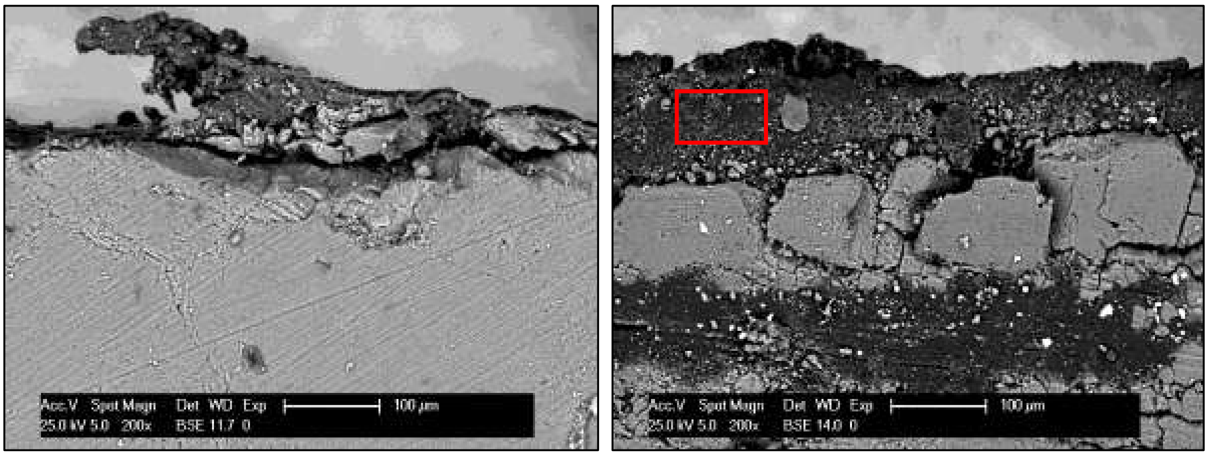


Figure 8.1: *SEM micrograph of Fluorophase superficial layer. The cross-section of both Carrara marble (on the left) and Vicenza limestone (on the right) samples also show the presence and penetration depth of the resin in the support.*

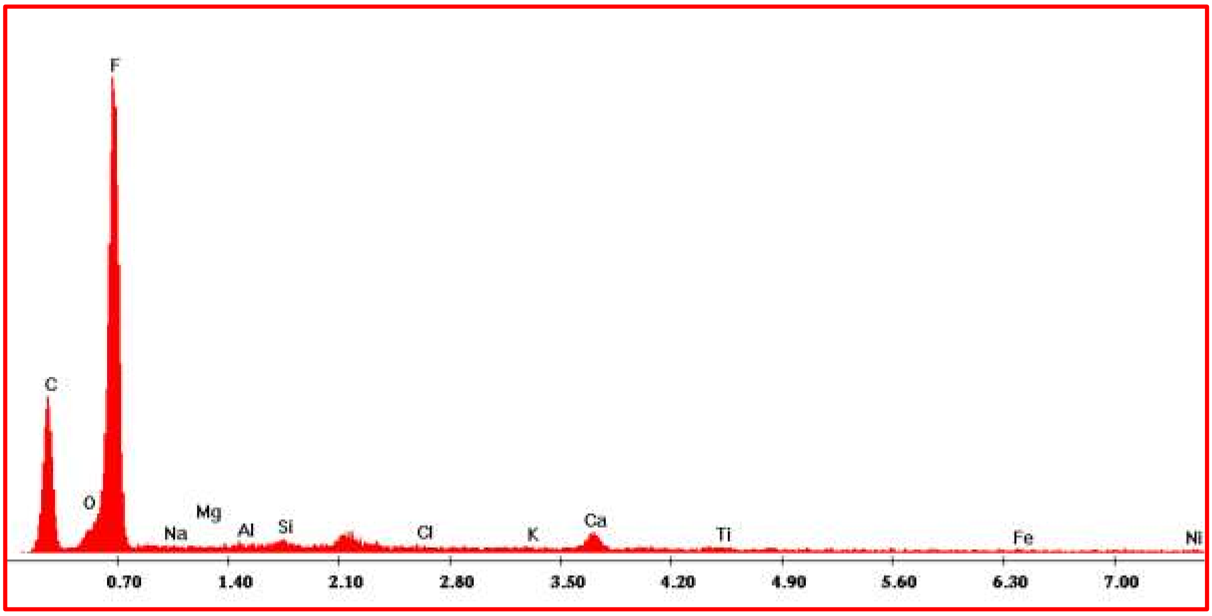


Figure 8.2: *EDS analysis of the protective superficial layer*

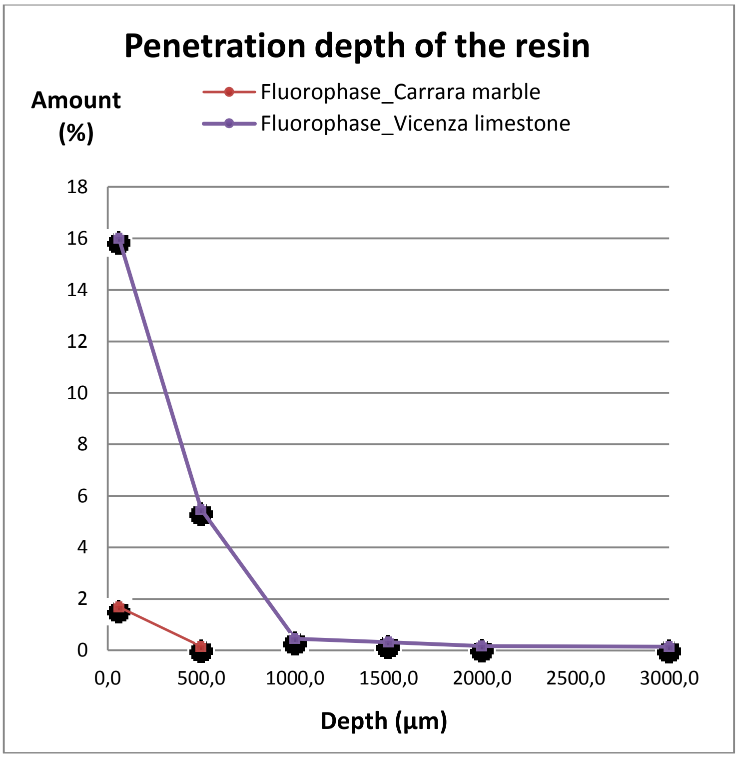
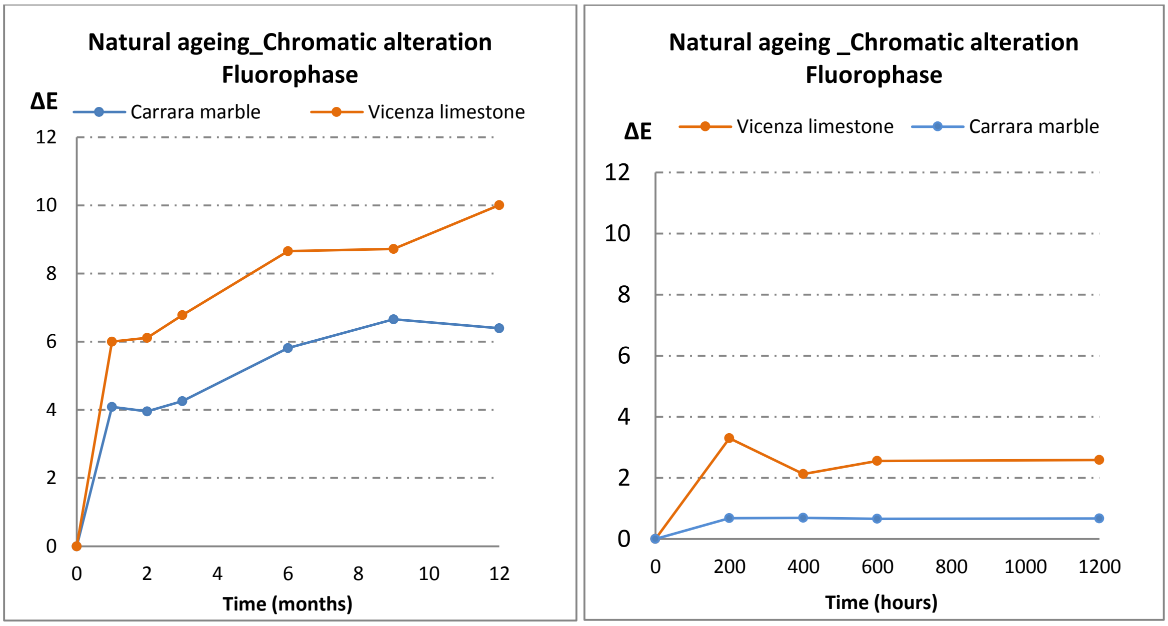


Figure 8.3:*Penetration depth of the resin into the treated specimens*

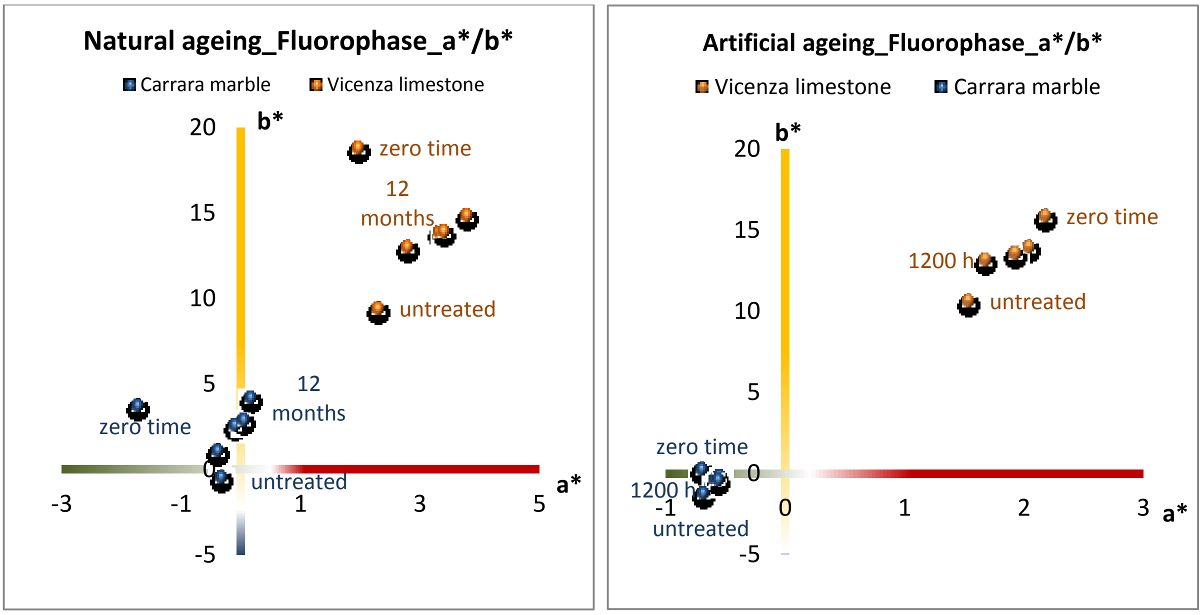
Microscopic observation of the film applied to stone surfaces and exposed to outdoor conditions showed over time a yellowing and browning of the film, to which many particles adhered. No biological growth was observed on either treated Carrara marble or Vicenza limestone. The resin maintained its elastic morphology throughout the entire period of exposure.

Measuring the chromatic variation of the treated samples and comparing the results with those obtained from treated specimens exposed to UV radiation, it was observed in both cases that there was a gradual increase of ΔE values and a final stabilization (graph 8.1). Also in this case, natural ageing caused a chromatic variation greater than artificial ageing, due to the interaction of the resin with weather but also due to the deposition of particles on the surfaces, as the elastic morphological aspect of the coating facilitates the adhesion of dust and atmospheric particles.

Observing the colour graphs (graph 8.2), it is possible to perceive a general yellowing of the resin exposed to outdoor conditions, while treated surfaces exposed to UV radiation tend to return to the "untreated value".

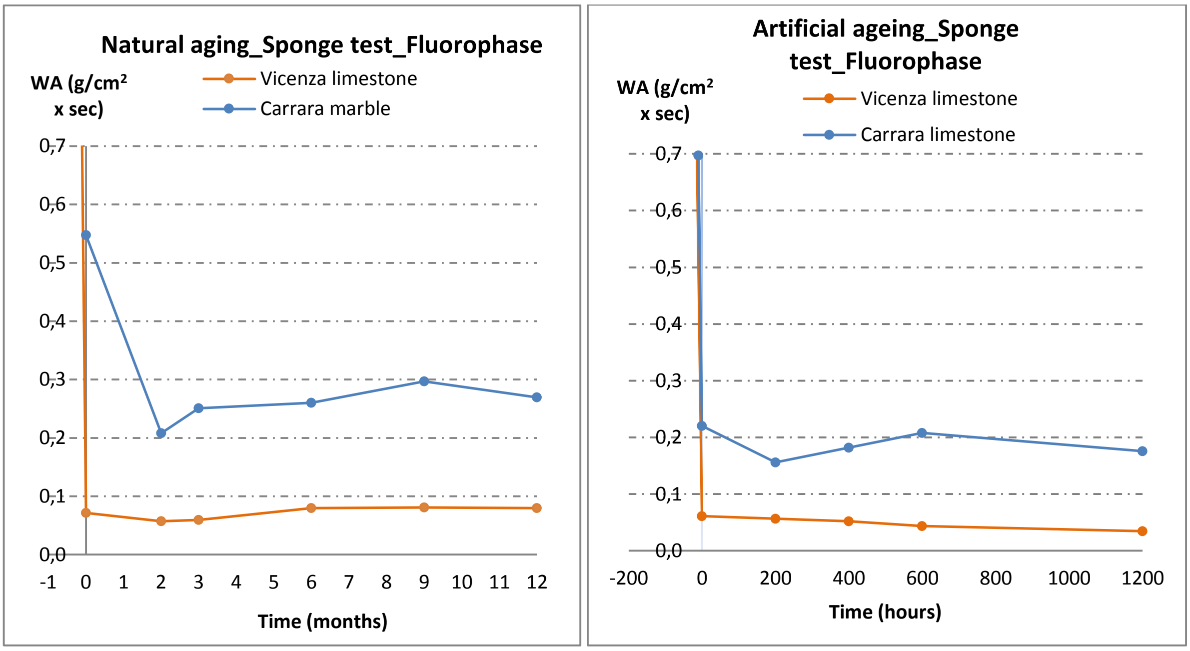


Graph 8.1: *Trend of colour change of surfaces treated with Fluorophase applied to both Carrara marble and Vicenza limestone and exposed to outdoor conditions (left) and UV radiation (right).*



Graph 8.2: *Chroma and tone variation calculated by a* and b* experimental values.*

The application of the resin confers hydrophobic features to the treated surfaces, which endured throughout the exposure time. It seems that neither weathering nor UV rays led to any alteration of the polymerized film, as shown in graph 8.3.



Graph 8.3: *Water absorption variation during outdoor exposure.*

μFTIR analysis confirmed the chemical stability of fluorinate products, and no significant alteration of the polymer was observed. However the spectra were not considered representative of the product due to the dust and calcite powder which adhered to the protective film. In table 8.1, the assignments of the main peaks are described in greater detail.

Wavenumber (cm^{-1})	*Functional groups*	*Assignments*
3400	*v O-H*	*Hydroxyl groups*
3030, 2980	*v $_2HC=CR_2$*	
2980, 2960, 2919, 2875, 2850	*v C-H*	
1795	*v C=O*	
1726	*v C=O*	
1643	*v C=C; v O-H*	*Olefinic groups*
1448	*δas CH*	*CH_2, CH_3*
1392	*δs CH_3*	*CH_2, CH_3*
1267	*v $C-F_3$*	
1188	*v C-F*	
1092	*v C-O-C;*	*Ether*
881	*v $_2HC=CR_2$*	
835	*v $_2HC=CR_2$*	
762	*v $C-F_3$*	
712	*v $C-F_3$*	

Table 8.1: *FTIR assignments of the main peaks observed for examined acrylic resin*

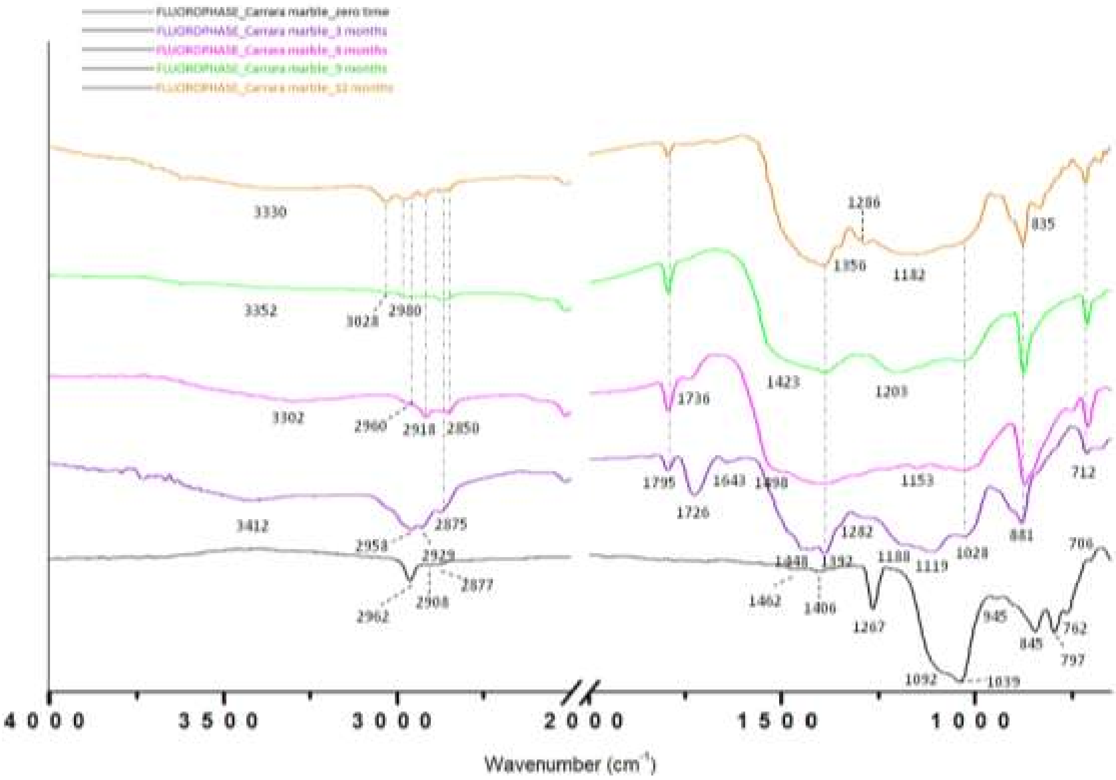


Figure 8.4: *µFTIR of Fluorophase applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

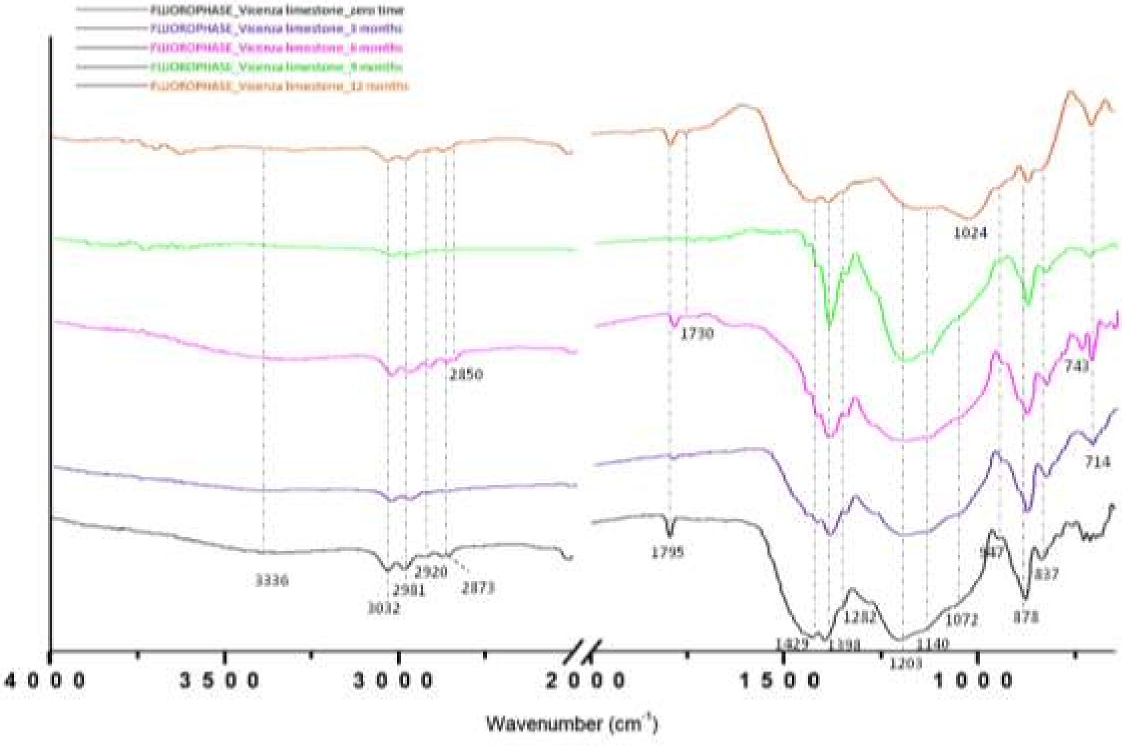


Figure 8.5: *µFTIR of Fluorophase applied toVicenza limestone and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

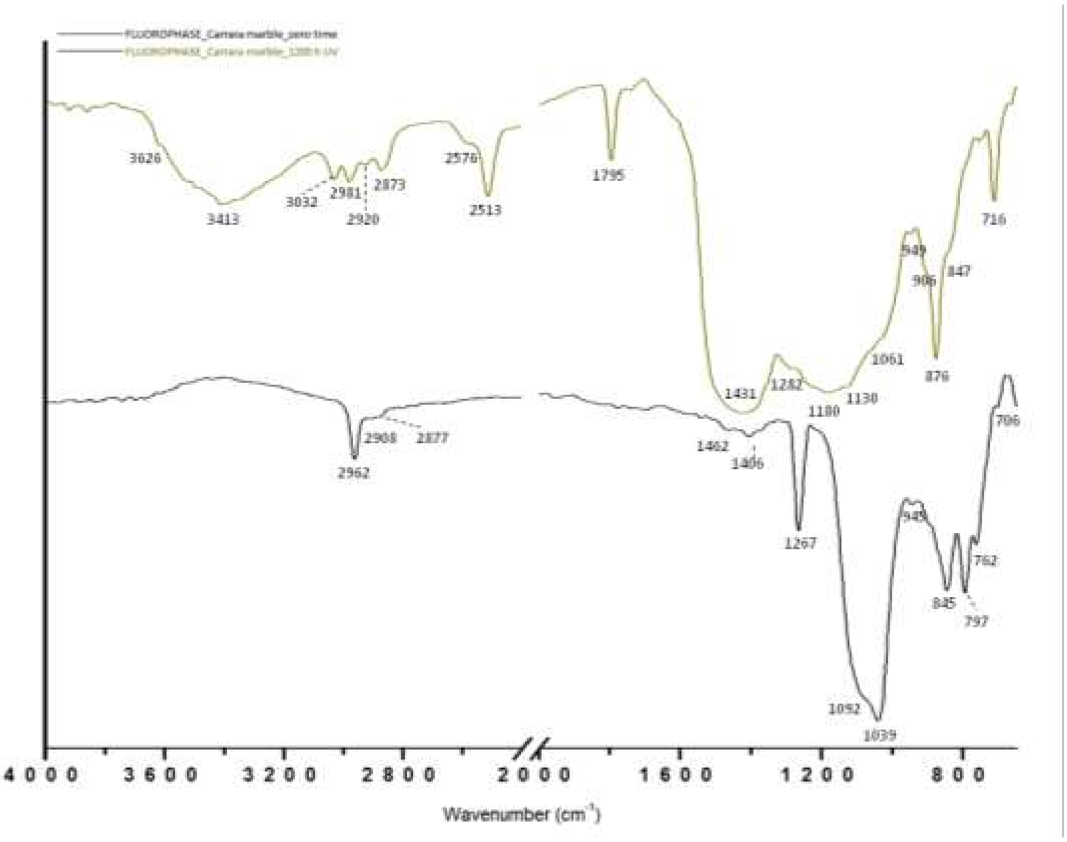


Figure 8.6: *µFTIR of Fluorophase applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was carried out at zero time (black line) and after 1200 h of exposure (dark yellow line).*

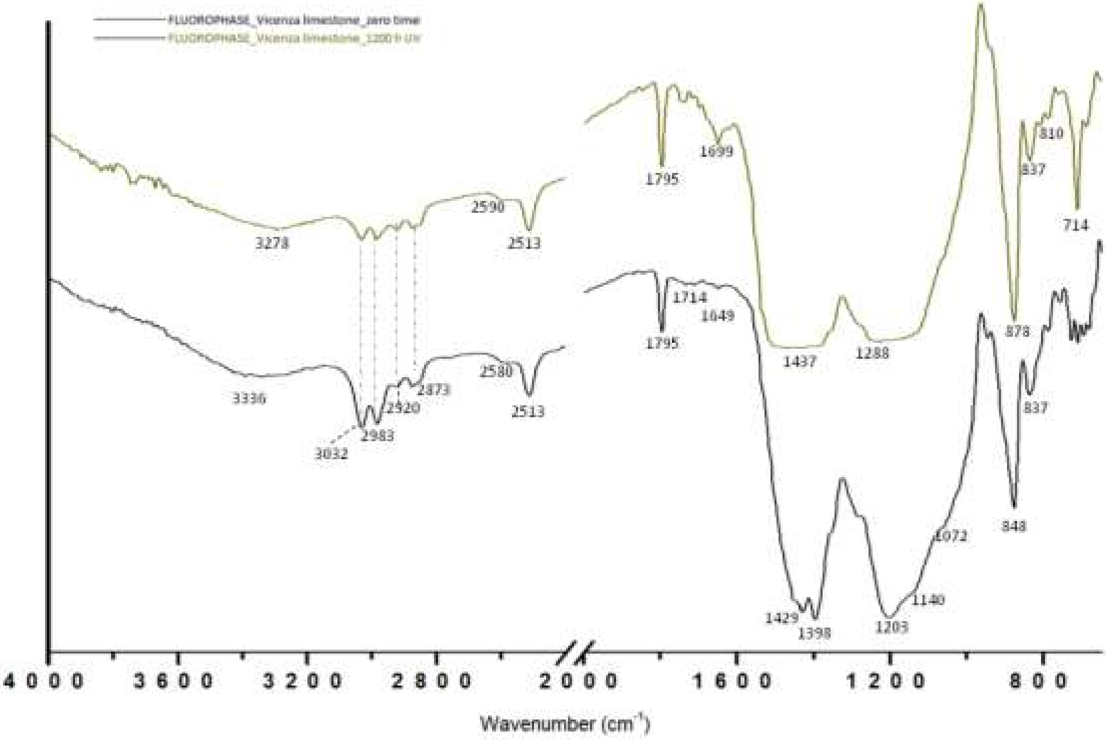


Figure 8.7: *µFTIR of Fluorophase applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line) and after 1200 h of exposure (dark yellow line).*

Chapter 9

Traditional and modern hydrophobic products

9.1 Traditional and modern hydrophobic products

In the past, beeswax, natural oils and, more rarely, animal fats were used as water repellent agents for the protection of stone surfaces. Beeswax is naturally secreted by the intra-abdominal glands of honey bees (*Apis mellifera L.*) and is usually purified by melting and filtering. It is a complex mixture principally composed of esters, saturated hydrocarbons and 12-14% free fatty acids [109-110]. It is slightly soluble in a small range of solvents, increasing considerable with temperature. Although it will turn yellow by ageing, presumably due to the oxidation of the unsaturated components, it can remain soluble over millennia. Today, for the protection of natural stones, microcrystalline waxes have replaced beeswax. They are aliphatic or cycle-aliphatic synthetic hydrocarbons, characterized by long branched chains and microcrystalline structure.

Compared with beeswax, microcrystalline waxes have good chemical stability, good resistance to thermo-oxidation and good hydrophobicity, the melting point is higher than that of beeswax and it is necessary to use aromatic or chlorate solvents to remove them [111].

For this latter reason, before the application of microcrystalline wax, the artifact must be heated. This is an operative complication which limits the use of microcrystalline waxes to only small artefacts. In recent decades, they were applied for the protection of the statue of St. Christopher in the church of the Madonna dell'Orto in Venice [112], or more often mixed with acrylic or siloxane resins [113-114], as for example for the restoration of the sepulcher of P. Ferrici cardinal in the church of S. Maria sopra Minerva in Rome [115].

Linseed oil is one of the most widely used drying oils in paint formulation, and is also used in restoration for the protection of stone surfaces. By oxidative cross-linking polymerization, it can form a water-repellent film with excellent optical and mechanical properties. Drying oils are natural triglycerides containing high percentage of polyunsaturated fatty acids that impart air drying properties to these oils. These polyunsaturated fatty acids readily oxidize to form a three-dimensional network [116].

When, exposed as a thin film, drying oils progressively adsorb, a significant amount of oxygen (20-30% of its weight) reacting with it in a oxidative chemical reaction to produce peroxide compounds [117]. The first step of oxidation involves hydrogen abstraction on a methylene group between two double bonds in polyunsaturated fatty acid chain [118-119].

Oxidation has been related to the presence of double bonds, and the first phase was thought to consist of the formation of either hydroperoxides [120] or cyclic peroxides [121].

In the early stages of auto-oxydation, volatile degradation products, e.g. carboxylic acids, aldehydes and carbon dioxide, are formed. The polymerization process essentially consists of the intermolecular coupling of radicals originating from the decomposition of the relatively unstable peroxide groups, with formation of cross-linked structures [122].

As a consequence, there is an increase of viscosity and alteration of the refraction index. A film of linseed oil becomes touch-dry in a few days but the drying reaction continues for many years and, as cross-linking proceeds, a progressive hardening occurs.

Linseed oil has good physical properties, such as a good resistance, cohesion and elasticity, but through degradation it suffers yellowing of the polymeric film. Yellowing occurs through oxidation in the dark or under low illumination. The yellowing can be bleached by sunlight and oxidizing agents, and can reappear in dark conditions as conjugated double bonds are created by oxidation. As soon as it is applied on a surface, linseed oil film is completely apolar and water-repellent but, with time, oxidative and hydrolytic processes cause the partial breaking of the reticular mail of the polymer, and the formation of carboxylic or oxydrilic terminal groups, which have great hydrophilic properties and make the film more sensitive to water. The film becomes much more polar and brittle from increased cross-linking [118].

In some cases of the conservation of stone materials, linseed oil and microcrystalline wax were used together in order to increase the water repellent effect and decrease the yellowing of the stone surface.

9.2 Laboratory tests

Linseed oil, as a traditional treatment, and microcrystalline wax, as a modern substitute for the bees wax used in the past, were tested in this study, both singly and together.

The treatment of Carrara marble and Vicenza limestone specimens was carried out using a brush until the substrate no longer accepted liquid. Three samples were treated for each product and three other samples were prepared by impregnation with oil and protected with microcrystalline wax. To allow application on the stones, microcrystalline wax was melted without solvent, and the surfaces of the specimens were heated.

After application of the products, the samples were maintained at room temperature until they were completely dried (15 days).

Macroscopically, as soon as the product dried, the specimens treated with linseed oil showed a yellowing of the surface noticeable to the naked-eye, whereas the aspect of the samples treated with microcrystalline wax looked unaltered.

Microscopically the oil was recognizable on the surfaces as light-yellow, small and bright crystals between calcite grains, while wax completely covered the stone surfaces and filled the superficial pores forming a white homogeneous patina. The specimens treated with linseed oil and protected with microcrystalline wax showed both characteristics, with observations showing a yellowing of the surface weakened by the presence of the wax on the surface (figure 9.1-2).

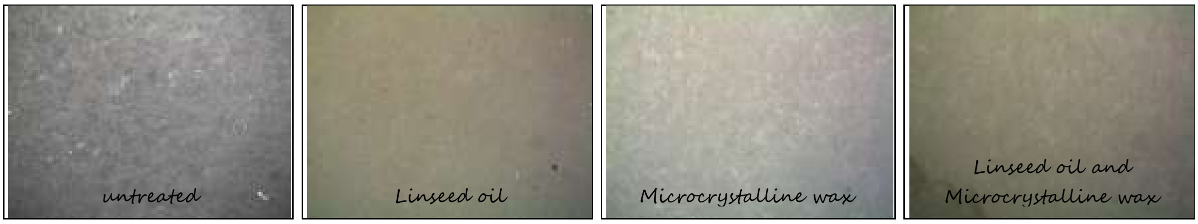


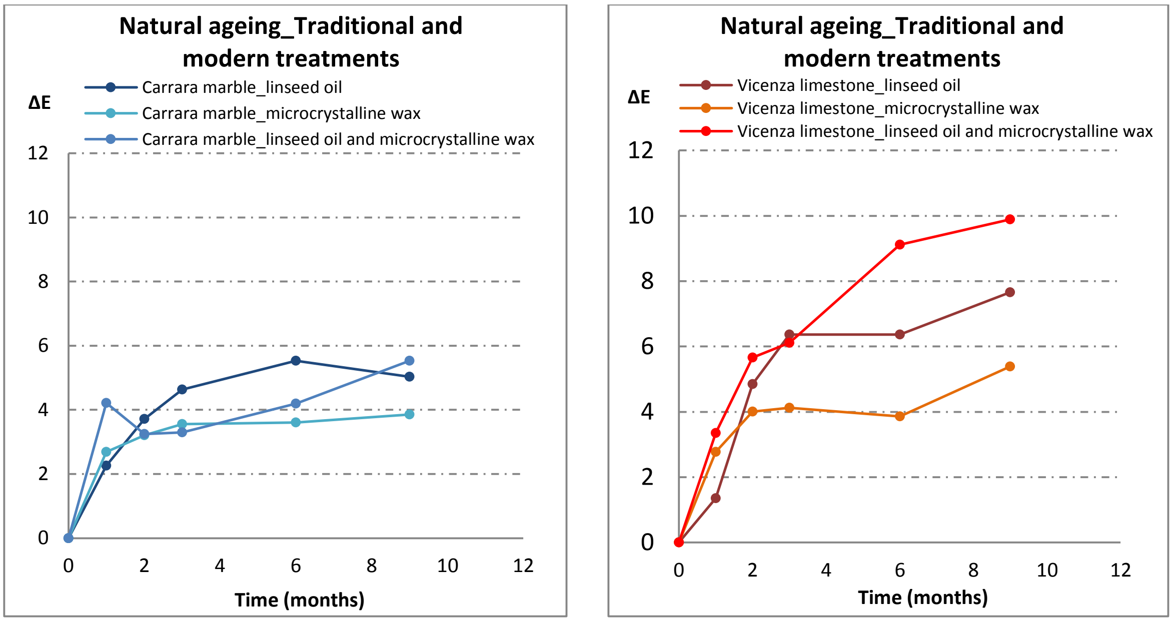
Figure 9.1: *Micrographs of Carrara marble samples untreated, treated with linseed oil, microcrystalline wax, and linseed oil-microcrystalline wax at zero time. Long side images 6.78 mm.*

Figure 9.2: *Micrographs of Vicenza limestone samples untreated, treated with linseed oil, microcrystalline wax, and linseed oil-microcrystalline wax at zero time. Long side images 6.78 mm.*

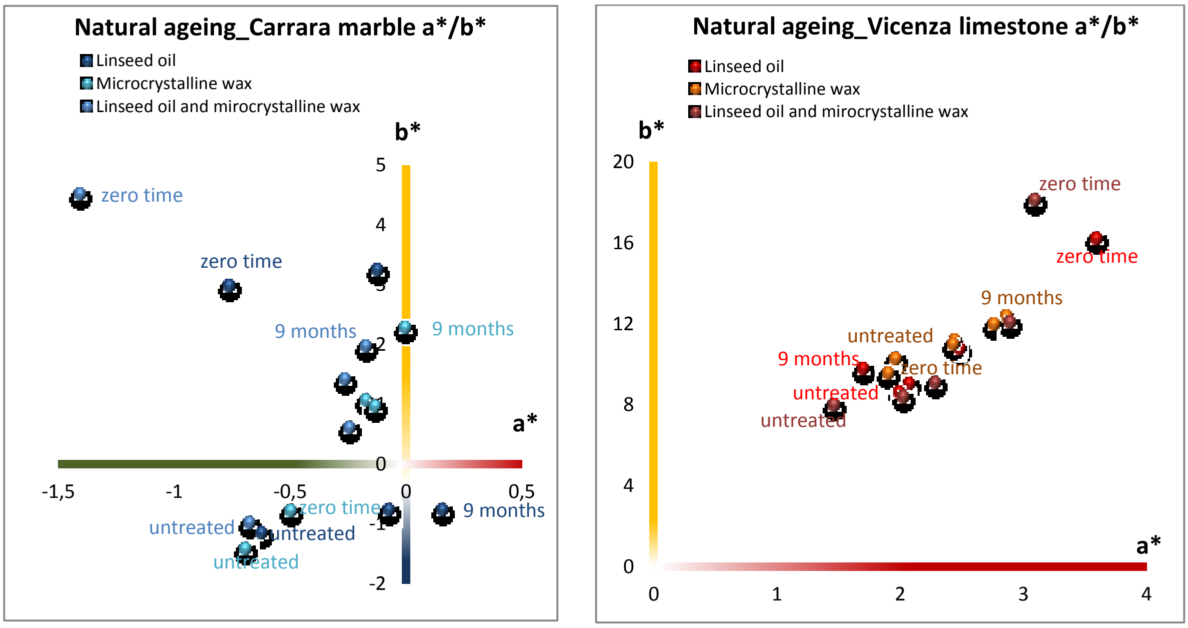
The specimens exposed to outdoor conditions for a year showed, from the first month, the presence of fungi on the treated surfaces, especially in the case of linseed oil. The cured oil formed an inhomogeneous superficial layer on the Carrara surface, which showed a diffuse craquelure and a brownish of the film from the third month. Nevertheless, it remained glossy throughout the exposure time. In the case of Vicenza limestone, oil did not form a compact layer but a whitening of the surface was observed with time. On the other hand, samples protected by microcrystalline wax, showed the presence of a thin, white and light-yellow, opaque and inhomogeneous film. Many particles were deposited on the surface and some black fungi were observed. The samples which were treated with linseed oil and microcrystalline wax showed a chromatic alteration of the surfaces which became darker.

Colour changes of the surfaces were confirmed by the spectrophotometric results.

In particular, linseed oil showed greater colour changing than microcrystalline wax, graph 9.1. From the colour graphs (graph 9.2), it is possible to observe a gradual yellowing of the surfaces treated with microcrystalline wax, whereas those treated with linseed oil and both linseed oil and microcrystalline wax, showed an initial yellowing and a following coming back to the untreated value.



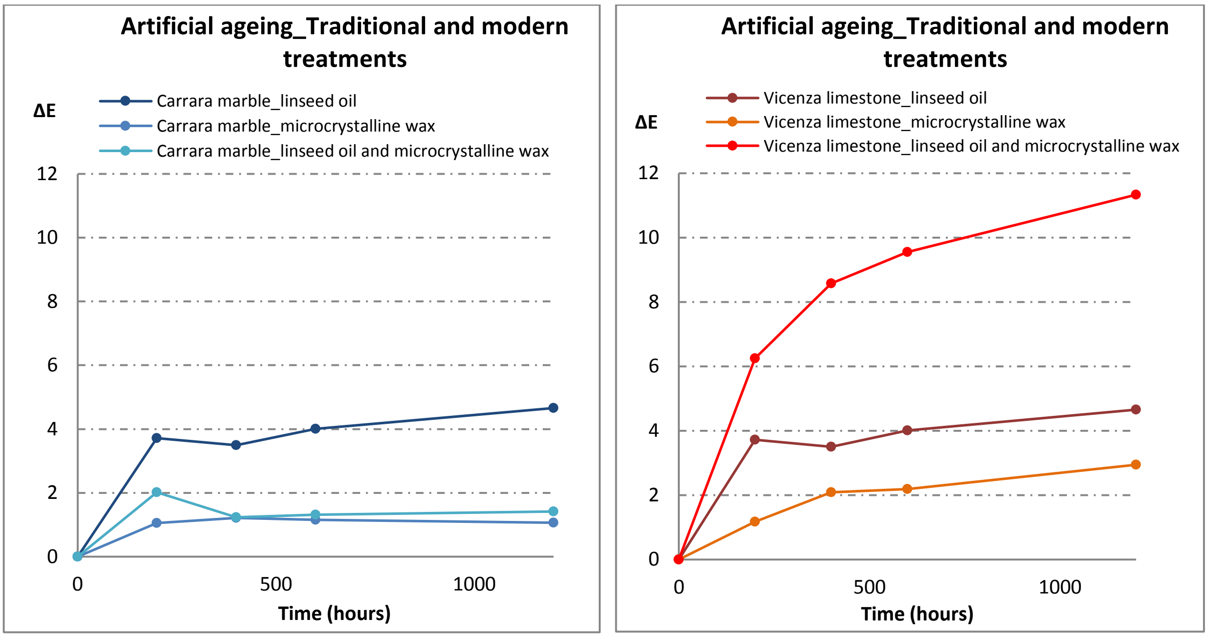
Graph 9.1: *Trend of colour change of surfaces treated with linseed oil (dark blue), microcrystalline wax (light blue) and both linseed oil and microcrystalline wax (blue) during exposure to outdoor conditions.*



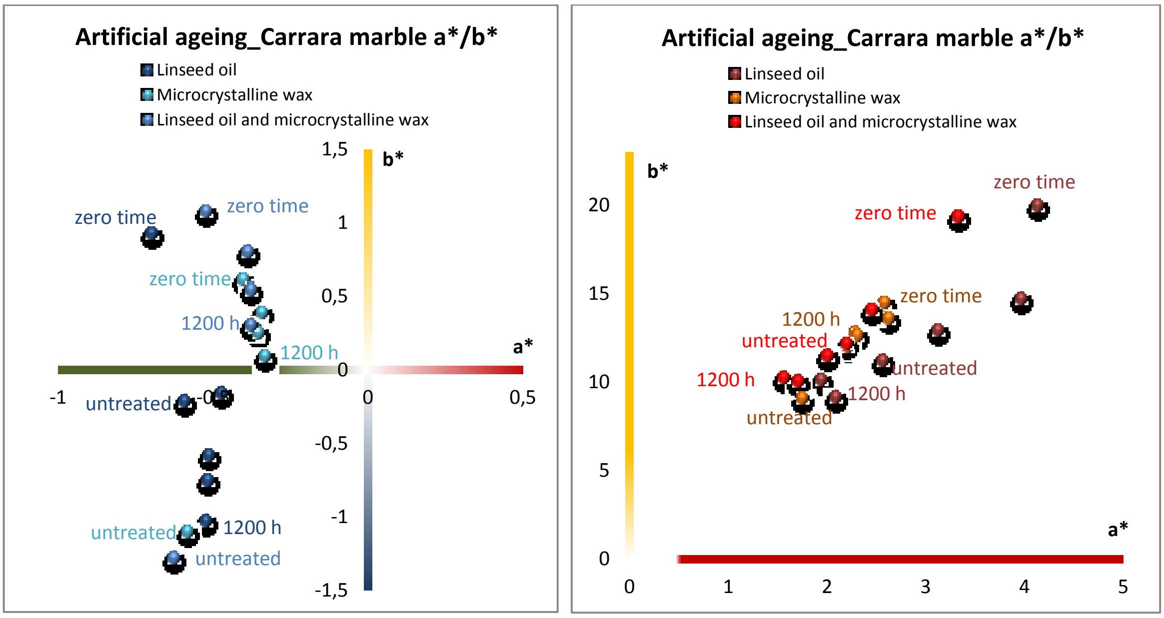
Graph 9.2: *Chroma and tone variation calculated by a* and b* experimental value. Natural ageing*.

The results obtained from the colorimetric variations by samples exposed to outdoor condition, are directly comparable with those obtained during exposure to UV rays. The trend of the lines as well as the values measured are comparable with each other (graph 9.3).

However, in this case, all samples showed a chromatic variation towards blue and green tones (graph 9.4).

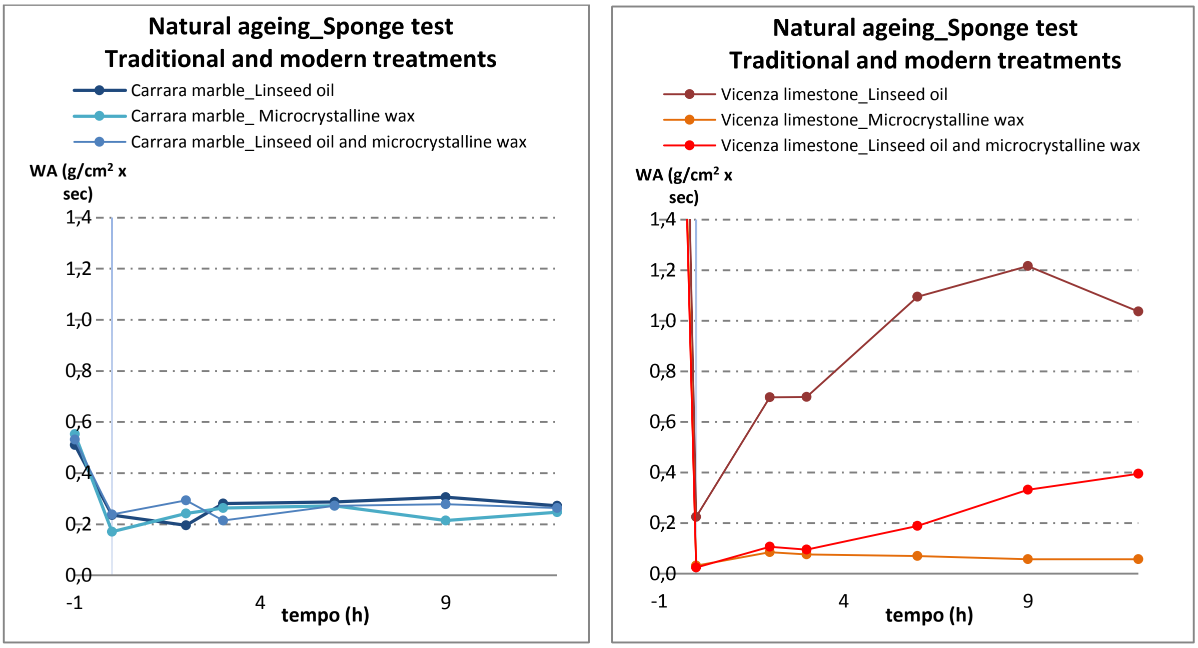


Graph 9.3: *Trend of colour change of surfaces treated with linseed oil (dark blue), microcrystalline wax (light blue) and both linseed oil and microcrystalline wax (blue) during exposure to UV radiations.*

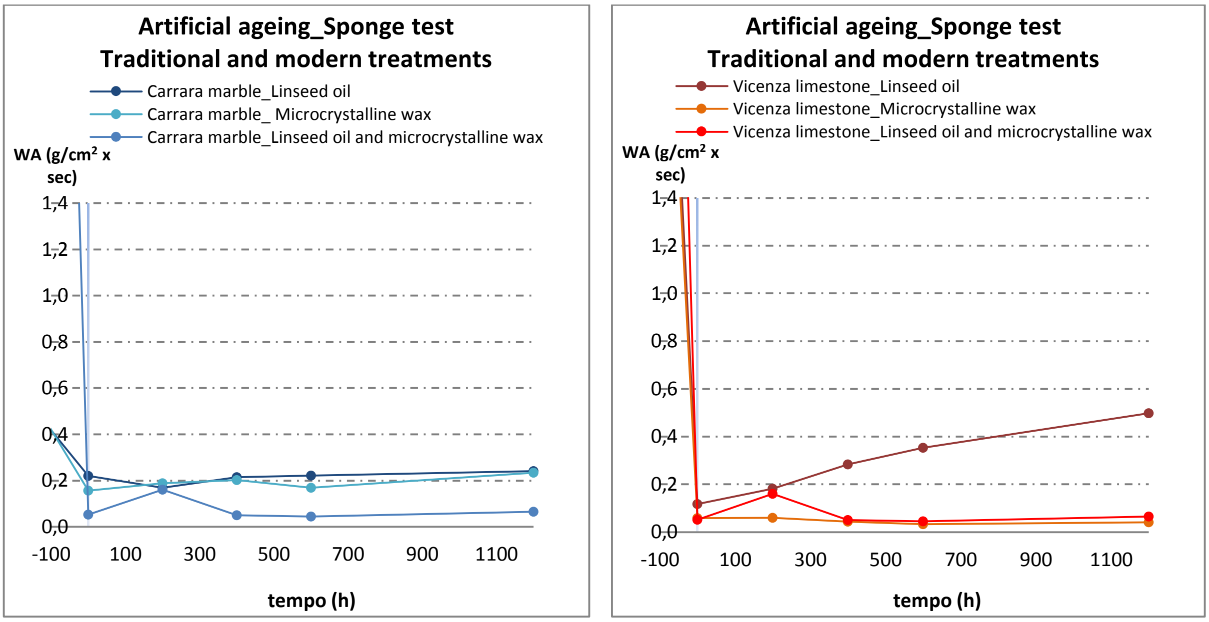


Graph 9.4: *Chroma and tone variation calculated by a* and b* experimental value. Artificial ageing.*

All treatments applied on stone surfaces conferred higher hydrophobicity to the stone. In fact, due to their apolar chemical nature, both linseed oil and microcrystalline wax are particularly water-repellent. The treated samples acquired a comparable value of water absorption each other, which in case of microcrystalline wax tends to be stable during the ageing processes. Linseed oil applied on Vicenza limestone and exposed to outdoor conditions and UV radiations, lost its initial hydrophobicity value and increased the amount of water adsorbed through time (graph 9.5 and 9.6).



Graph 9.5: *Water absorption variation during outdoor exposure*



Graph 9.6: *Water absorption variation during exposure to UV radiation.*

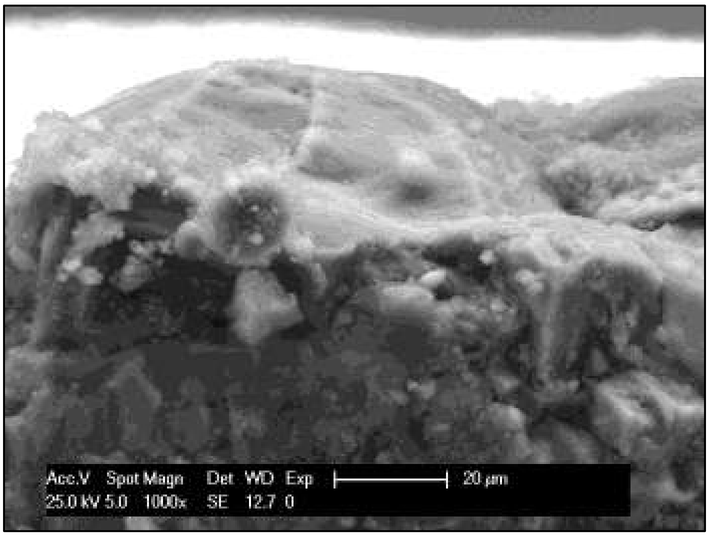


Figure 9.3: *SEM micrograph of the cross-section of C10 specimen.*

Studying the cross section of the treated samples after 12 months of outdoor exposure with SEM by secondary electrons, it is possible to observe the presence of a continuous, homogeneous patina which completely covered the surface and filled the holes. This morphological feature of the film may have supported the water repellent effect.

The chemical stability of microcrystalline wax was examined through µFTIR analysis.

During monitoring of both natural and artificial ageing, no particular modification of the spectrum was observed. The characteristic peaks of wax can be recognized by the ν C-H of CH_2 bonds, which gives strong and narrow bands at 2918 and 2848 cm^{-1} and a small band at 2956 cm^{-1} due to the methyl group CH_3, sharp doublets at 1462 and 1423 cm^{-1} related to CH_2 bending vibrations and rocking at 714 cm^{-1}. The resin also has ester groups, which are indicated by the ν C=O at 1736 cm^{-1}, the ν C-O at 1130 and 1053 cm^{-1}. For convenience, in this research, the monitoring of microcrystalline wax applied on Carrara marble and exposed to outdoor condition for 12 months and on Vicenza limestone and exposed to artificial ageing, as representative of the experiments are shown, in figure 9.4 and 9.5. In table 9.1 the assignments of the main peaks are summarized.

Wavenumber (cm^{-1})	*Functional groups*	*Assignments*
3420	*ν O-H*	*Hydroxyl groups*
2974, 2918, 2848	*ν C-H*	*Aliphatic bonds*
1736-1718	*ν C=O*	*Carbonyl groups in ester*
1462	*δas C-H*	*CH_2*
1423	*δas C-H*	
1377	*δs CH_3*	*COOR in EMA*
1130	*νas C-O*	*Ester*
1053	*ν O-C-C*	
714	*ρ C-H*	*Methylene groups*

Table 9.1: *FTIR assignments of the main peaks observed for examined microcrystalline wax.*

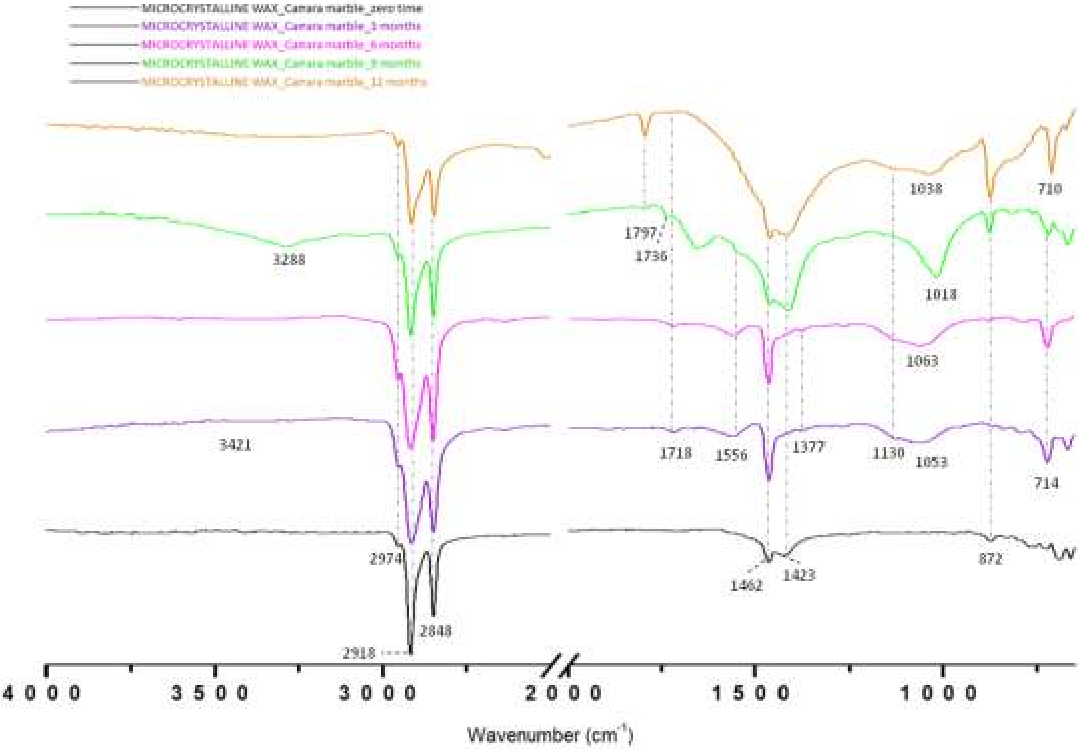


Figure 9.4: *µFTIR of microcrystalline wax applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

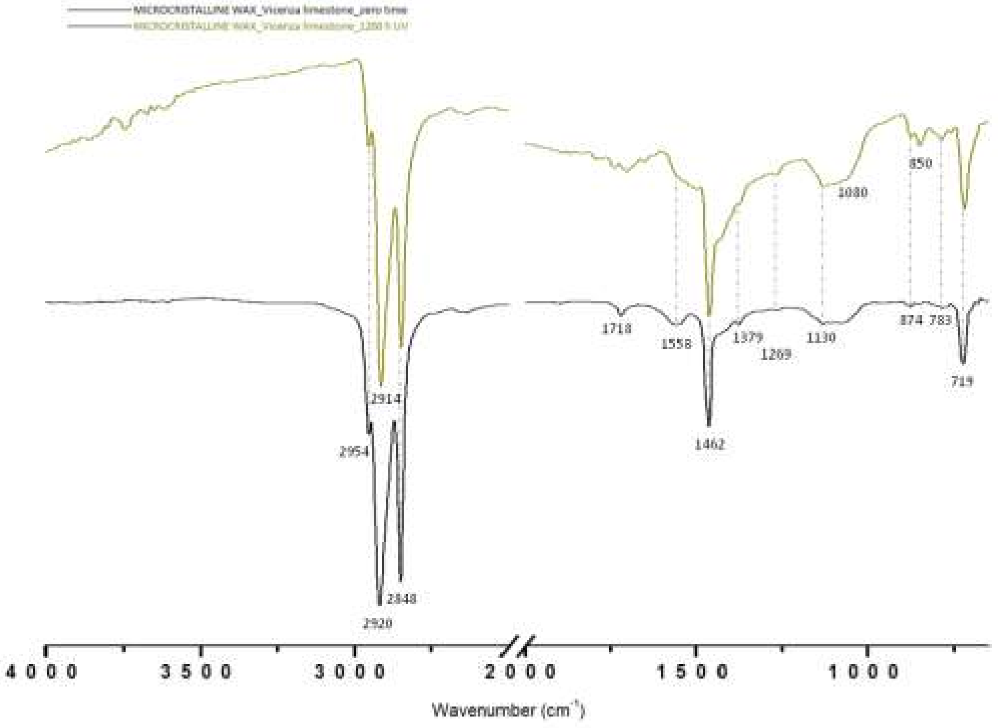


Figure 9.5: *µFTIR of microcrystalline wax applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 hours of exposure (dark yellow line).*

Study of the μFTIR monitoring of linseed oil applied on Vicenza limestone and exposed to natural ageing, allowed the observation of significant modification of the spectrum over time, whereas on Carrara marble no particular alteration was noticed.

In general, in both specimens, observations during the polymerization process (from zero time to 12 months for natural ageing), showed the appearance of a broad band centered at ca. 3430 cm^{-1}, due to the formation of hydroxyl groups, and of weak absorption at 1620 cm^{-1}, related to the formation of conjugated double bond, due to the cross-linking of oil as already explained at the premise of this section.

In particular, in Vicenza limestone, a gradual decrease of ν C=O and the disappearance of all the other characteristic peaks was found, summarized in table 9.2. Figure 9.6 shows that it is possible to observe from the third month only those peaks related to calcium carbonate of the stone substrate (1795, 1430, 870, 713 cm^{-1}).

Linseed oil exposed to UV radiation, applied to either Carrara marble or Vicenza limestone, suffered the same degradation and, in the spectra collected after 1200 hours of exposure, at which time only the peaks related to calcium carbonate are observable.

Wavenumber (cm^{-1})	*Functional groups*	*Assignments*
3421	*ν O-H*	*Hydroxyl groups*
2927, 2856	*ν C-H*	*Aliphatic bonds*
1740	*ν C=O*	*Carbonyl groups in ester*
1620	*Conjugated C=C*	
1564		
1454	δ_{as} *C-H*	
1417	*wag C-H*	
1377	*wag C-H*	
1319	δ_{as} *C-H*	CH_2
1238	ν_{as} *C-C-O*	*Ester*
1167	*ν C-O*	*Ester*
1097	ν_{as} *C-O*	*Ester*
1034	*ν O-C-C*	*Ester*
712	*ρ C-H*	*Methylene groups*

Table 9.2: *FTIR assignments of the main peaks observed for linseed oil.*

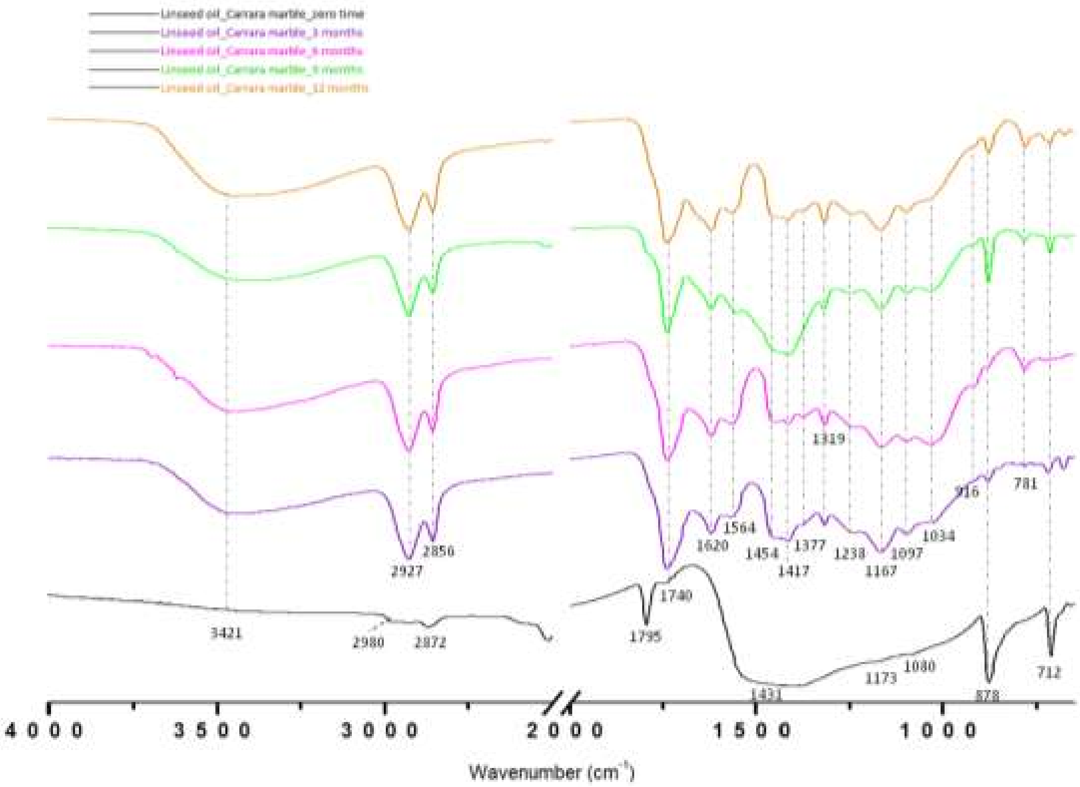


Figure 9.6: *μFTIR of linseed oil applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

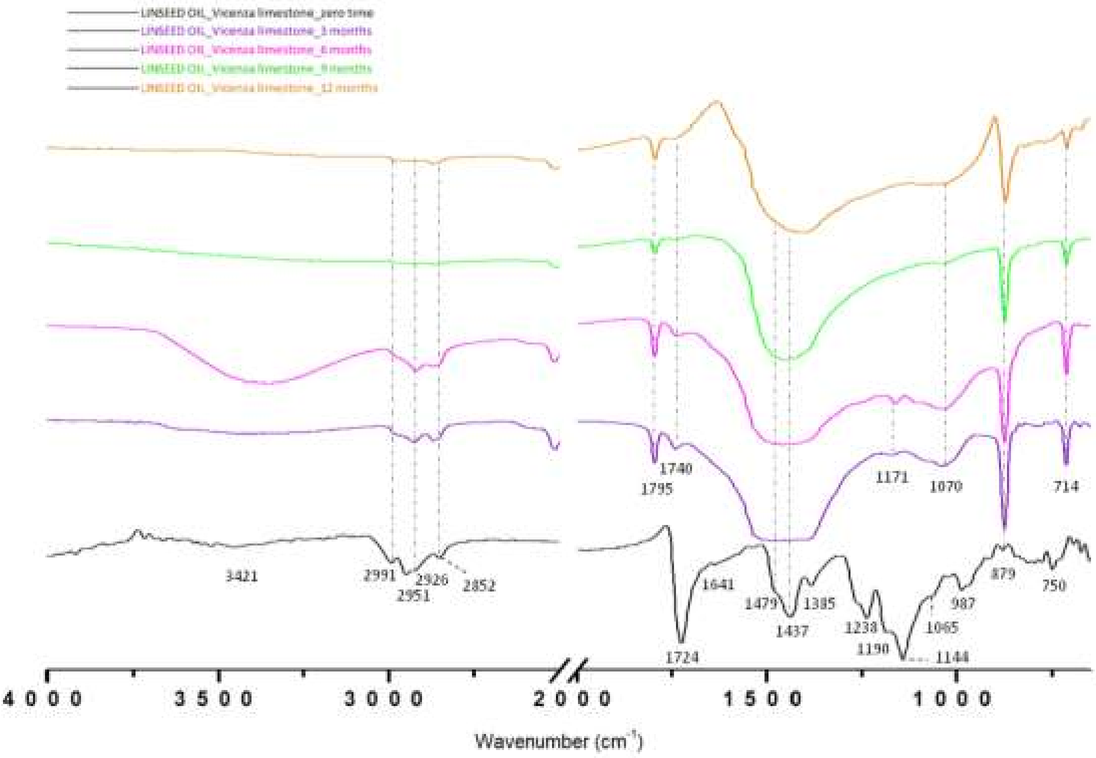


Figure 9.7: *μFTIR of linseed oil applied to Vicenza limestone and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line).*

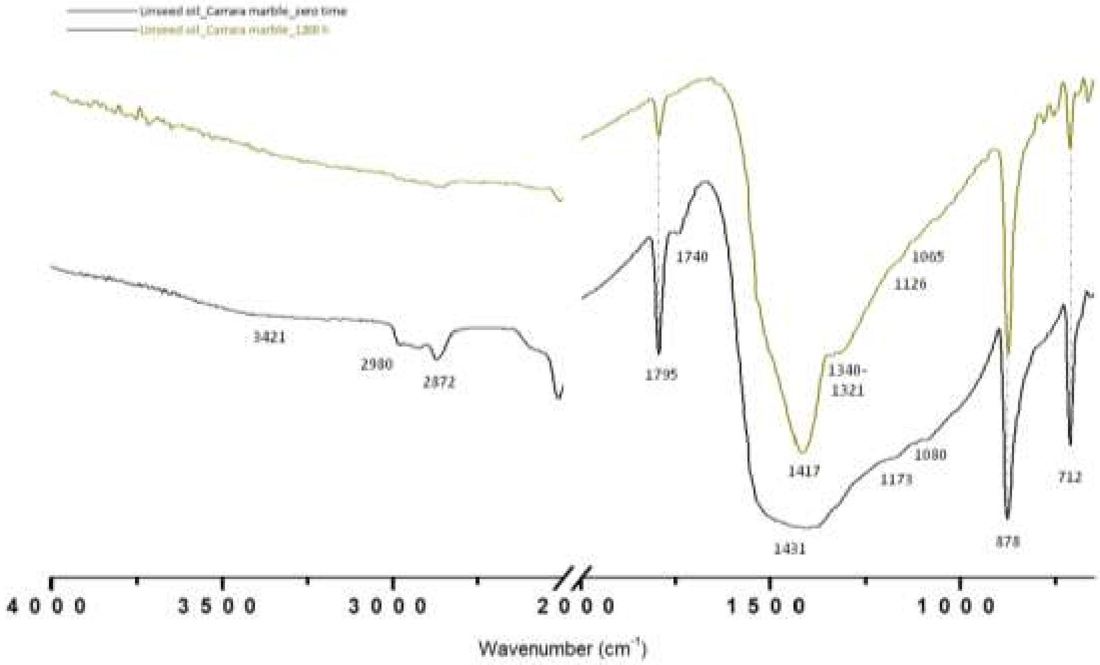


Figure 9.8: *µFTIR of linseed oil applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 hours of exposure (dark yellow line).*

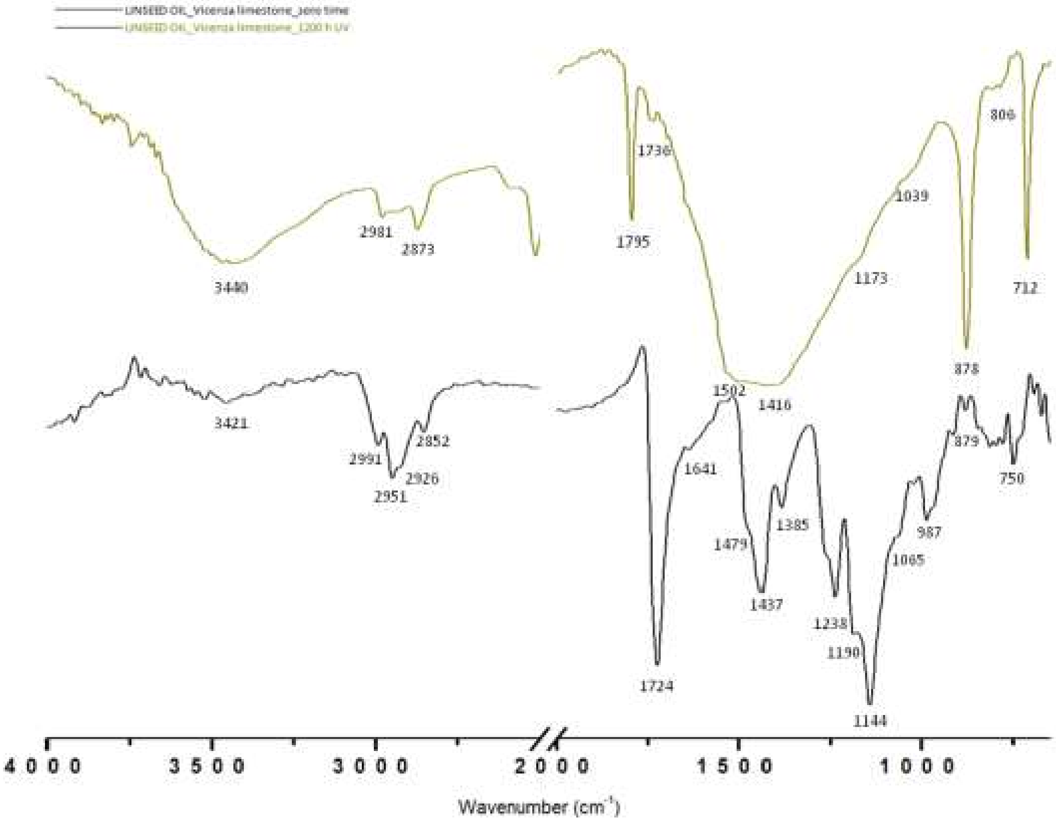


Figure 9.9: *µFTIR of linseed oil applied to Vicenza limestone and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 hours of exposure (dark yellow line).*

The FTIR analysis of the specimens treated using Linseed oil and protect with microcrystalline wax, showed the same variations already observed for the treatment based on Linseed oil.

9.3 Monitoring of past treatments in Venice

- **S. Giorgio Maggiore Church (16th c.) - (S. Giorgio island):** marble base of the High Altar
  Substrate: different kind of marble

PAST RESTORATIONS:
No information was available about past restoration.

SAMPLING:
17.10.2012
Operators: restorer Maxwell Malden (fellowship Venice in Peril)
Number of micro-fragments sampled: 2 samples from different areas of the artifact
2 micro-scales of superficial patina
The sampling was carried out using a scalpel.

Figure 9.10: *High Altar of S. Giorgio Maggiore church.*

Figure 9.11: *Sampling of superficial dark patina from different area oh the High Altar*

MACROSCOPIC OBSERVATIONS:

The fabric of the marble was in sound condition; with no friable areas evident. There was a yellow/brown surface coating evident on some of the panels of coloured marble and steps of pink marble.

The dark coating seen on the marble panel in the right of figure 9.12 was possibly a discoloured oil/wax previously applied to the surface. This was a common 'housekeeping' treatment in the past when a combination of beeswax and linseed oil was used as a polish for marble. The substance has only been applied to the front and the sides of the altar, further suggesting that it was a past surface treatment intended to improve the appearance of the stone for visitors to the church. If this was the nature of the coating, it was likely that the linseed oil has been yellowed over time and the wax had attracted and held dust/dirt. An Ultra Violet lamp was used to analyse the nature of the coating.

The coating appeared thick and waxy to the touch. Drip lines were visible suggesting that it was applied carelessly, thickly and in a liquid form.

Figure 9.12: *Dark coating seen on the marble panel on the right probably a past protective treatment.*

ANALYTICAL RESULTS:

- FTIR ANALYSIS

Samples SG01 and SG02 were analyzed by FTIR in KBr pellet. The spectra in figure 9.13 and figure 9.14 show all the characteristic peaks and typical shape of wax and oil materials spectra.

In particular, the peaks related to CH with the symmetrical stretching at 2922 and 2852 cm^{-1}, the bending at 1462 cm^{-1} and rocking at 723 cm^{-1} are well recognizable as well as those concerning ester group at 1741, 1633, 1163 and 1032 cm^{-1}.

The two spectra are in contrast only for the relative intensity of the bands.

In the case of SG02, the peaks related to wax have higher intensity than those related to oil.

Comparing the spectra obtained with the spectra of Jasco Europe library standard it is considered that the oil used was linseed oil and the wax was not beeswax but a synthetic one, with good correspondence of the main peaks.

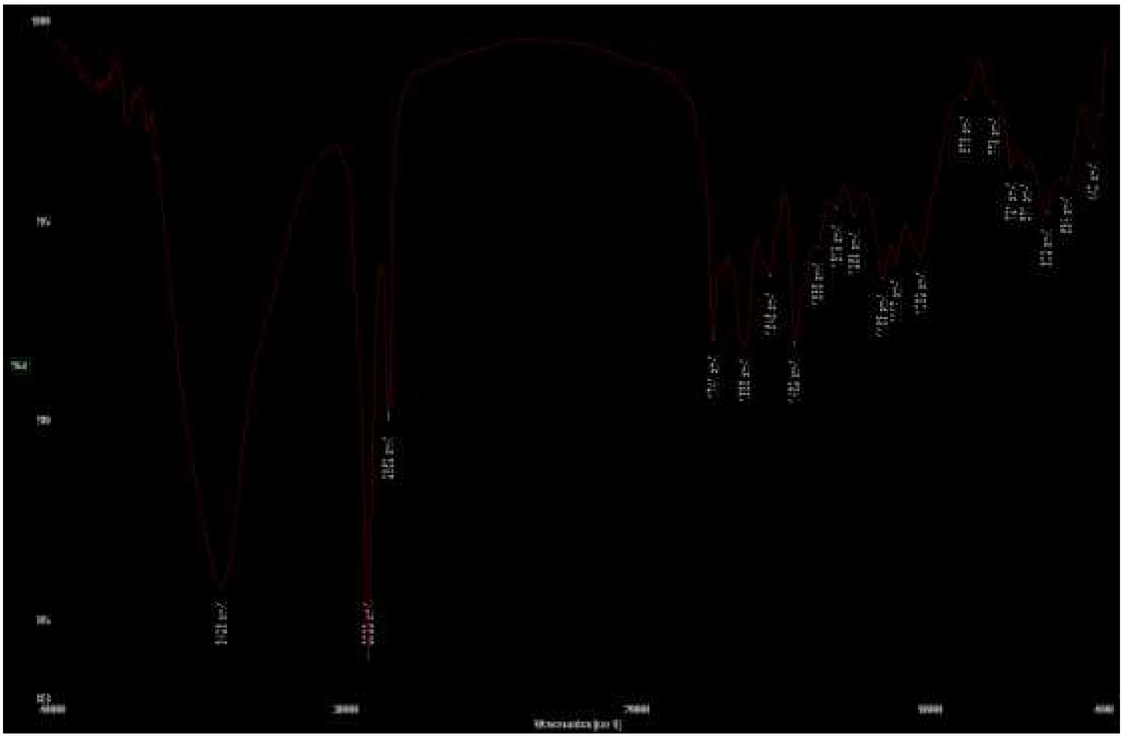


__Figure 9.13:__ FTIR spectrum of SG01 micro-fragment.

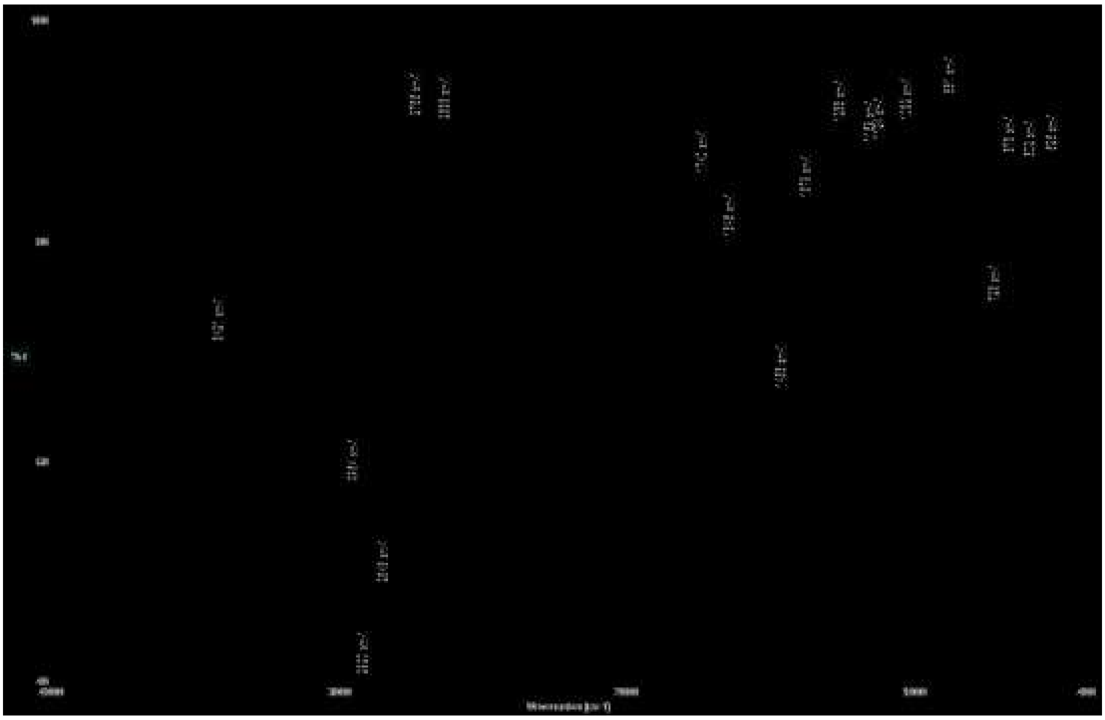


__Figure 9.14:__ FTIR spectrum of SG02 micro fragment.

9.4 References

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Chapter 10

Resistance of coatings to growth of mould

Exposed to the same conditions, the treated specimens showed a different resistance to growth of mould, which have been summarized in table 10.1.

The colonization increased steadily with time. Most of the treated samples showed an increase in the microbial flora in comparison with the untreated ones. The stone samples gave different results, probably depending on solvents, additives, or polymer resistance to biological attack. Carrara marble and Vicenza limestone samples, treated with the same protective or consolidant showed similar results.

Regarding the bioreceptivity of the coatings, the following considerations come out.

Epoxy resin as well as Hydrophase and microcrystalline wax samples inhibits the microbiological growth to the same degree as was found in the untreated samples. Acrylic resins, in particular Acrylic 33, and fluorinate products showed the lowest resistance to growth of mould. High receptivity was demonstrated also by PF3 and linseed oil. Silicone resins based on TEOS showed a moderate biological colonization on treated stone surfaces.

Specific treatments	***Carrara marble***	***Vicenza limestone***
Untreated samples	*1s*	*1*
$Ba(OH)_2$	*2s*	*4s*
EAS 40	*3s*	*2s*
RC90	*3s*	*3s*
RC80	*2s*	*2s*
H 224	*3s*	*1*
Hydrophase	*1s*	*1*
PF3	*3s*	*4s*
Paraloid B-72	*4s*	*2s*
Acrylic 33	*4s*	*3s*
EP2101	*1s*	*1*
Fluorophase	*4s*	*4s*
Linseed oil	*4s*	*3s*
Microcrystalline wax	*2s*	*1*
Linseed oil + microcrystalline wax	*3s*	*3s*

Table 10.1: *global evaluation of biological colonization in treated samples. 1 = 20%, 2 = 40%, 3 = 60%, 4 = 80%, 5 = 100%. S = presence of spores*

In order to study a possible correlation between fungi and the chemical nature of colonized coatings and assuming a selective bio-removal, the microorganisms were studied in detail by optical microscope and SEM.

Since not all the fungi were identified, it was not possible to find a correlation between the biological colonization and the nature of the treatment applied. However, Dematiaceous fungi, with sporularion clearly visible, are dominant, being represented by *Alternaria, Cladosporium* and *Aspergillus* genera. The microscopic observation and the micrographs collected for the main microorganism studied, are reported below.

For each one the coating in which the fungi grew are summarized.

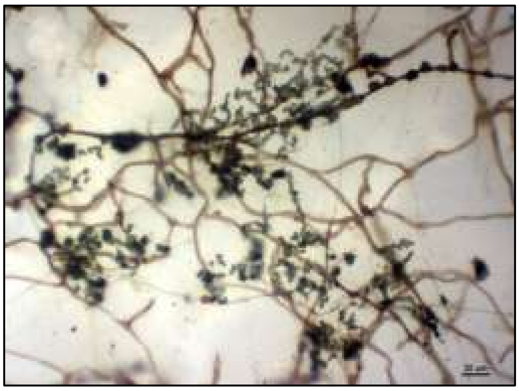
1. Hypothesis: _Alternaria alternata_

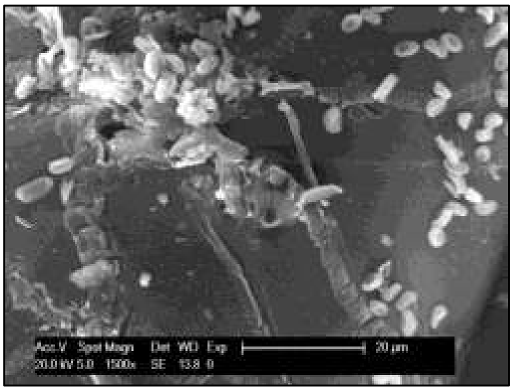
All the treated and untreated specimens:

Acrylic resins: *Paraloid B-72 – Acrylic 33; epoxy resin: EP2101; silicon based compounds: Rhodorsil RC90 - Rhodorsil RC80 – EAS 40 – Rhodorsil H 224 - Hydrophase*; nano-particle compounds: *PF3*; inorganic treatment: *Ba(OH)₂*; fluorinate products: *Fluorophase;* Traditional and modern treatments: *Linseed oil – microcrystalline wax – Linseed oil and microcrystalline wax*; untreated samples.

2. *Hypothesis:* _Penicillium Spp._

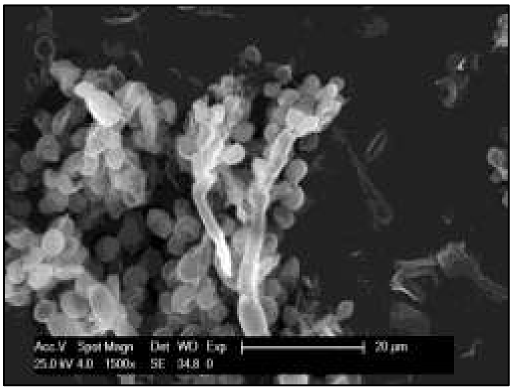
Acrylic resins: *Paraloid B-72*; inorganic treatment: *Ba(OH)₂*; nano-particle compounds: *PF3*; fluorinate products: *Fluorophase*.





3. *Hypothesis:* Cladosporium Spp.

Acrylic resins: *Paraloid B-72*

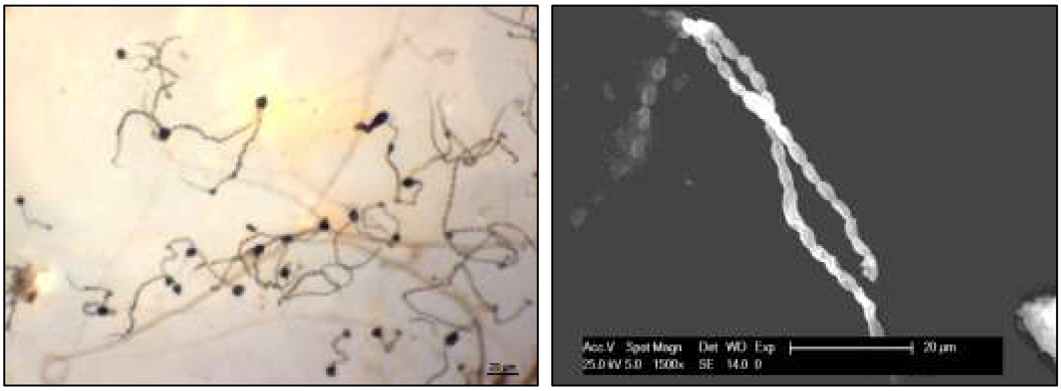


4. *Hypothesis:* Cladosporium oxysporum

Epoxy resin: *EP2101*; silicon based compounds: *Rhodorsil RC90 - EAS 40*; fluorinate products: *Fluorophase*; traditional and modern treatments: *microcrystalline wax.*

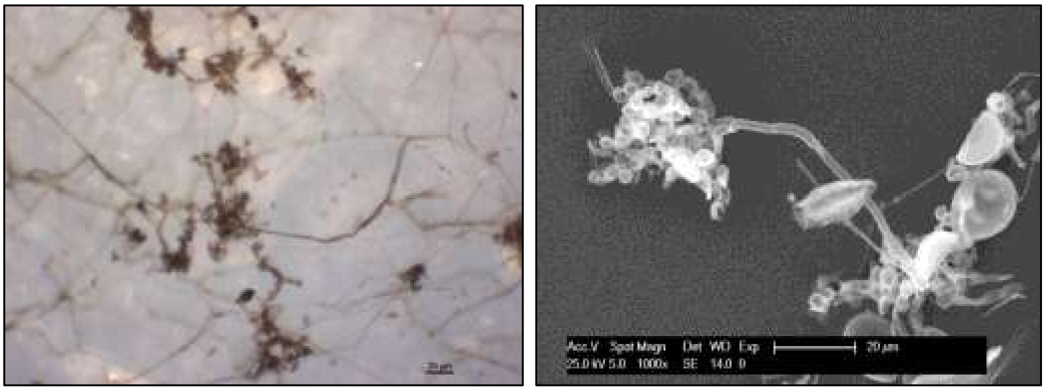
5. *Hypothesis: Cladosporium Spp.*

Inorganic treatment: $Ba(OH)_2$



6. *Hypothesis: Cladosporium Spp.*

Nano-compounds: *PF3*

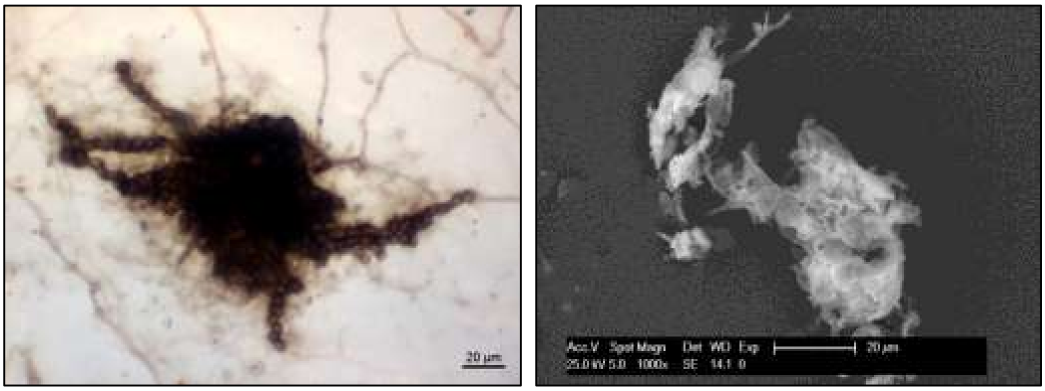


7. Hypothesis: *Cladosporium Spp.*

Silicon based compounds: *Rhodorsil H 224*

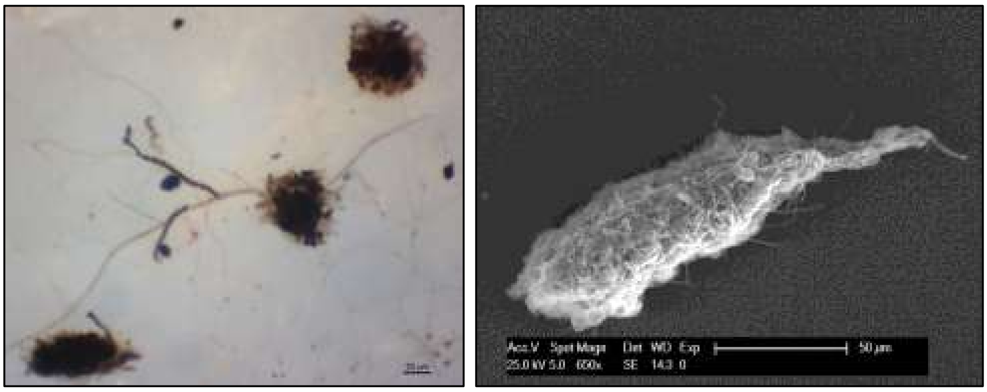
8. Hypothesis: *Chaetomium Spp.*

Epoxy resin: *EP2101*; inorganic treatment: *$Ba(OH)_2$*; Traditional and moden treatments: *Linseed oil and microcristalline wax.*



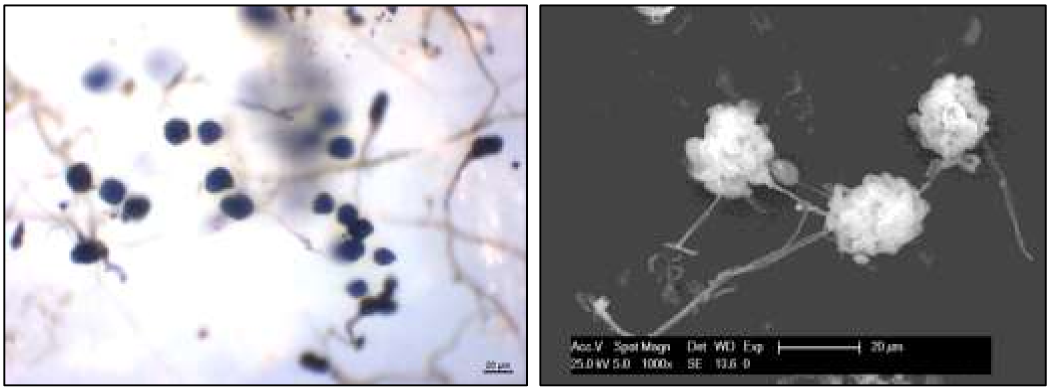
9. Hypothesis: *Chaetomium Sp.*

Acrylic resins: *Acrylic 33*; silicon based compounds: *Rhodorsil RC90 - Rhodorsil RC80 – Rhodorsil H 224 - Hydrophase*; inorganic treatment: *Ba(OH)*$_2$; fluorinate products: *Fluorophase*; Traditional and modern treatments: *Linseed oil and microcrystalline wax*.



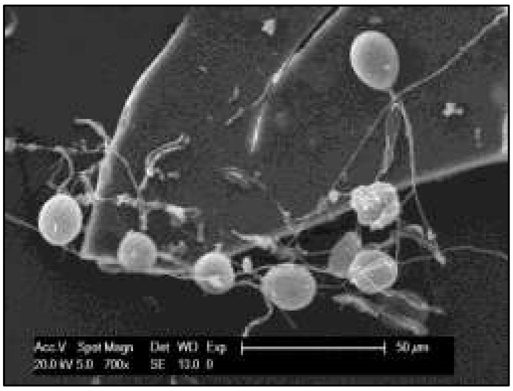
10. Hypothesis: *Aspergillus Niger*

Silicon based compounds: *EAS 40*; Traditional and modern treatments: *linseed oil and microcrystalline*; untreated sample.



11. Hypothesis: *Memnoniella Sp.*

Silicon based compounds: *Rhodorsil RC90 - Rhodorsil RC80 – EAS 40 - Hydrophase*; nano-compounds: *PF3*; inorganic treatment: *Ba(OH)₂*; Traditional and modern treatments: *Linseed oil – microcrystalline wax.*

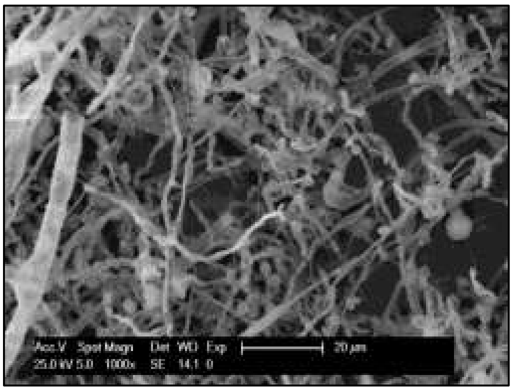


12. Hypothesis: not yet identified

    Acrylic resins: *Paraloid B-72*; silicon based compounds: *Rhodorsil RC90 - Rhodorsil RC80 – EAS 40 – Rhodorsil H 224 - Hydrophase*; Traditional and modern treatments: *microcrystalline wax.*

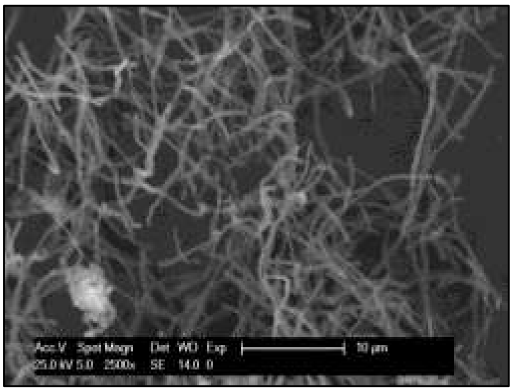
13. Hypothesis: not yet identified

    Silicon based compounds: *Rhodorsil RC90 - Rhodorsil RC80 – EAS 40 – Rhodorsil H 224 - Hydrophase*; nano-compounds: *PF3*; fluorinate products: *Fluorophase*; Traditional and modern treatments: *Linseed oil –Linseed oil and microcrystalline wax*.



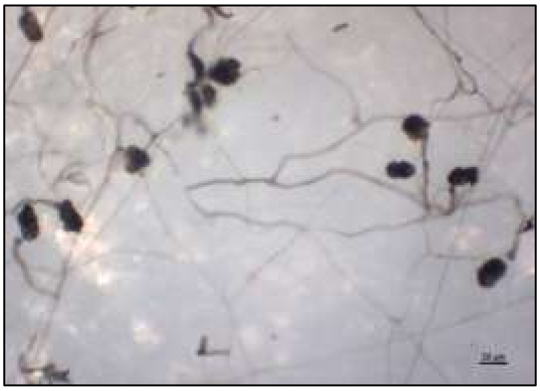
14. *Hypothesis:* not yet identified

    Inorganic treatment: *Ba(OH)$_2$*; fluorinate products: *Fluorophase*; traditional and modern treatments: *Linseed oil and microcrystalline wax.*



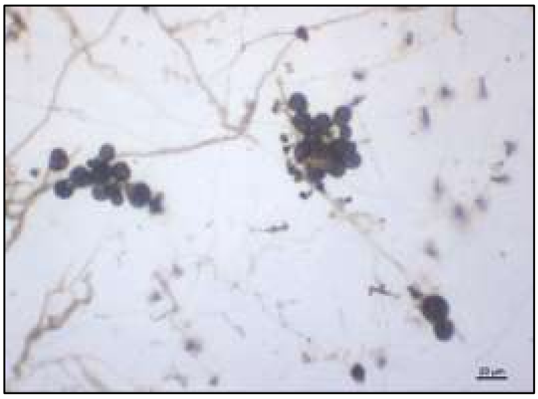
15. *Hypothesis:* not yet identified

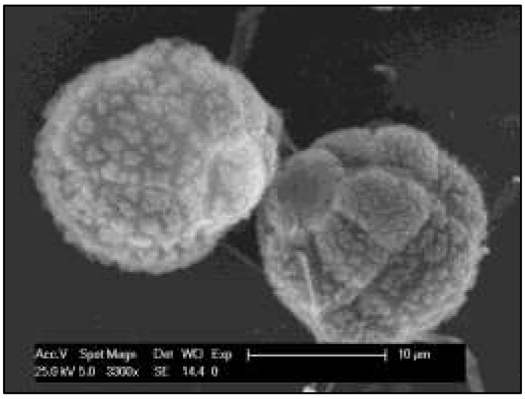
    Acrylic resins: *Acrylic 33; S*ilicon based compounds: *Rhodorsil RC90 - Rhodorsil H 224 - Hydrophase*; nano-compounds: *PF3*; fluorinate products: *Fluorophase*; Traditional and modern treatments: *Linseed oil –Microcrystalline wax.*



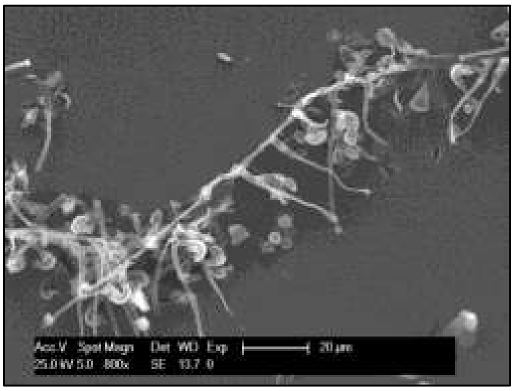
16. *Hypothesis:* not yet identified

Acrylic resins: *Acrylic 33*; Silicon based compounds: *Rhodorsil RC90 – EAS 40*; nano-compounds: *PF3*; Traditional and modern treatments: *Linseed oil –Linseed oil and microcrystalline wax*; untreated samples.

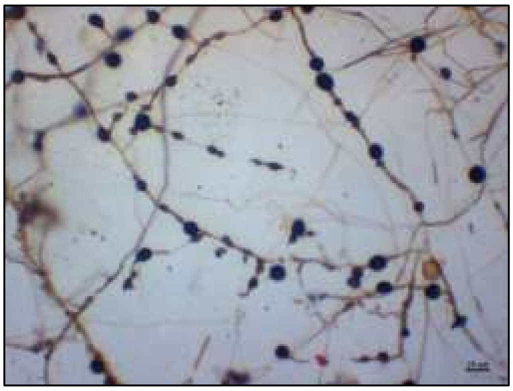




17. Hypothesis: not yet identified
    Silicon based compounds: *Rhodorsil RC80*

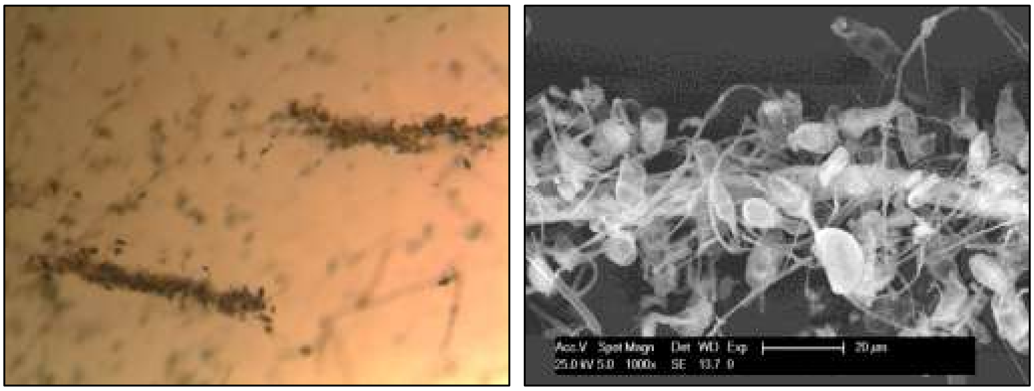


18. Hypothesis: not yet identified
    Silicon based compounds: *EAS 40*



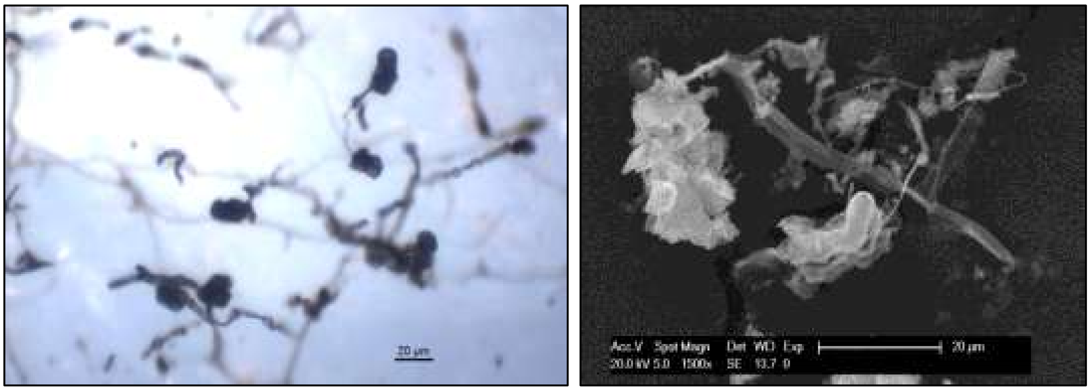
19. Hypothesis: not yet identified

Silicon based compounds: *EAS 40*



20. Hypothesis: not yet identified

Acrylic resins: *Acrylic 33;* Traditional and modern treatments: *m*icrocrystalline wax.



Due to difficulties which emerged from the identification of the fungi, two different culture media were prepared in the laboratory with the same procedure: Difco^{TM} Mycological agar and Gelose Rose Bengale chloramphenical agar, in order to obtain more information about their nature from the aspect and the morphology of the fungal colonies. However, Aspergillus was the only genera of fungi which grew on culture media. Consequently, the media chosen were unsuitable for the fungi developed on the specimens and the results obtained unsatisfactory to the aim of the research.

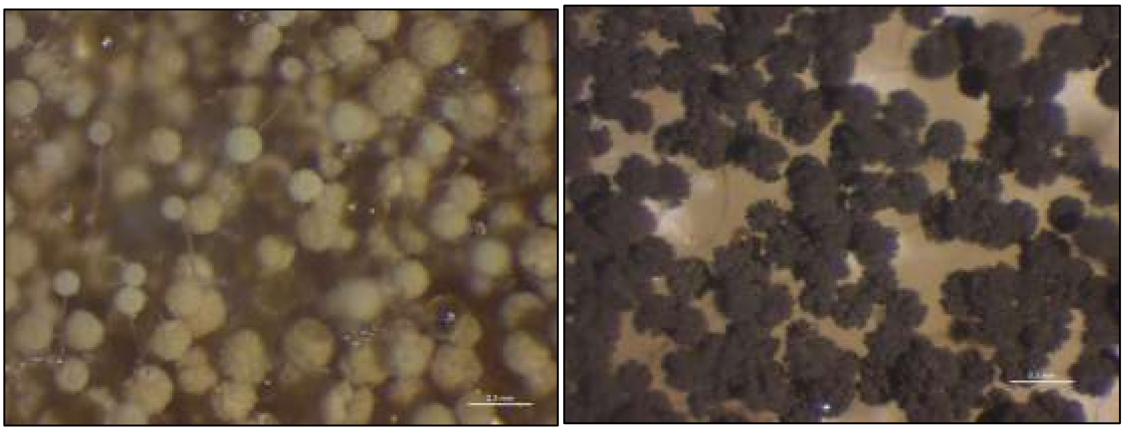


Figure 10.1: *Aspergillus ssp. on culture media of Agar*

Chapter 11

Conclusions

From the results obtained from the analytical study of different classes of inorganic and organic products widely used for the conservation of stone materials, it is possible to make the following considerations.

11.1 Inorganic compounds:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	Barium Hydroxide	No penetration Superficial whitening $\Delta E_{\text{untreated-0 time}} = 3.11$ $\Delta E_{\text{0-12 months}} = 2.96$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.180 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.422 Formation of a mixed carbonate, made of Calcium and Barium, and having an acicular shape. Secondary products: Barium sulphate UV rays= no effects Resistance to growth of mould:2s
Vicenza limestone *Laboratory specimen*	Barium Hydroxide	Penetration depth: 1 cm Superficial whitening $\Delta E_{\text{untreated-0 time}} = 4.44$ $\Delta E_{\text{0-12 months}} = 3.48$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 1.074 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 2.109 Formation of a mixed carbonate, made of Calcium and Barium, and having an acicular shape. Secondary products: Barium sulphate UV rays= no effects Resistance to growth of mould:4s
Carrara marble *Font in S. Fantin church*	Barium Hydroxide, urea and glycerine	Absence of barium (carbonate or sulphate) on the stone surface and in its pores.
Lumachella del Tasso *Column in Scuola di S. Giovanni Evangelista*	Barium Hydroxide, urea and glycerine	Penetration depth: 250 µm Secondary products: Barium sulphate Formation of a mixed carbonate, made of Calcium and Barium, and having an acicular shape.
Vicenza limestone *Laboratory specimens*	Barium Hydroxide	Penetration depth: greater than 3 mm Formation of a mixed carbonate, made of Calcium and Barium, and having an acicular shape.

Table 11.1: *summarizing table of Inorganic compounds results.*

The application of barium hydroxides to both Carrara marble and Vicenza limestone showed a whitening of the treated surfaces, visible to the naked-eye and confirmed by colour graph. Microscopically, the presence of a superficial white patina was observed, which covered the surfaces and on which biological colonization spread during the 12 months of natural ageing. From the study of the cross-section of the sample, the treatment did not seem to penetrate into Carrara marble, whereas on Vicenza limestone penetration was ascertained to a depth of 13 mm. The application of the product conferred an increase in the superficial hydrophobicity of the substrate, due to the filling of stone pores by the treatment, and the consequent crystallization of the salt in the stone porosity. However, atmospheric phenomena which may have removed the superficial layer of the treatment, caused a gradual decreasing of the water-repellent effect. The treatment did not suffer any alteration due to UV radiation. However, FTIR and EDS analysis showed the degradation of barium treatment exposed to outdoor conditions by sulphatation of the carbonate. The characteristic peaks of barium sulphate were observed on FTIR spectra after the third month of outdoor exposure, probably due to the air pollution caused by ships. Moreover, thanks to SEM observations and EDS analysis, the acicular shape of barium carbonate crystals was confirmed and the formation of mixed carbonates of barium and calcium.

11.2 Silicone resins:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	EAS 40 – Sinopia Restauro	Penetration depth: scarce penetration Diffused superficial craquelure Loss of several cracked polymeric film fragments and absence of a homogeneous protective layer. $\Delta E_{untreated\text{-}0\ time}$ = 24.88 $\Delta E_{0\text{-}12\ months}$ = 22.07 WA (g/cm^2 x sec)$_{0\ time}$ = 0.217 WA (g/cm^2 x sec)$_{12\ months}$ = 0.446 UV rays= no effects Resistance to growth of mould:3s
Vicenza limestone *Laboratory specimen*	EAS 40 – Sinopia Restauro	Penetration depth: 2 cm Diffused superficial craquelure Loss of several cracked polymeric film fragments and absence of a homogeneous protective layer. $\Delta E_{untreated\text{-}0\ time}$ = 11.99 $\Delta E_{0\text{-}12\ months}$ = 7.83 WA (g/cm^2 x sec)$_{0\ time}$ = 0.066 WA (g/cm^2 x sec)$_{12\ months}$ = 0.871 UV rays= no effects

		Resistance to growth of mould:2s
Carrara marble *Laboratory specimen*	Rhodorsil RC80 – Siliconi PD	No penetration Diffused superficial craquelure It tends to yellow when expoused to outdoor conditions $\Delta E_{untreated\text{-}0\ time} = 13.45$ $\Delta E_{0\text{-}12\ months} = 6.00$ WA (g/cm^2 x sec)$_{0\ time}$ = 0.257 WA (g/cm^2 x sec)$_{12\ months}$ = 0.306 UV rays= cross-linking and breakage of the siloxane chain with consequent formation of a linear chain and terminal groups Si-OH Resistance to growth of mould:2s
Vicenza limestone *Laboratory specimen*	Rhodorsil RC80 – Siliconi PD	Penetration depth: 7500 µm Diffused superficial craquelure It tends to yellow when expoused to outdoor conditions $\Delta E_{untreated\text{-}0\ time} = 4.44$ $\Delta E_{0\text{-}12\ months} = 3.48$ WA (g/cm^2 x sec)$_{0\ time}$ = 0.076 WA (g/cm^2 x sec)$_{12\ months}$ = 0.129 UV rays= cross-linking and breakage of the siloxane chain with consequent formation of a linear chain and terminal groups Si-OH Resistance to growth of mould:2s
Carrara marble *Laboratory specimen*	Rhodorsil RC90 – Siliconi PD	No penetration Diffused superficial craquelure Darkening of the polymeric film $\Delta E_{untreated\text{-}0\ time} = 22.58$ $\Delta E_{0\text{-}12\ months} = 14.96$ WA (g/cm^2 x sec)$_{0\ time}$ = 0.272 WA (g/cm^2 x sec)$_{12\ months}$ = 0.342 UV rays= cross-linking and breakage of the siloxane chain with consequent formation of a linear chain and terminal groups Si-OH Resistance to growth of mould:3s
Vicenza limestone *Laboratory specimen*	Rhodorsil RC90 – Siliconi PD	Penetration depth: 4500 µm Diffused superficial craquelure Darkening of the polymeric film $\Delta E_{untreated\text{-}0\ time} = 16.74$ $\Delta E_{0\text{-}12\ months} = 10.94$ WA (g/cm^2 x sec)$_{0\ time}$ = 0.099 WA (g/cm^2 x sec)$_{12\ months}$ = 0.294 UV rays= cross-linking and breakage of the siloxane chain with consequent formation of a linear chain and terminal groups Si-OH Resistance to growth of mould:3s
Proconnesian marble *Little column of the Ca' D'Oro façade*	Sogesil XR893	Homogeneous distribution of the resin which is still present in the inter- and intra-grain spaces. Secondary product: Calcium sulphate
Carrara marble *4 angels supporting the S. Sepulcher altar in S. Martino church*	Sogesil XR893	Sogesil XR893 was observed in the inter and intra grain spaces. The calcite was strongly degraded. Secondary product: Calcium sulphate

		Thin superficial layer made of microcrystalline wax.
Greek marble (probably Pario) *S. Alvise statue – s. Alvise church*	Sogesil XR893	Black crusts covered the greater portion of the sample. Presence of another previous conservative treatment based on barium hydroxide. Secondary product: Calcium and Brium sulphate.
Candogia marble *Lunette above the portal of Corner chapel "Madonna con bambino e angeli" – S. Maria Gloriosa dei frari church*	X54-802 – Rhone Poulenc	Good penetration of the resin in the inter and intra grain spaces. Alumina grains were distributed on the superficial layer. The resin still protects the stone surface and seems unaltered Secondary product: Calcium sulphate

Table 11.2: *summarizing table of Silicone based consolidants results*

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	Hydrophase – Phase Restauro	Penetration depth: 500 µm Diffused superficial craquelure Loss of several cracked polymeric film fragments and absence of a homogeneous protective layer. $\Delta E_{\text{untreated-0 time}}$ = 24.88 $\Delta E_{\text{0-12 months}}$ = 22.07 WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.217 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.446 UV rays= peculiar tendency to yellowing Resistance to growth of mould:1s
Vicenza limestone *Laboratory specimen*	Hydrophase – Phase Restauro	Penetration depth: 4000 µm Diffused superficial craquelure Loss of several cracked polymeric film fragments and absence of a homogeneous protective layer. $\Delta E_{\text{untreated-0 time}}$ = 11.99 $\Delta E_{\text{0-12 months}}$ = 7.83 WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.066 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.871 UV rays= the value of superficial hydrophobicity of the stone increased with time Resistance to growth of mould:1
Carrara marble *Laboratory specimen*	Rhodorsil H 224 – Siliconi PD	Penetration depth: 1000 µm No craquelure due to natural ageing was observed and the film remained bright and transparent for the entire exposure time. $\Delta E_{\text{untreated-0 time}}$ = 20.66 $\Delta E_{\text{0-12 months}}$ = 8.22 WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.266 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.275 UV rays= peculiar tendency to yellowing Resistance to growth of mould:3s
Vicenza limestone *Laboratory specimen*	Rhodorsil H 224 – Siliconi PD	Penetration depth: 5000 µm H224 did not form a continuous film but the resin showed transparent crystals in the pores of the stone.

		The initial superficial white patina turned yellow and cracked. $\Delta E_{untreated-0\ time}$ = 7.96 $\Delta E_{0-12\ months}$ = 1.46 WA (g/cm^2 x sec)$_{0\ time}$ = 0.061 WA (g/cm^2 x sec)$_{12\ months}$ = 0.059 UV rays= no effects Resistance to growth of mould:1

Table 11.3: *summarizing table of Silicone based protectives results*

In this work 5 silicone based product were studied: 3 consolidants based on TEOS (EAS 40, Rhodorsil RC90 and Rhodorsil RC80) and 2 water-repellent agents (Rhodorsil H224 and Hydrophase).

From the results obtained it was observed that consolidants based on TEOS did not tend to penetrate Carrara marble, whereas on Vicenza limestone the penetration depth seemed dependent on the dimension of the macromolecules of the product applied. In fact, EAS 40, which is based on pure TEOS, showed a good, homogeneous penetration, and distribution in all the sections of the sample. RC80, which is based on TEOS combined with a methyl resin, reached 7500 µm of penetration depth, whereas RC90, which is composed of TEOS combined with a methyl-phenyl resin, stopped at 4500 µm. During the polymerization process, the products applied on the stone surfaces, tended to crack due to the evaporation of ethanol during the hydrolysis chemical reaction, and the large amount of catalyst in the case of RC80. This caused the progressive disappearance of the superficial coatings and the decrease of the superficial hydrophobicity as time passed, especially in the case of EAS 40. RC90 is the product which is most sensitive to UV radiation, due to the presence of phenyl groups in its macromolecule, chemically linked to the siloxane chain. FTIR analysis showed a general chemical stability of the resins, and confirmed the cross-linking of the polymers by a shift towards higher wavenumbers for all the peaks related to the CH chemical bond. This trend suggests a shortening of the chemical bond due to the minor degree of liberty of the molecules during the polymerization process.

The protectives tested also seem chemically stable. In particular, they both formed a thin superficial layer on the specimens, which conferred water-repellent properties to the stone, stable through time. Hydrophase applied toVicenza limestone is distinct as the value of superficial hydrophobicity of the stone increased with time. This suggest a longer polymerization process. The products applied to Carrara marble both tended to yellow, either during natural or artificial ageing.

The evaluation of Venetian past treatment confirmed the high chemical stability of silicone resin. In particular, the artifacts treated using a particular siloxane resin or an alkyl-alkossy-silane resin showed a good state of conservation and a high penetration of the treatment into the stone porosity, probably due to the effectiveness of the application method. The presence of gypsum in the inter and intra-grain spaces was prior to the application of the treatments and it was due to an ineffectiveness cleaning.

11.3 Nano-particle products:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	PF3	Diffused superficial craquelure Initial chromatic alteration of the treated surfaces and a yellowing effect $\Delta E_{untreated\text{-}0\ time} = 3.03$ $\Delta E_{0\text{-}12\ months} = 3.05$ WA (g/cm^2 x sec)$_{0\ time}$ = 0.300 WA (g/cm^2 x sec)$_{12\ months}$ = 0.303 UV rays= the sample increased their superficial hydrophilicity Resistance to growth of mould:3s
Vicenza limestone *Laboratory specimen*	PF3	Diffused superficial craquelure Initial chromatic alteration of the treated surfaces and a yellowing effect $\Delta E_{untreated\text{-}0\ time} = 2.57$ $\Delta E_{0\text{-}12\ months} = 3.41$ WA (g/cm^2 x sec)$_{0\ time}$ = 0.043 WA (g/cm^2 x sec)$_{12\ months}$ = 0.282 UV rays= the sample increased their superficial hydrophilicity Resistance to growth of mould:4s

Table 11.4: *summarizing table of nano-particle products results*

The results obtained from the study of an experimental product named PF3, based on Titanium dioxide, could refer to what was already shown for silicone resins, because of the presence of an organic derivate of silicon, probably TEOS, as matrix of the system, and the inefficacy of TiO_2. In fact, also in this case, it was observed that there was a superficial cracking of the film during the polymerization process and a diffuse biological colonization. Moreover, the application of the commercial product caused a yellowing of the treated surfaces, and a progressive increase in total chromatic variation was noted, especially during the exposure to outdoor conditions. The product had no self-cleaning properties and it showed the lowest resistance to growth of mould.

11.4 Acrylic resins:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	Paraloid B-72	Penetration depth: no penetration It completely changed the original aspect of the stone $\Delta E_{\text{untreated-0 time}} = 9.66$ $\Delta E_{\text{0-12 months}} = 1.93$ WA $(g/cm^2 \text{ x sec})_{\text{0 time}} = 0.269$ WA $(g/cm^2 \text{ x sec})_{\text{12 months}} = 0.220$ UV rays= no effects Photo-oxidation Resistance to growth of mould:4s
Vicenza limestone *Laboratory specimen*	Paraloid B-72	Penetration depth: 400 μm It completely changed the original aspect of the stone. Chromatic variations through time $\Delta E_{\text{untreated-0 time}} = 11.22$ $\Delta E_{\text{0-12 months}} = 6.24$ WA $(g/cm^2 \text{ x sec})_{\text{0 time}} = 0.064$ WA $(g/cm^2 \text{ x sec})_{\text{12 months}} = 0.081$ UV rays= no effects Photo-oxidation Resistance to growth of mould:2s
Carrara marble *Laboratory specimen*	Acrylic 33	No penetration: undefined It partially changed the superficial aspect of the specimen Chromatic variations through time $\Delta E_{\text{untreated-0 time}} = 6.31$ $\Delta E_{\text{0-12 months}} = 9.26$ WA $(g/cm^2 \text{ x sec})_{\text{0 time}} = 0.269$ WA $(g/cm^2 \text{ x sec})_{\text{12 months}} = 0.273$ UV rays= no effects Photo-oxidation Resistance to growth of mould:4s
Vicenza limestone *Laboratory specimen*	Acrylic 33	Penetration depth: undefined It partially changed the superficial aspect of the specimen Chromatic variations through time $\Delta E_{\text{untreated-0 time}} = 7.98$ $\Delta E_{\text{0-12 months}} = 9.51$ WA $(g/cm^2 \text{ x sec})_{\text{0 time}} = 0.097$ WA $(g/cm^2 \text{ x sec})_{\text{12 months}} = 0.178$ UV rays= substantial increase in water absorption Photo-oxidation Resistance to growth of mould:3s
Lumachella di S. Vitale and Istrian stone *Altar of Sacresty – S. Stae church*	Raccanello ARD E0057 (acrylic-siloxane mixture) Raccanello ARD E0023 (acrylic-wax	The stone and marble surfaces are widely disaggregated. White opaque superficial layer. Photo-oxidation of Paraloid B-72.

	mixture)	
Istrian stone and Greek marble *Porta da Terra – main portal of Arsenal*	Paraloid B-72	Absence of a superficial treatment. Photo-oxidation of acrylic resin.

Table 11.5: *summarizing table of acrylic resins results*

Paraloid B-72 and Acryl 33 were tested as representative acrylic resins. The commercial products showed a similar behavior. In particular, the aged films showed neither cracks and other optical variations. Paraloid B-72 gave higher colour variation than Acrylic 33 when exposed to outdoor condition and it tended to yellow, whereas during the exposure to UV radiation chromatic changes of the film were negligible for both coatings. The application of the products guaranteed a water-repellent effect to the stone, comparable to each other and stable through time. Only in case of Acryl 33 applied to Vicenza limestone, a loss of the initial hydrophobicity was observed. FTIR analysis showed the degradation of the resin well. The formation of cyclic esters (γ-lactone), due to oxidation or the addition of O_2 to the radicals formed by the extraction of hydrogen bonded to the tertiary carbons in the methacrylate molecule, was noted. The results obtained from the laboratory examinations were confirmed by the study of micro-fragments of Venetian monuments treated in the past with acrylic resins. The resins showed the lowest resistance to growth of mould

11.5 Epoxy resins:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	Eurostac EP2101	Penetration depth: no penetration The polymeric film lost its brightness and became quite yellow Some cracks were visible $\Delta E_{\text{untreated-0 time}} = 24.60$ $\Delta E_{\text{0-12 months}} = 6.09$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.235 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.269 UV rays= tendency to yellowing, increasing until reaching stability over time Decay: opening of the cyclic structures and chain scission. Resistance to growth of mould:1s
Vicenza limestone *Laboratory specimen*	Eurostac EP2101	Penetration depth: 25 μm Discolouration and cracking effects Visible alteration of the surface by the formation of a thin layer similar to a white

		compact powder distributed throughout the entire superficial area. $\Delta E_{untreated\text{-}0\ time}$ = 13.60 $\Delta E_{0\text{-}12\ months}$ = 9.19 WA (g/cm^2 x sec)$_{0\ time}$ = 0.191 WA (g/cm^2 x sec)$_{12\ months}$ = 0.480 UV rays= tendency to yellowing, increasing until reaching stability over time Decay: opening of the cyclic structures and chain scission. Resistance to growth of mould:1
Misio marble (granite) *Vereri column in Murano island*	Eurostac EP2101	Disaggregation phenomena and scaling Presence of a dark, disaggregated and raised from the substrate superficial polymeric film. Biological growth Decay: opening of the cyclic structures and chain scission.
Proconnesian marble *S. Marco basilica*	Eurostac EP2101	Decay: opening of the cyclic structures and chain scission.

Table 11.6: *summarizing table of epoxy resins results*

The cycloaliphatic epoxy resin EP2101 was widely studied in its formulation and application to this work. In particular, GCMS and FTIR analysis gave more information about the chemical structure of the resin, and the results did not confirm the chemical structure initially assumed. The resin showed different behavior when applied to Carrara marble and Vicenza limestone.In the case of Carrara marble, the resin formed a transparent, homogeneous and bright film, which changed its morphological aspect during the ageing processes, losing its brightness, craking along the border and tending to yellow. On the other hand, on Vicenza limestone, the initial transparent, homogeneous and bright film suffered discoloration and cracking during its exposure to natural ageing, probably due to the evaporation of the solvent from the porosity of the stone during the polymerization process.

Changes in superficial hydrophobicity also varied depending on the exposure to degradative environments.

The μFTIR spectra collected during the monitoring of the ageing process showed that a degradation mechanism began for all the treated specimens and increased during the ageing time. It is possible to argue that EP2101 cycloaliphatic resin decays by the opening of its cyclic structure and chain scission. The results were confirmed by the study of micro-fragments of the Vereri column on Murano island treated in the past with the same resin.

11.6 Fluorinate products:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	Fluorophase – Phase Restauro	Penetration depth: no penetration The film appeared elastic and dust adhered well to it. It was incoherent and at some points had lifted up from the surface of the stone. Yellowing effect $\Delta E_{untreated\text{-}0\ time}$ = 5.84 $\Delta E_{0\text{-}12\ months}$ = 6.40 WA (g/cm^2 x sec)$_{0\ time}$ = 0.208 WA (g/cm^2 x sec)$_{12\ months}$ = 0.245 UV rays= chromatic alyteration Resistance to growth of mould:4s
Vicenza limestone *Laboratory specimen*	Fluorophase – Phase Restauro	Penetration depth: 2 mm Yellowing effect $\Delta E_{untreated\text{-}0\ time}$ = 10.31 $\Delta E_{0\text{-}12\ months}$ = 10.01 WA (g/cm^2 x sec)$_{0\ time}$ = 0.071 WA (g/cm^2 x sec)$_{12\ months}$ = 0.079 UV rays= chromatic alyteration Resistance to growth of mould:4s

Table 11.7: *summarizing table of fluorinate products results*

The tested fluorinate resin, Fluorophase, as a representative of fluorinate products was characterized by an elastic film on which dust and atmospheric particles adhered well. The resin is well-known as a protective for stone materials, and in fact it formed a superficial thin layer, which conferred a water-repellent effect to the treated substrate, which was stable through time. However, the product tended to yellowing and browning, especially during exposure to outdoor conditions. Some difficulties were found during the preparation of the sample for FTIR analysis, due to its elastic nature.

11.7 Traditional and modern hydrophobic treatments:

Stone substrate	**Treatment applied**	**Results**
Carrara marble *Laboratory specimen*	Linseed oil	Penetration depth: undefined The inhomogeneous superficial layer showed a diffuse craquelure and a browning of the film. $\Delta E_{untreated\text{-}0\ time}$ = 24.29 $\Delta E_{0\text{-}12\ months}$ = 5.03 WA (g/cm^2 x sec)$_{0\ time}$ = 0.232 WA (g/cm^2 x sec)$_{12\ months}$ = 0.272 UV rays= depolymerization by the radical reaction

		Resistance to growth of mould:4s
Vicenza limestone *Laboratory specimen*	Linseed oil	Penetration depth: undefined $\Delta E_{\text{untreated-0 time}} = 12.11$ $\Delta E_{\text{0-12 months}} = 7.66$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.236 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 1.036 UV rays= depolymerization by the radical reaction Resistance to growth of mould:3s
Carrara marble *Laboratory specimen*	Microcrystalline wax	Penetration depth: no penetration Presence of a thin, white and light-yellow, opaque and inhomogeneous film $\Delta E_{\text{untreated-0 time}} = 4.86$ $\Delta E_{\text{0-12 months}} = 3.86$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.238 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.248 UV rays= no effects High chemical stability Resistance to growth of mould:2s
Vicenza limestone *Laboratory specimen*	Microcrystalline wax	Penetration depth: no penetration Diffused superficial craquelure It tends to yellow when expoused to outdoor conditions $\Delta E_{\text{untreated-0 time}} = 1.53$ $\Delta E_{\text{0-12 months}} = 4.82$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.055 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.057 UV rays= no effects High chemical stability Resistance to growth of mould:1
Carrara marble *Laboratory specimen*	Linseed oil and microcrystalline wax	Chromatic alteration of the surfaces which became darker. $\Delta E_{\text{untreated-0 time}} = 21.35$ $\Delta E_{\text{0-12 months}} = 5.53$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.238 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.263 UV rays= depolymerization by the radical reaction Resistance to growth of mould:3s
Vicenza limestone *Laboratory specimen*	Linseed oil and microcrystalline wax	Darkening of the polymeric film $\Delta E_{\text{untreated-0 time}} = 12.55$ $\Delta E_{\text{0-12 months}} = 9.89$ WA (g/cm^2 x sec)$_{\text{0 time}}$ = 0.075 WA (g/cm^2 x sec)$_{\text{12 months}}$ = 0.395 UV rays= depolymerization by the radical reaction Resistance to growth of mould:3s
Different type of marble *Marble base of the High Altar of S. Giorgio church*	Linseed oil and microcrystalline wax	The coating appears thick, yellow/brown and waxy to the touch The FTIR spectra confirmed the use of linseed oil and a microcrystalline wax for the treatment.

Table 11.8: *summarizing table of traditional and modern hydrophobic treatments results*

Linseed oil and microcrystalline wax have been widely studied in the literature and the results collected in this work confirmed the previous experiments.

In particular, the tendency to yellowing and the depolymerization by the radical reaction of linseed oil were confirmed. Moreover, linseed oil applied to stone materials guaranteed an initial good hydrophobicity, which tended to decrease, in the case of Vicenza limestone, through time.

On the other hand, the microcrystalline wax tested, ensured chemical stability, did not cause colour variations to the treated stone and it maintained its natural hydrophobicity through time.

11.8 Holistic conclusions

The results obtained from this study have been consistent with the purpose of the research. The laboratory operating methodology developed to evaluate the efficacy of the commercial products studied and widely used for the restoration of stone materials was appropriate to characterize any associated degradation mechanisms and have been already applied successfully to the industry. XRD analytical technique did not give any additional results in order to verify the conclusions drawn and, for this resion, it was not mentioned in the results sections. Comparing the analytical data supplied from the research and evaluating critically the substrate and the expousure environment, it would be possible to carefully select the product best fitting future restoration process. Moreover, the look at past treatments and the evaluation to their stability, comparing them to fresh products, allowed to monitoring the state of conservation of monuments treated in the past and to hypothesize future restoration approaches. The supposed “bio-removal” of the aged treatments will be examined more in depth in future works, taking advantages of the observations and results obtained from this study.

Chapter 12

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Appendix A

Study of the stability of siloxane stone strengthening agents

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Study of the stability of siloxane stone strengthening agents

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The commercial organosilicone compounds *Rhodorsil Consolidante RC90* and *Rhodorsil Consolidante RC80*, commonly used as stone strengthening agents for the conservation of artefacts, were tested to ascertain their chemical nature, the mechanisms involved in the polymerization reactions and their stability under oxidative stress. The resins were first chemically characterized by means of GC/MS, FTIR and EDXRF techniques, then applied to slides and subjected to controlled photo-oxidative and thermo-oxidative weathering. The film's morphology was observed by SEM determinations, while DTA-TG techniques were used to determine polymer thermal stability. The features examined prompted a number of considerations on the effects of the resins applied on stone materials and were the reference point for speculation on the chemical nature and the performance of *Sogesil XR893*, a silicon resin which is no longer available on the market.

1. Introduction

Organosilicone compounds have been widely used as protective and consolidating agents to preserve stone materials from inevitable weathering due to environmental exposure. Good chemical stability resulting from the high strength of the silicon–oxygen bond, together with low surface tension, good elasticity and resistance to thermal stress foster their application on different stone substrates [1]. Silicone resins, such as polysiloxanes and alkyl-alkoxy-silane, have been applied in Venice since 1960, on various stone surfaces during well-documented restorations. The first consolidation treatment using organosilicone compounds in Venice took place in 1967 and was applied to the marble statue of St. Alvise, located on the main façade of the church dedicated to the saint. The statue was treated by vacuum impregnation in autoclave using the silicone resin *Sogesil XR893* [2]. To the best of our knowledge the resin, which was produced by Rhone Poulenc and is no longer available on the market, was a methyl-phenyl-polysiloxane dissolved in benzene with a solid content of 50%. Right away, it was judged very promising and began to be used elsewhere in the city: in the following year it was employed for the consolidation of the four angels supporting the Holy Sepulchre altar in the Church of San Martino, during the restoration of the Ca' D'Oro in 1969 and in 1977–78 for the consolidation of the statues located on the gable-end of the façade of Basilica of San Marco [3]. No datasheet is available to indicate the chemical composition of the resin actually used. Moreover no studies have been carried out to illustrate the characteristics of the resin or the mechanisms of the polymerisation process. However, several years after the applications cited above, authoptic observations were carried out to evaluate the efficiency of the past treatments: all the stone surfaces showed a good state of conservation and no new fracture planes were observed [4]. Nowadays the fact that the resin is not commercially distributed prevents detailed study of its chemical stability. In the intervening years however, other silicone-based commercial products based such as tetraethylorthosilicate (TEOS) and poly-dimethyl-siloxane (PDMS) have been studied in detailed laboratory examinations [5–7]. In general, analytical tests have demonstrated that the most important problem of silicone resin is related to the cracking of the derived gel, due to the evaporation of the solvent upon the gelification process, or in the case of products based on TEOS, to the TEOS/organometallic catalyst ratio [5]. In order to solve this drawback, alternative mixtures of acrylic and silicone polymers [8] or, more recently, mixed systems of epoxy-silicone resins have been synthesized in organic-inorganic formulation with acid catalysts [9].

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Nowadays, in the restoration field, a new silicone resin, *Rhodorsil Consolidante RC90*, has replaced the old Sogesil XR893. The chemical nature of these two resins is quite different, as shown in the literature [10]: in fact RC90 differs from XR893 because of the presence of TEOS as the main component, combined with a tin-siloxane catalyst and a methyl-phenyl resin. The consolidation effects of RC90 such as changes in porosity and pore size distribution, water absorption coefficient, mechanical resistance and colorimetric features have been well-documented [11–13].

Another silicone resin commonly used in the restoration field, is *Rhodorsil Consolidante RC80*, which is different from RC90 only in that it contains a methyl instead of a methyl-phenyl resin [14]. The effectiveness of *RC80* on stone surfaces has been examined [13,15].

Nevertheless, despite their applications, the features of both Rhodorsil resins and the polymerization process remain unclear.

This study aims to achieve a better understanding of the chemical nature and stability of *Rhodorsil Consolidante RC90*, by comparison with *Rhodorsil Consolidante RC80*, in a thermo-oxidative and photo-oxidative environment. Among the techniques used, Fourier Transform Infrared Spectroscopy (FTIR) has been invaluable for understanding the sol–gel processes, as well as any polymer structural changes due to UV radiation and thermal-oxidation. Thermal analysis (DTA-TG) was used to assess the resistance of the resins to heat [16]. The results obtained have clarified the hydrolysis reactions involved in the polymerization process and ascertained the general high stability of the resins, supplying users with useful information concerning the performance of the consolidants. Furthermore, the different thermal stability and resistance to UV radiation of RC90 and RC80, has revealed the important role played by the methyl-phenyl resin in the ageing process, and provide reasonable explanations for the causes of failure of the old *Sogesil XR893*. These hypotheses were tested by study of a fragment of a column of the Ca' D'Oro façade, treated in 1963 with the XR893 resin.

2. Experimental

2.1. Materials

The commercial products to be tested were *Rhodorsil Consolidante RC90* and *Rhodorsil Consolidante RC80* supplied by the Italian company *Siliconi Padova*. Both of them are composed of tetraethylorthosilicate (TEOS) combined with a tin-siloxane catalyst and a water repellent component, which is a methyl resin in the case of RC80 and a methyl-phenyl resin in the case of RC90. The solvent is white spirit with the addition of xylenes only in the case of RC90, presumably to improve dissolution of the methyl-phenyl resin [10–14].

The polymers were chemically characterized in liquid and dried form.

After the complete sol–gel changeover, films were subjected to UV radiation in a UV chamber equipped with four 8 W black light blue lamps, emitting in the near-UV range (315–400 nm; 3 mW cm^{-2}). The volume of the photoreactor was 25 ml. The films were also subjected to thermal-oxidation in a ventilated oven fixed at 60 °C [17]. These experiments almost simulate the ongoing degradation of resins exposed to outdoor conditions.

2.2. Investigation methods

RC90 and RC80 were chemically characterized in sol and gel form, following UV radiation and thermal treatment under laboratory conditions, the better to ascertain their chemical composition, microstructure and stability.

2.2.1. GC/MS measurements

The GC/MS analysis performed in this study was carried out using a TRACE GC 2000 Gas Chromatograph interfaced by the quadrupole Mass Spectrometer TRACE MS (Thermo Finnigan). The gas chromatograph was equipped with an HP5-MS column (length: 30 m, I.D.: 0.25 mm, film: 0.25 μm). The samples were injected in the split flow mode and the oven was set from 80 °C to 300 °C.

The identifications were supported by NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library, 2.0.

2.2.2. FTIR spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) using a Perkin–Elmer 1000 spectrometer and a Jasco-Europe model FT/IR4200 instrument in the spectral range of 400–4000 cm^{-1} was used to characterize both the sols and the xerogels. The sol samples were initially placed inside an AgBr cell with a Teflon spacer (0.05 mm thick) between the windows. In the case of the xerogels, they were homogenized with KBr and pressed to obtain a pellet using a vacuum hydraulic press. Sols and xerogels were recorded in the absorbance mode with a spectral resolution of 4 cm^{-1} and 75 consecutive scans were summed and averaged before applying the Fourier transform, in order to obtain a good signal-to-noise ratio. The spectra of sols and xerogels were recorded at various time intervals during the curing and ageing of resins, as follows: (a) the sols and the derived xerogels of both resins were analysed at time intervals of 0, 18, 48, 83, 155, 216 and 384 h from the application time in the laboratory ambient; (b) spectra were recorded for the resins subjected to UV radiation at time intervals of 0, 24, 72, 216, 288 and 1152 h; (c) spectra were also recorded for the resins subjected to a thermal-oxidation at time intervals of 83, 155, 323, 491, 1163, 2123 h [18,19].

In order to evaluate an old conservation treatment based on XR893 silicone resin and to compare it with the results obtained from the application of RC90 resin on a stone surface, as better explained in paragraph 2.3, μFTIR analysis was carried out. The instrument used is a Jasco IRT-5000 Irtron Infrared Microscope. A micro scale of the polymeric films was sampled from the stone surface, using a needle, laid and pressed on a standard KBr pellet, then analysed in transmittance mode.

2.2.3. Thermal analysis

The thermal decomposition of the nanocomposite coatings was assessed by means of differential thermal analysis (DTA) and thermogravimetric (TG) analysis with a Setaram LabSysEvo 1600. The TG analysis was performed under air atmosphere at a heating rate of 10 °C/min from 27 °C to 1000 °C, on samples dried at 60 °C for one day.

2.2.4. EDXRF technique

An EDXRF unit with ^{55}Fe and ^{109}Cd and ^{241}Am radioactive sources, Si(Li) semiconductor detector (resolution 150 eV at 5.9 keV) was employed for the identification of the catalyst included in the resins. The EDXRF analysis was performed in powders originating from cured films of the resins.

2.2.5. Scanning electron microscopy

Morphological observations and detailed chemical microanalyses of dried films polymerized on a slide and coated with a thin gold layer, were carried out by Philips XL 30 SERIES SEM instrument. The semi-quantitative elemental composition was measured using an EDS coupled with EDAX X-ray dispersive spectrometer, equipped with a thin beryllium window. The accelerating voltage was 25 keV.

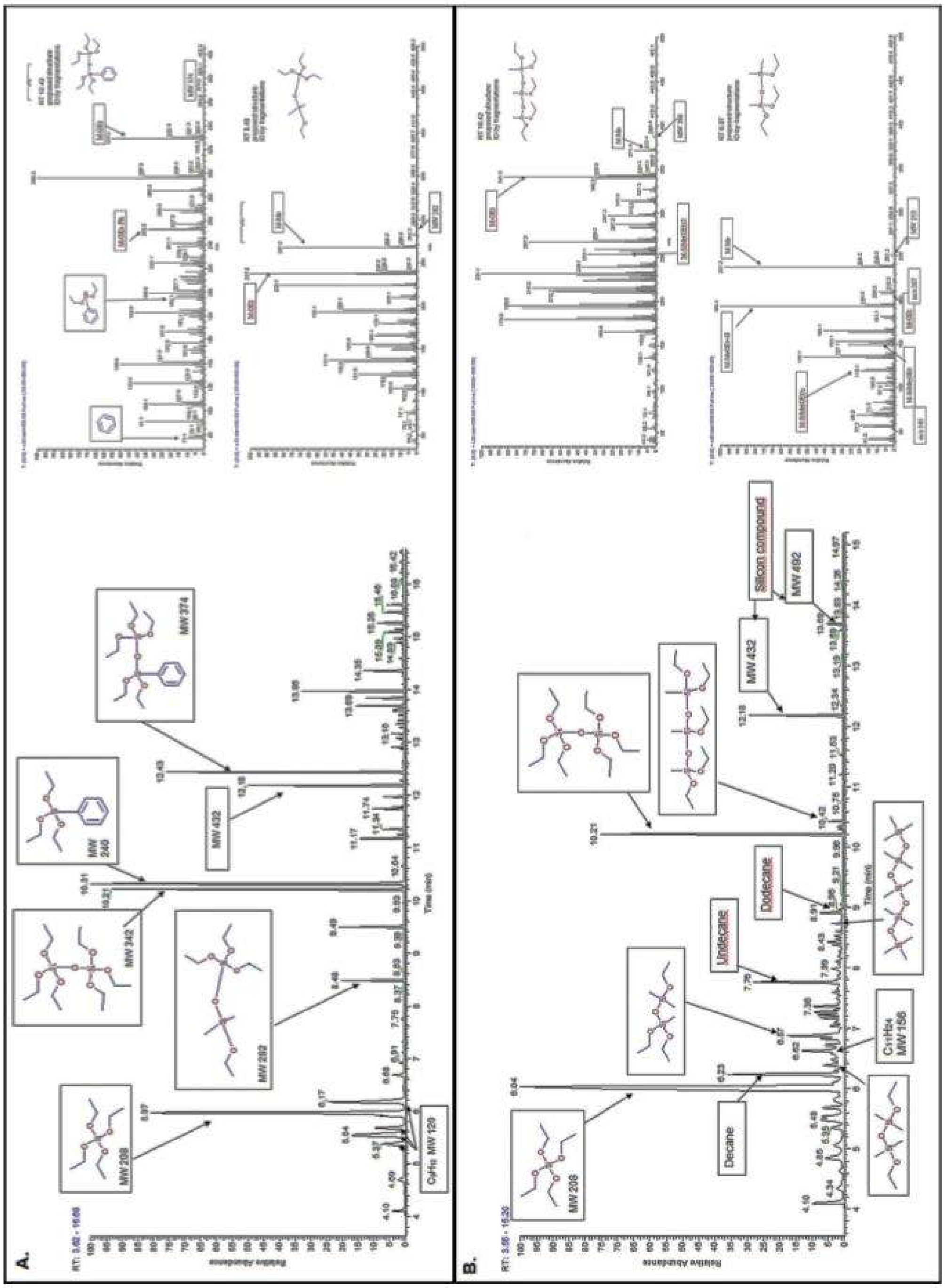


Fig. 1. Gas chromatogram of RC90 (A) and RC80 (B) resins analysed in liquid phase.

2.3. Evaluation of conservation treatments

A sample from a carved Proconnesian marble column of the Ca' D'Oro façade in Venice, which was treated in 1963 with *Sogesil XR893* by vacuum impregnation, was analysed in order to evaluate the performance of the treatment. Particular attention was devoted to assessment of the strengthening effects of the applied resin and its stability, taking into consideration the results obtained from the characterization of RC90 and RC80 resins. A minimum quantity of the sample was collected using a chisel, and studied by optical microscopy, μFTIR, FTIR and SEM-EDS analyses.

3. Results and discussion

3.1. RC80 and RC90 sol–gel characterization

The chromatograms of both resins (Fig. 1A and B) showed a mixture of TEOS monomer (MW 208), observable at a retention time (RT) of 5.97 (RC90) and 6.04 min (RC80), and dymer at RT 10.21 min with MW 342, identified by NIST commercial library. Prepolymers of a copolymer TEOS/methyl-ethoxy-siloxane are also observable, in particular at RT 8.48 min with MW 282 in RC90, 6.87 and 6.39 min in RC80, the last identified by the study of the fragmentations (Fig. 1). TEOS is the most abundant component in RC80. In contrast, in RC90 sol, monomer of phenyl-ethoxy-siloxane (MW 240), identified by NIST commercial library, is the component with the highest relative abundance (RT 10.31 min) and studying the fragmentations, at RT 12.43 min, a prepolymer of a copolymer TEOS/phenyl-ethoxy-siloxanes, with MW equal to 374, is also recognizable. The *m/z* of the components identified by the study of the fragmentations are readable in the corresponding mass spectra in Fig. 1(A and B).

FTIR spectra of the sol and gel form of resins confirmed the presence of the groups identified above (Fig. 2). More specifically, in the analysed sol phase of the resins the ethoxy groups were indicated by strong peaks at 1170–966, 1082 (1086 in RC80), and 478 cm^{-1} corresponding to ρ C–H, ν_s Si–O–C, δ O–C–C bonds, respectively [6].The characteristic Si–O–Si symmetrical stretching in linear structures at 1106 and 966 cm^{-1}, along with the Si–O–Si bending at 794 cm^{-1} indicate the presence of siloxanes in the resins. In RC90, the Si–Ph stretching and bending vibrational modes were indicated by the peaks at 1594–1432–1482 and 740–700–690 cm^{-1}, while the Si–(CH$_3$) bond was denoted by the peaks at 1264 and 810 cm^{-1} (Fig. 2(A)). The doublet at 3074–3052 cm^{-1} was attributed to C–H symmetrical stretching and bending, respectively, of aromatic hydrocarbon, while the absorptions at 1608, 1594 and 600 cm^{-1} to C–C of aromatic compounds. In RC80 the Si–(CH$_3$) bond was denoted by the peaks at 1254, 846, 810 and 690 cm^{-1} (Fig. 2(B)).

During the polymerization process, a shifting of some bands towards higher values of wavenumbers was observed. In the sols the peaks attributed to the C–H bond of the aliphatic groups, such as the triplet at 2974, 2928 and 2896 cm^{-1} shift in the gel to higher wavenumbers at 2980, becoming a shoulder of the main peak at 2962 cm^{-1}, and 2904 cm^{-1}; also the peak corresponding to δ_s C–H at 1392 cm^{-1} shifts to 1404 cm^{-1}. According to the literature, this trend suggests a shortening of the chemical bond due to the minor degree of liberty of the molecules during the polymerization process [20,21]. This is also in accordance with the subsequent condensation of the silanol groups, which were produced following the hydrolysis process, giving rise to the formation of cross-linked siloxane chains (Scheme 1).

Further evidence of the cross-linked siloxane chain, upon the polymerization process, derives from the broadening of the Si–O–Si peak, at 1080 cm^{-1} in RC80 and at 1074 cm^{-1} in RC90, and the appearance of a shoulder at 1192 cm^{-1} related to Si–O–Si symmetrical and asymmetrical stretching in cyclic structures, respectively [7]. Additionally, in RC90 the Si–O–Si shifting from 1082 to 1074 cm^{-1} along with the appearance of a shoulder at 1134 cm^{-1} can be related to the broadening of the Si–O–Si chemical bond due to the presence of the phenyl group.

The evolution of the hydrolysis and condensation is different in the resins studied. Macroscopic evidence suggests that RC80 became a gel after 4 h, while in RC90 the process took much longer. This is confirmed by the infrared analysis indicating that the O–H stretching at approximately 3600 cm^{-1} appeared in RC80 and RC90 after 18 and 83 h of gelation time, respectively (Fig. 2). The evolution of the hydrolysis becomes evident by plotting the ratios of the

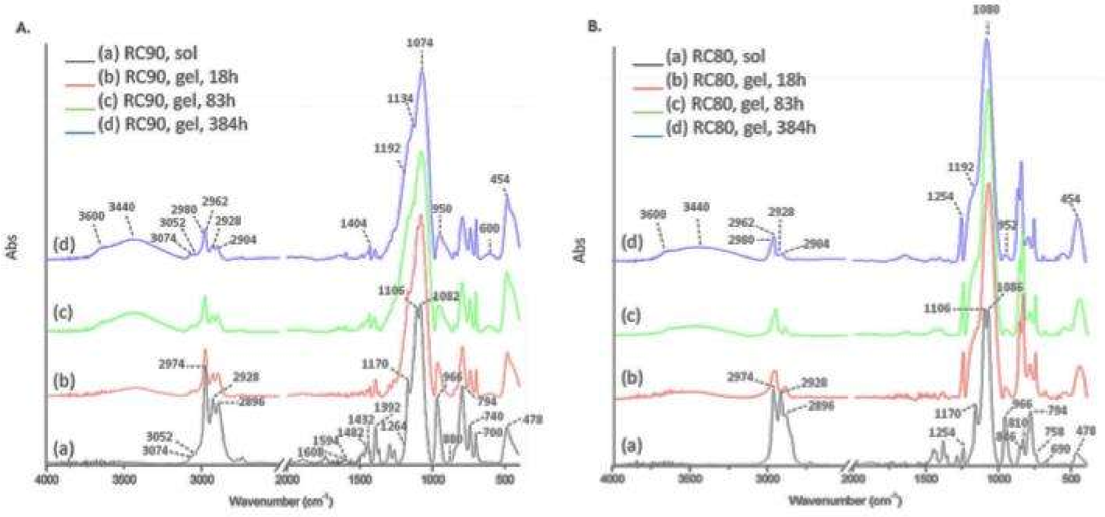
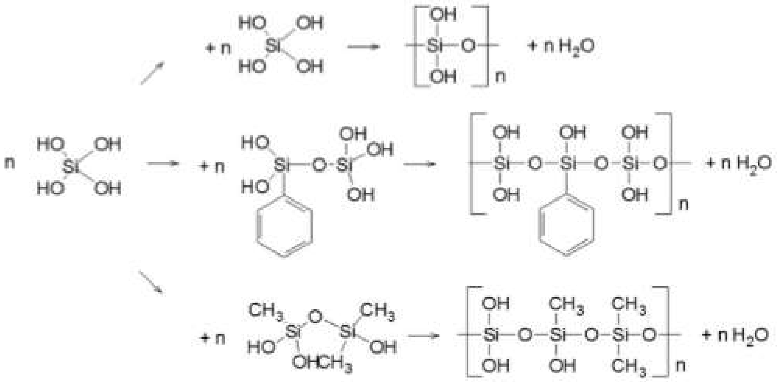


Fig. 2. FTIR spectra of RC90 (A) and RC80 (B) resins, in sol (a) and gel phase after 18 (b), 83 (c) and 384 h (d) of curing time.



Scheme 1. Possible condensation and polymerization reactions between monomers or dimers in the resins.

calculated area of the bonds Si–O–C, C–H, Si–OH and –OH versus the area of the Si–CH_3 bond. The results illustrated in Fig. 3 for the RC90 show a general decrease in the area of Si–O–C and O–C–H stretching bonds and an increase in the area corresponding to the Si–OH and –OH absorptions.

Optical microscope observations of RC80 (A) and RC90 (B) xerogels reveal the formation of micro-cracks (Fig. 4). More specifically, the RC80 was characterized by linear and cyclic cracks, while in the RC90 only linear cracks were observed.

With the aim of explaining the different performance of the resins, the amounts of the tin catalyst were quantified by EDXRF analysis; they were found to be 2.92% in RC90 and 2.09% in RC80 [22].

SEM observations of the microstructure of xerogels revealed linear cracks across a compact film for RC90, while RC80 film appears inhomogeneous, with a large number of cracks and micro-cracks with many white spots of different dimensions (Fig. 5). Detailed chemical microanalyses, by EDS, of various areas of RC80 film, revealed a generally higher concentration of tin in the white spots, previously observed, than in the surrounding areas (Fig. 5(B)). Consequently, it is reasonable to assume that the high concentration of tin in these particular areas can be accounted for by the shorter gelation time of RC80 compared to RC90. In addition, the high localized tin concentration may influence the formation of nuclei of germination and separate phases within the TEOS matrix [13].

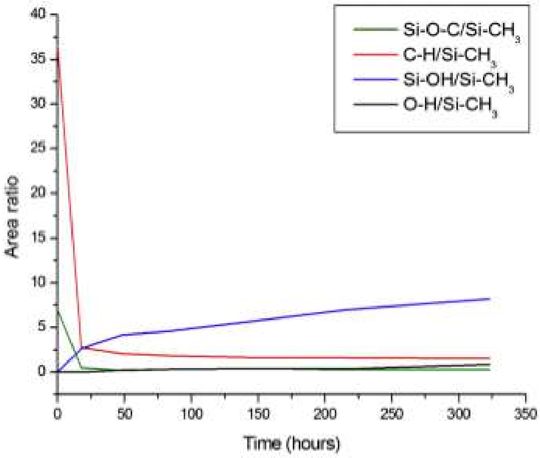


Fig. 3. Evolution of the ratios of the principal FTIR absorptions as a function of the curing time in RC90.

This feature may be the reason for the white colour of RC80 xerogel observed under the optical microscope, while RC90 remains colourless (Fig. 4).

In the polymerization process of both resins no differences were observed whether the experiment was carried out in the laboratory ambient or in a ventilated oven.

3.2. Degradation of resins

Both resins proved to have a high stability with respect to UV-thermo oxidation, since no macroscopic differences were observed after UV ageing. However, as is suggested by the FTIR technique, when exposed to an oven temperature of 60 °C for 2675 h in oven, RC90 was characterized by a progressive shifting of the Si–O–Si stretching band towards lower values of wavenumber, from 1074 to 1068 cm^{-1}, and an increase of a shoulder at 1134 cm^{-1} (Fig. 6).

This shift to a lower wavenumber was also observed upon the polymerization process of RC90 and can be related to the achievement of the desired network after the solvent evaporation. In particular, in the literature Grill [23] suggested at 1068 cm^{-1} the asymmetrical stretching of the Si–O–Si bond occurs with a specific angle of about 144° in a siloxane network. This shift occurred only in the case of RC90, probably due to the greater steric hindrance of phenyl groups in the polymeric structure.

In addition RC90 spectra exposed to UV radiation showed the appearance of a peak at 1080 cm^{-1} with a shoulder at 1054 cm^{-1} and a new band around 880 cm^{-1} (Fig. 7). This confirmed the shifting of the 1074 cm^{-1} band to a lower wavenumber (1054 cm^{-1}), due to the cross-linking, but also the breakage of the siloxane chain induced by UV light with the consequent formation of a linear chain (1080 cm^{-1}) and terminal groups Si–OH (878 cm^{-1}).

The resins studied showed different TG curves during the thermal analysis (Fig. 8). Both the commercial products lost 20% of their weight up to 600 °C, which according to the literature, indicated that branched structures were formed, since the cross-linking

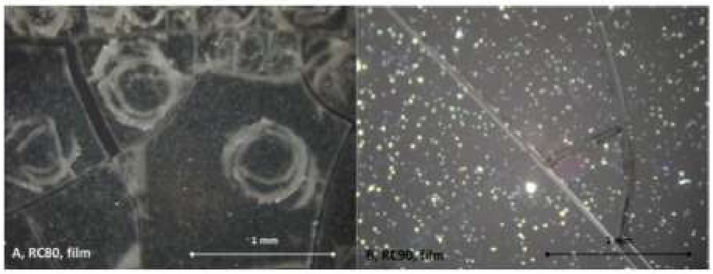


Fig. 4. Optical microscope images of RC80 (A) and RC90 (B) xerogels. Micro-cracks and inhomogeneous aspect characterize RC80, whereas linear cracks are observed in RC90.

phenomenon reduces the flexibility of the molecules, thus delaying pyrolysis. RC80 almost decomposes up to 600 °C (Fig. 8(A)), while the major thermal decomposition of RC90 was observed at a temperature higher than 500 °C (Fig. 8(B)). The percentage of the amorphous SiOxCy residue at 800 °C is higher in RC80 than in RC90, being 75.8% and 61.1%, respectively. Generally, at low temperature phenyl side groups provide higher thermal stability than pure methyl side groups, while at high temperature they speed up the degradation of the Si–O bond [24].

3.3. Stability of resins and comparison with past treatments

The difference in the chemical nature of *Sogesil XR893* compared to the RC90 and RC80 resins is well known, and some considerations about it can be suggested on the basis of the results obtained.

A small chip sampled from a column of the Ca' D'Oro façade in Venice, carved in Proconnesian marble and treated in 1963 by profs. L. Marchesini and L. Lazzarini using *Sogesil XR893*, by vacuum

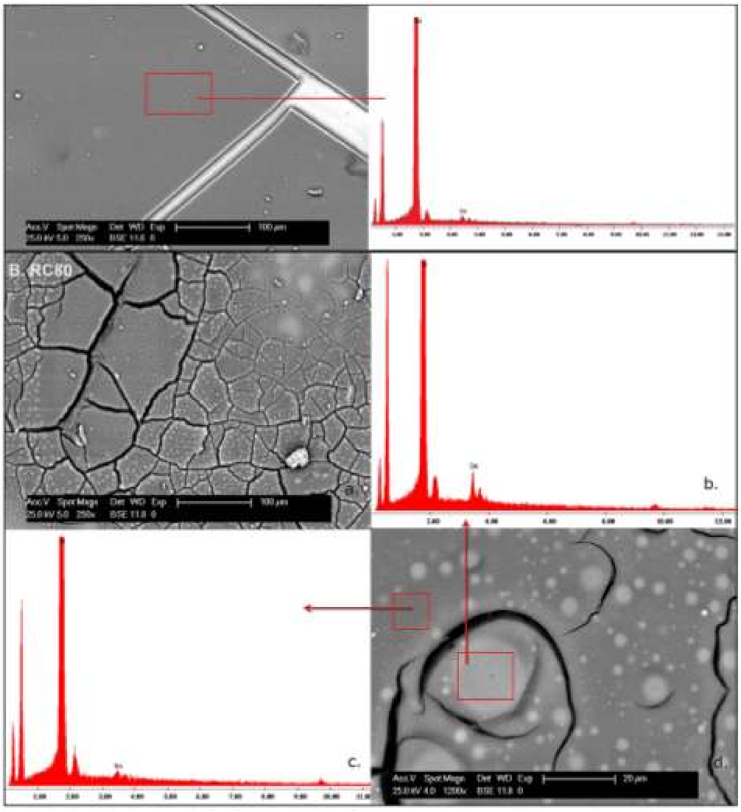


Fig. 5. SEM micrographs of RC90 (A) and RC80 (B) xerogels showing micro-cracks and white spots in RC80. The EDS study of the RC80 revealed an inhomogeneous distribution of tin with localization in the white spots.

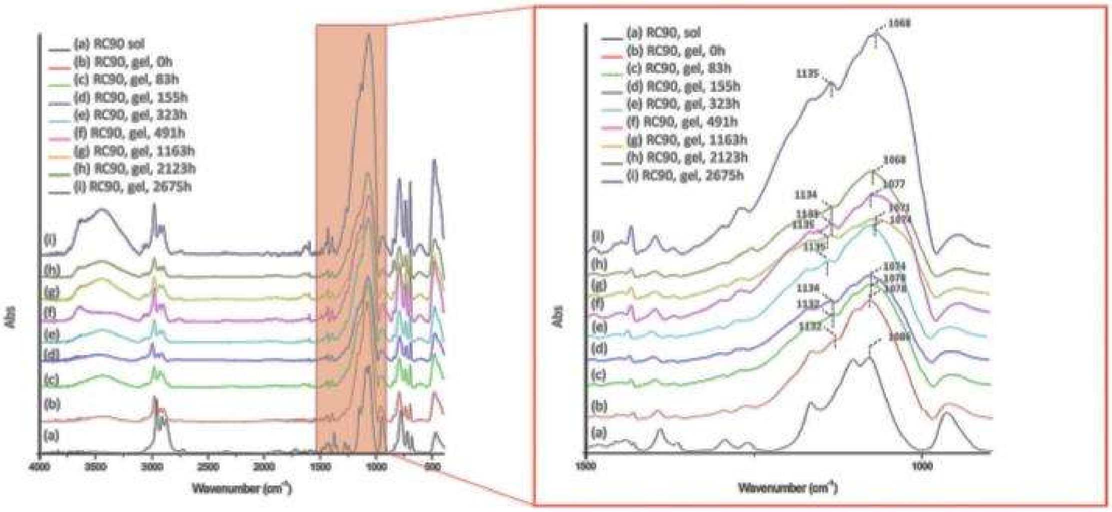


Fig. 6. Comparison between RC90 sol and gel at different time intervals of the thermal-oxidation test.

impregnation, has been chemically analysed. The cross-section of the sample showed a homogeneous distribution of the resin, confirmed by SEM-EDS analysis, still present in the inter- and intra-grain spaces (Fig. 9).

The study of the wavenumbers of each μFTIR peak of the spectra collected, confirmed the chemical nature of methyl (1267 cm^{-1}) – phenyl (3068, 1464–1429, 706 cm^{-1}) – polysiloxane (1082, 1030 cm^{-1}) and its cross-linked structure. In addition the characteristic peaks of gypsum (3400–3550, 1146–1117, 1620, 1684 cm^{-1}) revealed the sulphatation of the calcium carbonate (substrate).

By comparing the spectrum of XR893 resin with that obtained from the analysis of *Rhodorsil Consolidante RC90* applied on a Carrara marble specimen and exposed for 9 months to the Venetian environment, a general correspondence with all the peaks was observed (Fig. 10). However, the peaks from 2000 to 1600 cm^{-1} show alkyl groups in XR893 whereas in RC90 they are not observable.

The reason for this is the different chemical composition of the resins. In the case of XR893, the resin was a pure methyl-phenyl-siloxane dissolved in toluene, whereas RC90 is an ethyl silicate admixture with a methyl and a phenyl resin. Thus in XR893 alkyl groups may be more abundant than in RC90. The use of benzene as a solvent and its high volatility could, in all probability, generate cracked polymeric films, allowing penetration of water and

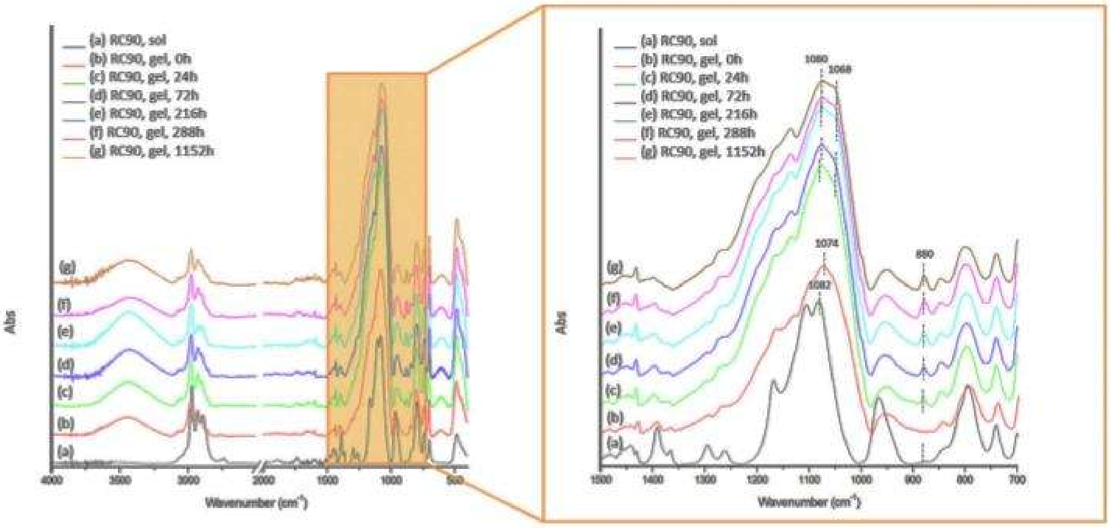


Fig. 7. Comparison between RC90 sol and gel at different time intervals of UV-oxidation.

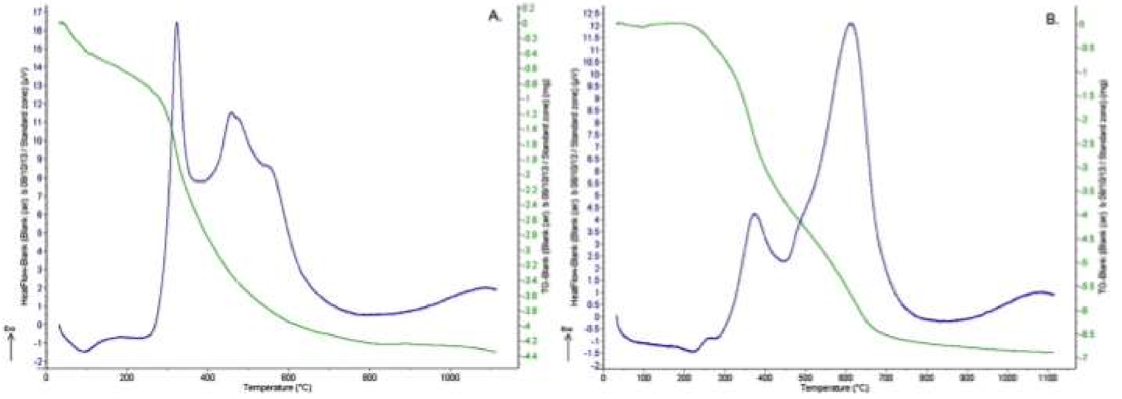


Fig. 8. TG curves of RC80 (A) and RC90 (B) resins in air.

pollutants into the cured layer and the consequently sulphatation of the carbonatic substrate.

4. Conclusions

Organosilicone compounds have been extensively used as preserving agents for building materials exposed to outdoor environments. Focussing on the polysiloxane most used in Venice, *Sogesil XR893*, a methyl-phenyl-polysiloxane which is no longer available on the market, this work has been carried out through the chemical characterization of the present substitute silicon resin, *Rhodorsil Consolidante RC90*, and a similar one, *Rhodorsil Consolidante RC80*, both commonly used in the restoration field. On the basis of the results obtained from the monitoring of curing processes and the consequent polymerization mechanism, supported by the existing literature, it is possible to make some observations about the effects of RC90 and RC80 resins applied on stone materials as strengthening agents. Due to the development of branched siloxane structures during the polymerization process and the hydrophobic feature of methyl groups in their formulation (assured by GC/MS and FTIR techniques), the resins also provide waterproofing properties. They are both really durable with respect to UV and thermo oxidation. In particular RC80 does not suffer any chemical transformation, whereas UV rays and oxidation cause cross-linking in RC90, probably limiting the removability of the polymers from treated surfaces whenever should become necessary. These modifications in RC90 result in a gradual shifting towards lower values of wavenumber of the main peak, related to the Si–O–Si stretching bond in a cycle structure and to the appearance of Si–OH bonds. However, the limited deterioration process on polymers, ascribed to the low permeability to oxygen, reduced the photo-oxidative reactions [25].

RC80 film is characterized by cracks, which were microscopically observed, and an irregular distribution of the organometallic catalyst, as was proved by SEM-EDS and EDXRF analysis. This peculiarity could not preserve carbonate rocks from sulphatation. In addition, this also determines the macroscopic opacity and whitening of the RC80 polymeric film.

RC90, which macroscopically is characterized by a transparent film, could undergo less chromatic alteration than RC80. Nevertheless, the phenyl groups in RC90 could arouse a colorimetric change of the treated surface after natural ageing. Moreover, at low temperatures, the phenyl groups guarantee a better thermo stability than that assured by RC80.

The identification of some degradation markers of RC80 and RC90 resins could be really useful for the enhancement of incoming products and for understanding of the decay of stone treated by these two commercial products. It also suggests some

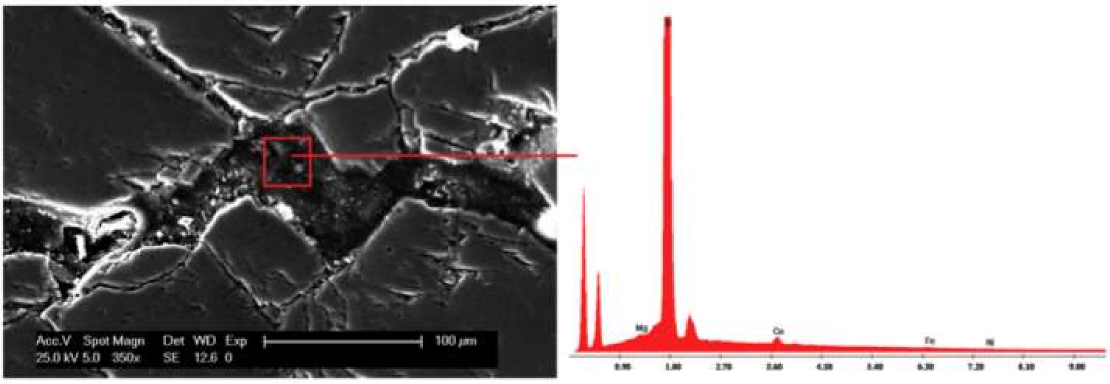


Fig. 9. Detail of a cross-section of the fragment sampled from a portion of a column at Ca' D'Oro. SEM observations and EDS analysis showed the presence of the resin in the inter- and intra-grain spaces.

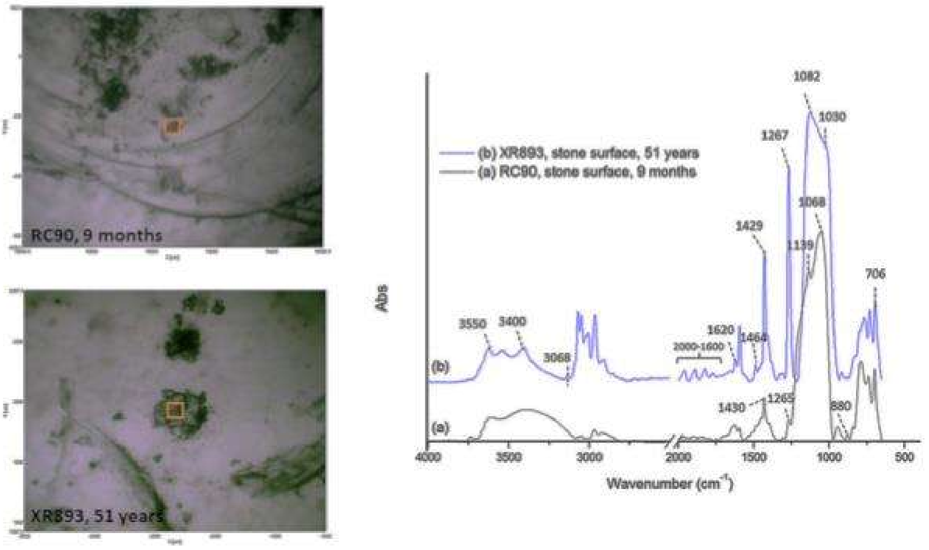


Fig. 10. Micrographs and FTIR spectra collected by μFTIR instrument of RC90 resins, applied on a marble surface and exposed to the Venetian environment for 9 months, and XR893 resin, applied on a marble surface and aged for 51 years in Venice. Comparison of the spectra shows a general correspondence with all the peaks.

considerations concerning the chemical behaviour of *Sogesil XR893* silicon resin during its ageing process. The assumed chemical nature and cross-linking tendency of *Sogesil XR893* have been confirmed by examining the 51-year-old polymerised resins from a marble artefact.

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Appendix B

Valutazione dell’applicabilità e studio del degrado di alcuni prodotti commerciali della ditta Tenax spa, per il loro impiego nel settore della conservazione e del restauro.

RELAZIONE CONSUNTIVA SULL’ATTIVITA’ DI RICERCA

1. ATTIVITA’ SVOLTA

Il presente progetto nacque dall’esigenza di creare un’attiva collaborazione fra Tenax spa e il Laboratorio di Analisi dei Materiali Antichi (L.A.M.A.), al fine di rispondere da un lato ad esigenze di tipo tecnico-commerciale per lo sviluppo aziendale, e dall’altro ampliare e finalizzare un settore della ricerca accademica interna al laboratorio universitario.

Il Laboratorio di Analisi dei Materiali Antichi ha recentemente intrapreso un lavoro di ricerca basato sullo studio del degrado di prodotti commerciali di tipo consolidante e protettivo, applicati su supporto lapideo in occasione di operazioni di restauro ben documentate.

Lo sviluppo di Tenax negli anni è stato tale da farla diventare leader nella produzione e distribuzione di prodotti per la lavorazione ed il trattamento dei materiali lapidei. Attualmente il progetto Restauro si colloca all’interno di un piano di sviluppo aziendale volto ad individuare e testare scientificamente, tra la vasta gamma di prodotti a marchio Tenax, quelli che meglio si adattano alla manutenzione, ripristino, sanatura e conservazione della pietra naturale.

Per questo il Laboratorio di Analisi dei Materiali Antichi, ampliando il settore d’indagine ai prodotti individuati da Tenax, ha soddisfatto le esigenze aziendali, mettendo a disposizione conoscenze teoriche e prove pratiche di laboratorio.

L’obiettivo del progetto è stato lo studio dell’applicabilità e del degrado nel tempo di prodotti commerciali, in particolare resine consolidanti di tipo epossidico a basso o zero ingiallimento, protettivi per i materiali lapidei, cere, e prodotti in nano particelle con azione foto-catalittica, al fine di introdurre nel settore del restauro lapideo nuovi formulati di cui se ne conoscano preventivamente le caratteristiche chimico-fisiche e le possibili interazioni con gli agenti esterni ed i substrati lapidei.

Un ulteriore obiettivo in procinto di attuazione è stato la divulgazione dei risultati ottenuti in riviste specializzate e la presentazione degli stessi a congressi specialistici nazionali ed internazionali.

Durante il primo semestre, la ricerca si è proposta di individuare fra i prodotti suggeriti dall'azienda Tenax i più tecnicamente adatti all'applicazione nel settore del restauro e della conservazione. In collaborazione con i responsabili aziendali sono stati selezionati 6 prodotti con formulazioni e caratteristiche tecniche differenti l'uno dall'altro. I formulati sono stati preventivamente caratterizzati e ampiamente studiati in forma sol e gel presso il laboratorio L.A.M.A., quindi sono stati applicati su provini in marmo di Carrara e Pietra bianca di Vicenza, infine monitorati ad avvenuta polimerizzazione. I provini trattati sono stati esposti all'esterno per la durata di 3 mesi consecutivi.

Nei successivi 6 mesi del progetto, i provini sono stati monitorati mediante specifiche tecniche analitiche, quindi sottoposti ad ulteriori 3 mesi di esposizione ambientale e nuovamente monitorati in laboratorio. In questo secondo periodo inoltre i prodotti oggetto di valutazione sono stati applicati su altri provini in marmo di Carrara e Pietra bianca di Vicenza, analoghi a quelli già citati in precedenza. Se una parte di essi è stata utile al fine di studiare la propensione al biodeterioramento delle superfici trattate, una seconda parte invece dei provini è stata sottoposta, presso i laboratori aziendali di Tenax, ad invecchiamento artificiale in apposita camera climatica Q-Sun per un totale di 400 ore, monitorando l'effettivo degrado ogni 200 ore di esposizione.

Parallelamente è stata condotta un'indagine su un prodotto commerciale noto e tuttora in uso nel settore del restauro con il nome di Paraloid B72, impiegato sia come consolidante che come protettivo dei manufatti lapidei. La metodologia analitica utilizzata per lo studio di questo prodotto è stata la medesima di quella a cui sono stati sottoposti i prodotti Tenax. I risultati ottenuti sono stati utilizzati come riferimento per la valutazione finale dell'efficacia dei consolidanti e protettivi oggetto della ricerca.

2. METODOLOGIE OPERATIVE

2.1 MATERIALI:

PRODOTTI COMMERCIALI OGGETTO DELLA RICERCA:

I prodotti commerciali selezionati e oggetto di studio sono stati:

- RESINA EPOSSIDICA CONSOLIDANTE A BASSO INGIALLIMENTO + INDURENTE A BASSO INGIALLIMENTO: resina epossidica formulata appositamente per essere un intermedio fra le resine CONSOLIDANTE STANDARD e RESINA GLAXS, miscelata in rapporto 1:1 con indurente a basso ingiallimento;
- RESINA EPOSSIDICA CONSOLIDANTE STANDARD + INDURENTE STANDARD: resina epossidica consolidante RCC miscelata in rapporto 1:1 con indurente ICC4/100;
- RESINA GLAXS RC + HARDNER GLAXS 200: resina consolidante bicomponente di nuova generazione a zero ingiallimento al sole, miscelata in rapporto 1:2 con indurente GLAXS 200;
- SKUDO MARMO: protettivo in soluzione acquosa (resistente all'acqua e all'olio e antimacchia);
- SELF-CLEANER: trattamento autopulente foto-catalitico a base acquosa con nanoparticelle di biossido di titanio;
- SEALUX: cera in soluzione acquosa.

<u>SUPERFICI OGGETTO DI STUDIO:</u>

La ditta Morseletto srl, partner del progetto di ricerca, ha messo gentilmente a disposizione del Laboratorio di Analisi dei Materiali Antichi (L.A.M.A.) e della ditta Tenax spa, alcuni provini in marmo di Carrara e pietra bianca di Vicenza con dimensioni regolari di 5 x 5 x 2 cm.

I provini sono stati posti in stufa per 48 ore a 70°C, quindi in essiccatore per 24 ore, e successivamente pesati utilizzando una bilancia analitica.

I provini sono stati caratterizzati mediante le tecniche analitiche illustrate in seguito (osservazioni microscopiche, valutazioni colorimetriche, misure di idrofobicità, analisi FTIR), e su ciascun provino è stato effettuato un trattamento superficiale a pennello con uno specifico prodotto fino a completa imbibizione (solo una delle due facce ad area maggiore è stata sottoposta a trattamento).

I provini sono stati suddivisi in tre gruppi con denominazioni differenti a seconda della tipologia di invecchiamento a cui sono stati sottoposti.

2.2 TIPOLOGIE DI INVECCHIAMENTO

- <u>Esposizione ambientale</u>

Alcuni fra i provini trattati sono stati esposti all'ambiente per 6 mesi, alloggiati su appositi espositori inclinati di 60° dal suolo.

- Invecchiamento artificiale

Alcuni fra i provini trattati sono stati sottoposti ad invecchiamento artificiale in apposita camera climatica aziendale Q-Sun: Xenon Test Chamber, model Xe-3-H/HS/HBS di Q-Lab Corporation, secondo normativa ISO 11341 per un totale di 400 ore.

2.3 METODOLOGIA ANALITICA:

Prima di effettuare alcun trattamento superficiale, i provini sono stati caratterizzati tal quali mediante la medesima metodologia analitica che si è scelto di adottare per i monitoraggi del degrado degli stessi. Analisi spettroscopiche del tipo FTIR, osservazioni micro e macroscopiche, valutazioni del grado di assorbimento d'acqua mediante sponge test e variazioni colorimetriche, sono stati reputati procedure utili e adatte allo scopo della ricerca.
Di seguito, nello specifico:

ANALISI SPETTROSCOPICA DEL TIPO FTIR (Fourier Transform Infrared Spectrometer):

Lo strumento utilizzato è un Jasco FT/IR-4200 Fourier Transform Infrared Spectrometer collegato ad un Jasco IRT-5000 Irtron Infrared Microscope, in dotazione presso il Laboratorio di Analisi dei Materiali Antichi (L.A.M.A.).
I prodotti sono stati analizzati sia in forma liquida sia in forma polimerizzata. I risultati ottenuti sono stati confrontati con quanto ottenuto dall'analisi FTIR effettuata sugli stessi prodotti, sia in forma liquida che polimerizzata, utilizzando uno strumento Perkin-Elmer messo gentilmente a disposizione dal politecnico di Chania presso cui è stato effettuato uno stage.
Per ragioni di riservatezza aziendale non verranno presentati gli spettri ottenuti né le relative interpretazioni. Ciononostante è possibile affermare che grazie a questo studio è stato possibile studiare il meccanismo di polimerizzazione di ciascun prodotto.

MICROSCOPIA OTTICA:

I provini sono stati osservati utilizzando lo stereomicroscopio Leica Wild M3Z e il microscopio ottico Leitz Laborlux 12 POL S, entrambi in uso presso il laboratorio L.A.M.A..

Servendosi di fogli di acetato sono state costruite delle maschere di forma quadrata e dimensioni 5 x 5 cm, con 5 fori anch’essi di forma quadrata, uno centrale e uno in ciascuna zona angolare, ciascuno di dimensioni 1 x 1 cm, come illustrato in fig. 2. Adagiando la mascherina sulla superficie prima e dopo il trattamento, cos’ come durante i monitoraggi dei processi degradativi, sono state registrate 3 immagini per ciascun foro, ognuna ad ingrandimento differente: 10x, 16x, 25x. Questo procedimento ha permesso di avere una corretta documentazione fotografica sempre della stessa zona del provino, a fasi dell’invecchiamento differenti.

ANALISI COLORIMETRICA:

Utilizzando una maschera analoga a quella descritta nel paragrafo precedente ed illustrata in figura 2, ma con fori circolari del diametro di 6 mm ciascuno, sono state effettuate delle indagini colorimetriche impiegando uno spettrofotometro portatile Konica Minolta CM-2600d/2500d, messo gentilmente a disposizione dal Dipartimento di Scienze Molecolari e Nanosistemi (DSMN), partner del progetto. Per ciascuna area sono state effettuate 3 misurazioni e per ognuna ne è stato calcolato il valore medio. I valori così ottenuti per ciascuna area sono stati impiegati per il successivo calcolo della variazione colorimetrica media totale caratteristica di ciascun provino.

Lo studio è stato effettuato secondo la normativa “NORMAL – 43/93 Misure colorimetriche di superfici opache”.

SPONGE TEST:

Il metodo della spugna di contatto è un metodo per la determinazione della capacità di assorbimento di acqua di un materiale lapideo per unità di superficie in funzione del tempo. La prova avviene mediante contatto, a pressione costante, di una spugna imbibita di acqua deionizzata (spugna di contatto) e la superficie del materiale. È una metodologia analitica che si applica ai materiali lapidei, non trattati e a seguito di trattamento, ed è effettuabile sia in laboratorio che “in situ” su superfici piane.

La metodologia analitica è stato applicata seguendo la normativa “UNI 11432 Beni culturali – Materiali lapidei naturali ed artificiali: misura della capacità di assorbimento di acqua mediante spugna di contatto”.

PER MOTIVI DI SEGRETEZZA AZIENDALE NON VENGONO QUI RIPORTATI I RISULTATI OTTENUTI DALLA RICERCA.

CONCLUSIONI

Il lavoro di ricerca ha permesso di raggiungere gli obiettivi prefissati e di creare nuovi spunti per il proseguo della ricerca.

I risultati ottenuti hanno permesso a Tenax di approfondire le conoscenze riguardo i prodotti da loro formulati e parzialmente sperimentati, aprendo da un lato all'effettiva possibilità di migliorare alcuni fra questi, grazie alla messa in luce di aspetti negativi degli stessi, dall'altro lato all'eventualità di aprire il proprio mercato al settore del restauro proponendo alcuni fra i prodotti sperimentati che già denotano buone caratteristiche tecniche. L'assegnista ha avuto la possibilità di approfondire le proprie conoscenze nel settore dei consolidanti e dei protettivi, acquisendo maggiore manualità ed esperienza con le strumentazioni utilizzate, e confrontarsi con una realtà aziendale ed accademica di elevata professionalità. Il laboratorio L.A.M.A. infine ha potuto validare una metodologia analitica messa appunto per lo specifico studio di prodotti consolidanti e protettivi impiegati nel settore del restauro, ampliare il proprio settore di ricerca ed individuare possibili futuri sviluppi.