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CONSERVAZIONE E RESTAURO DI PIETRE ARCAICHE DELLE CITTÀ ANTICHE DI EUROMOS E IASOS – SVILUPPO DI NUOVI POLIMERI PER LA PROTEZIONE DI MANUFATTI LAPIDEI

CONSERVATION AND RESTORATION OF ARCHAIC STONES OF ANCIENT CITIES OF EUROMOS AND IASOS – DEVELOPMENT OF NEW POLYMERS FOR THE PROTECTION OF ARCHAIC STONES

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CHAPTER 1

1. Introduction

Since the end of the last century the use of scientific tools and methodologies to improve the knowledge of materials and their properties has increased not only in the conservation field of historic, artistic and architectural assets, but also in the archaeological conservation where the development of scientific research on materials is pivotal prerequisite for restoration and preservation work. The scientific technologies and methodologies are also indispensable evaluating the deterioration rate and developing procedures for stopping or slowing down further degradation. However, the scientific approach applied to restoration and conservation of archaeological sites, as in the case of the marble artifacts of the ancient cities of Euromos and Iasos, shows more difficulties than in the other fields of conservation. This is mainly due to the unavoidable interaction among different disciplines such as archaeology, history, art as well as the scientific disciplines of geology, chemistry, biology and physics. The areas under investigation in this thesis are the ancient cities of Euromos and Iasos that are under the liability of the Ministry of Culture and Tourism of Turkey, the Directorship of Euromos Excavation Muğla University (Turkey), Mission of Iasos di Caria (Italy) and the Directorship of Museum of Milas (Turkey).

In the study; applied research composed in the two parts. First part of research performed in the in-situ analyses that concern to investigation of the physical environmental characteristics of research areas; in relation to the environmental conditions which the stones are submitted, they have been properly identified and realized. In situ analyses have been carried out by thermal camera and portable thermometer for monitoring temperature and relative humidity on stone surfaces and the environment. Measurement of moisture performed by the protimeter on the stone artefacts. Second part of the research was performed in the laboratories. Determination of physical properties of various kinds of stones from Euromos Temple area performed by the optical and water porosity methods due to identify their organic and inorganic components, as well as to evaluate their physical, chemical and biological characteristics in order to estimate the degradation conditions and propose suitable conservative treatments. The author performed optical methods experiment for the stones from Agora of Iasos in his master thesis. In addition, this thesis, he is also performed water porosity experiments for these stones. Stones samples were taken from modern quarry of Mugla province exposed to extreme conditions (temperature, humidity) then the decay of the stones was determined via water repellence test by the water capillary absorption method for understanding degradation process of stone artefacts. In particular, innovative hydrophobic compounds to be used as protective agents have been designed, synthesized, tested on Turkish quarry marble samples, and compared with some commercial products. In situ tests with the same compounds used for the laboratory experiments have also been carried out. The innovative compounds belong to the partially fluorinated polymers (oligoamides with pendant perfluoropolyether segments). Tests for the evaluation of the efficacy and durability of conservative treatments, in relation to the environmental conditions which the stones are submitted, have been properly identified and realized. These compounds have been studied and tested on laboratory, also as well as in situ. Several organic/inorganic treatments have been performed in laboratory and in situ to select the more suitable compounds and application methodologies for consolidation and protection of these ancient stones.

CHAPTER 2

2.1. General Information on Research Areas

2.1.1. Ancient City of Euromos and Zeus Lepsynos Temple

The ancient City of Euromos is located at the southwestern of Turkey within boundaries of today’s Muğla province. It is near to the main road from Bodrum to İzmir and the settlement area is located in the northern part of Selimiye plain which is on the road that runs through Miletos, to the north-west of Mylasa (Map 1, Chapter 8, page 81).

Zeus Lepsynos temple was built near the eastward city walls of Euromos city walls of and the temple is one of the best preserved in Anatolia that is arrived until today. A major part of temple's columns is still standing. The type of structure is a peripteros (a building surrounded by a single colonnade). Six columns decorate each of front and back parts (short sides), while eleven columns decorate each of the long sides. The highest layer of the stone base of the temple is the Stylobate; it has dimensions of 14.40 x 26.80 m. The columns stand on the plinths in Attic-Ion style and are completed with Corinthian capitals. Sixteen of the are still standing today, together with architraves in groups -of octet, quintet and trio. Four columns of the temple haven't groove; three of them are in the south edge and another column is in the south-west part, this disposition shows that the construction of the temple was not realized at the same time, or it was partially destroyed and later reconstructed [1] (Figure 1, Chapter 8, page 82).

The standing column line is preserved mostly in the north and west directions and a column is missing in the northwest corner. In north long row eight columns are still complete with architrave and frieze blocks over. The eastern side, along with the pronaos, is the place where the temple was most destroyed. The three stylobate blocks, slipped through the overturned column, support this. [1]

The column bases of the temple are the attic-ion sitting on Plinthos. The Plinthos is 1.25 x 1.25 in height and 0.17m in height. The lower heel diameter of the pedestal sitting on the top is 1.21m. [1]

2.1.2. Ancient City of Iasos and Agora

Iasos is found in Caria, the region belongs to the south-western extremity of the Anatolia, overlooking the Aegean Sea. The city is situated inside of a deep gulf (famous in ancient like the Iasos Kolpos, today Mandalya Körfezi) approximately 70 km north of Bodrum (the ancient Halikarnassos) (Map 1, Chapter 8, page 81). The area of the city corresponds to a peninsula, approximately 900 m length and 450 m width, the altitude is between one and 80 meters above sea level (Fig 2, Chapter 8,page 83) The conformation of the site has guaranteed the presence of a naturally closed and protect main port on the western side, but also the possibility of berthing and ports of call on the opposite depositor, rendering it an ideal place for the exploitation of the peach and the development of trans marine traffics.

The city stood on a high rocky island, now connected to the Mainland by an isthmus. The Harbor was located on a Bay on the West side ("small sea"), with Roman docks on which was built a Byzantine defence tower (10-11th century). It preserves the layout and short stretches of the Hellenistic walls that surrounded the island. The theatre was built in the IV century BC on the North-Acropolis Eastern and restored in the 2nd century BC, as evidenced by an inscription; it was partly dismantled in Ottoman time. The temple is near the theatre dedicated to Dionysus. [2]

2.2. Previous Conservation Interventions

Ancient city of Euromos and Euromos Zeus Lepsynos Temple have been remained in-situ since they built. Euromos Zeus Lepsynos. The temple was restored using Portland cement and an iron crowbar used to reinforce the temple structure in the 1972-1979.Temple has been remained in-situ since 1979 without any interventions.

Ancient city of Iasos consists of three main parts and all of them have been restored in different periods in the past.

Comprehensive conservation interventions occurred on the stone-artworks in Iasos Fish Market Museum. The studies began in 2007 and completed in 2008.The study consisted of two main parts, the quantitative analysis done in 2007 and the application of the conservation work done in 2008 [3]. A water extraction process removed soluble salts from the easy lifted items for avoiding efflorescence.

The items were immersed into water for a 5-6 hour of continuous extraction. The process was repeated 2 times with drinkable and 1 time with distilled water.

After extraction the items were wrapped a few times with paper towel to control the drying. The stone objects with too large dimensions for immersion were wrapped with a poultice prepared from cellulose pulp and distilled water. The poultice was kept on the stone surface just before it was not completely dry. After this process, the amount of salt on the pulp was measured and when it reached a reasonable level (the conductibility was approximately 150 *μs)* the process was stopped. [3]

Detached layers from surface were reinforced with Paraloid B72 (*weight / volume in Toluen*) by order of 3% and 5% after desalination. However, foliated crusts that could not endure the washing processes were reinforced with concentrated Paraloid B72 before salt extraction, and the extraction process was carried out 3-5 days after the application of Paraloid B72. To prevent the rapid temperature changes on the surfaces of the stone-works, a temporary remediation could be to cover porticos and arched windows. [3]

On the other hand, the important stone artifact (Epigraph), were cleaned by a chemical method, i.e. the AB57 mixture. This stone, in fact, showed a high level of sulphate (mainly gypsum, $CaSO_4 \cdot 2H_2O$), not fastly dissolvable in water. Firstly, the metallic parts present on the stone were protected from the contact with the chemical agent, then a gentle cleaning with a soft brush was performed, followed by a scrubbing with plastic brushes and water. Finally, the jelly mixture of AB57 was applied on the sulphated surface, covered with polyethylene film and left overnight (15 h). The morning after, the polyethylene film was removed and the jelly paste containing gypsum was removed from the artifact with the assistance of water and brushes. In case all the gypsum was not removed from the artifacts the same application was repeated once more. After the second treatment with AB57 analyses for the presence of additional Cl^- and SO_4^{2-} were carried out. In this case, all the salts were removed, and a further salt extraction was not necessary. [3]

A study of the durability of some protective treatments has been realized on Iasos stone artefacts. Considering that these marbles, exposed outdoor in sheltered position, suffer of superficial decohesion and foliation in 2011[4,5]. Samples coming from Yatağan-Muğla has been used as substrate for the treatments. Two acrylic polymers (Paraloid B72 and Paraloid B67), three perfluorinated elastomers (NH, N935 and N215) and a natural polymer (animal glue) have been tested as protective agents. The specimens have been artificially aged, both in a climatic chamber, where temperature and relative humidity changes have been performed for simulating the natural decay, and under UV irradiation for simulating solar radiation. The efficacy and durability of the treatment have been evaluated by testing the water capillary absorption, the peeling resistance and the chromatic behaviour of the treated samples [4]. Although the exposition of the marble samples to artificial ageing is too short for selecting the polymers with the best performances, the fluoroelastomer having relatively low average molecular weight (N215) may be considered eligible protective and aggregating agent in these studies [4,5].

2.3. Conservation problems of Stone Artefacts of Research Areas

The stone show heavy biodegradation problems on all surfaces and various biological formations are well visible to the naked eye onto the stone artifacts in both areas. The main biological growth is represented by lichens (black, white, some yellow) (Figure 3). Biological growth and biological degradations on stone artifacts are effective when water and CO$_2$are present. As matter of fact, micro-plants that use minerals of the stone for their growth give rise to micro-cracks on the surface structure and contribute to the degradation of the material. Lichens, algae and bacteria that develop in the masonry are the cause of the deterioration of the stone surface.

Figure 3. Some biological formations on stone artefacts of Euromos Temple and Agora of Iasos

2.3.1. Biological problems

According to another study on the biodegradation problems of Euromos Zeus Temple, the presence of lichens proved that they may contribute to the formation of calcium oxalate monohydrate ($CaC_2O_4 . nH_2O$) [6]. Calcium oxalate monohydrate is most likely being formed on exposed surfaces of the marble monuments examined [6] (Figure 4). As calcium oxalates, and various clay minerals, phosphate ions and iron minerals are important compounds for vegetation [6], they should also contribute to the degradation of stones by favouring biological and microbiological growth on stone surfaces, Calcium oxalates and the other components above mentioned are, in fact, frequently found in decayed zones of calcareous monuments (exterior surfaces and cracked surfaces) [6]. Calcium oxalates may play similar roles in decayed zones of monuments like in soils. Lichens and mosses contribute to the formation of soil on the rock by catching organic residues such as dust, plant fibers, seeds, insect measurements, animal wastes coming from the wind. They form a thin layer of soil on the rock surface.

Figure 4. Calcium oxalate monohydrate ($CaC_2O_4 . nH_2O$) formation in architrave of Euromos Temple.

Lichens and mosses also release very dilute carbonic acid (H_2CO_3), causing the dissolution of $CaCO_3$-based rocks and accelerating soil formation. Leading plants, such as lichens, allow the development of higher plants by creating soil rich in organic matter, necessary for their growth. Organisms (lichens, etc.) give out CO_2 by breathing and when the rock is wet, CO_2 is dissolved in the water, so that the weak acid occurred after this process (carbonic acid, H_2CO_3) dissolves $CaCO_3$-based rocks that are in direct contact with the organism and this dissolution process reduces the cohesion of stones and pieces break away from the stone by the effects of rain drops [6].

Heterotrophic sulfate and nitrate bacteria are known to live on the stones. Sulfate bacteria (sulfate oxide bacteria), lead carbonate and lead oxide which are in composition of rock formation bring the white lead coming from the chemical pathway to the black PbS. This form of lead carbonate is greyed out and can be diagnosed in this way. As initially identified in this study; fungi in the lichen can only be observed under the microscope and fungi are involved to (with sports of fungi) reproduction of lichens. In addition, fungi are wrapping algae cells with their hyphae that would have protected them from being dry and free from external influence. When the algae and fungus cells come together, and they formed to lichen; they start producing substances in diverse colours and it is become a new creature with a different appearance on stone surfaces [6].

Micro-Plants that use minerals of the stone for their growth give rise to micro-cracks on the surface structure and contribute to the degradation of the material [7]. Lichens, algae and bacteria that develop in the masonry are the cause of the deterioration on the surface of the stone. Lichens are difficult to remove from the surface of marbles or stones composed of $CaCO_3$, because they live in symbiosis between their roots and the stone surface [7]. Autotrophic bacteria are classified as follows according to the cleavage activities on significant role in carbonate stones [7]. Atmospheric pollution and weathering of stone surfaces in urban historic buildings frequently results in disfigurement or damage by salt crust formation (often gypsum), presenting opportunities for bioremediation using microorganisms [7]. Conventional techniques for the removal of these salt crusts from stone have several disadvantages: they can cause colour changes; adversely affect the movement of salts within the stone structure; or remove excessive amounts of the original surface [7]. Although microorganisms are commonly associated with detrimental effects to the integrity of stone structures, there is growing evidence that they can be used to treat this type of stone deterioration in objects of historical and cultural significance [7]. In particular, the ability and potential of different microorganisms to either remove sulphate crusts or form sacrificial layers of calcite that consolidate mineral surfaces have been demonstrated [7]. Current research suggests that bioremediation has the potential to offer an additional technology to conservators working to restore stone surfaces in heritage buildings [7].

2.3.2. Soluble Salts and Other Compounds

Preliminary chemical analyses on the stone objects showed that insignificant amounts of chlorides and phosphates were present on all the stone objects.

These salts are visible on the stone items as efflorescence, as well as sub-efflorescence, depending on the exposition of the objects to sun light that it means to different changes in temperature and relative humidity. Temperature decreases during the night in all the stone objects, but the surfaces exposed to sun during the morning are subjected to a rapid increase of temperature and the formation of sub-efflorescence. On the other surfaces, efflorescences are more frequently found.

CHAPTER 3

3. Basic Operations and Concepts in Stone Conservation Processes

3.1. Materials in Use and Under Study

3.1.1. Cleaning

Cleaning is often one of the first steps to be undertaken by removing the dirt, one can better see the condition of the underlying stone and thus judge what further conservation may be necessary. Several authors have emphasized the damage that can be caused by cleaning: loss of surface, staining, deposition of soluble salts, or making the stone more vulnerable to pollutants or biological growths [8,9,10]. In situations where soluble salts are a major contributor to decay, it makes sense to try to remove the salts. The removal of water-soluble salts sounds tantalizingly easy, but it can prove difficult in practice. Desalination of masonry is usually attempted using poultices, which may consist of clay, paper pulp, or cellulose ethers. In those instances where calcium sulphate is to be removed, additional materials may be added in order to increase its solubility. Clearly there are overlaps here with cleaning, especiallyin the removal of black crusts. The additives may include EDTA and its sodium salts, sodium bicarbonate, ammonium bicarbonate, and ammonium carbonate [11,12,13]. More exotic methods of desalination may invoke the movement of ions and of solutions under the influence of electric fields. Skibinski in particular has advocated the use of membrane electrodialysis for artefacts, although it has not gained wide acceptance. Friese has described a system that can be applied to masonry, although few details are given whereby its effectiveness and potential hazards can be assessed. [14,15]

Hempel was one of the first to raise the possibility of biological cleaning. He had been surprised by the effectiveness of a clay poultice containing urea and glycerol and proposed that microorganisms were at least partially responsible [16]. Kouzeli has reported favourably on the technique in comparison with pastes based on EDTA or ammonium bicarbonate [17]. Biological cleaning, in general, has been little researched. Gauri, however, has demonstrated the use of the anaerobic sulfur-reducing bacterium *Desulfovibrio desulfuricans* in removing the black crust on marble [18]. He has argued, moreover, that the bacterium was converting calcium sulphate back to the calcium carbonate from which it was originally formed [19].

The use of bacteria in desalination may merit further attention. Gauri's use of sulfur-reducing bacteria to eliminate the black crust has already been mentioned [19], and Gabrielli gives an anecdotal account of the use of cow dung to convert nitrates to elemental nitrogen. One wonders, however, how many other salts are added at the same time [20].

3.1.2. Consolidation

Where stone is severely weakened by decay, some form of consolidation may be necessary to restore some strength. One of the properties that a consolidant must have is the ability to penetrate the stone. This requires a low viscosity and a low contact angle. The consolidant needs to stiffen or set once it is in place in order to strengthen the stone. These requirements can be met in three ways: First, one can apply a wax at elevated temperatures that stiffens as it cools down. In practice, it is hard to get a low enough viscosity without excessive heat, and the wax tends to be sticky and to pick up dirt. The second approach is to use a consolidant dissolved in a solvent. Consolidants are usually applied to the surface of the stone by brush, spray, pipette, or by immersion, and are drawn into the stone by capillarity. Domaslowski experimented with a "pocket system" that was intended to hold the consolidant against the stone [21], and Mirowski has described a system of bottles for maintaining a steady supply of the consolidant at a large number of points [22]. Schoonbrood has developed a low-pressure application technique that maximizes capillary absorption [23]. Vacuum systems may also be used to facilitate penetration into movable objects [24]; the vacuum system developed by Balfour Beatty Limited for use on monuments did not find extensive application in practice [25].

Two compounds, in particular, have been dominant: methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS). The silanes are hydrolyzed by water to form silanols, which then polymerize in a condensation reaction to give a silicone polymer. Epoxy resins have had a very bad press as far as consolidation is concerned.

Many conservators see them as viscous, brittle, yellowing materials that may make admirable adhesives in some circumstances, but which are certainly not to be considered as consolidants. Although in situ polymerization of methyl methacrylate (and another acrylic monomers) has its advocates, the high rigidity and glass transition temperature of polymethyl methacrylate are generally considered to make it unsuitable as a stone consolidant. Far more attention has been given to the use of acrylic resins dissolved in solvents, and the ubiquitous Paraloid B72 (Acryloid B72) inevitably makes its appearance. Many conservators have experimented with B72 dissolved in an alkoxysilane such as MTMOS, the reasoning being that the B72 brings adhesive properties that the alkoxysilane lacks. The B72 is capable of securing pigment or loose flakes, for example, while the alkoxysilane provides deep consolidation. However, Wheeler and coworkers have shown that the resulting composite gel is weaker than the polymers derived either from neat MTMOS or from a solution of B72 in a nonreactive solvent [26,27].

3.1.3. Protection

Surface coatings is a bit of a catchall category that includes a range of materials applied to stone─protective water repellents, emulsions, antigraffiti coatings, salt inhibitors, protective oxalate layers, sacrificial lime coatings, colloidal silica, biocides, and bioremediation treatments. A substantial research effort in the 1970s and 1980s was aimed at finding a single treatment that would both consolidate and protect stone.

Protective treatments need to be maintained, and this means retreatability needs to be taken into consideration when designing a treatment system. Surface coatings can be renewed at regular intervals, but the initial consolidation will, it is hoped, last much longer.

Water repellency has been provided largely by alkoxy silanes, silicones, and fluoropolymers. The development of the fluoropolymers provides an interesting, and regrettably rare, instance of "tailor-made" products. The polymers are close relatives of polytetrafluoroethene (PTFE, or Teflon), renowned for its non-stick properties. The early fluoropolymer coatings worked well, except for a rather poor ability to stick to the stone! Subsequent development has entailed the synthesis of compounds containing functional groups that can adhere to the stone surface, thereby providing more persistent protection [28].

Another example of "tailor-making" is provided by Fassina and Coworkers, who have synthesized a range of fluorinated acrylic polymers [29,30]. The intention, which was partially achieved, was to improve water repellency and resistance to photooxidation, by comparison with nonfluorinated analogues such as Paraloid B72. The use of fluorinated polyurethanes has also been reported [31].

Aqueous emulsions have been studied by a number of researchers. The emulsions have included acrylics and silicones [32, 33], silanes [32], and fluorinated polyurethanes [34]. Performance varies from stone to stone but is generally promising.

Water-repellent coatings prevent the ingress of liquid water, but they do not prevent the passage of water vapor. Moreover, many surface coatings are also permeable to harmful gases such as sulphur dioxide [35], for example, have shown that calcium sulphate forms on the surface of calcareous samples that are exposed to sulphur dioxide after treatment with a silicone resin. However, have emphasized the potential of polymeric membranes that are permeable to some gases and not others. It is possible, in principle, to deposit on the surface of stone a membrane that is permeable to water vapor, for example, but not to sulphur dioxide. It should also be possible to deposit "directional" membranes, which are more permeable in one direction than in the other [36]. The membranes can be deposited from solution, but further work is required to demonstrate whether the technology can be transferred from the clean conditions of the laboratory to the conditions that are found on the surface of monuments.

There is a long history of research into surface treatments that will kill biological growths and, if possible, inhibit regrowth. Such treatments must meet a large number of criteria, and this can prove difficult in the outdoor environment, where there is a continual supply of moisture to promote regrowth. The existing research on biocides has been concerned with algae, lichens, and higher plants like weeds, mosses, and ivy. Some of the research has been based on cultures in the laboratory, while most of it has been based on site trials. Examples of such research are provided by Agarossi, Ferrari, and Monte and Anagnostidis [37,38]. The latter also emphasize the need for regular observation and retreatment and they suggest "early warning systems" to indicate the moment for retreatment. Caneva, Nugari, and Salvadori provide a valuable account of the many available biocides, which are normally applied to the surface of the stone by brush or spray [39]. Portable objects may also be treated by fumigation: for example, report the use of ethylene oxide [40]. Bassier reports the use of ultraviolet radiation to sterilize mineral surfaces [41]. Caneva mention the possibility of preventive conservation by the deliberate introduction of suitable vegetation in the vicinity [39]. It is possible that some water repellents may have a biocidal effect. Sorlini, Falappi, and Sardi report the inhibition of fungal growth by a methyl phenyl silicone resin [42], but other workers have reported the opposite effect: the biodegradation of silicones [43,44,45]. In some cases, polymeric treatments of stone become food for microbes, leading to the production of organic acids and other biological activity related to the consumption of surface treatments [46,47]. However, this biological affinity for certain otherwise insoluble, cross-linked organic material has also been used as a bioremediation treatment to remove the hardened glue from the surface of a fresco fragment in storage for twenty years [48].

Accelerated or artificial tests of hydrophobic coatings as a method for reducing the effects of air pollutants on porous, calcareous stone have had mixed results, with the protective effect decreasing rapidly with time in bulk samples [49].

3.2. Basic Concepts of Stone Restoration

Polymers generally are used in conservation of stone and mainly in consolidation, protection and joining of small pieces. Polymers for consolidation treatment have:

An improvement in the cohesion of mineral constitutes,

A good penetration inside the porous material in order to obtain a uniform distribution between the deteriorated and sound areas.

An increase is in the mechanical resistance of the consolidated stone.

Waterproofing is not an essential requisite for a consolidation agent, as this characteristic can be achieved by the application of a protective treatment.

Expected performances of the polymers to be used for protective treatment are:

Water repellence, permeable to vapor, colorless and transparent

Chemical stability (temperature, humidity, acid, base and UV irradiation)

Reversibility

Not reactive with the substrate (protective agent does not produce by –product)

Homogenous absorption by the stone surface and inside the pores

3.2.1. Products for Consolidation and Protection

Compounds for consolidation and protection can be achieved both inorganic and organic products. Organic products are mainly polymers. Polymer products for stones generally are collected under two main classes; silicon-based polymer and acrylic polymer.

Silicon Based Products

This group includes a large number of products different in chemical composition, ranging from alkaline silicates to silicone resins. Inorganic alkaline silicates and fluosilicates have been used since the second half of the last century. In the class of consolidants which produce silica after a hydrolytic reaction, silica esters (mainly ethyl silicate) are presently widely use. They have the advantage of good penetration and do not produce dangerous by-products.

Acrylic Resins

Acrylic resins are a group of related thermoplastic or thermosetting plastic substances derived from acrylic acid, methacrylic acid or other related compounds [50]. Among thermoplastic resins, acrylic polymers are probably most commonly used for stone consolidation. Acrylic resin is a general term for any one of the plastics (resin) generated through chemical reaction by applying polymerization initiator and heat to a monomer. The chemical name for the resin produced from the methyl methacrylate monomer (MMA) is polymethyl methacrylate (PMMA). MMA is a transparent and colourless fluid substance. [50] One of the main characteristic features of PMMA is its high transparency with its relatively weather resistance; it has been known to last over 30 years. [50] However the most frequently acrylic polymer used in the field of stone conservation is poly (ethyl methacrylate-*co*-methyl acrylate) (PB72), which is a polymer with suitable Tg and good stability. In fact, it is considered the most stable polymer among the acrylic and methacrylic polymers.
Some polymers these groups (silicon and acrylic resins) together the stones where they are prudentially applied.

All materials, including stones, attempt to reach a state of equilibrium regarding environmental parameters (temperature, relative humidity, air quality, etc.). If one or more of these parameters change, a new state of equilibrium must be reached through some modification of the stone conditions (chemical composition, content of water, etc).

These modifications as a whole produce the deterioration of the stone; the more frequent the environmental variations, the faster the alteration of the stone. The aim of any protective treatment is to reduce the probability of alteration process or, at least, slow them down.

This can be achieved either by modifying environmental conditions or by applying a suitable product to the stone, or both.

Sequences are joining, integration and replacement applications in restoration of stone artefacts. Epoxy resins are commonly used for bonding of stone artefacts. Epoxy resins are thermosetting resins, which are cured using a wide variety of curing agents via curing reactions. Their properties depend on the specific combination of the type of epoxy resins and curing agents used because of their excellent mechanical properties, high adhesiveness to many substrates, and good heat and chemical resistances [51,52]. In the case of restoration of large blocks of stone artefacts can be used epoxy resins with stainless steel rods due to increase adhesion strength.

Integration applications are usually made by ready plaster on the historical stone artefacts. Main features of these plasters must respect values determined by standard methods such as UNI / EN 1015/ 12 (water repellence and penetration depth standard), UNI / EN 1015 /19 (Vapour permeability standard) and WTA (Standard of resist against efflorence) [53, 54]. FRP (Fiber Polymer Bars) are used with plasters in some case of low adhesion areas.

When repairs are being planned for a large building (like a temple); quarrymen and geologists are often asked: “Which of the available stones will provide good durability and a compatible match to the existing stone?” [55]. Finding appropriate replacement stone requires tools for stone selection such as atlases and databases [56,57]. A useful discussion of aspects of selecting replacement stone based on material properties can be found in two recent works [58,59].

CHAPTER 4

Aim of Thesis

Ancient cities of Euromos and Iasos are in the region of Caria, in the modern Southwest Anatolia (Turkey). The cities were built in natural stones (mainly marble) extracted from the quarries close to the ancient cities. These ancient cities have stood for at last 2000-2200 years. Nowadays, what remains of the ancient cities are just some items and the ruins of the old buildings; however, they are important testimony of the old civilization.

Research for understanding the degradation processes of stones of Iasos, the disintegration of the surfaces where inscriptions are present, and for evaluating the possibility to protect the surfaces started in 2007.

In order to identify the processes of degradation of the stone surfaces, diagnostic analyses (for the identification of natural organic compounds used in previous restoration treatments and for characterization and semi-quantification of soluble salts), and acquisition of thermo-hygrometric data, realized both on the surface and in the vicinity of the object (for evaluating the effect of the environmental parameters on the degradation) were carried out.These analyses were followed by a preliminary restoration of some items; the restoration concerned the extraction of soluble salts and the consolidation of stone by injection of an acrylic resin (Paraloid B72).

A possible strategy to protect the stone surfaces was investigated during the thesis work after the mineralogical and chemical characterization of samples of marble coming from the archaeological area of Iasos quarry samples of marble (quarry of Kozağaç – Yatağan-Milas) like the marble of Iasos, were treated with some synthetic and natural polymers commonly used as consolidants and protective agents for stone. Their performances were evaluated before and after a short artificial ageing test.

The degradation processes of stones of the Euromos area (Euromos Zeus Temple and other part of temples of the ancient city) are like those observed in Iasos, however here the main conservation problem seems to be related to wrong restoration methodologies. In fact, restoration treatments with Portland cement are well visible in many parts of the temples.

In August 2012, a campaign of measurements has been realized by a thermal camera (for emission values), a protimeter (for humidity on stone surfaces) and a thermometer (for environmental climatic values).

Research objectives

In this PhD thesis, I intend to obtain results which may be of support for conservators and responsible for conservation of this cultural heritage.

The main objectives of the research may be summarized in the following steps:

Extended characterization of ancient marbles sampled on different but pre-selected items of the Euromos and Iasos areas. This characterization is finalized to the evaluation of the alteration state of the stone and to identify the main causes of decay, included previous treatments;

Monitoring, on stone surfaces and in the environment, of temperature, relative humidity, and solar radiation or, eventually, other parameters, if they will be considered relevant for this study. The results of this monitoring will be taken in consideration for planning artificial ageing conditions of quarry samples (treated and untreated);

Testing of several organic/inorganic treatments (traditional and/or innovative) in order to select the more suitable compounds and application methodologies for protection of ancient stones. The tests will be carried out in laboratory, on quarry samples having similar characteristics than the ancient stones, and will concern the evaluation of the properties of the products used (hydrophobic properties, permeability to water vapor, color change, penetration depth, resistance to ageing etc.);

Innovative compounds or formulations have been designed based on the results obtained with the traditional ones. They may be synthesis new protection in the class of partially fluorinated polymers;

The selected compound(s) have been also tested in situ, on some areas used as area test for monitoring the natural ageing of the treatment(s).

CHAPTER 5

5.Results and Discussions

5.1. Environmental Conditions of Research Areas

In the natural environment, changes in temperature and moisture are supposed to be key factors in stone degradation. They can cause a pronounced loss of relief structure due to granular decohesion. [60] The often-cited bowing of marble panels is also discussed as being due to the anomalous expansion-contraction behaviour of crystals [60].

Research areas Euromos Zeus temple and Agora of Iasos located in the same province however, Agora of Iasos has been established near the sea. Between of the two areas there is a mountain (altitude is 681 m). In this case, weather and climate conditions of two areas must be investigating to understand the stone degradation processes for the beneficial research.

Meteorogical parameters have been taken from local environmental database (between years 2012- 2017, generally August) as well as from in-situ settlements. Environmental database from 1970 to 2011 in Milas province were taken from Meteorological Department, Water Affairs and Forestry Ministry of Turkey for comparison with current values.

Average environmental values of August from 1970 to 2017 in Milas province are reported in the Table 1.

Year(s)	Month	Temperature (^{0}C)			RH (%)		
		Min.	Max.	Average	Min.	Max.	Average
2012	August	19.0	33.4	26.2	21.4	36.2	28.8
2013	August	20.0	41.4	30.7	12.0	84.0	48.0
2014	August	20.4	42.0	31.2	13.0	98.0	55.5
2015	August	22.1	41.2	31.6	14.0	95.0	54.5
2016	August	19.2	41.3	30.2	12.0	93.0	52.5
2017	August	22.0	40.0	31.0	35.4	88.6	62.0
1970 -2011	August (40 years Average)	20.2	43.6	31.9	7.0	51.2	29.1

Table 1. Environmental Average Values of August in Milas Province*

**Meteorological Department, Water Affairs and Forestry Ministry of Turkey*

Local environmental values found in situ during August 2017. The values are reported as average values from morning earlier (06:30 am), noon (12:30 pm) and the evening (06:30 pm) in the research areas are representing in Table 2.

August 2017	Temperature (^{0}C)			RH (%)		
	Min.	Max.	Average	Min.	Max.	Average
Euromos Temple Area	28.9	37.6	33.25	18.1	56.7	37.4
Agora of Iasos	16.6	38.0	27.3	29.5	36.5	33.0

Table 2. Local environmental conditions of Settlements in August 2017

According to Table 1 and 2, average values have been not changed relatively in August from 1970 to 2017, but we can observe differences between the two archaeological areas. Euromosis hotter than Iasos and more humid.

According to values of imaging; the temperature conditions of stone artefacts of temple are similar to environmental values. Except, the average heat values of the filled parts with Portland cement that have been found lower than about 10 ^{0}C in respect to the environmental values found in stones artefacts of temple (Figure 5,6, Chapter 8,page 84). Portland cement is generally recognized as a resource of soluble salts. This characteristic is dangerous for natural stone that efflorescence and their phenomenon (dissolution and re-crystallization of salts). Moreover, it must be noticed that the thermal and hygrometric expansion coefficient among the three materials (natural stone, Portland cement and iron reinforcing bar) are different. This difference is emphasized by the differentiated condensation conditions, according to the thermal camera imaging data found in other parts of the temple.

Investigation of environment of Agora performed in summer of 2017. Thermal camera imaging had been performing in some periods of May, June, July and August (Table 3, Chapter 8, page 86).

Even the time is limited, according to the measurements of temperature and relative humidity, the surface temperature of the stone-works on the west portico increases quickly because they receive morning sun and in conclusion they dry suddenly. The surface temperature increases till the sun changes its direction. The surface temperature of the stone-works on the north and east porticos increases till receive sun light directly, when the light comes directly, the increasing of the surface temperature is accelerated. The stone-works on the south portico are prone to both conditions. (Figure,7, 8 Chapter 8, page 85).

In addition, the temperatures of the parts filled with Portland cement were less than about 10 ^{0}C in respect to the environmental values in stones artefacts of Bouleuterion of Agora (Figure 9, Chapter 8, page 85).

Evaluation of all results shows us that there is condensation on all surfaces due to high relative humidity in the air and low surface temperature during morning hours. The rapid vaporization of the condensed water on the surfaces is faster during the morning when the temperature increases quickly.

Moisture is one of the causes of swelling and shrinking that can be observed for a large quantity of stones upon exposure to humid (or wet)–dry cycles [60] and this has been mainly attributed to the swelling and shrinking to clay minerals. However, the terms hygric and hydric should not be referred to the mechanism but rather to the condition under which the wetting of the material occurs. Thus, the general term ‘‘moisture expansion’’ will be used to describe the volume change processes that result by either condition. The water with lower electrolyte concentration has the effect of balancing the concentration. Consequently, water is taken up by osmosis between the mineral particles thus pushing them apart. This process is known as ‘‘osmotic swelling’’ [61,62].

The results of moisture measurements show that the stone blocks of the temple do not have a dangerous fluctuation of moisture. In addition, the humidity measurement was made separately from the bases to the columns of all the façades of temple. Also, these results show that no water transfer from the base to the column occurred (Figure 10, Chapter 8, page 86). Nevertheless, a dangerous fluctuation of moisture was not detected in the architectural stone blocks in the Agora of Iasos.

Rain is another source of water in natural stones [62]. For this reason, the rainfall rate is another important parameter to understand the deterioration of these architectural stones. According to data of rainfall of Milas province taken from Meteorological Department, Water Affairs and Forestry Ministry of Turkey; rain falls most intensively in December and January in all average. Amounts of total rainfall are 677,6 kg/m^2 in February and March according to values of 2012 and 2017 (Table 4,5, Chapter 8, page 87). These rainfall amounts of Milas province is not seen in the other months of years. Considering that sweltering summers have been occurred in this area, rainfall is not too much dangerous parameter for degradation of stone artefacts in the Milas province.

5.2. Descriptions of Stones from Research Areas

5.2.1. Stones from Euromos Temple Area

Rock fragments called Degraded Grey (DG), Degraded White (DW), Degraded Vein (DV) and Euromos Quarry (EQ), have been analysed. Degraded Grey (DG), Degraded White (DW), Degraded Vein (DV) were taken from the surrounding of Euromos temple area. Rock fragments of Euromos, Quarry (EQ) was taken from ancient quarry close to Euromos Temple area. Thin sections obtained from rock samples were examined under an optical microscope and their water porosity was evaluated. Physical descriptions of samples are given below.

Degraded Grey (DG)

This sample is mainly composed of quartz and feldspar grains (Figure11 A and B). The quartz grains are sub-rounded and well sorted. There is no cement in this section. All grains are well sorted, grain supported by each other. Quartz (SiO_2) and feldspar are equilibrium grains and metamorphism direction are well observed. Moderate grains, K- feldspar, quartz (SiO_2) are heterogeneous grains.

Plagioclase is clearly observed in this section and orientation of twins indicates to low metamorphism. Sub-angular grain is from immature to mature grains and this Sub-angular grain demonstrated that the decompositions level is high (Figure 11 C and D). Moreover, sedimentary rocks fragments are also clearly visible in this section. Hematite (Fe_2O_3) solutions are also observed among the grains. According to the water porosity test, DG has 0,75 % porosity.

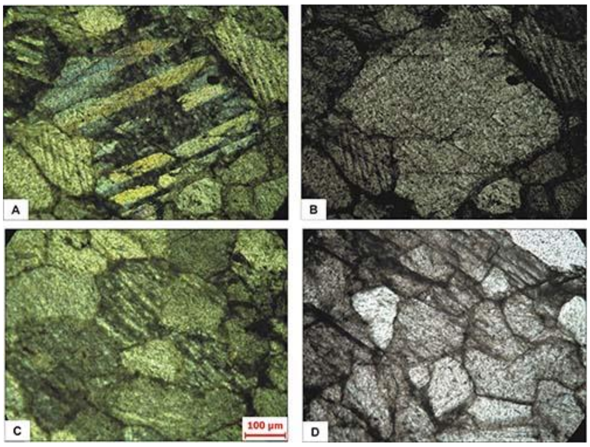


Fig. 11. The images of thin sections obtained from Degraded Gray (DG) samples. Quartz and feldspar grains are clearly observed

Degraded White (DW)

This thin section (DW) composes of moderate-sorted quartz and mostly consists of plagioclase grains (Figure 12 A and B). Plagioclase grains are highly altered, DW consists of about 80 % of feldspar grains, only a few quartz (SiO_2) grains and alteration traces of plagioclase are clearly observed. Grains are sub-angular, very fractured, grain supported and DW has no matrix, boundary which is among all grains are clearly visible. Plagioclase grains are quite larger than quartz (SiO_2) grain and these are generally altered, fractured and amorphous (not regular shape) (Figure 12 C and D). This is most probably related to tectonic activity of the region.

DW has also a small amount of Hematite (Fe_2O_3) solution but less than DG sample. This sample indicates immature rock with low-grade metamorphism and strongly affected by tectonic movements of the surrounded area. According to the water porosity test, DW has 0,67 % porosity.

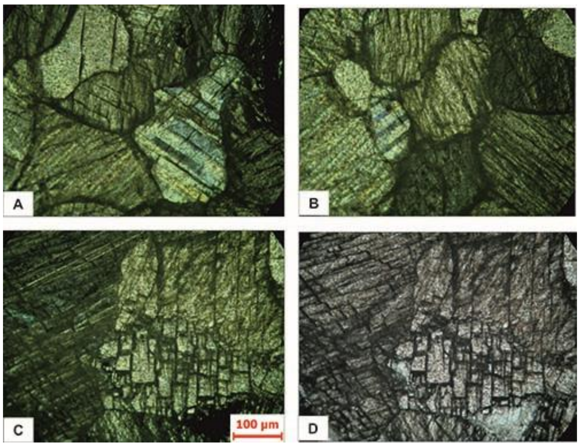


Fig.12. The image of thin section of Degraded white (DW) sample and fractured grains are clearly visible

Degraded Vein (DV)

Degraded Vein (DV) sample mainly consists of quartz (SiO_2), K- feldspar and plagioclase with poor sorted and coarse grains (Figure 13). The grain size of sub-angular and angular grains of DV is smaller than that of DW sample. Plagioclase grains are altered and hematite cement (Fe_2O_3) fills the space among the grains.

The poor-sorted and angular grains are related with transportation distance. Sample has not moved very far from the source and directly deposited and lithified.

Moreover, tectonic activity could have critical role on the sedimentary rock in this region. According to the water porosity test, DV has 1.00 % porosity.

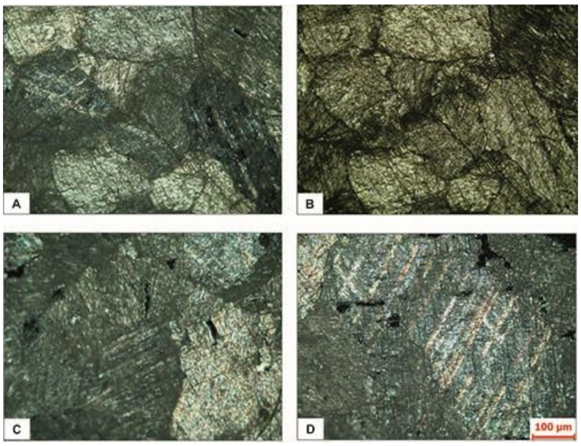


Fig.13. The image of thin section of Degraded Vein (DV) sample. The quartz and feldspar grains have been altered

Euromos Quarry (EQ)

The grains are angular and poor sorted (Figure 14 A and B). Euromos quarry (EQ) sample dominantly consists of feldspars, quartz (SiO_2) grains and some rock fragments (Figure 16 C and D). Quartz (SiO_2) is polymetric and plagioclase are altered, grain oriented by metamorphism (Figure 14 E and F). Grains are moderate-well sorted. Iron cement has filled the space among to grains. According to the water porosity test, EQ has 0,50 % porosity.

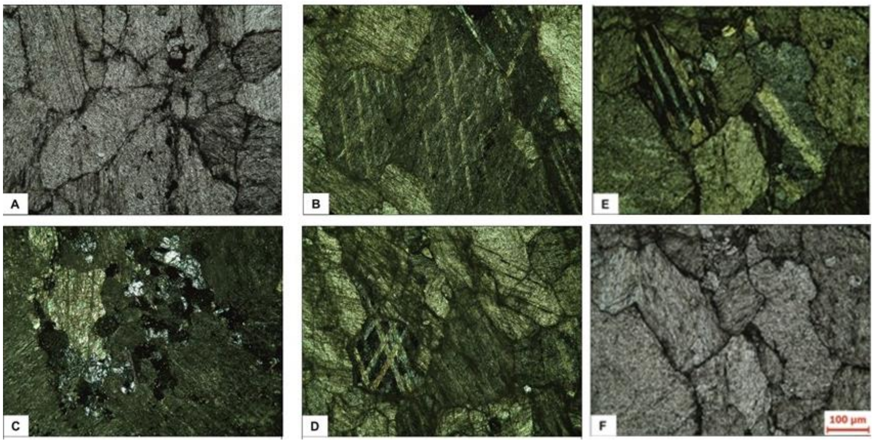


Fig.14. The image of thin section of Euromos Quarry (EQ) sample. The quartz and feldspar grains have been altered**.**

5.2.2. Stones from Agora of Iasos

The description of stones of Agora of Iasos has been reported in the author's master degree thesis. In addition, water porosity tests were performed on some stones samples of Agora of Iasos in this research. Stones samples of Agora of Iasos have been called HC1, HC2 and HC5.

Although, not used in this work for the application of protective agents, we give information about modern marble quarry samples from MY (Mugla / Yatagan) (Figure15, Chapter 8, page 88) in this section, because this kind of marble used to test some treatments application in author's master thesis shows similar properties to the stones of Iasos of Agora. In addition, this marble was also used on artificial ageing tests in this research.

HC1 is low-grade metamorphic and pure marble stones [63]. The water porosity of HC1 is 0.16 %. Sample of HC2 is a low grade metamorphic, impure marble [63] and water porosity of is 0.11 %. Sample of HC5 is a high- grade metamorphic pure marble [63] and water porosity is 0.10 %.

Modern marble quarry samples of MY is high- grade metamorphic marble [63] and their water porosity is 0.27 %.

Results of mineralogical and physical properties of stones samples show that samples have low-grade metamorphisms, except, MY and HC5.

Their water porosity of the stones analyzed ranges from 0.10 % to 1.00 %. According to mineralogical and physical results; the stone samples of the research areas show different physical and chemical- mineralogical properties. Therefore, their water capillary absorption properties are different. Moreover, porosity properties of stones are important parameter to apply protection materials. These physical and chemical data must be considered when protection materials application is performed.

The results of the mineralogical and petrographical analyzes will be used to understand the phenomena of decay in these types of marble / stones; under ambient conditions. The mineralogical composition and the texture characteristics of the marbles / stones are the main parameters for evaluating the resistance to deterioration.

At this point the field needs to move beyond basic characterization to a better understanding of material behaviour and the maintenance necessary to sustain long-term performance. In the process of stone characterization, it is important to recognize that while some stones have a similar composition, their behaviours may have few things in common. For example, Istrian stone, Lecce limestone, and Carrara marble are all carbonate materials, but their contrasting modes of deterioration depend more on their porosity, pore shapes, pore size distribution, and grain size than their chemical composition. One division of stone types is based on the percentage and relative ratio of pore-shaped and fissure-shaped voids [64].

The water is the main weathering agent, pores and micro-cracks have considerable effects on the fluid storage and diffusion capacity within the building material inevitably favouring its deterioration and lowering the mechanical resistance [65]. Benavente et al. examined the effect of the water permeability and pore structure on the strength of natural stone. They observed a linear and strong relationship between water permeability and capillary water absorption coefficient and defined that the parameter affecting the strength is the water content rather than water itself and the characteristic features of the natural stone [66]. Ioannou et al. tried to model the capillary water absorption behaviour of porous limestone using different liquids. They observed that the large pore structure reduces the capillary water absorption ability in contrast with the small pore structure [67].

5.3. Determination of Biological Growth on Stone Artefacts

According to introduction on biological problems affecting the sites under investigation, we confirm that heavy biodegradation problems on all surfaces and various biological formations are well visible to the naked eye onto the stone artifacts in both areas. In this case, primary characterization of biological growth on stone artifacts was carried out on a rock fragment coming from the ancient quarry of Euromos Temple.

This rock fragment was chosen because of its similarity with several biological formations on stone artefacts in both areas. Six points with evident growth of microorganisms were chosen on the rock fragment for the biological identification in laboratory (Figure 16).

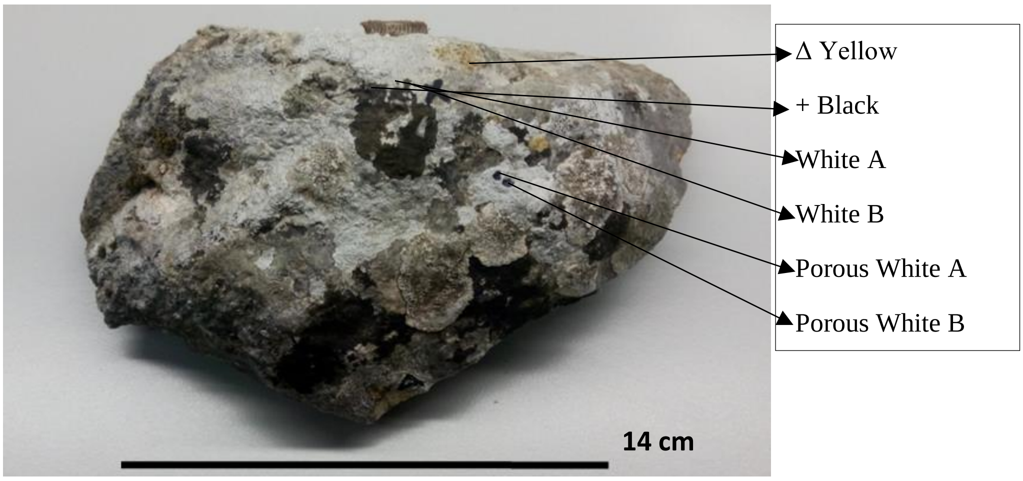


Fig.16. Microorganism sampling from rock fragment with names

Six samples of microorganisms were re-created in sterile conditions in six different plates. Each of the six samples that re-created of microorganism observed under the stereo microscope (X200 and X400). Primary results show that microorganisms are very complex live forms. Lichens and Fungi with were bacteria detected on White Porous B, Δ Yellow and +Black. Results are shown in following figures.

Sample of White Porous B and Δ Yellow

They are typical fungi with movement bacteria. This live form is composed of a large domain of prokaryotic microorganisms (Figure 17).

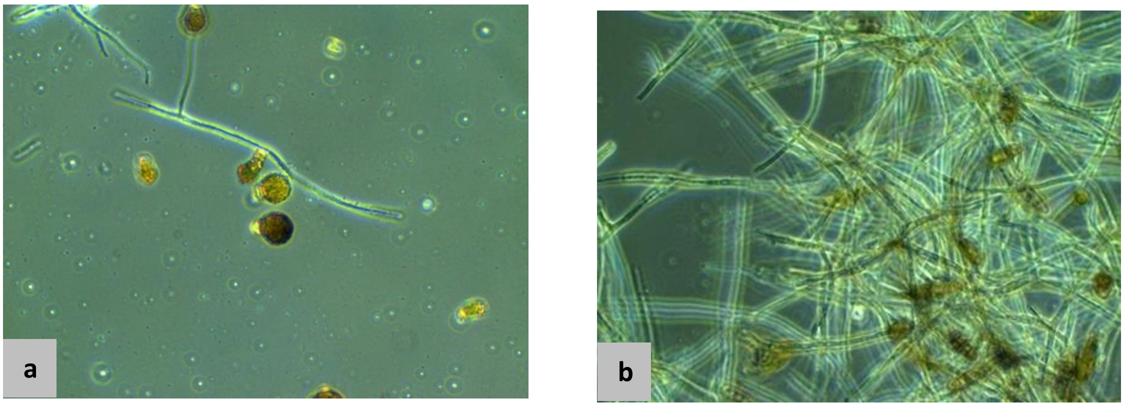


Figure 17. White Porous B (a) and Δ Yellow, fungi with bacteria (b)

From the biological point of view stone is an extreme environment poor of nutrients, with enormous changes of humidity, with mechanical erosion due to wind and rain and high doses of UV radiation. Nevertheless, stone is inhabited by fungi and other microorganisms in all climate regions of the earth [68]. Due to their thick, melanised cell walls fungi also resist to chemical attack and cannot easily be killed by biocides or other anti-microbial treatments [69]. In here, according to the environmental results on research areas have not enormous changes of humidity and temperature. UV radiation may cause an acceleration fungi growth on stone artefacts of research areas.

Bacteria are found on exposed surfaces, and consequently the stone is chemically attacked. Under experimental conditions, bacterial activity, on stone substrates has been associated with low pH and metabolic acid formation [70].

A physical deterioration mechanism has recently been postulated for cyanobacteria and algal films involving lifting of microbial films containing adherent mineral grains in periods of dryness [71]. Fungi produce a variety of inorganic and organic acids [72]. Organic acids such as oxalic, lactic and gluconic function as chelating agents and can demineralize a variety of stone substrates in which calcium, silicon, iron. manganese or magnesium are leached. Chemical degradation of stone by fungi has been demonstrated experimentally [73]. Fungal acid production has been studied using strains isolated from decaying monuments [73,74]. Solubility of cations differs according to the substrates and the cations leached [74]. The dissolution, recrystallization and re-deposition of calcite by fungi have been also studied [75]. Hyphal penetration along etched channels and etching of grains of calcite and dolomite have also been demonstrated [76]. Fungi have also been shown to oxidize manganese in the laboratory, causing staining [77,78], and have been associated with deteriorated stone *in situ* exhibiting a powdery, surface [79].

Sample of the + Black

Sample of + *Black* is a typical black lichen (figure 18). Lichens are a self-sufficient association of fungi and algae or cyanobacteria [80]. Both lichens and algal-fungal protolichenous symbiotic associations are associated with stone deterioration [80].

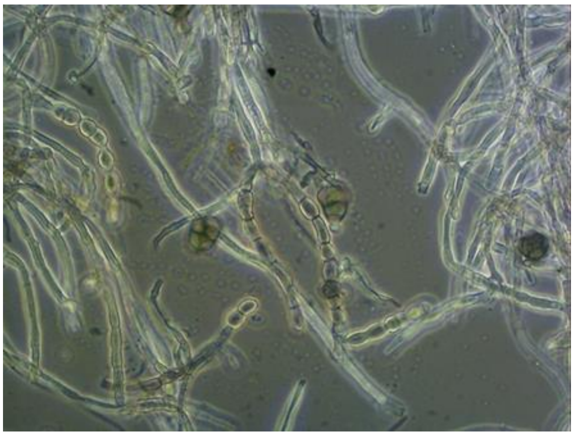


Figure 18. Sample of + *Black* is a typical black lichen

Lichens cause stone degradation mechanically and chemically [80]. Mechanical weathering involves growth of the hyphae into the stone and periodic detachment of the thallus related to fluctuations in humidity, resulting in the loss of adherent mineral fragments [80].

Chemical degradation includes the production of carbonic acid. oxalic acid. and water-soluble organic chelating agents.

The role of such chelating agents, primarily polyphenolic compounds, in stone deterioration is established but less well studied than the role of oxalic acid in stone weathering [80]. Carbonic acid is produced when carbon dioxide from respiration is dissolved in water held by the thallus [80]. Deterioration involves depletion of basic cations such as calcium, magnesium, and silica, and accumulation of aluminium and iron. Carbonic acid is a strong weathering agent over extended periods of time [81].

5.4. Results of Artificial Decay Experiments

The artificial ageing experiments were carried out on marble samples coming from of a modern quarry (MY). The general physical properties of this marble are given in section 5.2.2 of chapter 5. The aim of the experiment was to find the best deterioration conditions of marble samples in laboratory simulating a natural process. Artificial decay cycles were performed until the average water absorption capacity of the marble samples reached about 0.200 g (about a 75 % of increase in respect to the sound samples). The number of marble samples were 24 and these samples were selected from 130 samples according to their first average water absorption capacities. The first average water absorption values of the 24 samples were 0.054g (Table 6, Chapter 8, page 89) before the artificial decay processes.

The artificial decay experiments were performed with 10 cycles. Water absorption test by water capillary absorption method was carried out after each artificial decay cycle in marble samples. Marble samples were subjected to different water absorption methods in the first 5 cycles and they were not subjected to water absorption methods in the subsequent test cycles. The conditions of the first three cycles were selected according to the environmental values that were found on the study areas (as reported in Table1 and Table 2, Chapter 5, section 5.1.). According to results of the first three artificial ageing experiments, hot and cold cycles were applied on extreme conditions in order to accelerate the degradation process in the subsequent tests cycles. These extreme conditions gave an effective deterioration on the marble samples. Artificial decay processes and results of their evaluations with water uptake test by water capillary absorption methods are reported in table 7 (in page 30).

Ageing Process	**Temperature (°C) / Hour (h)**				**Average Water Uptake Test in 2 hours**
	Oven	**Freezer**	**Oven**	**Freezer**	
1st	+40 / 15	+3 / 7 *	-	-	0.153 g
2nd	+40 / 15	+3 / 7 •	-	-	0.126 g
3rd	+45 / 15	+3 / 7 *	-	-	0.126 g
4th	+55 / 6	+3 / 15 *	-	-	0.127 g
5th	+100 / 2	+3 / 19 Δ	-	-	0.142 g
6th	+110 / 15	+3 / 7	-	-	0.141 g
7th	+110 / 13	+3 / 4	+110 / 3	+3 /4	0.145 g
8th	+110 / 8	+3/ 14	-	-	0.171 g
9th	+110 / 3	+3/ 3	+110 / 3	+3/ 14	0.188 g
10th	+110 / 3	+3/ 3	+110 / 3	+3/ 14	0.188 g

*** *Samples wetted with distilled water by spray and put in plastic bags before the introduction in freezer.***

• *Samples wetted with distilled water by 2 hours of water capillary absorption and put in plastic bags before freezer.*

Δ *Samples wetted with distilled water by spray and put in freezer without bags.*

Table 7. Artificial decay processes and results of their evaluations with water uptake test by water capillary absorption

According to the average water absorption values of the marble samples after the first artificial degradation test; water absorption capacities of the marble samples increased by 65 % respect than average values of before the artificial decay processes (0,054g). The water absorption capacity of marble samples increases to approximately 70-75 % after the 9th and 10th artificial aging experiments in extreme conditions. The presence of water in the marble samples can also be achieved - as seen in the first artificial decay experiment - under the normal conditions.

The water uptake by water capillary absorption tests has been also carried out on stone samples from research area of Euromos (EQ, DW, DG and DV). The water uptake tests performed on the same samples three times. According to average of water absorption tests results (Table 8, Chapter 8, page 89); the behavior of water absorptions of DW (0.184g) and DG (0,179g) are similar to samples of MY (188g) after the artificial decay processes. EQ (0.112 g) has lower water absorption capacity than the other stone samples. DV samples (0,299g) show higher water absorption behavior than the other samples.

Several studies about the effects of environmental conditions on the deterioration of monuments have been carried out. Mostly, attention is focused on the effects of anthropogenically induced decay [82,83]. The effects of marine aerosols on the stone decay process have attracted the attention of researchers since many years [84]. Air pollution causes decay, but the unfavourable marine environment (in e.g. Venice) also enhances the decay [83]. The building materials deteriorate under the action of environmental weathering factors, e.g. in Mediterranean cities, where the presence of salts in combination with movement and evaporation of water which forms solutions of soluble salts in the stone [85]. However, artificial decay processes can be also obtained in marble in the presence of water and in extreme conditions.

Artificial decay experiments had been completed positively according to all results of water uptake tests by the water capillary absorption method in all marble samples.

5.5. Synthesis of New Partially Fluorinated Oligoamide for Protection of Stone Artefacts

Perfluoropolyethers are liquid materials having approximately the same chemical stability as polytetrafluorethylene.

Their properties make them eligible products as protective agents of stone. The protection of stone exposed to atmospheric agents is carried out by applying on its surface products acting as water repellents which, as a result, reduce the contact and penetration of rain carrying contaminants.

Partially fluorinated oligoamides were obtained through a two steps reaction. In the first step, an oligoamide containing two terminal amino groups for molecule was obtained from diethyl suberate and ethylenediamine (R1) (in page 32).

$n\ EtO - CO - (CH_2)_6 - CO - OEt + \alpha n\ H_2N - (CH_2)_2 - NH_2$

$$\text{-2mEtOH} \quad \downarrow$$

$m\ H_2N - (CH_2)_2 - NH - CO - (CH_2)_6 - CO - \{HN - (CH_2)_2 - NH - CO - (CH_2)_6 - CO\}_p - HN - (CH_2)_2 - NH_2$

whrere α=,2,3,5

R1

The molar ratio ester / amines were 1/2; 1/3 and 1/5 in order to favorite the formation of molecules with NH_2 terminal groups.

The second step consisted in introducing a perfluoropolyetheric group into the reaction (R2). The oligoamides where characterized by FT-IR, NMR and their solubility in some solvents (water, acetone, 2-propanol, THF) were evaluated.

$m\ H_2N - (CH_2)_2 - NH - CO - (CH_2)_6 - CO - \{HN - (CH_2)_2 - NH - CO - (CH_2)_6\}_p - HN - (CH_2)_2 - NH_2 + 2m\ Rf - COOEt$

$$\text{-2mEtOH} \quad \downarrow$$

$m\ Rf - CO - HN - (CH_2)_2 - NH - CO - (CH_2)_6 - CO - \{HN - (CH_2)_2 - NH - CO - (CH_2)_6\}_p - HN - (CH_2)_2 - NH - CO - Rf$

where $Rf = CF_3 - O - (CF_2 - CF(CF_3) - O)_m - (CF_2 - O)_n - CF_2 -$

R2

5.5.1. Synthesis of Not-Fluorinated Oligoamide

Synthesis of not fluorinated oligoamine began from the synthesis of Diethyl Suberate; through the esterification reaction of Suberic acid, with EtOH and Sulfuric acid used as catalyst (Table 9) (in page 33). The esterification process was obtained at 65 ^{0}C. Generally, the progress of the reactions has been periodically checked by recording FT-IR spectra.

The synthesis was considered finished only when the spectra showed the complete disappearance of the peaks attributable to the reagents (peak of the C=O stretching of the suberic acid at about 1700 cm^{-1}).

The product obtained was characterized by FT-IR and also checked with $NaHCO_3$ to ensure no more acid remains.

Suberic Acid (g)	EtOH (ml)	Sulfuric Acid	Temp. ^0C	Time (hour)
7.00	20.00	3-4 drops	65	22

Table 9. Experimental conditions used in the synthesis of Diethyl Suberate

Three different molar ratios of non-fluorinated oligoamides have been synthesized as reported in table 10.

Ratio	Etyhdia. (g)	Dsub. (g)	Solvent (ml)	Tempt. (^0C)	Reaction Time (h)	Product (g)
1:5(1st)	1.45	1.12	1 (EtOH)	95	17	1.483
1:5(2nd)	1.74	2.00	-	50	25	1.974
1:3	1.56	2.00	2 iso pro	80	35	1.557
1:2(1st)	0.75	1.43	4 iso pro	65	42	1.005
1:2(2nd)	0.78	1.38	5 iso pro	70	45	0.894
1:2*(3rd)	0.58	1.00	1 iso pro	70	45	0.785
1:2(4th)	0.58	1.00	1 iso-pro	70	52	0.980

Table 10. Reaction conditions of non-fluorinated oligoamide with three different molar ratio Diethyl Suberate / Ethylendiamine

According to calculations of molar ratios of reagents (as reported in the table); all reactions started under the N_2 atmosphere and dithyl suberate has been added slowly in the flask at ambient temperature under stirring to obtaining long chain. The temperatures was raised to 60 ^{0}C – 80 ^{0}C (as reported in the table) and maintained until the end of the reactions. The reactions carried out as described above required extended periods of time for obtaining the product and this was attributed to the presence of the solvent which would not allow to reach the desired temperature. All synthesis carried out with very little amount of solvents showed the problem of inadequate stirring due to presence of solid oligoamide formed during the reaction. The synthesis of non-fluorinated oligoamides have been started with EtOH as solvent (boiling point is 78°C), but it was observed that EtOH evaporated faster due to elevated temperature of reaction (e.g.95 °C in 1:5 1st). Therefore, 2-Propanol (boiling point is 82°C) was used in the other syntheses of non-fluorinated oligoamides of 1:5(1st) hereafter in all other synthesis.

Generally, the kinetics of the reactions has been periodically checked by recording FTIR spectra on sampling. The syntheses were considered finished only when the spectra showed the complete disappearance of the peaks ascribable to the reagents (1733 cm^{-1}, for ester).

The unreacted ester, in cases where the reaction is not able to go up to completion (1727 cm^{-1}), the excess of ethylendiamine and a few amounts of oligoamide (detected by the peak at 1635 cm^{-1} of amide 1), probably that at lower molecular weight, were washed from the crude product. However, the very small amount of oligoamide present in the washings compared to the amount of product obtained from the reaction, did not generally greatly influence the yield of the reaction.

The FT-IR and the ^{1}H-NMR spectra of oligo ethylensubramide (ratio 1:2, 4th) are reported, as example, in figure 19 and 20, respectively (in page 35).

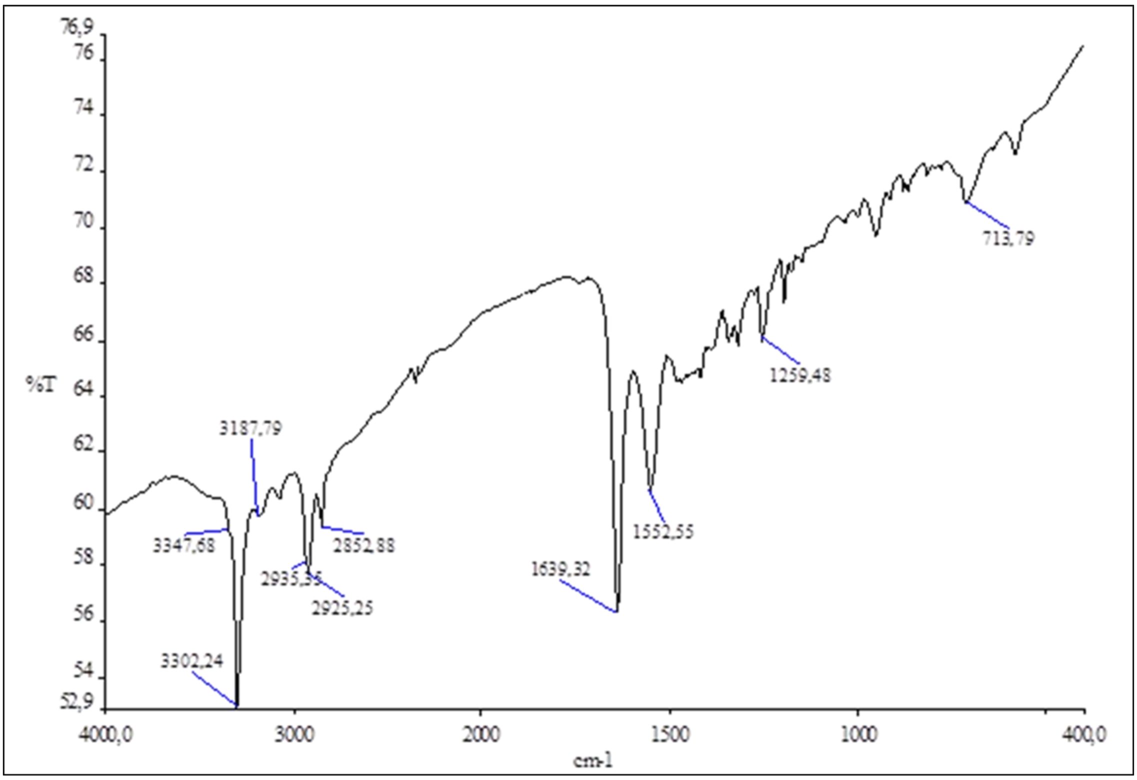


Figure 19. FT-IR Spectra of Oligo Ethylensubramide (ratio 1:2, 4th)

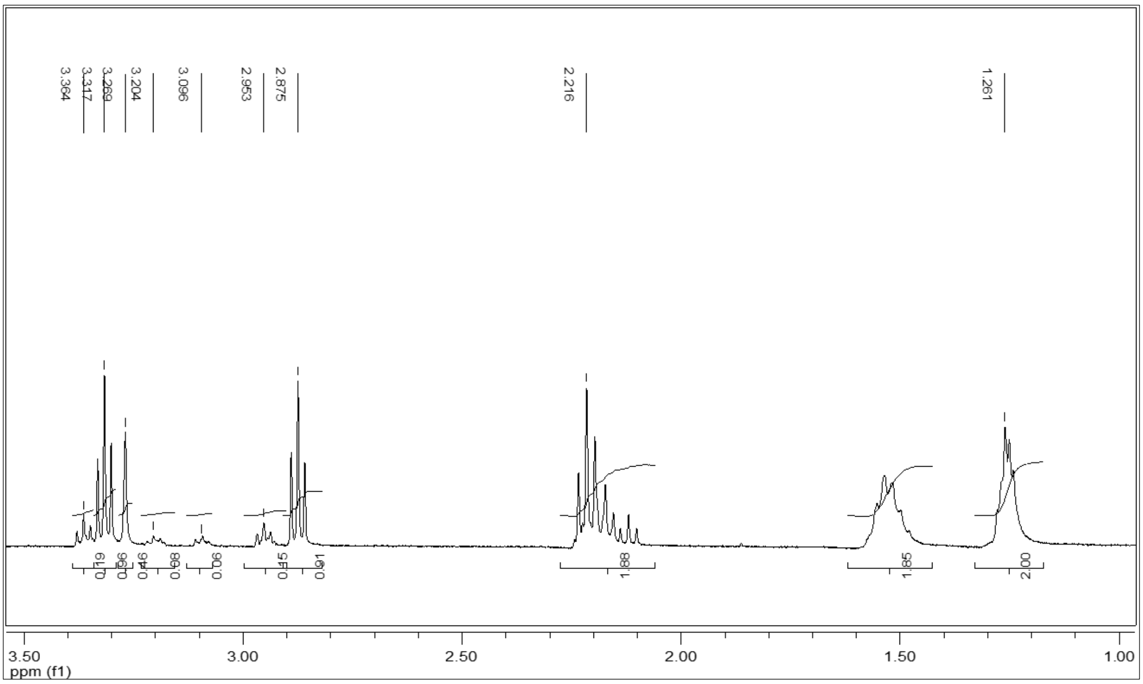


Figure 20. ^{1}H-NMR Spectra of Oligo Ethylensubramide (ratio 1:2, 4th)

5.5.1.2. Evaluation of Not-Fluorinated Oligomide

All reactions gave white solids of non-crystalline appearance and of waxy consistency. Solubility tests carried out with different solvents in cold and hot conditions are reported in table 11 and 12, respectively.

Non-Fluorinated Oligoamide	**Acetone (%)**	**THF (%)**	**EtOH (%)**	**H_2O (%)**	**2-Propanol (%)**	**2-Propanol: H_2O 90:10 (%)**
1:5(1st)	0	0	0	100	0	0
1:5(2nd)	0	0	0	100	0	0
1:3	0	0	0	100	0	0
1:2(1st)	0	0	0	100	0	0
1:2(2nd)	0	0	0	100	0	0
1:2 (3rd)	0	0	0	100	0	0
1:2(4th)	0	0	0	100	0	0

Table 11. Solubility of Non-Fluorinated Oligoamide in cold condition (room temperature, about 25°C)

Non-Fluorinated Oligoamines	**Acetone (%)**	**THF (%)**	**EtOH (%)**	**H_2O (%)**	**2-Propanol (%)**	**2-Propanol: H_2O 90:10 (%)**
1:5(1st)	0	15	20	-	20	25
1:5(2nd)	0	15	20	-	20	30
1:3	0	10	0	-	-	-
1:2(1st)	0	5	0	-	10	50
1:2(2nd)	0	5	0	-	-	55
1:2*(3rd)	0	5	0	-	-	55
1:2(4th)	0	5	0	-	-	45

Table 12. Solubility of Non-Fluorinated Oligoamide in hot condition (about boiling point of the solvent)

Solubility test of not fluoridated oligoamides were calculated starting from 10 mg of product in 1 g of solvent. The solubility data show that the not fluoridated oligoamides are completely soluble in cold water. Instead, generally, the solubility of not-fluoridated oligoamides in the organic solvents are better in hot conditions. Among the tested organic solvents, the mixture of 2-Propanol: H_2O (90:10 ratio) has been proved to be the most effective. Among the various synthesized not fluoridated oligoamides, those obtained with the ratio 1:2 show better solubility in the mixture 2-propanol/water (90:10). The higher solubility can be justified by the higher length of the oligomeric chain.

Most important things that the not fluoridated oligoamides are soluble in water because this solubility allows the determination of molecular weight by ^{1}H -NMR.

According to ^{1}H -NMR spectrum (Figure 21), reported as example, all the oligo amides obtained with different ratio were not pure. In fact, too much signals are present in the spectrum in respect to the expected formula. The extra signals can be assigned to the excess of diamine that may be linked via H-bonding to the oligoamide. In support of this hypothesis there is the impossibility of a further purification of the oligoamide. In the case of oliogoamide with ratio 1:2 (3rd) the purification was carried out by extracting 9 times the excess of diamine with diethyl ether. After the last extraction no ethylenediamine was recovered from the solvent. The same was obtained with the oligo amide 1:2 (4th) where the extraction was repeated 12 times. In any case, the oligoamides obtained in the 3th and 4th syntheses were considered the best purified.

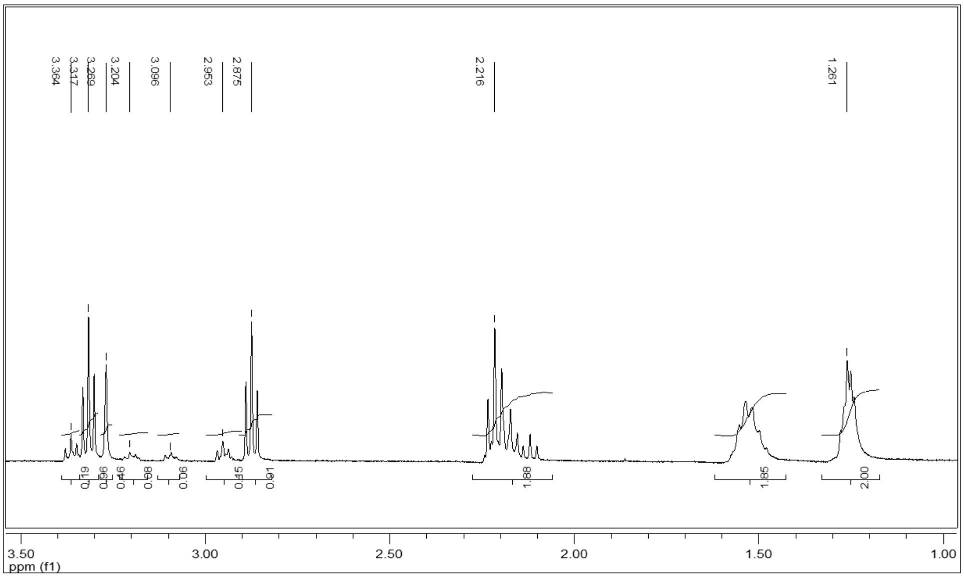


Figure 21. ^{1}H -NMR spectra of Oligo Ethylensuberamide with ratio 1:2 (4th)

5.5.2. Synthesis of Partially Fluorinated Oligoamide

Three types of partially fluorinated oligoamides have been synthesized with two different fluorinated esters which commercial name were Fomblin and Krytox. Fluorinated esters of FomblinY (F3100 and G900) and Krytox used with two different ratios of not fluorinated oligoamide for obtaining partially fluorinated oligoamides as represented in Table 13.

Reaction	**(1:5) (g)**	**(1:5) (g)**	**(1:2) (g)**	**EF (g)**	**Solvent (ml)**	**Temp. (^{0}C)**	**Time (h)**	**Product obtained (g)**
(1:5) [1st] + F3100	0.250			0.615	15 EtOH	65	111	0.745
(1:5) [2nd] + Krytox		0.214		0.012	-	-	-	-
(1:2) [4th] + G900			0.300	0.767	45 2-prop.	85	65	0.848

Table 13. Reaction Conditions used in the Synthesis of Partially Fluorinated Oligoamides

First synthesis was performed between not fluoridated oligoamides (1:5 ratio) and ethyl ester of perfluoropolyether Fomblin Y (F3100) at high molecular weight (MW=3100).

Basic formula of FomblinY (F3100);

Fomblin Y = CF_3-O- [CF_2- CF_3-O-]$_m$ - [CF_2-O]$_n$ – CF_2 -CH_2-$COOC_2H_5$

Not fluorinated oligo amides with ratio 1:5 [1st] and fluorinated ester of F3100 reaction occurred under N_2 atmosphere and 70 ^{0}C. 2-propanol was used as a solvent in this reaction and fluorinated ester of F3100 added drop by drop in the reaction system under the N_2 atmosphere. The reaction was periodically controlled by FT-IR spectroscopy.

According to FT-IR spectra; the shift of the peak from 1793 cm^{-1} to about 1710 cm^{-1} showed that the C=O stretching passed from the fluorinated ester to the fluorinated amide.

The ratio between the peak height of the C=O stretching of amide I and ester Increases slowly, but the reaction was faster at 70 ^{0}C temperature than room temperature. After a long time (111hours) the peak of perfluorinated ester was still present, but the reaction was not really completed, because, the amount of F3100 was much less than that necessary to have a molar ratio of not fluorinated oligoamide / F3100 (1:2). However, the reaction was stopped because no differences in the FTIR spectrum were observed after two consecutive times. The low reactivity of this ester may be due to its insolubility in the organic solvent.

In any case, the solubility of the product obtained from this reaction was tested. The results are reported in Table 14. According to results of solubility tests, the product was considered not good for application.

Acetone (%)0	**THF (%)**	**EtOH (%)**	**H_2O (%)**	**2-Propanol (%)**	**2-Pro: H_2O 90:10 (%)**
0	15	35	-	25	10

Table 14. Solubility test on partially fluorinated oligoamide (1:5) [1^{st}] + F3100

Another point to be noted about the solubility test of (1:5) [1^{st}] + F3100 with Acetone is that the colour of the mixture changes from transparent to dark yellow after one hour. This is another confirmation of the presence of an excess of diamine.

Another synthesis between not fluoridated oligoamides (1:5 ratio) with a fluorinated ester is referred to Krytox (MW 1500). Krytox is made by base catalyzed polymerization of hexa-fluoropropylene oxide

Ethyl ester of Krytox = CF_3-CF_2-CF_2-O-[CF(CF_3)-CF_2-O-$]_m$ CF_2-$COOC_2H_5$

The ethyl ester of Krytox was obtained by reacting the corresponding Krytox acid and thionyl chloride in dry conditions, then the acyl chloride was reacted with EtOH to form the corresponding ethyl ester.

Synthesis process between not fluoridated oligoamides (1:5 ratio 2nd) with a fluorinated ester of Krytox occurred under N_2 atmosphere and reaction started at room temperature and continued at 70°C in presence of EtOH as a solvent.

However, according to FT-IR spectra collected after two hours and after four hours at 70 ^{0}C showed that reaction did not occur. After 1 and 2 days more the reaction was checked again, but no expected fluorinated oligoamide was obtained. The difficult of this synthesis may be due to the different structure of the fluorinated chain in respect to the Fomblin one.

The synthesis between not fluoridated oligoamides (1:2 ratio3rd) and a fluorinated ester of G900 occurred under N_2 atmosphere and 65 ^{0}C under stirring and 2-propanol used as solvent. During the reaction the expected product the mixture became solid and, for this reason, more solvent respect than beginning was added. The ethyl ester of G900 was added drop by drop do the not fluorinated oligoamide. The progress of reaction was monitored by FT-IR spectroscopy, and the reaction was considered terminated when the peak of fluorinate ester (C=O stretching at 1793 cm^{-1}) was not more present. The recovered product shows good solubility in some solvents, and particularly in 2- propanol (in hot condition); however final product was not enough for application (table) and another synthesis was necessary. The not fluoridated oligoamides (1:2 ratio3rd) and (1:2 ratio 4th) were then reacted with the ethyl ester of G900. Solubility tests results of not fluoridated oligoamide (1:2 ratio 4th) reacted with the fluorinated ester of G900 in cold and hot conditions are reported in table 15 and 16, respectively.

Acetone (%)	**THF (%)**	**EtOH (%)**	**H_2O (%)**	**2-Propanol (%)**	**2-Pro: H_2O 90:10 (%)**
0	15	35	-	25	10

Table15. Solubility of partially fluorinated oligoamide (1:2 ratio 4th) +G900 in cold conditions

Acetone (%)	**THF (%)**	**EtOH (%)**	**H_2O (%)**	**2-Propanol (%)**	**2-Pro: H_2O 90:10 (%)**
0	51	78	-	90	45

Table16. Solubility of partially fluorinated oligoamide (1:2 ratio 4th) +G900 in hot conditions

The solubility tests in two conditions show that the solubility of oligoamide (1:2 ratio 4th +G900) in 2-propanol in hot conditions is about 90%. The mixture becomes a colourless suspension that can be applied on samples surfaces. Moreover, 2-propanol is useful for the in-situ application because its boiling point is higher than that of other organic solvents reported in table 17 (82.6°C). The better results were obtained with the oligomide 1:2, instead of 1:5. This result is due to the better purification of the oligoamide from the excess of amine (ethylene diamine).

5.6. Evaluation of New Partially Fluorinated Oligoamide for Protection of Stone Artefacts

5.6.1. Evaluation of Water Repellency

Evaluation of water repellency of New Partially Fluorinated Oligoamide (G900) was carried out in three parts: water capillary absorption and contact angle methods in laboratory and through the "*Contact Sponge*" method in situ (research areas).

The treatment with the new protective materials G900 was carried out by pipette, applying a mixture of the product at 1% (w/w) in 2-propanol directly on one of the larger surfaces of the stone samples. The product was applied with the technique wet on wet until a theoretical amount of 4 g/m^2 were deposed on the stone surface. The water capillary absorption test was performed after forty-eight hours from the treatment.

Commercial products, Fluoline HY and SILO 112, were also used as reference products. Fluoline HY was applied as 1% (w/w) solution in butyl acetate. Applied method was wet on wet by pipette on the stone samples. SILO 112 was applied as 1 % (w/w) dispersion in distilled water. Applied method was wet on wet by pipette on the stone samples. Water capillary absorption test was performed after treatment and after each step of artificial ageing.

The water uptake was determined after two hours of water absorption. The water repellency was calculated and expressed as Protective Efficacy (PE %).

Calculation of efficacy of protective (EP %) with formula;

PE % = ($A_0 – A_1$) / A_0 *100

where A_0 and A_1 are the mass of water absorbed by the same sample before and after treatment, respectively.

The Protective efficacy (PE %) of the three treatments on all the stones is reported in table 17 and figure 22.

Treatments	**G900**		**Fluoline HY**		**SILO 112**	
Sample	**Applied (g / 25 cm²)**	**PE% 2h**	**Applied (g / 25 cm²)**	**PE % 2h**	**Applied (g / 25 cm²)**	**PE % 2h**
EQ	0.006	60	0.008	55	0.006	32
DW	0.007	37	0.007	39	0.005	25
DG	0.005	45	0.004	30	0.005	51
DV	0.004	38	0.006	59	0.005	15
MY	0.003	31	0.005	30	0.003	24

Table 17. Protective efficacy at 2h of water absorption of different coatings on stone samples after treatment

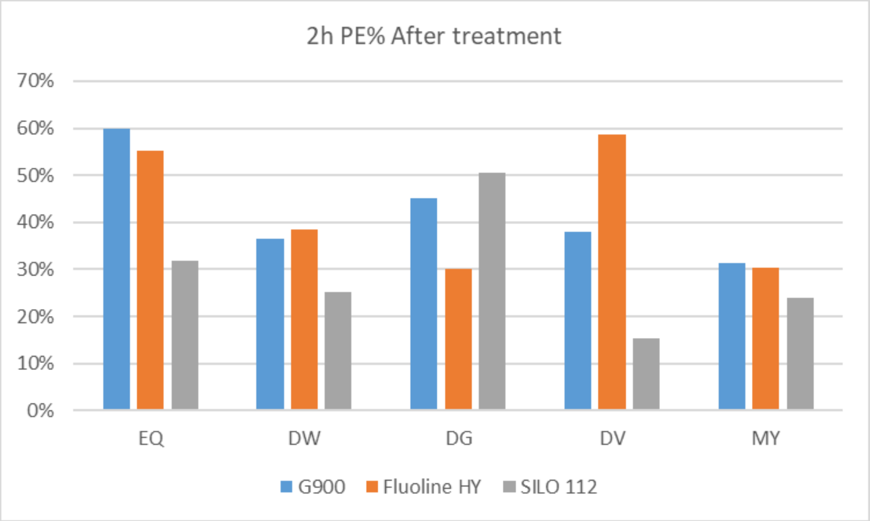


Figure 22. Protective efficacy at 2h of water absorption of different coatings on stone samples after treatment

According to the first results, G 900 shows better water repellency on marble samples EQ than on the other marble samples.

Considering the amount of G 900 applied, it can be considered that the product has higher water repellence properties than the other compounds. However, the sample DW, where slightly higher amount of G 900 was applied, the protective efficacy is lower or similar to that of other products.

Artificial degradation process was carried out on treated samples under the thermo-ageing cycles with UV irradiation. Each step of artificial ageing has been performed with ten cycles. These ten cycles repeated at three times in the artificial degradation processes. The thermo-ageing conditions for each cycle are reported in table 18.

Time (h)	1	2	6	10	4	1
Temperature (^{0}C)	-5	5	10	25	30	35
RH (%)	0	0	90	80	65	50

Table 18. Artificial Ageing Cycle

First artificial ageing was carried out with 10 cycles and the results of protective efficacy (PE%) are reported in table 19 and figure 23 (page 44) .

Treatments	**G900**		**Fluoline HY**		**SILO 112**	
Sample	**PE% (2h)**		**PE % (2h)**		**PE % (2h)**	
	After treatment	**After 1st Ageing**	**After treatment**	**After 1st Ageing**	**After treatment**	**After 1st Ageing**
EQ	60	60	55	53	32	24
DW	37	43	39	32	25	15
DG	45	40	30	27	51	11
DV	38	37	59	37	15	24
MY	31	25	30	33	24	14

Table 19. PE% of different coating materials on stone samples after treatment and after the 1st ageing step

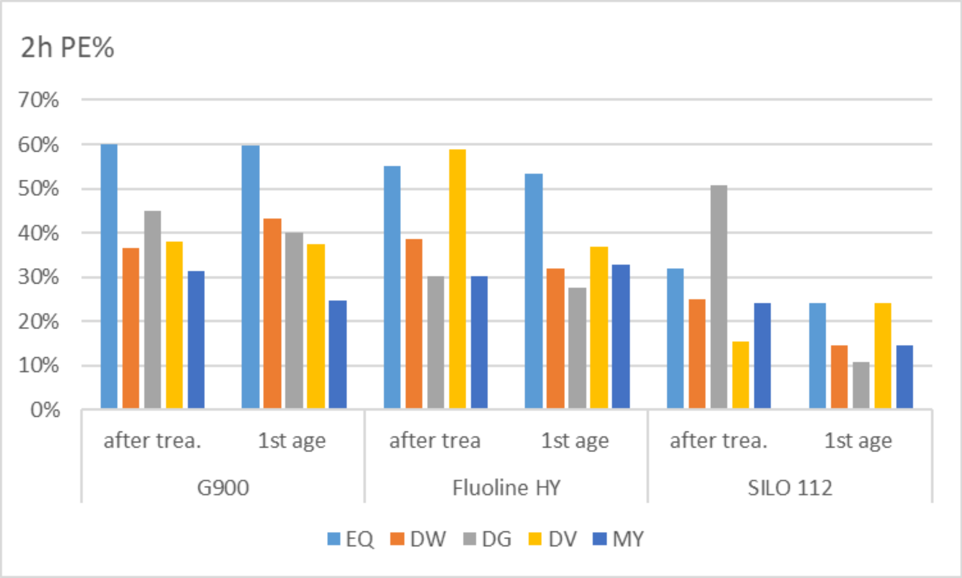


Figure 23. PE% of different coating materials on stone samples after treatment and after the 1st ageing step

EQ samples show good protective efficacy when coated with G900 and Fluoline HY. On the contrary, the SILO 112 treatment provides lower protective efficacy in respect to fluorinated compounds. The protective efficacy of SILO 112 decreased of about 25% after the 1st ageing period.

Treatments with G900 and Fluoline HY also show better protective efficacy than SILO 112 on DW stone samples after the 1st ageing evaluation.

Moreover, treatments with G900 and Fluoline HY show better protective efficacy than SILO 112 after 1st ageing step on DG stone samples. The PE% decrease after the 1st ageing step for G900 and Fluoline HY on this samples are very similar: in fact, their decrease is 11 % and 10%, respectively. On the contrary, relevant decrease occurred when DG samples were treated with SILO 112 (decrease of 78% after the 1st ageing step).

Treatment with G900 shows better protective efficacy on DV stone samples after the 1st ageing step. Fluoline HY has an intermediate decrease, while SILO 112 gives lower protective efficacy (lower resistance) than fluorinated compounds.

Finally, treatment with G900 shows better resistance of protective efficacy on MY samples after the 1st ageing step. Treatment with SILO 112 shows relevant decrease after the 1st ageing and the decrease is 41%.

Stone samples treated with Fluoline HY gives protective efficacy resistance similar to that observed on samples treated with G900.

Second artificial ageing was carried out with ten (10) cycles and the results of protective efficacy (PE%) are reported in table 20 and figure 24.

Treatments	**G900**		**Fluoline HY**		**SILO 112**	
Sample	**PE% (2h)**		**PE % (2h)**		**PE % (2h)**	
	After 1st Ageing	**After 2nd Ageing**	**After 1st Ageing**	**After 2nd Ageing**	**After 1st Ageing**	**After 2nd Ageing**
EQ	60	49	53	48	24	21
DW	43	43	32	27	15	13
DG	40	34	27	22	11	10
DV	37	36	37	34	24	22
MY	25	19	33	28	14	13

Table 20. PE% of some coatings materials applied on stone samples after the 1st and the 2nd ageing step

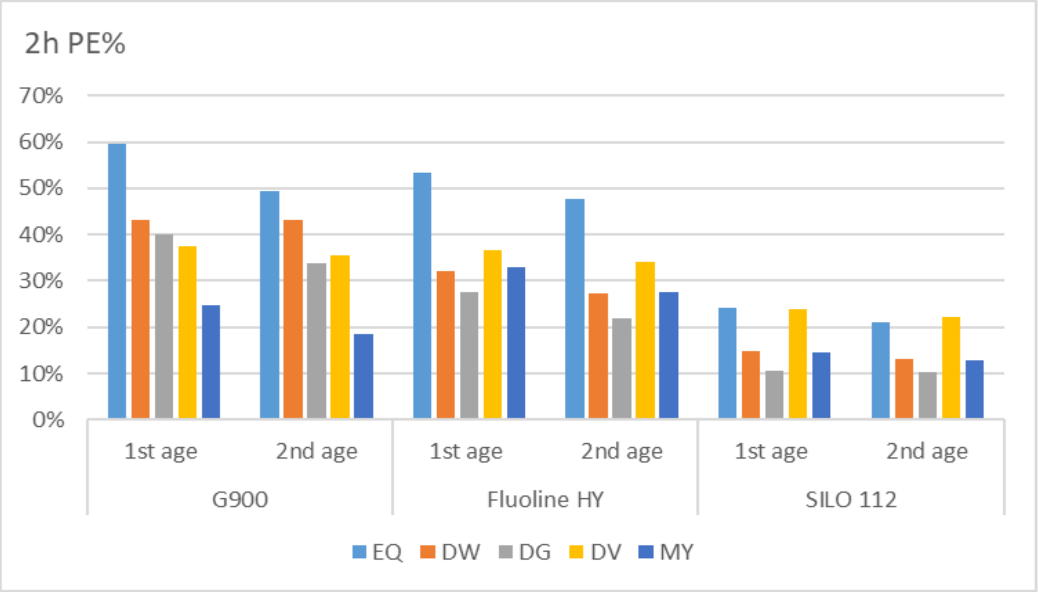


Figure 24. PE% of some coatings materials applied on stone samples after the 1st and the 2nd ageing step

EQ samples treated with G900 and Fluoline HY show good protective efficacy. Treatment with SILO 112 gives lower protective efficacy than fluorinated compounds and its values of protective efficacy decreased of about 45% from before ageing to the end of the 2nd ageing period.

On DW stone samples, the treatments with G900 and Fluoline HY show better protective efficacy than treatment owith SILO 112 after the 2nd ageing evaluation. No changes from the 1st to the 2nd artificial ageing step are observed for all treatments, except the treatment with SILO 112 are similar.

On DG stone samples treated with G900 and Fluoline HY the protective efficacy changes from the 1st to the 2 nd artificial ageing step are more evident than that observed for the treatment with SILO 112. The protective efficacy decreases for G900 and Fluoline HY are 15 % and 18%, respectively from the 1st to the 2nd ageing step. The percentage decrease of protective efficacy due to two ageing steps for all treatments is:e G900= 20%, Fluoline HY= 23% and Silo 112= 80%.

On DV stone samples, the changes of protective efficacyfrom the 1st to the 2nd artificial step are similar for all the treatments. The decrease for G900 and Fluoline HY are 3% and 8%, respectively from the 1st to the 2nd ageing step. On the other hand, the decrease of protective efficacy from the values after treatment and those after the end of 2nd ageing are: G900 =5%, Fluoline HY= 42% and Silo 112= 35%.

Treatments with G900 and Fluoline HY show higher protective efficacy changes from the 1st to the 2nd artificial step in respect to the treatment with SILO 112 on MY stone samples. The decrease for G900 and Fluoline HY are 24 % and 15% respectively, from the 1st to the 2nd ageing step, while the decrease for SILO 112 is 7%. The decrease of protective efficacy from the values after treatment and those after the end of 2nd ageing step for all treatments are: G900 = 39%, Fluoline HY= 6% and Silo 112 = 49%.

Stone samples treated with Fluoline HY present protective efficacy similar to samples treated with G900, while those treated with SILO 112 show lower resistance to ageing.

The third artificial ageing was carried out with additional 10 cycles and the results of protective efficacy (PE%) are shown in table 21 and figure 25 (in page 47).

Treatments	**G900**		**Fluoline HY**		**SILO 112**	
Sample	**PE% (2h)**		**PE % (2h)**		**PE % (2h)**	
	After 2nd Ageing	**After 3rd Ageing**	**After 2nd Ageing**	**After 3rd Ageing**	**After 2nd Ageing**	**After 3rd Ageing**
EQ	49	35	48	40	21	16
DW	43	32	27	32	13	15
DG	34	33	22	20	10	17
DV	36	17	34	7	22	10
MY	19	17	28	22	13	14

Table 21. PE% of some coatings materials applied on stone samples after the 2nd and the 3rd ageing step

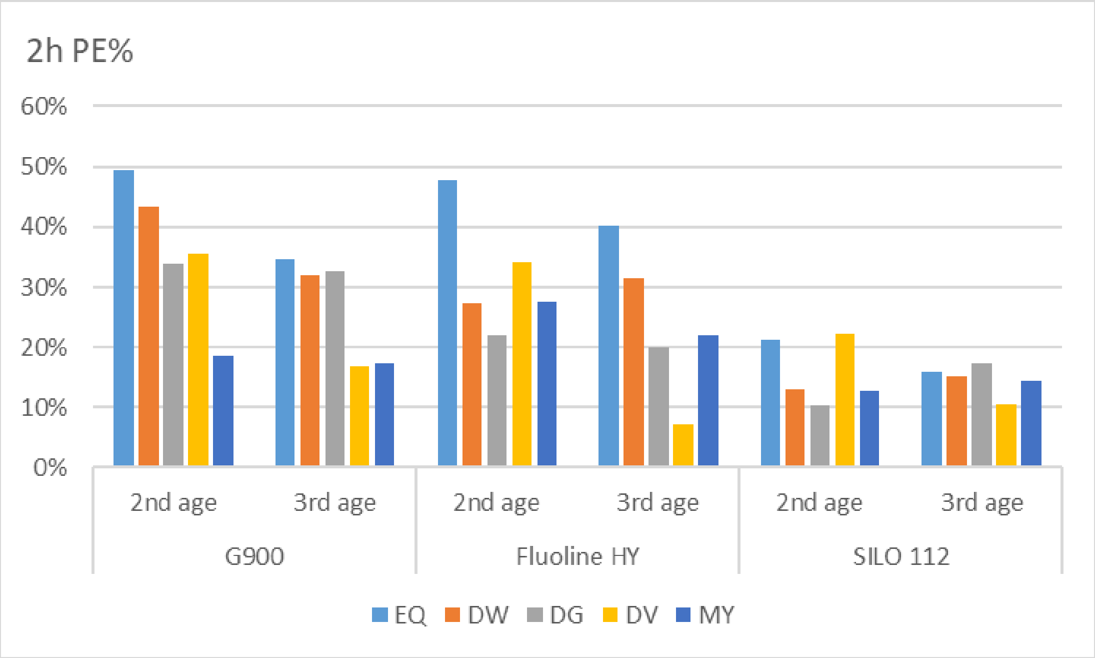


Figure 25. PE% of some coatings materials applied on stone samples after the 2nd and the 3rd ageing step

EQ samples treated with G900 and Fluoline HY show good protective efficacy. Treatment with SILO 112 gives lower protective efficacy than fluorinated compounds and its values of protective efficacy decreased of about 50% from before ageing to the end of the 3rd ageing period.

On DW stone samples, the treatments with G900 and Fluoline HY show better protective efficacy than treatment with SILO 112 after the 3rd ageing evaluation. No changes from the 2nd to the 3rd artificial ageing step are observed for all treatments, except the treatment with SILO 112 are similar.

On DG stone samples treated with G900 and Fluoline HY the protective efficacy changes from the 2nd to the 3rd artificial ageing step are more evident than that observed for the treatment with SILO 112. The protective efficacy of G900 and Fluoline HY are same values, respectively from the 2nd to the 3rd ageing step. The percentage decrease of protective efficacy due to three ageing steps for all treatments is:e G900= 26%, Fluoline HY= 33% and Silo 112= 67%.

On DV stone samples, the changes of protective efficacy from the 2nd to the 3rd artificial step are similar for all the treatments. The decrease for G900 and Fluoline HY are 52 % and 79 %, respectively from the 2nd to the 3rd ageing step. On the other hand, the decrease of protective efficacy from the values after treatment and those after the end of 3rd ageing are: G900 =55%, Fluoline HY= 88% and Silo 112= 33%.

Treatments with G900 and Fluoline HY different protective efficacy changes from the 2nd to the 3rd artificial step in respect to the treatment with SILO 112 on MY stone samples. The decrease for G900 and Fluoline HY are 10 % and 21% respectively, from the 2nd to the 3rd ageing step, while the increase for SILO 112 is 7%. The decrease of protective efficacy from the values after treatment and those after the end of 3rd ageing step for all treatments are: G900 = 45%, Fluoline HY= 26% and Silo 112 = 41%.

Stone samples treated with Fluoline HY present protective efficacy similar to samples treated with G900, while those treated with SILO 112 show lower resistance to ageing.

5.6.2. Water Repellency in Research Fields

The evaluation of water repellency in situ was performed by the "*Contact Sponge"* method. Evaluation time periods were 15 minutes, because weather conditions and other practical reasons did not allow longer times of water contact in field.

Water capillary absorption was carried out; before treatment, after treatment and three times in monthly.

5.6.2.1. Sample and Application Information

Euromos Zeus Lepsynos Temple

Two architectural stone blocks were chosen for water repellency test in temple's area. First architectural block was in the east area (EA) and second inside the temple, nearest alter (IA) (Figure 26). Treatments with protective materials were; G900 (Partially Fluorinated oligomers), FLUOLINE HY (is a water-repellent protective ready to use based on copolymers fluorinate with molecular weight around 400,000 u.m.a.) and SILO 112 (is a compound from a mixture of organosiloxanes oligomers). The theoretical amount of product applied was the same than the laboratory specimens (4 g /m^2). The concentration of the formulates (solutions) was 1% in the same solvents used for the laboratory tests. Applied method was wet on wet with brush on samples.

Figure 26. Architectural block east of area **(EA)** and close to alter **(IA)**

Agora of Iasos

Two architectural stones were chosen for water repellency test in Agora. Two blocks were selected in the west side of the area; AE1 and AE2 (Figure 27). Treatments with protective materials were; G900), FLUOLINE HY and SILO 112. The amount of product, the concentration of the solution/formulation and the application method were the same used for the Euromos site.

Figure 27. Architectural blocks of AE1 and AE2 in Agora

Water uptake test with "*Contact Sponge"* was performed just before treatment, and one week after the treatment. The water repellency was calculated in accordance with the following formula:

Wa (g/cm^2.min) = (Pi-Pf) / 23.76 *t

Where;

t= time of contact in minutes,

Pi = Beginning weight in grams

Pf= Final weight in grams

23.76 = Surface of sponge in cm^2

Before the application, thermal camera imaging was performed on architectural stones artifacts in-situ in order to registered environmental conditions.

The results of water repellency test before the treatment and after treatment are reported in table 22.

After Treatment	**EA**		**IA**		**AE1**		**AE2**	
	Wa (g/cm^2.min)	**PE** %	**Wa** (g/cm^2.min)	**PE** %	**Wa** (g/cm^2.min)	**PE** %	**Wa** (g/cm^2.min).	**PE** %
G900	0.17	80	0.21	70	1.14	67	0.65	41
FLUOLINE HY	0.21	75	0.12	83	0.29	91	0.45	60
SILO 112	0.34	60	0.28	60	2.41	30	0.41	63

Table 22. Water repellency measurements after treatment and Protective efficacy of some hydrophobic coatings on marbles of Euromos and Iasos archaeological sites

First values of water repellence on stone architectural artefact in-situ show that protective materials with fluorinated compounds give valuable properties against water. Moreover, according to results of water absorption before treatment, stone artefacts (EA and IA) of Euromos Zeus Temple area show lower absorption properties than stone artefacts of Agora of Iasos (AE1 and AE2). The discuss relatively to the result in percentage; EA and IA show good water repellence properties when both fluorinated compounds were applied in respect to the treatment with organo siloxanes Moreover, higher percentage values of protective efficacy than AE1 and AE2.

According to result of percentage, the protection with organ siloxanes compounds shows better water repellence properties on stone artefacts of AE2 than fluorinated compounds and lower percentage values in the other sites.

This happening may be the effect of degradation level of stone or treatments were not good penetrated in stone surfaces.

After treatment, water repellence test with "*Contact Sponge"* had been performed monthly and during these months the environmental conditions were registered. In addition, meteorological data of last 5 years of province (Milas) from minister of meteorology of Turkey for understand changes of weather situations have been taken.

According to values of water repellence tests with "*Contact Sponge*" collected in monthly it has been demonstrated that values do not show relevant change in all stone artefacts. Normally, in this case study; three months is not enough for understanding how the protective materials can be transformed (deteriorated).

General discussion about water repellence results; fluorinated compounds demonstrate to have good water repellence properties. However, according to a previous study on these kind of marbles, it was observed that the acrylic resins (mainly PB67) show the best hydrophobic properties. This may be due to their good ability to form film on the surfaces, and to the fact that they have higher Tg than the fluoroelastomers (PB72 and PB67 have Tg at 41 ^{0}C and 51 ^{0}C, respectively, while the fluoroelastomers have Tg around -18 ^{0}C). As a matter of fact, acrylic resins (mainly PB72 and PB67) are not good resistance against UV light inside of the sunlight and for this reason they may not be used outside. Ones of the aim of this study was to try the synthesis of new protective materials with good resistance against sunlight on these kinds of marbles.

5.6.3. Results of Contact Angle Test

Contact angle test has been performed by contact angle goniometry standard method. In goniometry, a back-lit drop (silhouette) is optically imaged and the angle subtended by the drop at the point of solid–liquid contact (on left and right sides) estimated with an optical goniometer (manual) or by image analysis (computerized) [86].

Contact angle hysteresis is the phenomenon in which a solid–liquid–vapor system at an arbitrary state may adopt a finite number of different configurations (contact angles), according to the path taken to attain that state [87].

Small contact angle is observed when the liquid spreads on the surface, while a large contact angle is observed when the liquid beads on the surface. More specifically, a contact angle less than 90° indicates that wetting of the surface is favourable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally means that wetting of the surface is unfavourable, so the fluid will minimize its contact with the surface and form a compact liquid droplet [87].

Contact angle of coating film measures up greater than 90^0 on stone surfaces due to good hydrophobic properties.

The contact angle measurement test was carried out on the marble samples of MY, DV, DW, DG and EQ with 5x5x2 cm dimensions. First, the contact angle measurement was performed on marble samples without a protective film layer. After completion of this measurement,1% concentration of G900 solution was applied on same marble samples (4 g/ m^2) that prepared by dissolving in 2 -propanol. We have waited for a week from the application day due to the thorough completion of the formation of the film layer. Second contact angle measurement was performed on treated marble samples. Contact angle measurement was always made at the exact midpoint of the marble samples. Contact angle measurement results of shown in the following charts and photographs. Photographs of measurements were taken from first drop of water bubble on sample surfaces. In this measurement was also made a 30 second recording due to understand behaviour of surfaces equilibrium. These graphic data are shown in appendix part (chapter 8).

DW

Contact angle measurements of DW is reported in table 23 (in page 54) and figure 28.

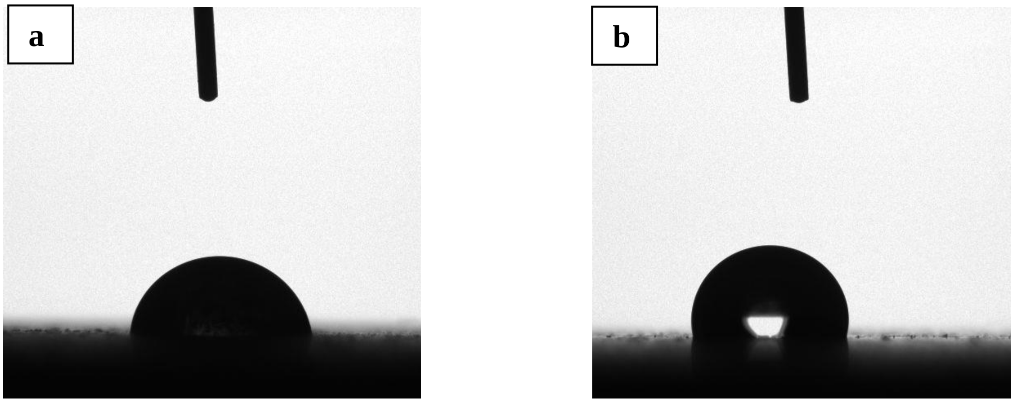


Figure 28. Imaging of angle measurements of DW. Untreated (a) and treated (b)

Sample	**Time [s]**	**CA [L] ϴ**	**CA [R] ϴ**	**CA [M] ϴ**	**L [mm]**	**M [mm]**	**Vol[ul]**	**A[mm^2]**
DW (untreat.)	28.984	84.230	81.431	82.831	2.874	1.224	5.25845	11.654
DW (treated)	28.968	103.465	103.390	103.427	2.424	1.421	4.93500	11.211

Table 23. Parameters of contact angle of untreated and treated of DW

New Partially Fluorinated Oligoamide (G900) provided an increase the water repellency properties of DW. The increase of contact angle from the value after treatment is 22%. (The contact angle behaviour of DW (untreated /treated) in 30 seconds reported in Figure 41, 42 Chapter 8, page 105).

MY

Contact angle measurements of MY is reported in table 24 and figure 29.

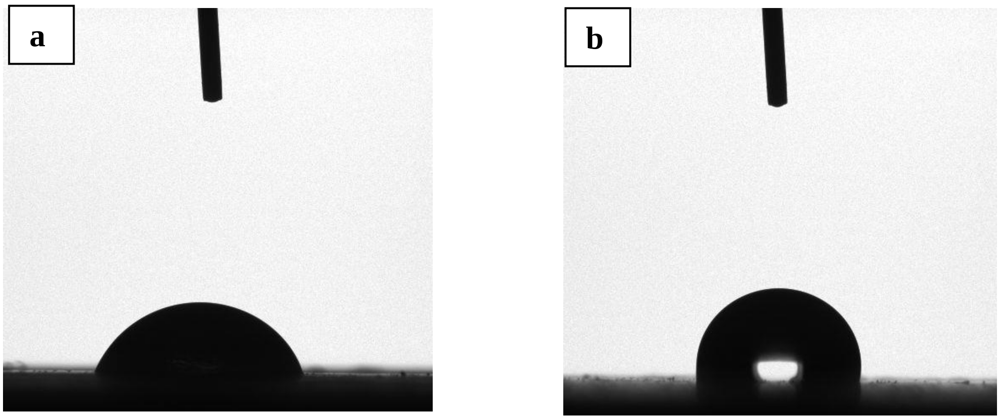


Figure 29. Imaging of angle measurements of MY. Untreated (a) and treated (b)

Sample	**Time [s]**	**CA [L] ϴ**	**CA [R] ϴ**	**CA [M] ϴ**	**L [mm]**	**M [mm]**	**Vol[ul]**	**A[mm^2]**
MY(untreat.)	28.984	68.630	70.923	69.777	3.216	1.086	5.41630	12.266
MY (treated)	28.985	103.246	103.579	103.413	2.450	1.408	4.97902	11.267

Table 24. Parameters of contact angle of untreated and treated of MY

According to measurement of contact angle that G900 provided an increase the water repellency properties of MY. The increase of contact angle from the value after treatment is 50%. (The contact angle behaviour of MY (untreated /treated) in 30 seconds reported in Figure 43,44, Chapter 8, page 106).

EQ

Contact angle measurements of EQ is reported in table 25 and figure 30.

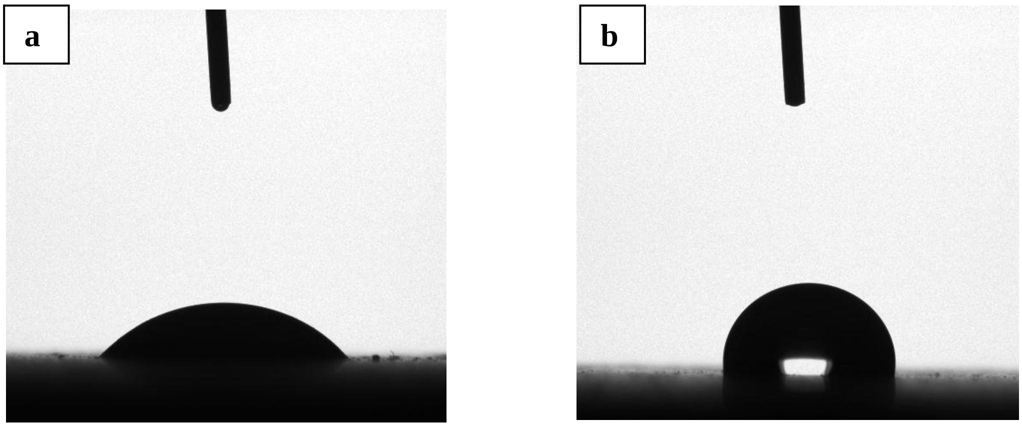


Figure 30. Imaging of angle measurements of EQ. Untreated (a) and treated (b)

Sample	**Time [s]**	**CA [L] ϴ**	**CA [R] ϴ**	**CA [M] ϴ**	**L [mm]**	**M [mm]**	**Vol[ul]**	**A[mm^2]**
EQ(untreat.)	28.984	50.133	50.507	50.320	3.729	0.833	4.94978	13.187
EQ (treated)	28.984	101.241	99.847	100.544	2.536	1.355	4.95987	11.195

Table 25. Parameters of contact angle of untreated and treated of EQ

According to measurement of contact angle that G900 provided an increase the water repellency properties of EQ. The increase of contact angle from the value after treatment is 101 %. (The contact angle behaviour of EQ (untreated /treated) in 30 seconds reported in Figure 45,46, Chapter 8, page 107).

DV

Contact angle measurements of DV is reported in table 26 and figure 31.

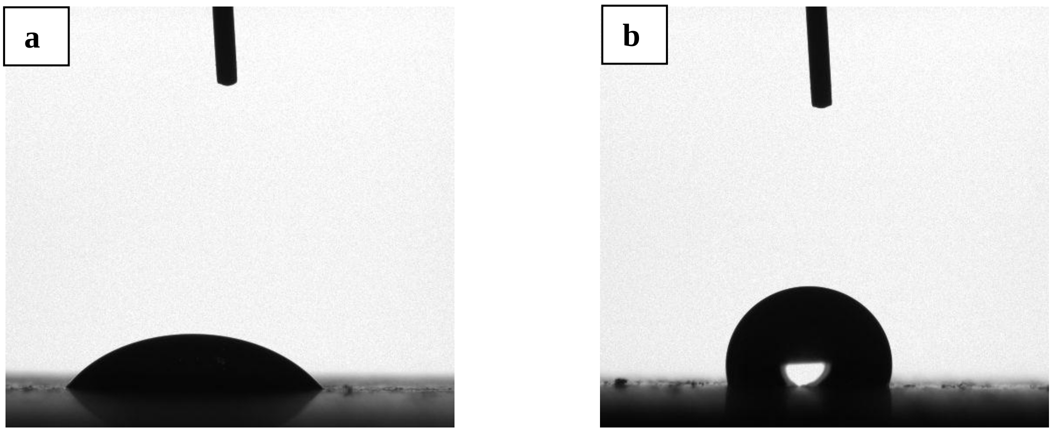


Figure 31. Imaging of angle measurements of DV. Untreated (a) and treated (b)

Sample	Time [s]	CA [L] ϴ	CA [R] ϴ	CA [M] ϴ	L [mm]	M [mm]	Vol[ul]	A[mm^2]
DV(untreat.)	28.984	52.881	51.372	52.126	3.771	0.801	4.98230	13.377
DV (treated)	28.984	107.848	107.874	107.861	2.536	1.461	5.00714	11.389

Table 26. Parameters of contact angle of untreated and treated of DV

According to measurement of contact angle that G900 provided an increase the water repellency properties of DV. The increase of contact angle from the value after treatment is 103 %. (The contact angle behaviour of DV (untreated /treated) in 30 seconds reported in Figure 47, 48, Chapter 8, page108).

DG

Contact angle measurements of DG is reported in table 27 and figure 32.

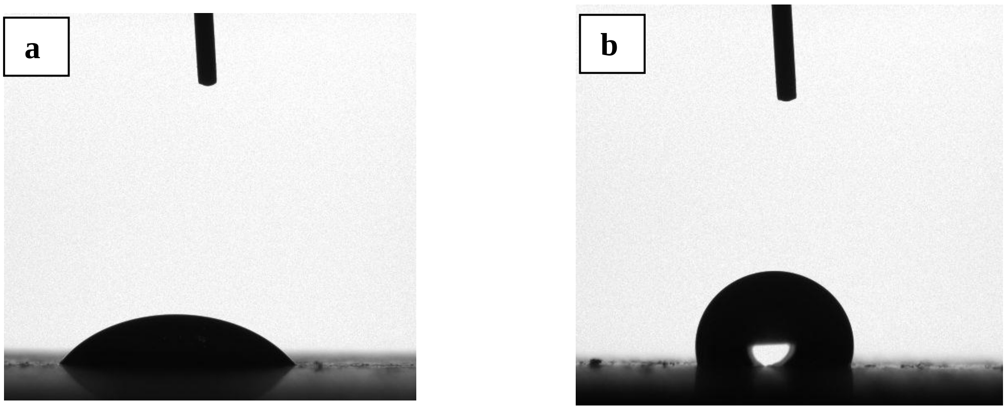


Figure 32. Imaging of angle measurements of DG. Untreated (a) and treated (b)

Sample	Time [s]	CA [L] Θ	CA [R] Θ	CA [M] Θ	L [mm]	M [mm]	Vol[ul]	A[mm^2]
DG(untreat.)	28.984	70.254	69.688	69.971	3.085	1.023	4.47112	10.864
DG (treated)	28.984	133.091	131.775	132.433	1.710	1.740	4.9688	12.204

Table 27. Parameters of contact angle of untreated and treated of DG

According to measurement of contact angle that G900 provided an increase the water repellency properties of DG. The increase of contact angle from the value after treatment is 91 %. (The contact angle behaviour of DG (untreated /treated) in 30 seconds reported in Figure 49, 50, Chapter 8, page 109).

According to the all results of the contact angle test, the G900 product shows best water repellence properties of increasing on stone sample of DV.

5.6.4. Vapour Permeability Test

The vapor permability test was performed with the Bicchierino method. It was evaluated for marble samples (5x5x2 cm) by measuring the mass of water vapour passing through the unit surface in 24 hours, at 30°C and %50 RH under controlled conditions. The mass of water evaporated in 24 hours was measured when the system had achieved equilibrium. In a typical 'permeability test' the mass change of the bicchierino/stone sample/water system is recorded every 24 hours for 8 days, and equilibrium is considered to be achieved when the mass of water evaporated in 24 hours remains constant or differs by less than 1% in two consecutive weighing**.**

The parameter RP% (percent residual permeability) was calculated from the sample permeability, after (P_1) and before (P_0) the treatment, by the formula:

$RP\% = (\Delta_{m1} / \Delta_{m0}) * 100 = (P_1/P_0) * 100$

Where Δ_{m0} is average value of water vapor evaporated in 24 h for the untreated sample and Δ_{m1} is average value of water vapor evaporated in 24 h for the treated sample.

The maximum standard deviation achieved on each sample for RP% was 1 %. The representatively of the samples was ±8%

The vapor permability results for the stone samples treated with the partially fluorinated oligoamide G900 are reported in Table 28.

Treatment	Sample	App.Amount (g)	RP %
G900	EQ	0.004	100
G900	DG	0.003	100
G900	DV	0.003	98
G900	MY	0.002	100
G900	DW	0.004	100

Table 28. The vapor permability results for the stone samples treated with the partially fluorinated oligoamide G900

The residual permeability of the treated stone to water vapour (RP%) shows high values in all the cases observed.

5.6.5. Color Determination

Color measurements have been collected; before treatment, after treatment and after each degradation process. The results of color determinations are separated for each kind of protective materials and for each stone artefacts.

The new partially fluorinated oligomide (G900), together the other two coatings, applied on stone samples have been also exposed to UV light in the same ageing conditions previously described (climatic chamber with temperature and relative humidity changes) , in order to test their resistance to photo-oxidation.

First experiment on color determination was performed after treatments applied on stone surfaces. The results were calculated as difference of the chromatic parameters before and after application of treatments, after 1st ageing, after 2nd ageing and after 3rd ageing. The results of color determinations after the treatment is reported in table 29 and Figure 33 (in page 60).

Sample	**ΔE After Treatment**		
	G900	**Fluoline HY**	**SILO 112**
EQ	0.0	0.0	0.1
DW	0.1	0.1	0.1
DG	0.1	0.1	0.0
DV	0.0	0.1	0.1
MY	0.1	0.1	0.1

Table 29. Chromatic change (ΔE) of stone samples after treatment with different coatings

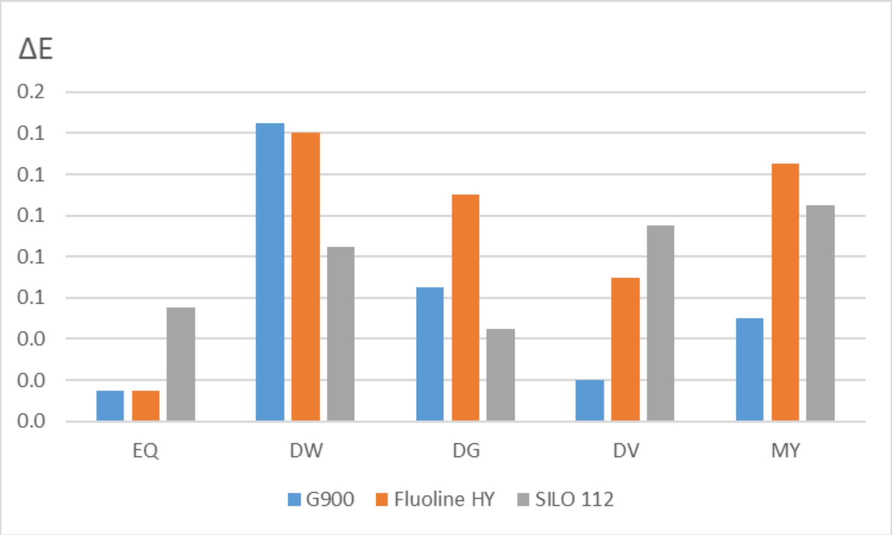


Figure 33. Chromatic change (ΔE) of stone samples after treatment with different coatings

EQ stone samples have lower color changes after the treatment respect than other samples, while DW samples have higher color changes in all the treatments. In any case, color change values (ΔE) are below the level that human eye detected.

The treated samples were exposed to UV light with wavelength > 280 nm in the 1st ageing test which duration was 240 hours. The results of color changes (ΔE) after 1st ageing is reported in table 30 and figure 34 (in page 61).

Sample	**ΔE After Treatment and after the 1st ageing step**					
	G900		**Fluoline HY**		**SILO 112**	
	After trea.	**1st age**	**After trea**	**1st age**	**After trea.**	**1st age**
EQ	0.0	0.2	0.0	0.1	0.1	0.4
DW	0.1	0.2	0.1	0.1	0.1	0.2
DG	0.1	0.1	0.1	0.3	0.0	0.2
DV	0.0	0.1	0.1	0.1	0.1	0.3
MY	0.1	0.1	0.1	0.1	0.1	0.2

Table 30. Chromatic change (ΔE) of stone samples after treatment and after the 1st ageing step

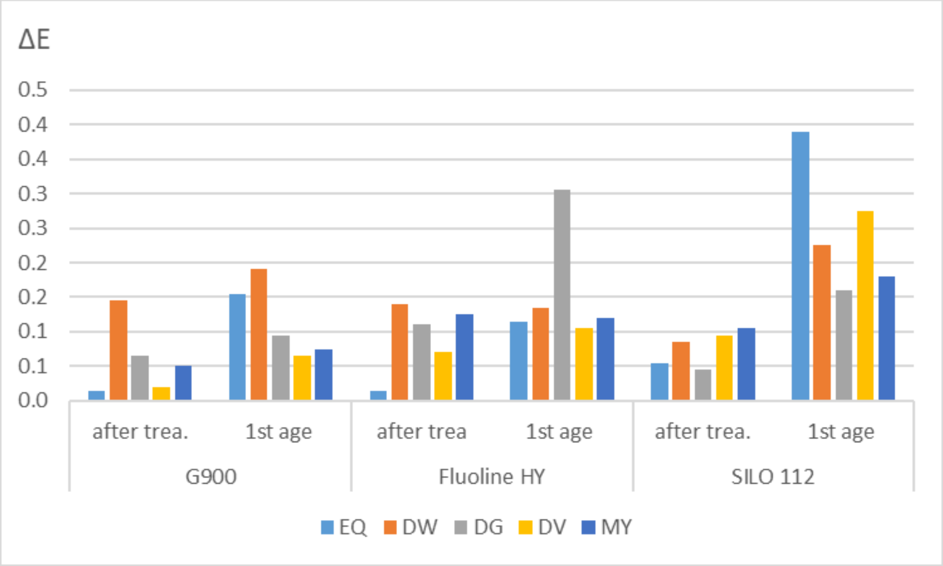


Figure 34. Chromatic change (ΔE) of stone samples after treatment and after the 1st ageing step

Samples treated with SILO 112 show higher color changes respect than samples which are treated with fluorinated compounds. DG Samples show more relevant change with treatment Fluoline HY after the 1st ageing process. Samples with treated G900 show lower color changes. However, color change values (ΔE) of all treated samples are still below the level detected by human eye (ΔE = 3.00).

The new partially fluorinated oligomide (G900) was also controlled by FT-IR after the UV exposition. The FTIR spectrum of G900 after 240 hours under the UV light is reported in Figure 35. The spectrum of G900 does not show changes in the chemical structure.

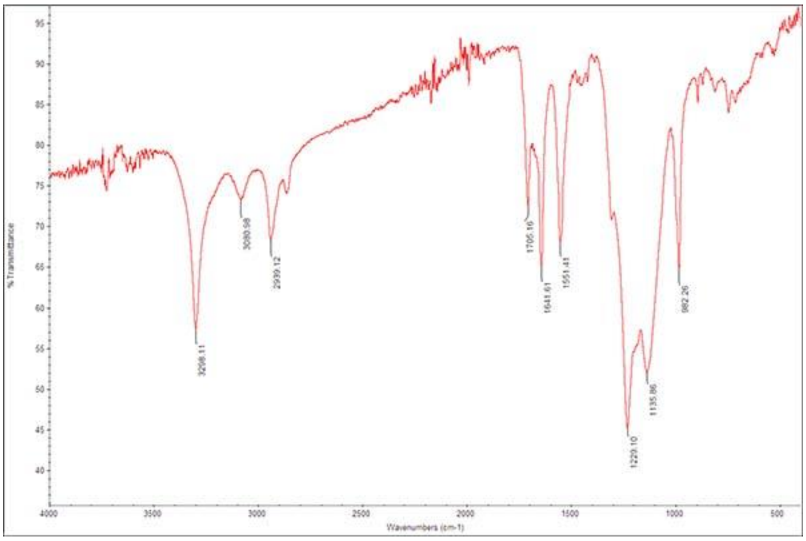


Figure 35. FT-IR spectrum of G900 after 240 hours under the UV light

The treated samples were again exposed to UV light for other 240 h (2nd artificial ageing step) + 240 h (3rd artificial ageing step) for a total of 720h.The results of color determinations (ΔE) after the 2nd ageing (480 h) are reported in table 31 and figure 36, while those after the 3rd ageing (720 h) are reported in table 32 (in page 63) and figure 38 (in page 64).

	G900		**Fluoline HY**		**SILO 112**	
Sample	**1st age**	**2nd age**	**1st age**	**2nd age**	**1st age**	**2nd age**
EQ	0.2	0.6	0.1	0.4	0.4	0.8
DW	0.2	0.6	0.1	0.8	0.2	1.0
DG	0.1	1.2	0.3	5.9	0.2	2.9
DV	0.1	1.8	0.1	0.8	0.3	3.9
MY	0.1	1.0	0.1	1.6	0.2	2.3

Table 31. Chromatic change (ΔE) of stone samples after the 1st ageing step and after the 2nd ageing step

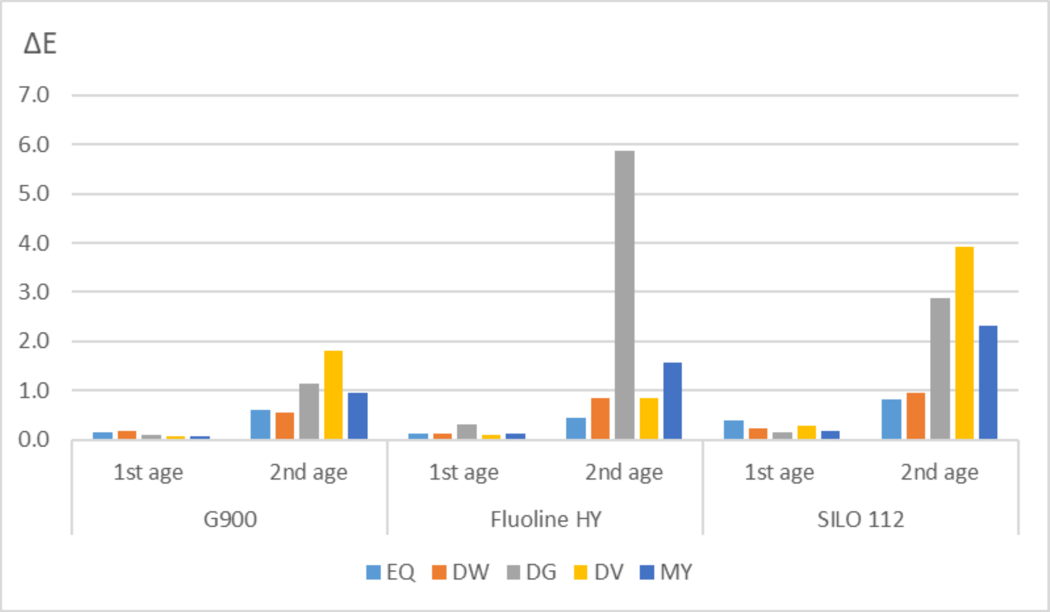


Figure 36. Chromatic change (ΔE) of stone samples after the 1st ageing step and after the 2nd ageing step

According to results of color determinations (ΔE) after 2nd ageing; relevant color change is observed for DG and MY samples treated with Fluoline HY color changes are +5.9 for DG sample and +1.5 for MY sample. This relevant change may due to some contamination of the stone surface during the experiment. Important chromatic changes were also observed on DV, DG and MY samples treated with SILO 112 (ΔE = 3.9, 2.9 and 2.3, respectively)

The new partially fluorinated oligomide (G900) was again controlled by FT-IR s after the 480 hours under UV light and the spectrum was not changed as reported in figure 37.

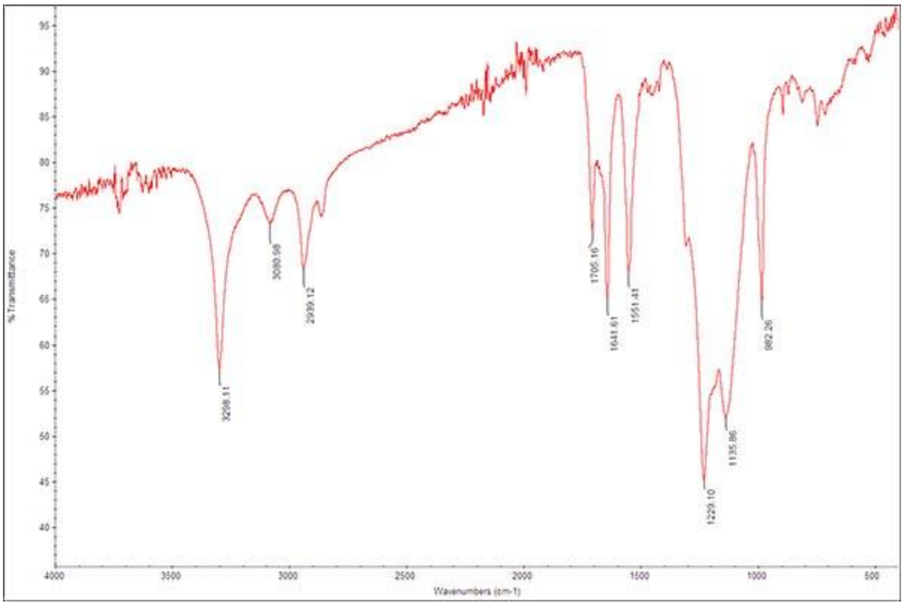


Figure 37. G900 after 480 hours under UV light

	G900		Fluoline HY		SILO 112	
Sample	**2nd age**	**3rd age**	**2nd age**	**3rd age**	**2nd age**	**3rd age**
EQ	0.6	1.2	0.4	3.8	0.8	3.6
DW	0.6	1.7	0.8	1.3	1.0	1.0
DG	1.2	1.9	5.9	8.3	2.9	5.9
DV	1.8	4.9	0.8	2.1	3.9	5.4
MY	1.0	2.4	1.6	6.2	2.3	4.2

Table 32. Chromatic change (ΔE) of stone samples after the 2nd ageing step and after the 3rd ageing step

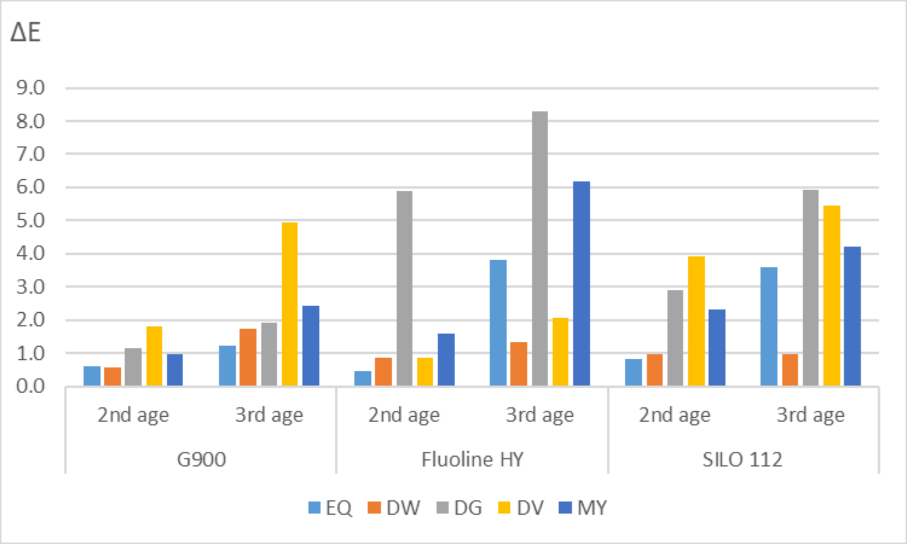


Figure 38. Chromatic change (ΔE) of stone samples after the 2nd ageing step and after the 3rd ageing step

According to results of color determinations (ΔE) after 3rd ageing; relevant color change is observed for DG and MY samples treated with Fluoline HY color changes are +8.3 for DG sample and +6.2 for MY sample. This relevant change may due to some contamination of the stone surface during the experiment. Important chromatic changes were also observed on DV, DG and MY samples treated with SILO 112 (ΔE = 5.4, 5.9 and 4.2, respectively)

The new partially fluorinated oligomide (G900) was again controlled by FT-IR s after the 720 hours under UV light and the spectrum was not changed as reported in figure 39.

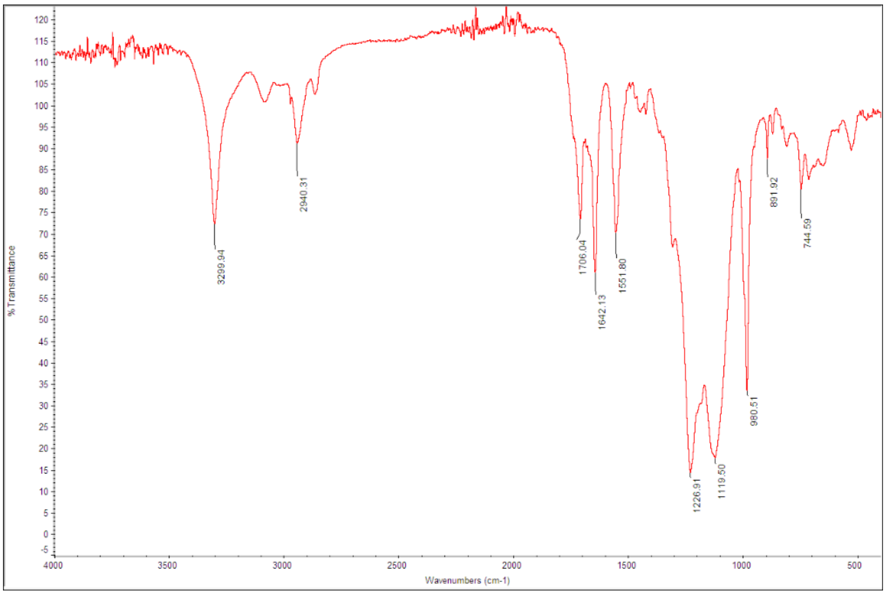


Figure 39. G900 after 720 hours under UV light

The photo-stability of G900 is better visualized in figure 40, where the comparison of spectra acquired after 240, 480 and 720 h of UV irradiation are showed.

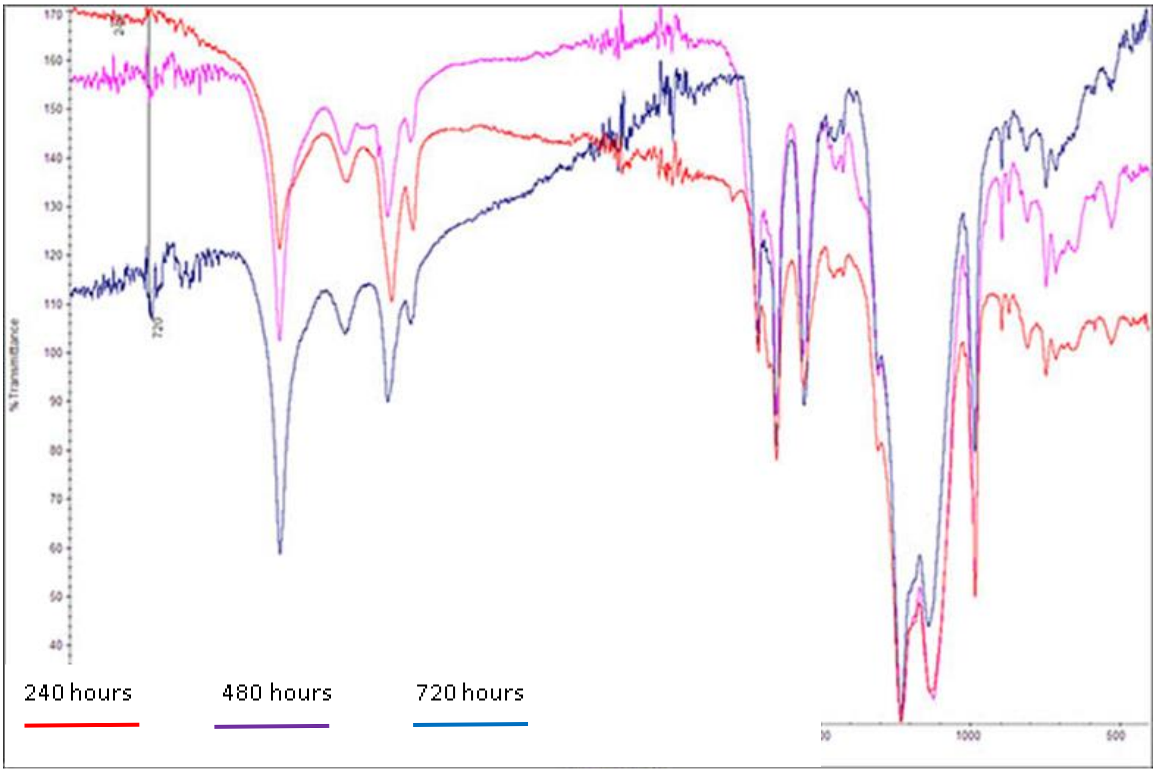


Figure 40. The comparison of spectra G900 acquired after 240, 480 and 720 h of UV irradiation

CHAPTER 6

6. Conclusions

Decohesion of stone artefacts in Euromos Zeus Temple and their area is mainly due to biological growth on surfaces of stone and water condensation favorite by temperature and relative humidity fluctuations during the daytime. As matter of fact; condensation facilitates the growth of microorganisms and decomposition of stone artefacts. Some minerals are highly susceptible to thermal expansion and some are not homogeneously expanded. Calcite shows different expansion coefficient along the crystal axes. This phenomenon creates different elongation with forces acting in opposite direction. Repeated heating cyclic can cause cracking of the interstitial spaces of calcite grains combined in different directions like a Temple's area. This process can be accelerated by water condensation as observed in some parts of temple' s area, where condensation problems are possible. High relative humidity accelerates degradation of stone artefacts with vapor diffusion on top of temple's stones artefacts; however, according to protimeter results that proved no water movement upwards in a partially dry porous structure, water may migrate from the region at higher vapour pressure or evaporate in one pore and re-condense in another wherein there is no water passage. Condensation occurs in the low sunlight zone of temple's and close the Portland cement filling parts.

Temperature parameters are normal, and anomaly of weather was not detected during the research period. According to average values of last forty (40) years; an increase of 2°C in 40 years was observed for the average temperature of August Rainfall intensity has been increased from year of 2012 to year of 2017.

The coefficients of thermal expansion of structural elements are different and expansion coefficients of the different structural elements, as marble and cement, can cause physic-mechanical stress that improve the decohesion of stone artefacts of temple. Although, as a reported before; this problem is not topic of this research, it is an important and urgent issue in terms of the static condition of the temple.

In all the area of stone artefacts of Iasos Agora are not observed condensation problems, although higher average relative humidity values than Euromos Temple's area were found. Here fast drying phenomena occur; they are due to the fact that stones are in large and open-area, but biological occurrences are present on stones artefacts located near trees.

Condensation phenomena are seen mainly in these parts. Synthesis of a new partially fluorinated oligomide; it is not easy to obtain in short time because the reaction needs two steps, long time of reaction, and difficult purification. However, according to results of PE%, contact angle, color determination, photostability and residual permeability (RP%), the new product provides better performance than commercial products, although the fluoroelastomer FLUOLINE HY, in some case, has comparable performance to G900.

EQ stone samples (quarry from Euromos Temple territory) have been demonstrated to be better protected by all the tested products because with this stone better protective efficacy is obtained and the chromatic variations after treatment and after ageing are not relevant. In addition, with this stone the better protective efficacy has been found for the partially fluorinated oligoamide (G900).

On the contrary, on MY stone samples lower values of protective efficacy and higher chromatic changes are observed for the treatments, probably due to the very low porosity (0.27%) that limits the penetration and homogeneous distribution of the coatings.

MY stone samples have been used to set up an ageing methodology simulating natural ageing without the introduction of soluble salts. Different conditions have been tested and an increase in water absorption (related to an increase of porosity) of about 75% have been achieved with 10 cycles.

The evaluation of the durability of the treatment under natural ageing has been evaluated on the treatments performed in situ. However, the period tested is only three months and cannot be considered long enough for evaluating the stability of products to be used on cultural heritage items. At the same time, the artificial ageing carried out in this research gives us an indication on the durability of the treatments under conditions simulating the natural environment. However, also in the case of artificial ageing, longer tests than that carried out in this research are desirable.

The new partially fluorinated oligoamide (G900) has been designed against photo-oxidation. Actually, it shows good photo-stability according to FT-IR spectra acquired after UV irradiation. The low molecular weight of the fluorinated oligoamide is usually preferred to high molecular weight in the protection of marbles or very low porous materials, because of the better solubility in common and environmentally friendly solvents.

Another performance expected from G900 is the inhibition of biological growth on stone surfaces due to its hydrophobicity and to its chemical composition. This parameter will see in-situ applications on stone artefacts in research areas during the time and this parameter will be checked periodically in the next year.

CHAPTER 7

7. Experimental Part

7.1. Equipment and Analytical Methods

7.1.1. Environmental Condition of Research Areas

Thermal Camera and Portable Thermometer

Two varied brands and models of thermal camera used in-situ imaging in the research. First equipment was FLIR brand and IX SERIES model that used at Euromos Temple and their area in years from 2012 to 2016. Second equipment was TROTEC brand, IC080 LV model used at Agora of Iasos and Euromos Temple and their area in year of 2017. Instrument of portable thermometer was TROTEC brand, BC20 model that used both research areas in research years that write above.

Protimeter

TROTEC brand, BM 20 model protimeter used for moisture imaging at both research areas in years of 2012-2017.

7.1.2. Petrography and Mineralogical Definition

The study in transmitted polarized light microscopy has provided information on the structure and crystal size and on the mineralogical composition. These characteristics have led to the classification of the examined rocks.

7.1.2.1. Porosity

Porosity test occurred with two different methods on samples which came from two search areas.

First were water porosity methods performed; samples of DW6, DV4, DG12 and EQ4 put in oven at 110 ^{0}C in twenty-four (24) hours and samples put in the desiccator for came to colder. Before had been burying the water, samples were balanced and then suddenly put in water pool which is in the desiccator. This system was closed engage to pump for vacuum helps to deplete of air in the porous of stone samples.

Vacuum process had been performed three (3) hours and then system remained twenty-four (24) hours closed without vacuum process. Samples were balanced again after twenty-four (24) and values of balance had been calculated.

Porosity had been calculated with equation;

Porosity (%) = $(V_A - V_P) / V_S * 100$

Where;

V_A = Weight of wet saturated samples

V_P = Weight of Dry Samples

V_S = Volume of Sample

7.1.3. Determination of Biological Growth on Stone Artefacts of Euromos Zeus Temple

Microorganisms which were on rock fragment separated and cleaned for the preparation of recreation processes in the laboratory. Sterile soil used that prepared malt extract agar of OXOID CM0059 (Malt extract 30.0) with solution 25g / 500ml (in distilled water) in the recreations of microorganisms. Solution of sterile soil inserted sterilising instrument and sterilisation process has been starting with under the temperature of 121^0C and 0.7 bar pressure and sterilisation process has been stopped after twenty (20) minutes. Sterile soil put in the oven at 50^0C temperature after the sterilisation process. Sterile soil removed from oven Sterile after one (1) hour and sterile soil was added to sharing in the six (6) plates (25 ml for each plate). Microorganisms that separated put in the these six (6) plates than plates put in oven at 30 ^{0}C temperature for recreation process. Plates removed from oven after the three (3) days than observed under the stereo-microscope in the laboratory

7.1.4. Artificial Decay Experiments

Thermo- ageing process were performed with samples which have been came from modern quarry (MY). Thermo-ageing process was occurred ten (10) cycles with different conditions except 9th and 10th cycles. Fridge was used for winter conditions (until 3°C) and oven for hot conditions (115°C) in this experiment.

Sample Information

Marble samples obtained from sheets of a massive block which came from the quarry of the Yatagan* (province of Mugla / Turkey) and several samples had a come one hundred and thirty (130) with 5x5x2 cm dimensions after finished cutting process from marble sheets.

Preparation of Samples

Samples had glossy surfaces, rub with emery paper to prevent this situation and all samples had washing process under the flowing water with the brush the after grinding process. Samples leave to dry in room temperature conditions after the washing process.

1st Ageing Process

The process had started with samples were placed in an oven at + 40 ^{0}C temperatures during the fifteen (15) hours, after then samples wetted with distilled water by spray and put in plastic bags and samples placed with seven (7) hours in the fridge at + 3 ^{0}C ±1°C then samples were extracted from the plastic bag and punt again in the oven at 40°C (1 cycle).

2nd Artificial Ageing Process

The process had started with samples were placed in an oven at + 40 ^{0}C temperatures with fifteen (15) hours after then samples wetted with distilled water at two (2) hours by water capillary absorption method and samples put in plastic bags before the freezer. Samples were in plastic bags remains in the freezer at + 3 ^{0}C temperature with seven (7) hours. These circles repeated in ten (10) times.

3rd Artificial Ageing Process

The process had started with samples were placed in an oven at + 45 ^{0}C temperatures with fifteen (15) hours then samples wetted with distilled water by spray and samples put in plastic bags before the freezer. Samples were remains in the freezer at + 3 ^{0}C temperature with seven (7) hours. These circles repeated in ten (10) times.

4th Artificial Ageing Process

A process had started with samples were placed in an oven at + 55 ^{0}C temperatures with six (6) hours then samples wetted with distilled water by spray and put in plastic bags before the freezer. Samples were within plastic bags remains in the freezer at + 3 ^{0}C temperature with fifteen (15) hours, in this case, we tried samples remain in the cold condition a long time. These circles were repeated in ten (10) times.

5th Artificial Ageing Process

A process had started with samples were placed in an oven at + 100 ^{0}C temperatures with two (2) hours after then samples wetted with distilled water by spray and samples were put in freezer at + 3 ^{0}C temperature without plastic bags with nineteen (19) hours.

According to previously results of water uptake tests that marble samples had to react slowly to the physical conditions and we decided for in this cycle, a temperature of hot condition was a raised to +100 ^{0}C and residence time of samples was reduced to two hours (2) in an oven.

A temperature of cold condition remained same + 3 ^{0}C, however, a residence time of samples in the freezer has been extended up to seventeen (17) hours. Considering about extreme conditions of this process; we decided that cycle consisted in five (5) repeat time.

6th Artificial Ageing Process

A process had started with samples were placed in an oven at + 115 ^{0}C temperatures with fifteen (15) hours then samples put in freezer at + 3 ^{0}C without wetting and without plastic bag.

8th Artificial Ageing Process

A process had started with samples were put in oven at 110 ^{0}C temperature with eight (8) hours and then samples put in distilled water pool; samples waited two (2) hours in water with laboratory conditions (about 25 ^{0}C) and then put in freezer at +3 ^{0}C during the last of the day about forty (14) hours.

9th Artificial Ageing Process

As results of water uptake test with water capillary absorption method after the 8th artificial ageing process; thought that samples were degraded with wintry conditions after water pool application, therefore water pool application repeated two times in this cycle.

10th Artificial Ageing Process

A process was according as 9th artificial ageing circle due to more degradation on stone samples.

7.1.5. Solvents and Reagents

7.1.5.1. Solvents and Salts

2-Propanol purity > 99.8 % from EMSURE

Acetone purity > 99.8 %   from J.T. Baker

Distilled Water produced in the laboratory before use

Absolute Ethanol purity > 99.8 %   from J.T. Baker

Thionyl Chloride purity > 99.8 %   from Sigma- Aldrich

Diethyl Ether purity > 99.8 %   from J.T. Baker

CFC purity > 99.8 %   from Montefluos

7.1.5.2. Reagents

Suberic Acid purity > 99.8 %   from Aldrich

Ethylenediamine purity > 99.8 %   from Aldrich

F3100 Perfluoropolyether Esters from SOLVAY- SOLEXIS

G898 Perfluoropolyether Esters from SOLVAY- SOLEXIS

Krytox Polhexafluoropropylene Oxide from DuPont

7.1.5.3. Commercial Products for Treatment

Fluoline HY, is a water-repellent protective ready to use. It is a poly (hexafluoropropene-co-vinylidene fluoride (molecular weight around 400,000 u.m.a.), supplied by CTS Italia.

Silo 112, is a compound from a mixture of organosiloxanes oligomers, supplied by CTS Italia.

7.1.6. Synthesis of Partially Fluorinated Oligoamides

7.1.6.1. Synthesis of Not-Fluorinated Oligoamides

1:5 (1st)

First synthesis of not fluorinated oligomers performed; in two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). Etilendiamine 1.450 g put in the flask under N_2 and 1 ml solvent of EtOH and start stirring with room temperature and temperature had been raised slowly until 95 ^{0}C. Di-ethyl suberate added slowly in the flask with amount of 1.222 g. After FT-IR checking (spectra 1, chapter 8, page 90) and after 17 hours the reaction was considered finished by FT-IR control. Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 1.483 g and final product characterized by FT-IR and ^{1}H-NMR.

1:5 (2nd)

Second synthesis of not fluorinated oligomers performed; two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). Etilendiamine 1.741g put in the flask under N_2 without solvent and start stirring with room temperature and temperature had been raised slowly until 50 ^{0}C. Desuberate joint slowly in flask with amount of 2.0 g. After FT-IR checking (spectra 2, chapter 8, page 91) and after 25 hours, was considered finished by FT-IR control. Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 1.974 g and final product characterized by FT-IR and ^{1}H-NMR.

1:3

Synthesis of 1:3 started with two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). Etilendiamine 1.565g put in the flask under N_2 with solvent of 2-propanol (2 ml) and start stirring with room temperature and temperature had been raised slowly until 80 ^{0}C. Desuberate joint slowly in flask with amount of 2.0 g. After FT-IR checking (spectra 3, chapter 8, page 92) and after 35 hours, was considered finished by FT-IR control. Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions).

The final product (white waxy solid) obtained 1.557 g and final product characterized by FT-IR and ^{1}H-NMR.

1:2 (1st)

Synthesis of not fluorinated oligomers 1:2 performed; two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). Etilendiamine 0.746 g put in the flask under N_2 with solvent of 4 ml 2-propanol and start stirring with room temperature and temperature had been raised slowly until 65 ^{0}C. Desuberate joint slowly in flask with amount of 1.43 g. After FT-IR checking (spectra 4, chapter 8, page 93) and after 25 hours, was considered finished by FT-IR control. Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 1.005 g and final product characterized by FT-IR and ^{1}H-NMR.

1:2 (2nd)

Second synthesis of not fluorinated oligomers 1:2 performed; two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). Etilendiamine 0.782 g put in the flask under N_2 with solvent of 5 ml 2-propanol and start stirring with room temperature and temperature had been raised slowly until 70 ^{0}C. Desuberate joint slowly in flask with amount of 1.38 g. After 45 hours, was considered finished by FT-IR control. Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 0.894 g and final product characterized by FT-IR and ^{1}H-NMR.

1:2 (3rd)

Third synthesis of not fluorinated oligomers 1:2 performed; two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min) Etilendiamine 0.290 g put in the flask under N_2 with solvent of 1.00 ml 2-propanol and start stirring with room temperature and temperature had been raised slowly until 70 ^{0}C. After 24 hours, 0.290 g Etilendiamine put in the flask under N_2 due to complete amount 0.580 g for ratio of 1:2. After 45 hours, was considered finished by FT-IR control. Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 0.785 g and final product characterized by FT-IR and ^{1}H-NMR.

1:2 (4^{th})

Forth synthesis of not fluorinated oligomers 1:2 performed; two -neck flask (100 ml) with magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). Etilendiamine 0.580 g put in the flask under N_2 with solvent of 1.00 ml 2-propanol and start stirring with room temperature and temperature had been raised slowly until 70 ^{0}C. After the 52 hours, was considered finished by FT-IR control (spectra 5, chapter 8, page 94). Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 0.980 g and final product characterized by FT-IR and ^{1}H-NMR.

7.1.6.2. Synthesis of Partially Fluorinated Oligoamides

1:5 +F3100

Synthesis of partially fluorinated oligoamides started with two -neck flask (100 ml) within magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). 0.250 g of not fluorinated oligoamides with 1:5 ratio (First synthesis) put in flask and process started with ambient temperature (about 25 ^{0}C) with stirring and heating; heat grade had been raising until temperature reached to 65^{0}C. Homogeneous solution observed in the flask, 0.038 g of perfluoropolyether esters of F3100 (ready to use) added in the solution after five (5) hours from the beginning of reaction. FT -IR spectra checked after three (3) hours and 0.048 g of perfluoropolyether esters of F3100 had been adding in the reaction at 65^{0}C temperature. Perfluoropolyether esters of F3100 had been adding drop by drop during the reaction period due to obtained long chain. Product is in the flask had been coming to harden and, in this case, stirring had been poor attendance and in this reason, solvent of EtOH put with fragmentary in the flask under N_2 and EtOH had used totally 15 ml in the end of the reaction. Perfluoropolyether esters of F3100 had been adding drop by drop after the solvent of EtOH and totally 0.615 g of perfluoropolyether esters of F3100 used in the reaction. After 111 hours, was considered finished by FT-IR control (spectra 6, chapter 8, page 95). However, esters which are not reacted had been determinate and reaction had been continuing more 29 hours and end of the 140 hours, was considered finished by FT-IR control (spectra 7, chapter 8, page 96). Then the crude product was purified by the unreacted reagents through several extractions with diethyl ether (typically 7-8 extractions). The final product (white waxy solid) obtained 0.745 g.

1:5 +Krytox

Synthesis for the obtained ester of Krytox started with two -neck flask (100 ml) within magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). 1.003 g Krytox with put in the flask under the N_2 atmosphere and then had been starting reaction at room temperature then 0.1 ml thionyl chloride and 4 ml EtOH added in the flask under the N_2 atmosphere, respectively. Reaction has been heated until temperature reached 70 ^{0}C. Reaction checked by FT-IR spectra after two (2) four (4) hours and twenty-two (22) hours, respectively.

After 22 hours, was considered finished by FT-IR control (spectra 8, chapter 8, page 97). After the obtained Ester of Krytox; reaction of 1:5 +Krytox has been started with two -neck flask (100 ml) within magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). 0.214 g of not fluorinated oligoamides with 1:5 ratio (second synthesis) put in the flask under the N_2 atmosphere. Reaction has been started with room temperature and add 0.012 g ester of Krytox in the flaks under the N_2 atmosphere. According to observation of reaction that ester of Krytox not diffused in the solution and ester of Krytox was like a deposition in the flax. All these results decided that reaction was not to come into existence; finished experiment.

1:2 (4th) + G900

Synthesis of partially fluorinated oligoamides started with two -neck flask (100 ml) (100 ml) within magnetic stirring and this system was closed and three (3) times circulation of N_2 (1 min) and O_2 (5 min). 0.300 g of not fluorinated oligoamides with 1:2 ratio (forth synthesis) put in flaks and then 20 ml 2-propanol solvent added in flax under N_2 atmosphere.

Process started with ambient temperature (about 26 ^{0}C) with steering and heating; heat grade had been raising until temperature reached to 85 ^{0}C. 5 ml solvent of 2-propanol added in the solution after six (6) hours from the beginning of reaction that due to help steering more facility. Homogeneous solution observed in the flask, 0.092 g of perfluoropolyether esters of G900 has been add in the flax after twenty-four (24) hours from the beginning of the reaction. FT-IR spectra checked after two (2) hours from the beginning of the reaction then 0.101 g of perfluoropolyether esters of G900 has been added into the reaction. 5 ml 2-propanol has been added more into the reaction for help to steering magnetic bar, because, product was a turn from liquid faze to rigid faze due to evaporation of 2-propanol due to high reaction temperature. 0.767 g of perfluoropolyether esters of G900 has been added into the reaction in the end of the reaction process. 45 ml of solvent of 2-propanol has been used in the 65 hours of reaction time, according to FT-IR spectra; reaction is over and then began purification process with diethyl ether washing for to eliminate esters which are not reacted. After the 45 hours, was considered finished by FT-IR control (spectra 9, chapter 8, page 98) and decided that reaction has been continued about one day due to react with more unreacted esters of G900 after according to FT-IR spectra 9. After the 65 hours, was considered finished by FT-IR control (spectra 10, chapter 8, page 99) Then the crude product was purified by the unreacted reagents through several extractions with CFC (4 extractions) (spectra 11, chapter 8, page 100). The final product (white waxy solid) obtained 0.848 g.

7.1.7. Evaluation of Partially Fluorinated Oligoamides

7.1.7.1. FT-IR Spectroscopy

FT-IR spectra were recorded using a Perkin Elmer spectrometer model Spectrum 1000 in the range 4000-400 cm^{-1} and PC managed by spectrum software Spectrum One. Samples were analyzed on KBr windows and diamond cell using a resolution of 2 cm^{-1} and 16 or 32 scans, respectively on KBr windows or diamond cell.

7.1.7.2. Measures of Water Repellency Tests

7.1.7.2.1. Capillary Water Capillary Absorption Test

The water capillarity absorption measures have been carried out in accordance with the recommendation UNI-EN 15801 – 2010 “Conservation of Cultural Heritage” -Test Method-. Determination of absorption of water by capillarity in laboratory.

Measurements was performed by the effectiveness of a water-repellent treatment of stone surfaces and plasters, NORMA UNI 11432:2011 in-situ.

Calculation of efficacy of protective (EP %) with formula;

$PE\ \% = (A_0 – A_1) / A_0 *100$

where A_0 and A_1 are the mass of water absorbed before and after treatment, respectively.

7.1.7.2.2. Contact Sponge Test

Water uptake test with "*Contact Sponge"* was performed before treatment and after treatment in the research areas. Calculation of water repellency with formula;

Wa ($g/cm^2.min$) = (Pi-Pf) / 23.76 *t

Where;

t= time of contact in minutes,

Pi = Beginning weight in grams

Pf= Final weight in grams

23.76 = Surface of sponge in cm^2

7.1.7.2.3. Color Determination

Colorimetric measurements of opaque surfaces were performed using a portable reflector colorimeter model 3nh NS810 portable spectrometer uses d/8 structure with 400- 700 nm and high accuracy Delta E^*ab 0.04, and 8 mm aperture makes accordance with the recommendation UNI-EN 15801 – 2010 "Conservation of Cultural Heritage" -Test Method-. Measuring the color of surfaces. On each measurement were recorded by the tool and tool a placing in the same point of the sample. Color Determination values are expired as

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

where ΔE is the difference of the concluding parameters (a* b* and L*):

- after treatment and before treatment (to evaluate the influence of the treatment);
- after ageing and before ageing (to evaluate the influence of the ageing process).

7.1.7.2.4. Thermal Hygrometric ageing and UV Ageing

Tests of equipment were samples which that applied treatments and climatic chamber. Climatic chamber brand and model were Weathering chamber BGD 852 model of BIUGED for ageing process. Process was 30 cycles, and every 10 cycles the samples were controlled by capillary absorption test and chromatic changes. Cycles are representing in the table 33.

Time (h)	1	2	6	10	4	1
Temperature (^{0}C)	-5	5	10	25	30	35
RH (%)	0	0	90	80	65	50

Table 33. Thermal Hygrometric ageing cycle

7.1.7.2.5. Vapour Permeability Test

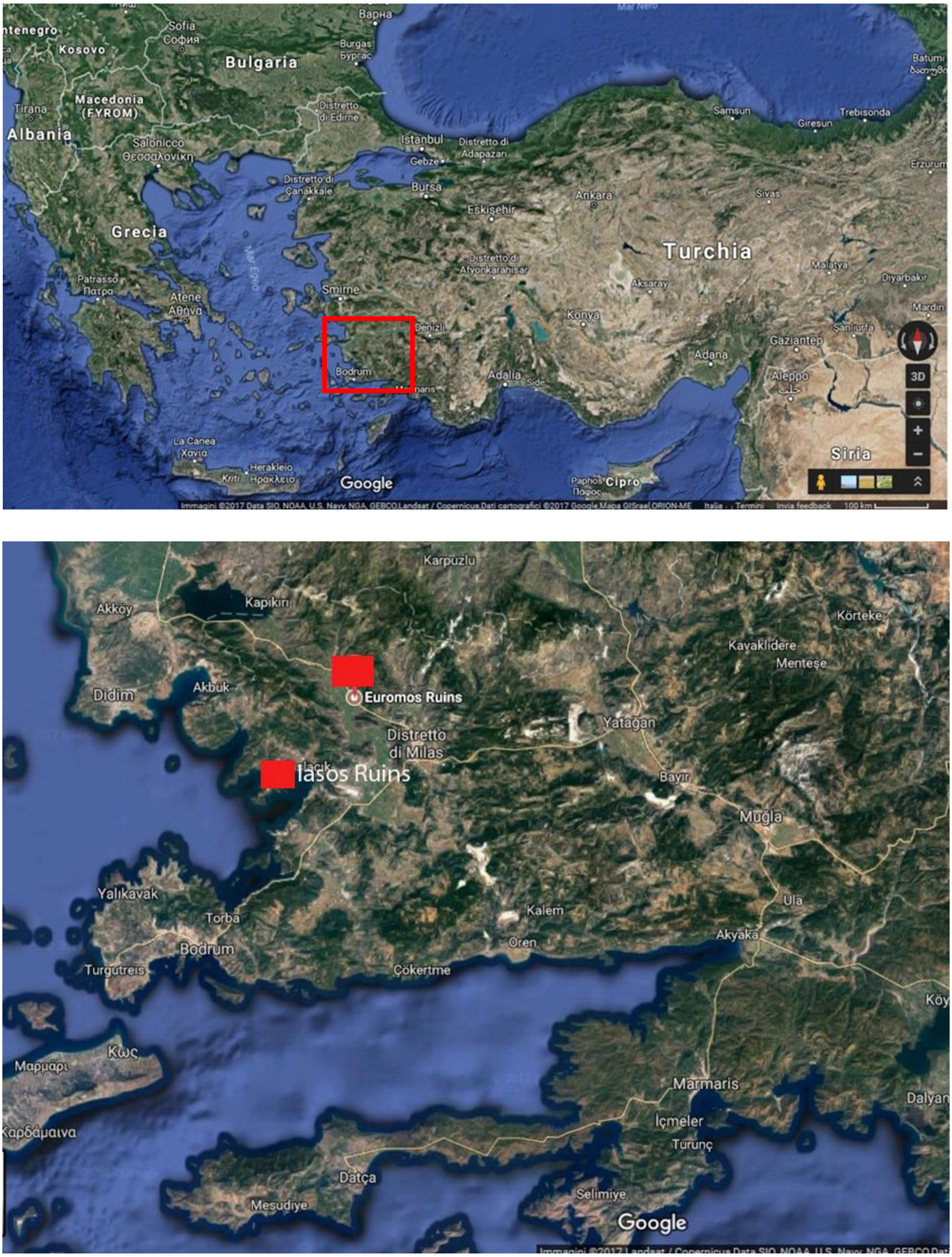
The water vapor permeability measurements were carried out with *"Cup"* method, according to recommendation of UNI- EN 15803 -2010. "Conservation of Cultural Heritage " -Test Method-. Determination of water vapor permeability.

7.1.7.2.6. Measurement of Contact Angle

The contact angle between the film and water was measured by using a KSV Instruments Cam 200 contact angle meter at room temperature. The measurements were carried out with the latex films coated on lamellas. The volume of water drops in all the measurements was equal to 5.073 ml and A =11.98 mm^2. Five readings of contact angles were taken for each drop. The final contact angle of each sample was obtained by averaging the results of the least five measurements.

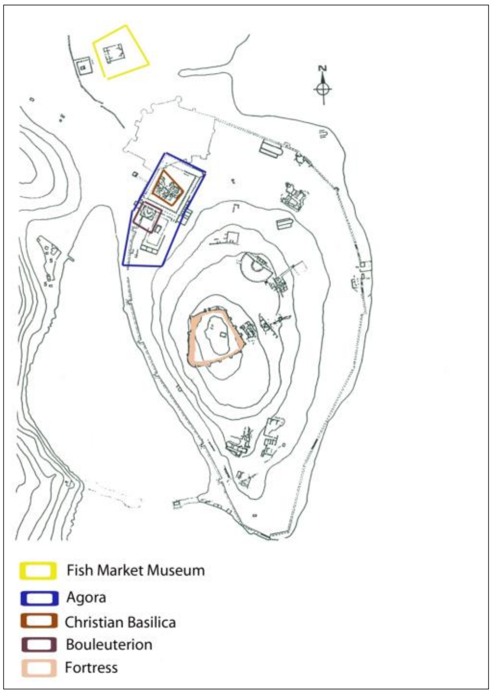
Chapter 8

Appendix

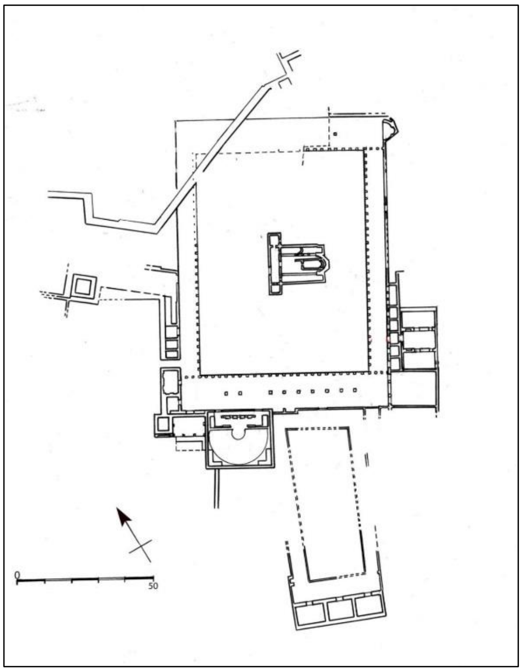


Map1. Location of Euromos and Iasos

Fig 1. Plan and View of Euromos Zeus Temple



General Plan of Iasos Ancient City



Plan of Agora of Iasos

Fig 2. Plans and Views of Iasos of Agora

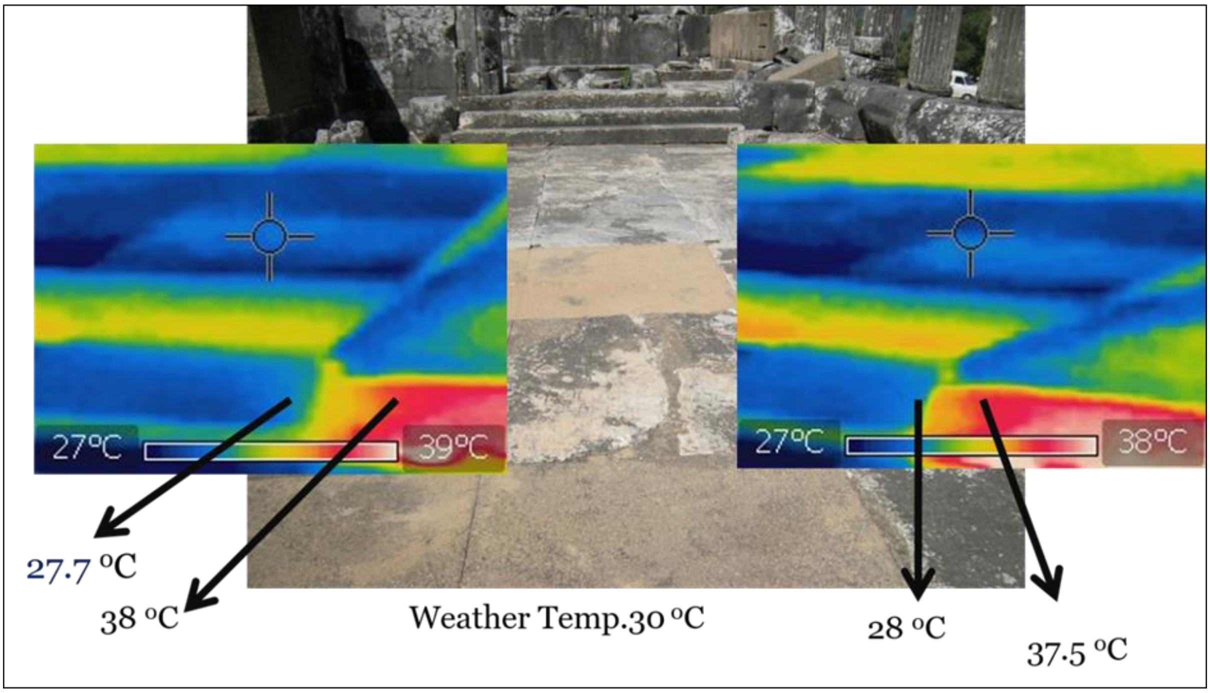


Fig.5. View of Zeus Temple's floor with thermal camera imaging; blue colour parts are Portland cement filling and red colour parts are natural stones.

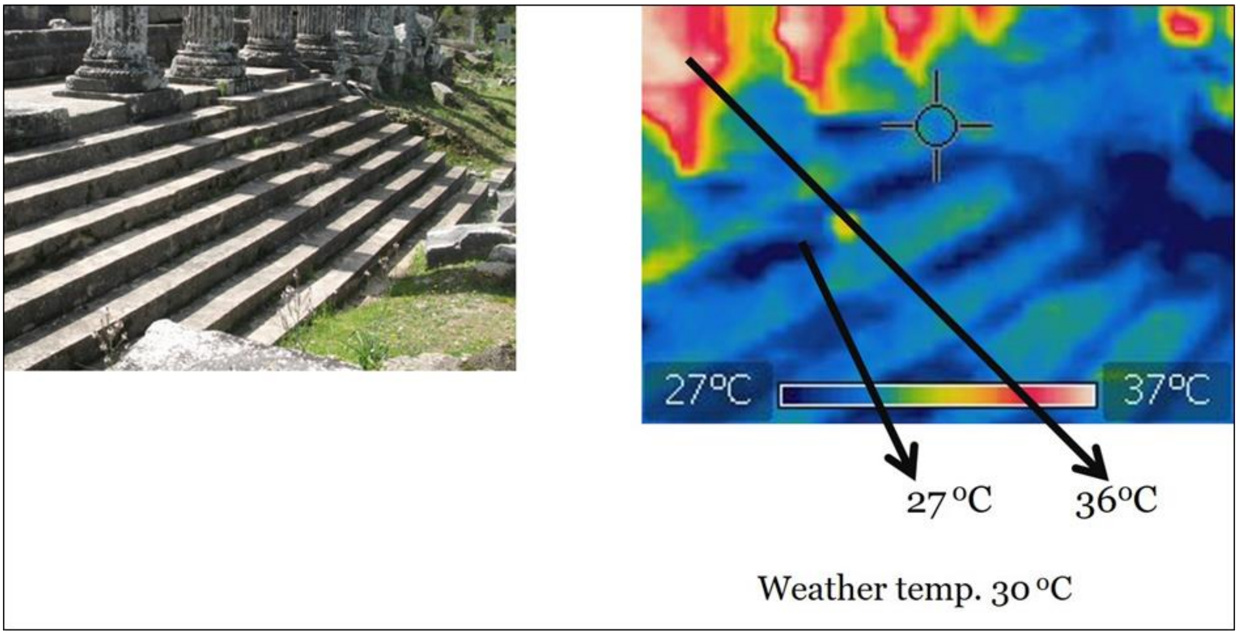


Fig.6. View of Zeus Temple's stairs that reconstructed with Portland cement; blue colour parts are Portland cement filling and red colour parts are natural stones.

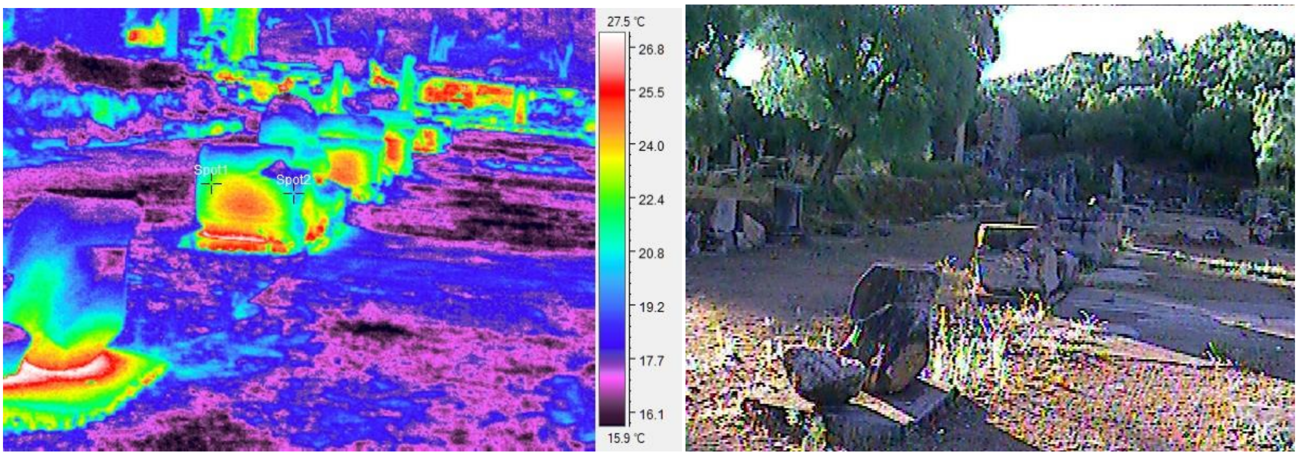


Fig.7. Bouleterion of Agora’s south path, temperature of stones artefacts similar to ambient temperature was 27.3 ^{0}C.

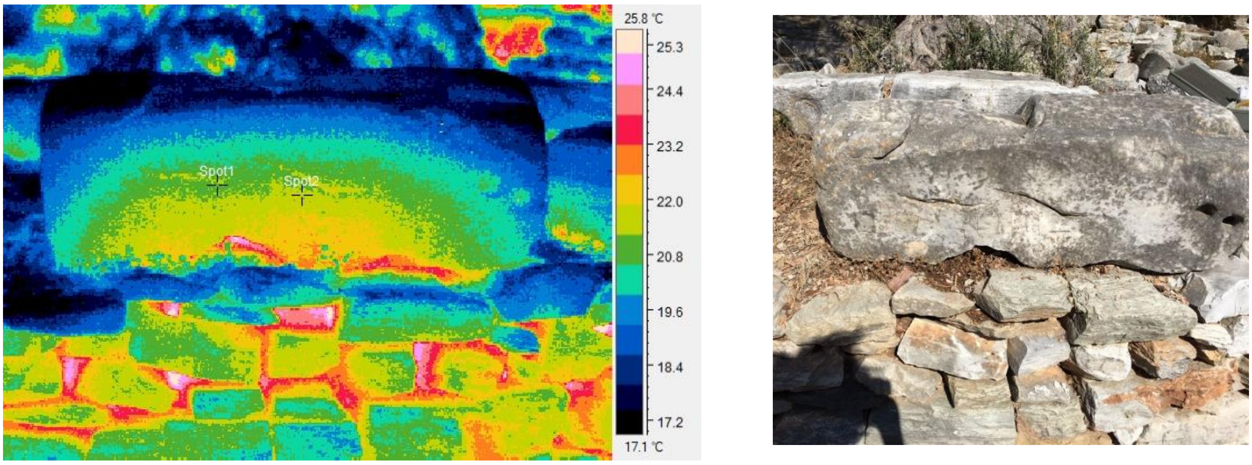


Fig.8. Bouleterion of Agora’s south-east path, temperature of stones artefacts similar to ambient temperature was 27.3 ^{0}C.

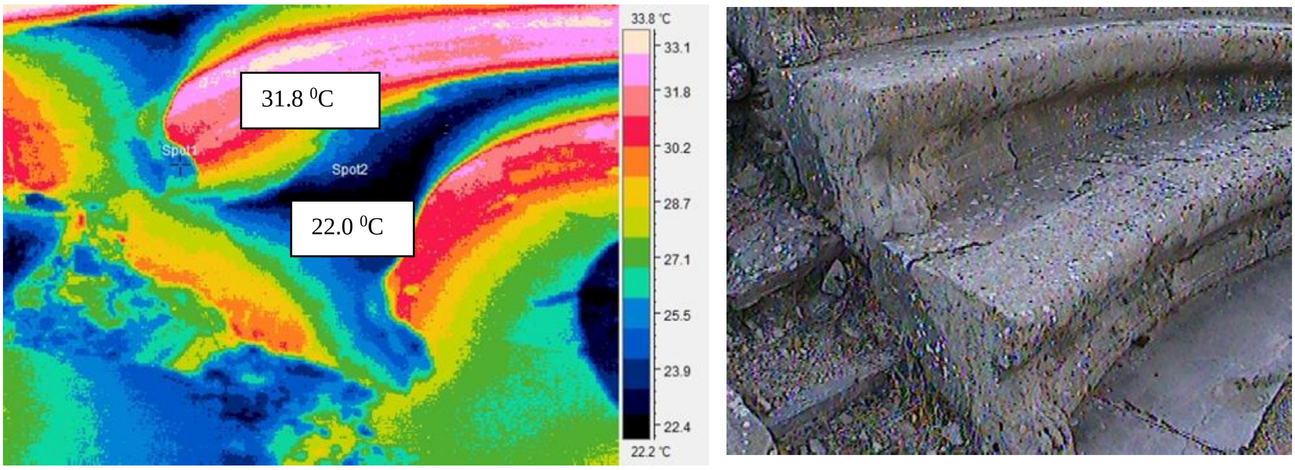
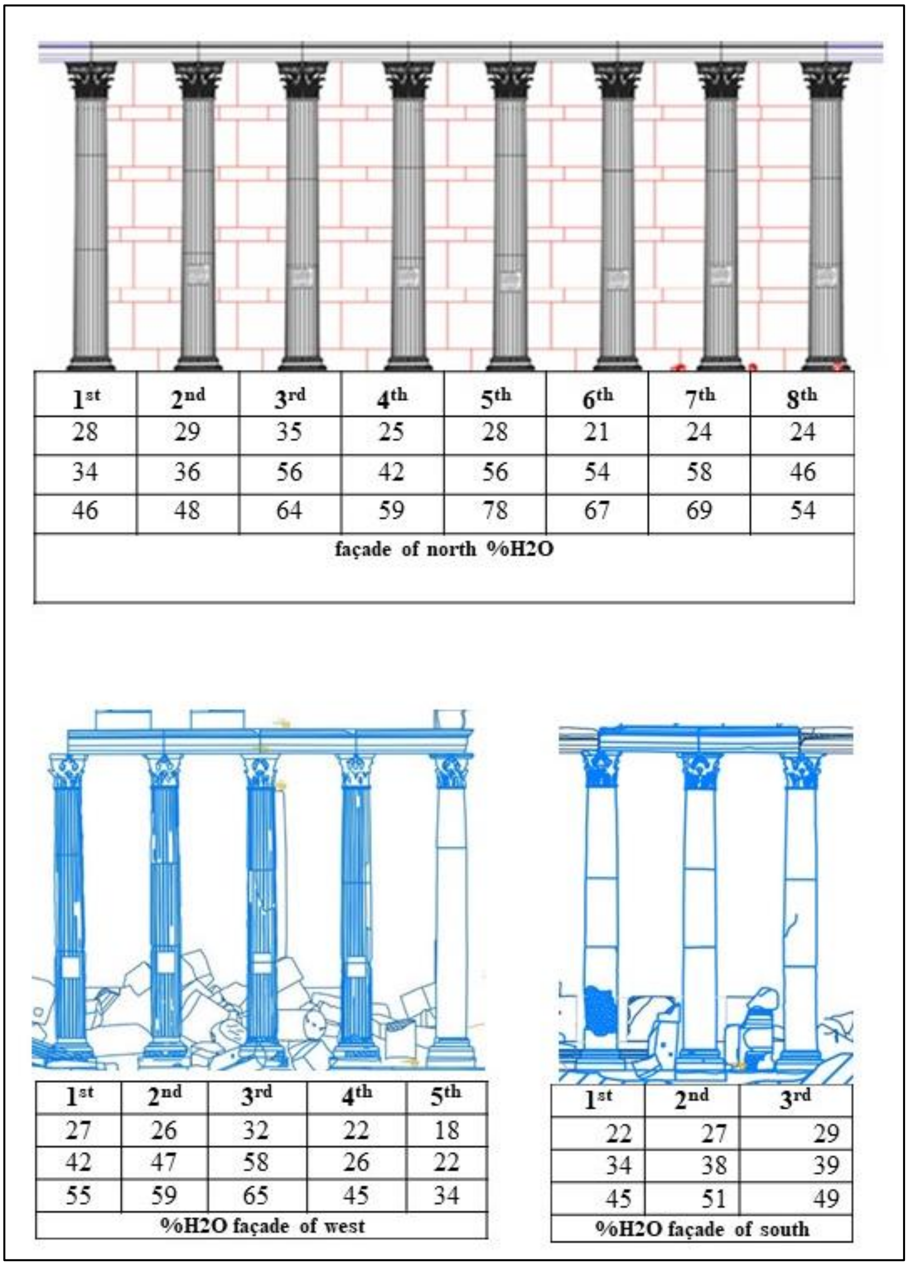


Fig. 9. Bouleterion of Agora’s stairs that reconstructed with Portland cement; blue colour parts are Portland cement filling and red colour parts are natural stones. Ambient temperature was 27.3 ^{0}C.

2017	Temperature (ºC)			Relative Humidity (RH %)		
Day/ Hour→	**6:30am**	**12:00am**	**6:30 pm**	**6:30am**	**12:00am**	**6:30 pm**
25th May	13.4	22.1	18.6	45.2	38.4	39.0
25th June	21.0	24.6	23.5	55.0	35.0	32.0
25th July	26.1	35.2	34.5	65.0	66.0	67.3
25th August	27.2	35.01	30.5	46.6	54.20	45.0

Table 3. Local weather values of Agora of Iasos in August 2017



1st	2nd	3rd	4th	5th	6th	7th	8th
28	29	35	25	28	21	24	24
34	36	56	42	56	54	58	46
46	48	64	59	78	67	69	54

façade of north %H2O

1st	2nd	3rd	4th	5th
27	26	32	22	18
42	47	58	26	22
55	59	65	45	34

%H2O façade of west

1st	2nd	3rd
22	27	29
34	38	39
45	51	49

%H2O façade of south

Fig. 10. Protimeter values of Temple’s columns

2012	Rainfall	
Month	**Sum (kg/m^2)**	**Maximum (kg/m^2) / Day**
January	214.0	46.6
February	210.8	55.0
March	30.2	14.6
April	102.2	32.6
May	53.4	20.4
June	0.0	0.0
July	0.0	0.0
August	7.8	7.8
September	0.0	0.0
October	75.2	46.8
November	33.0	15.8
December	252.6	44.6

Table 4. Year of 2012 rainfall intensity in Milas Province*

2017	Rainfall	
Month	**Sum (kg/m^2)**	**Maximum (kg/m^2) / Day**
January	241.4	53.2
February	23.2	15.4
March	83.8	24.4
April	36.6	12.8
May	30.2	9.0
June	4.2	4.2
July	0.0	0.0

Table 5 Year of 2017 rainfall intensity in Milas Province*

**Meteorological Department, Water Affairs and Forestry Ministry of Turkey*

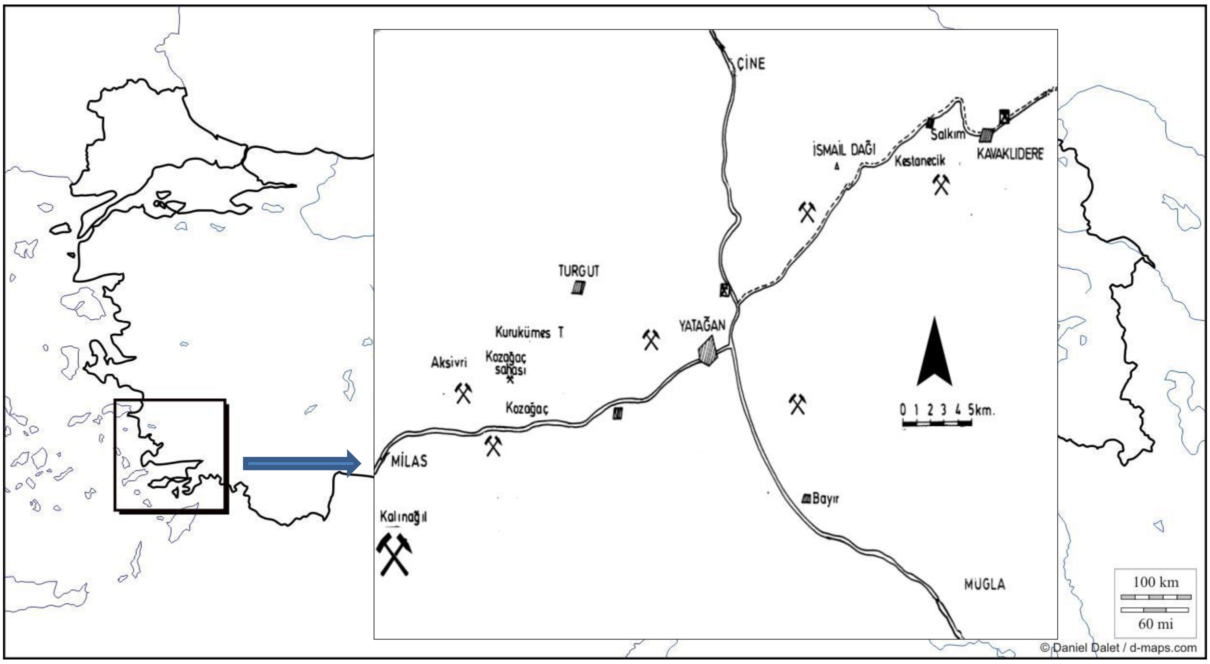


Fig. 15. Location of Kozağaç (Yatağan) region

Water uptake test by water capillary absorption test (g) Artificial Decay Experiments

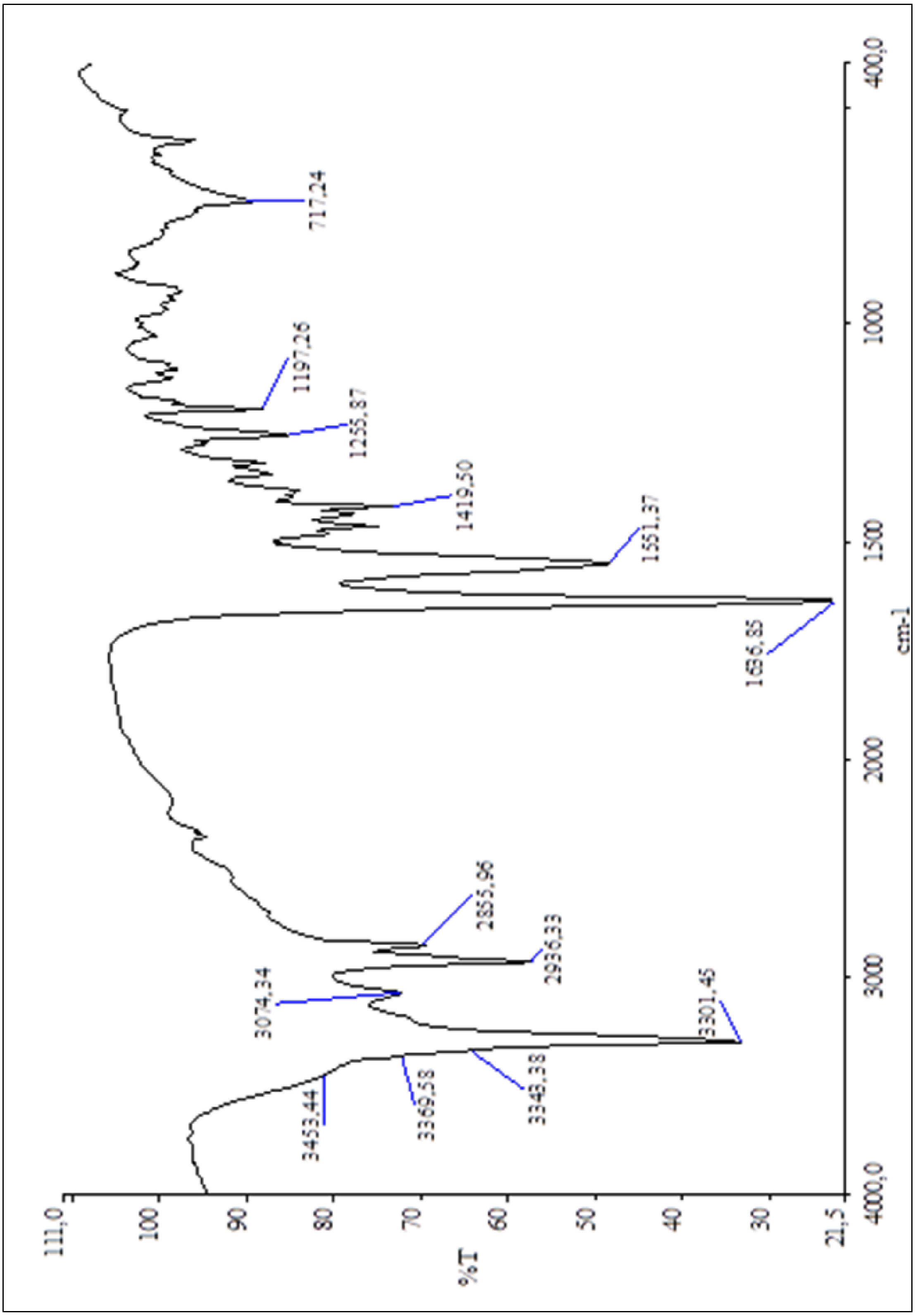
Sample	t=2h bef.age.	t=2h after 1st	t=2h after 2nd	t=2h after 3rd	t=2h after 4th	t=2h after 5th	t=2h after 6th	t=2h after 7th	t=2h after 8th	t=2h after 9th	t=2h after 10th	
MY1	0.064	0.135	0.133	0.134	0.133	0.153	0.149	0.151	0.189	0.208	0.186	**g**
MY3	0.070	0.153	0.137	0.145	0.123	0.161	0.159	0.170	0.204	0.222	0.192	**g**
MY6	0.049	0.130	0.125	0.117	0.109	0.133	0.138	0.133	0.153	0.177	0.158	**g**
MY7	0.045	0.114	0.129	0.111	0.123	0.122	0.125	0.123	0.154	0.170	0.148	**g**
MY10	0.107	0.172	0.190	0.167	0.178	0.199	0.183	0.179	0.224	0.226	0.220	**g**
MY12	0.073	0.138	0.135	0.133	0.157	0.152	0.155	0.150	0.179	0.190	0.183	**g**
MY15	0.074	0.160	0.148	0.142	0.144	0.163	0.162	0.223	0.201	0.213	0.194	**g**
MY18	0.073	0.127	0.118	0.130	0.126	0.130	0.134	0.147	0.177	0.192	0.185	**g**
MY20	0.066	0.145	0.143	0.131	0.142	0.146	0.148	0.165	0.187	0.208	0.181	**g**
MY23	0.056	0.138	0.120	0.115	0.155	0.148	0.165	0.163	0.177	0.198	0.167	**g**
MY24	0.086	0.142	0.155	0.150	0.159	0.161	0.166	0.173	0.194	0.214	0.189	**g**
MY30	0.070	0.146	0.127	0.152	0.142	0.161	0.154	0.187	0.190	0.197	0.178	**g**
MY31	0.070	0.134	0.127	0.127	0.122	0.137	0.139	0.143	0.160	0.183	0.160	**g**
MY32	0.073	0.160	0.145	0.144	0.147	0.165	0.172	0.169	0.200	0.217	0.194	**g**
MY35	0.067	0.131	0.126	0.117	0.130	0.138	0.143	0.148	0.170	0.188	0.170	**g**
MY36	0.086	0.171	0.148	0.180	0.161	0.162	0.177	0.164	0.189	0.218	0.187	**g**
MY37	0.072	0.145	0.149	0.181	0.147	0.157	0.170	0.164	0.189	0.209	0.162	**g**
MY40	0.076	0.130	0.125	0.136	0.130	0.149	0.149	0.150	0.169	0.201	0.173	**g**
MY41	0.053	0.126	0.127	0.129	0.129	0.151	0.141	0.149	0.175	0.183	0.155	**g**
MY44	0.076	0.140	0.138	0.138	0.155	2.164	0.166	0.174	0.196	0.204	0.203	**g**
MY45	0.058	0.117	0.123	0.128	0.117	0.150	0.149	0.140	0.175	0.187	0.162	**g**
MY47	0.064	0.127	0.123	0.120	0.131	0.138	0.139	0.140	0.161	0.198	0.158	**g**
MY54	0.087	0.175	0.145	0.142	0.150	0.155	0.158	0.155	0.180	0.207	0.175	**g**
MY58	0.106	0.173	0.154	0.173	0.169	0.174	0.177	0.180	0.211	0.224	0.222	**g**
MY59	0.045	0.172	0.118	0.118	0.121	0.131	0.133	0.139	0.154	0.168	0.189	**g**
Average	**0.054**	**0.153**	**0.126**	**0.126**	**0.127**	**0.142**	**0.141**	**0.145**	**0.171**	**0.188**	**0.188**	**g**

Table 6. Water uptake Tests results of the Artificial Decay Experiments in 2 Hour

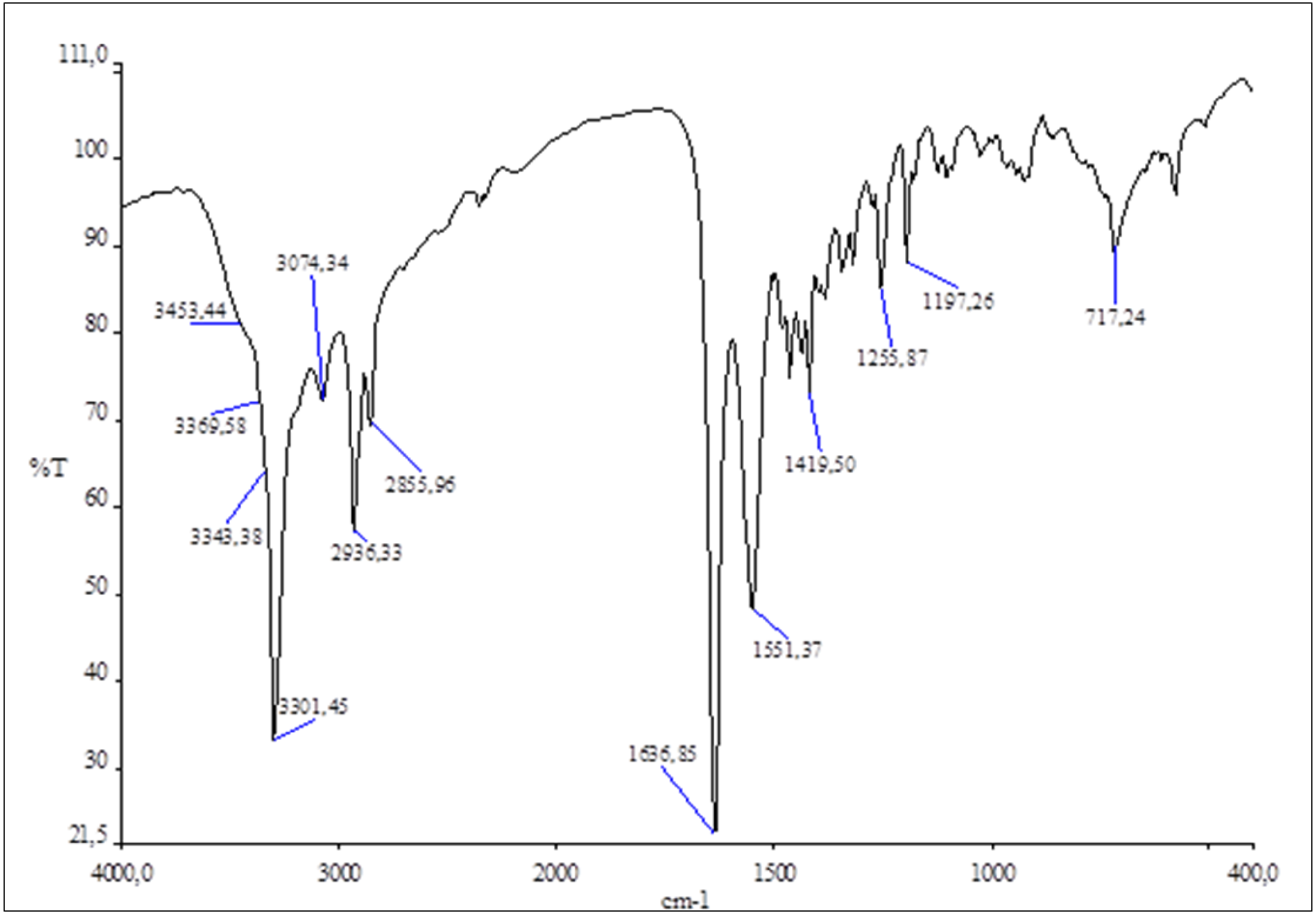
Sample	(Av.) t=2h-t=0		Sample	(Av.) t=2h-t=0		Sample	(Av.) t=2h-t=0		Sample	(Av.) t=2h-t=0	
EQ1	0.103	g	**DW1**	0.180	g	**DG1**	0.155	g	**DV1**	0.288	g
EQ2	0.114	g	**DW2**	0.204	g	**DG2**	0.125	g	**DV2**	0.336	g
EQ3	0.117	g	**DW3**	0.165	g	**DG3**	0.154	g	**DV3**	0.423	g
EQ4	0.106	g	**DW4**	0.223	g	**DG4**	0.195	g	**DV4**	0.316	g
EQ5	0.120	g	**DW5**	0.160	g	**DG5**	0.135	g	**DV5**	0.319	g
EQ6	0.129	g	**DW6**	0.169	g	**DG6**	0.199	g	**DV6**	0.440	g
EQ7	0.098	g	**DW7**	0.142	g	**DG7**	0.127	g	**DV7**	0.300	g
EQ8	0.117	g	**DW8**	0.172	g	**DG8**	0.139	g	**DV8**	0.347	g
EQ9	0.129	g	**DW9**	0.154	g	**DG9**	0.111	g	**DV9**	0.298	g
EQ10	0.121	g	**DW10**	0.188	g	**DG10**	0.202	g	**DV10**	0.310	g
Average	**0.112**	g		**0.184**	g		**0.179**	g		**0.299**	g

Table 8. Results of average water absorption tests of marble stones at three times

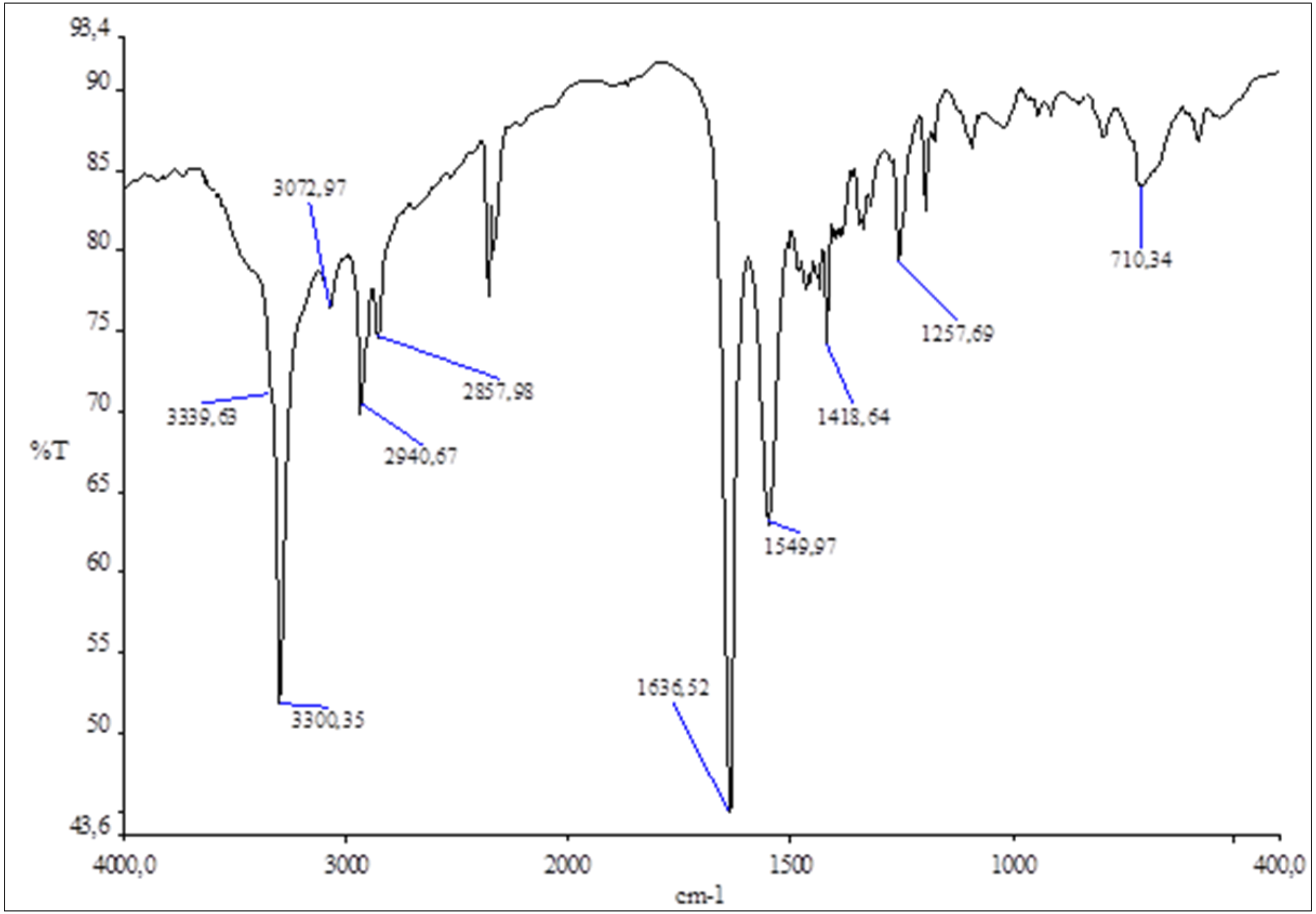
FT-IR Spectra



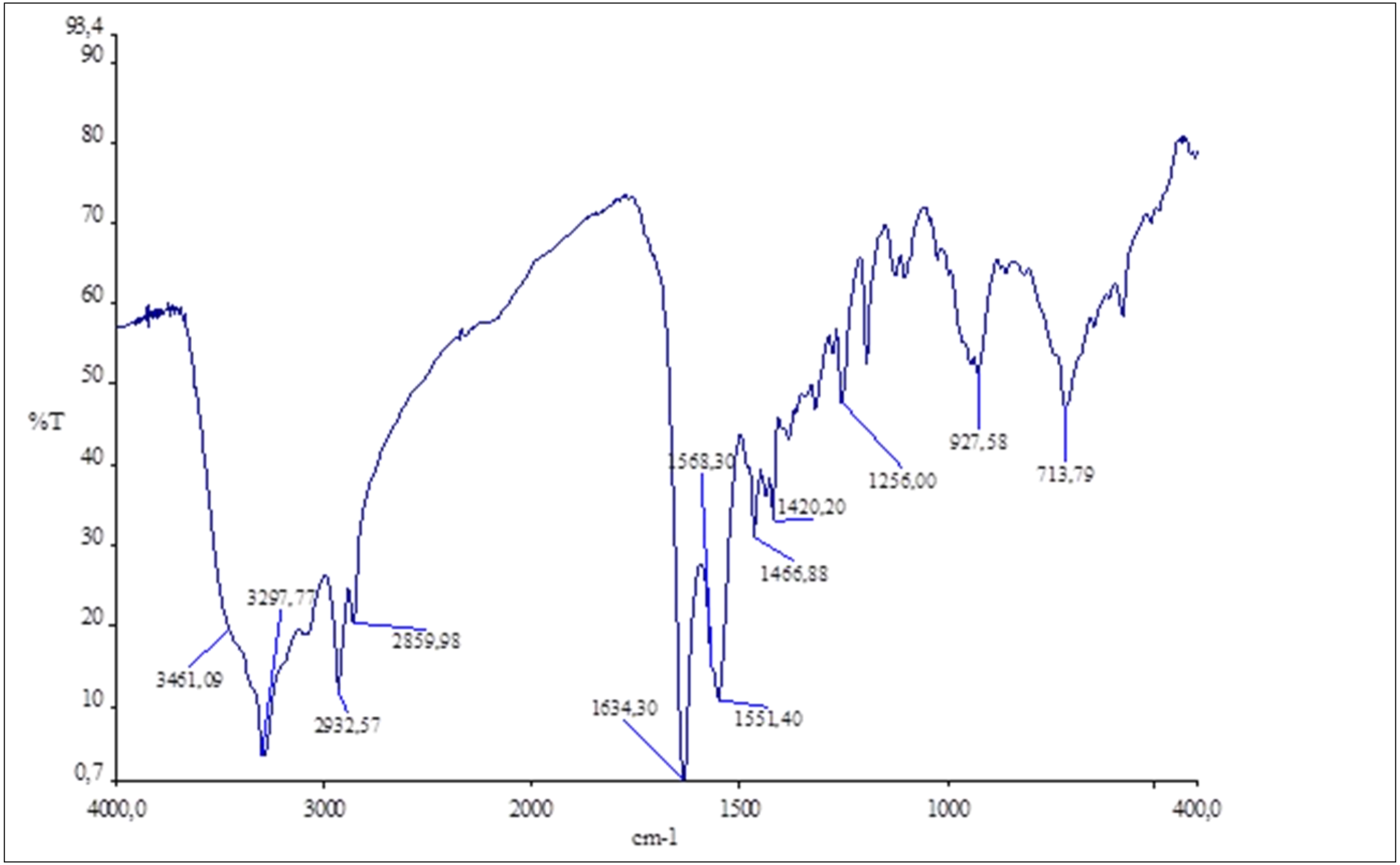
Spectra 1. SubC (1:5)



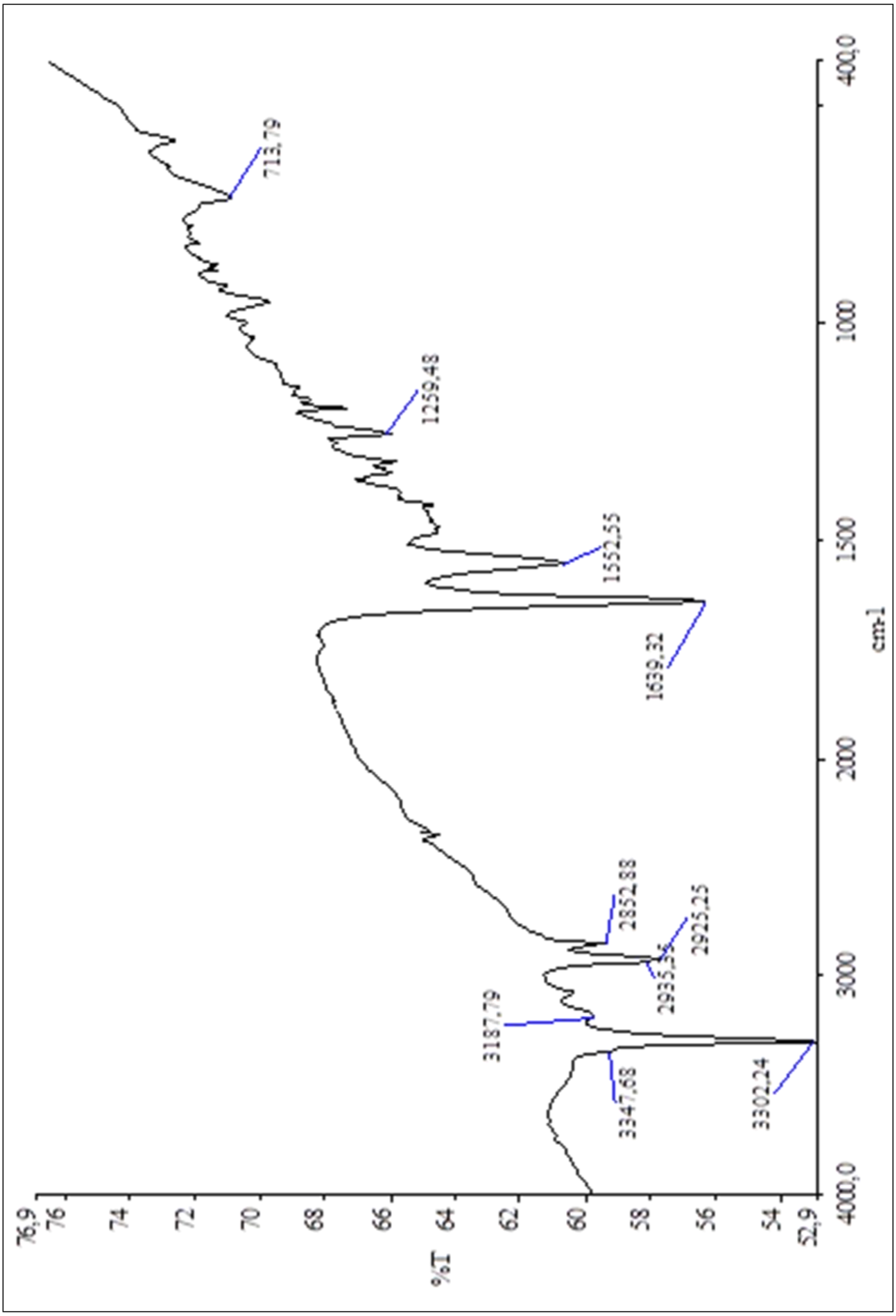
Spectra 2. SubC (1:5) after 4th washing



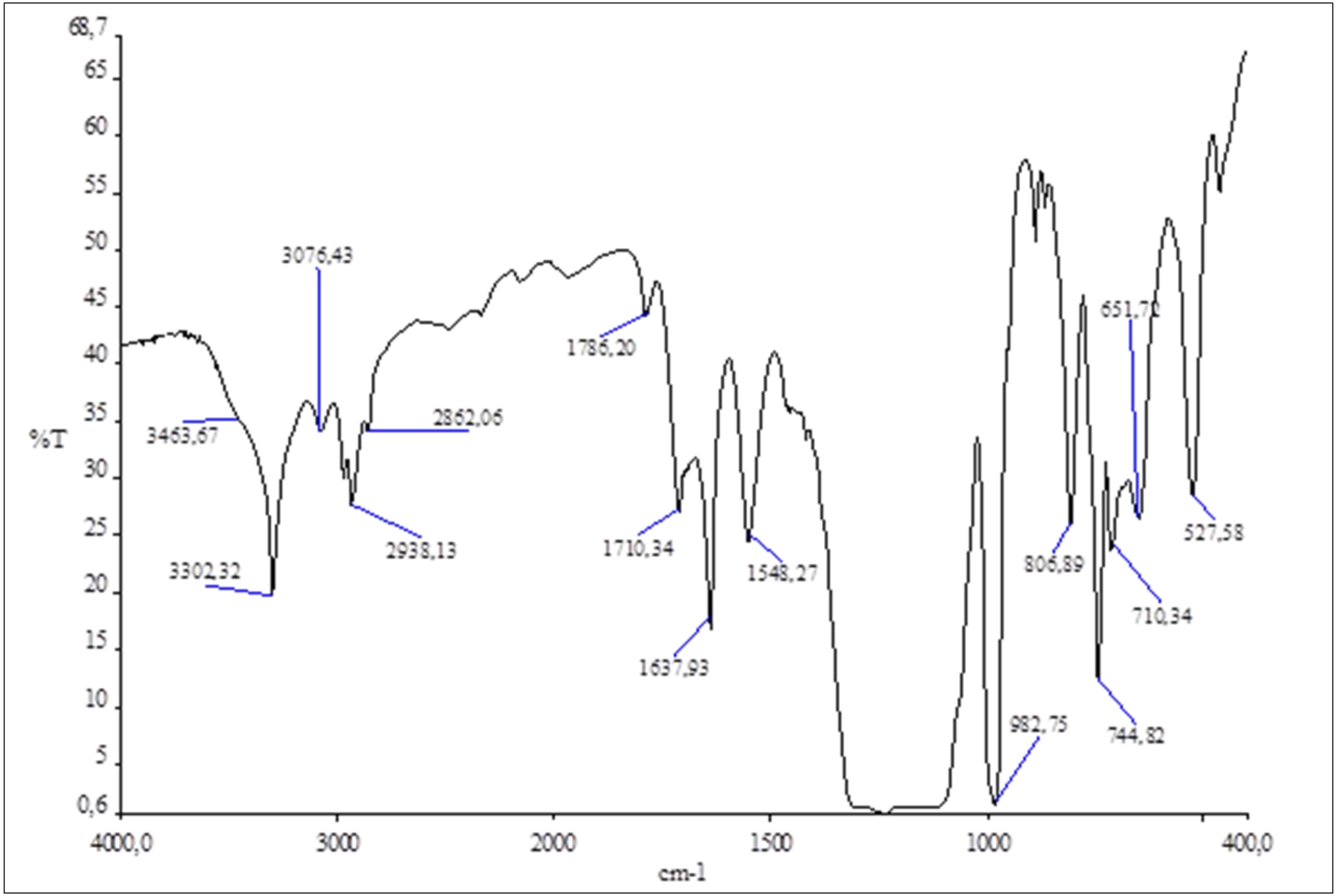
Spectra 3. SubC (1:3)



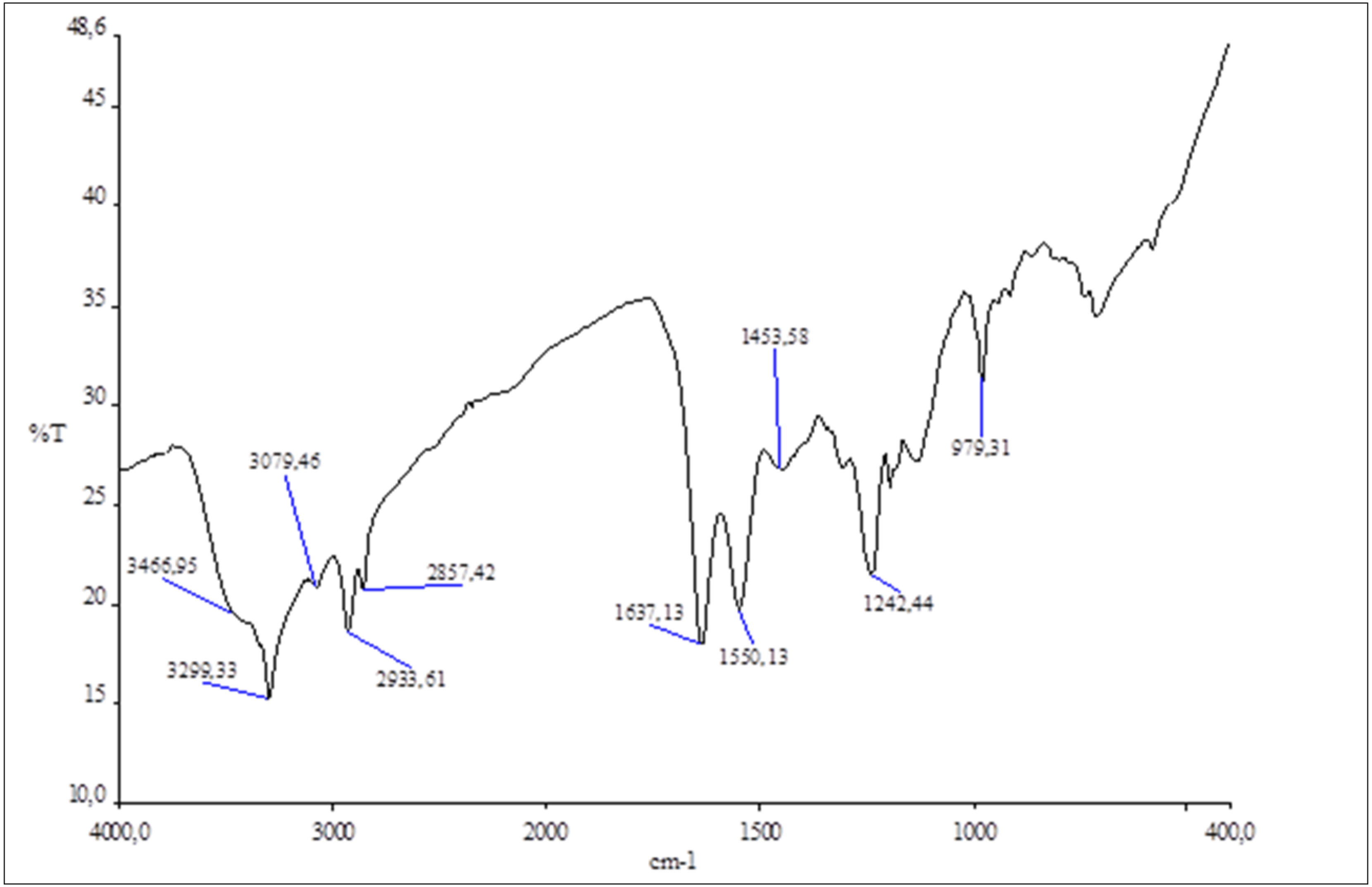
Spectra 4. SubC (1:2) 1st



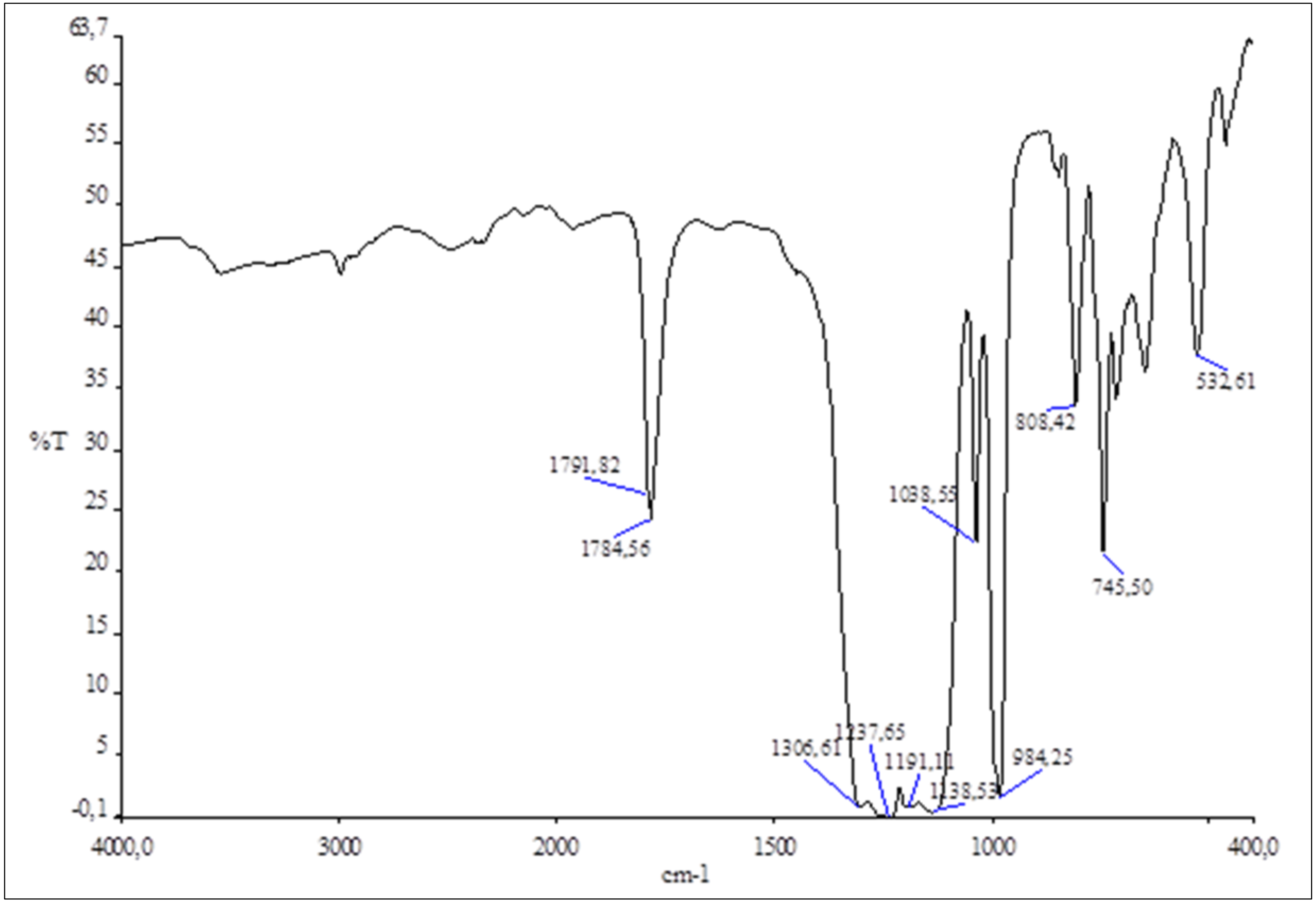
Spectra 5. SubC (1:2) 4th



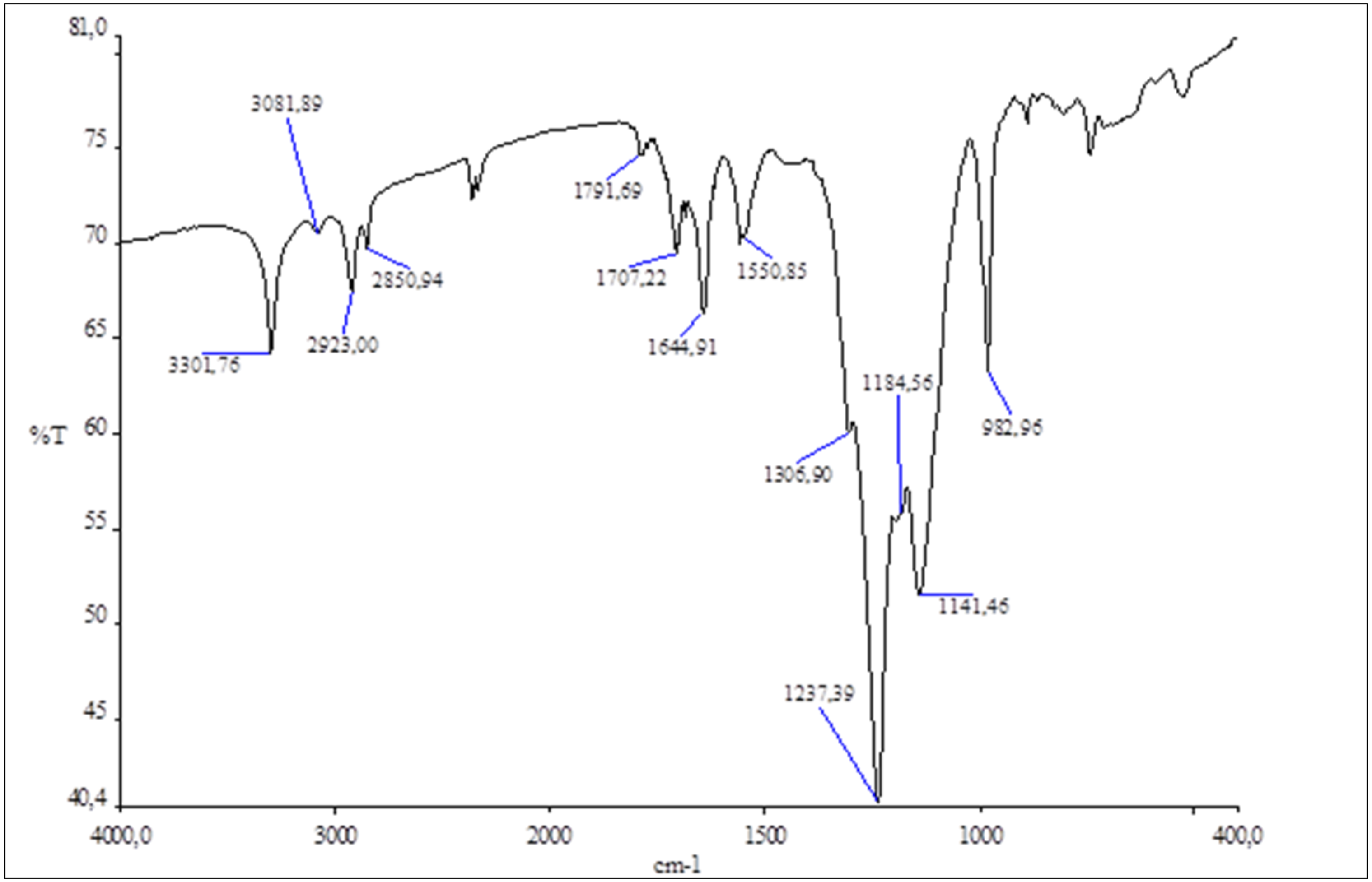
Spectra 6. SubC (1:5)1st + F3100 after 111 hours reaction



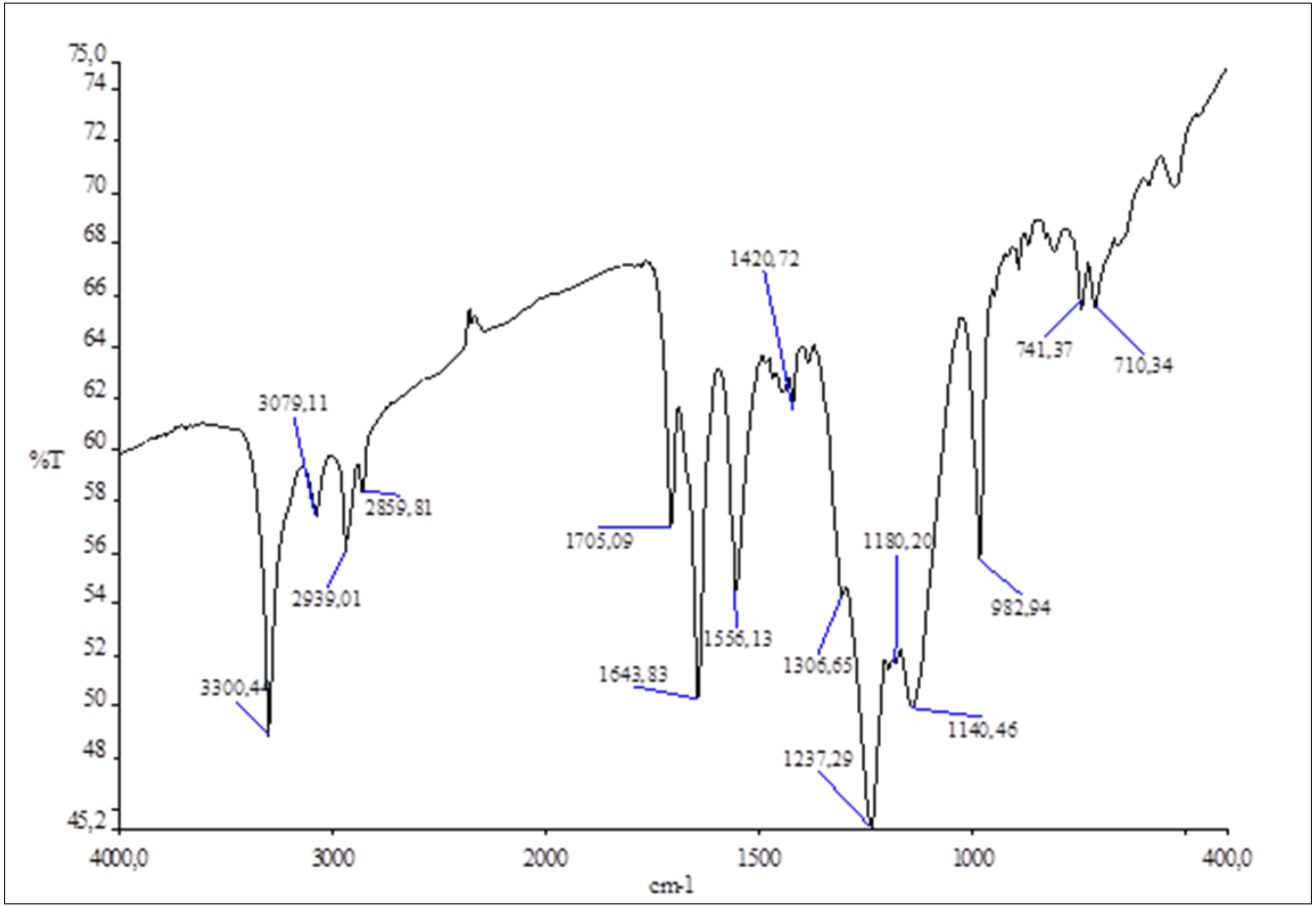
Spectra 7. SubC (1:5)1st + F3100 after 140 hours reaction



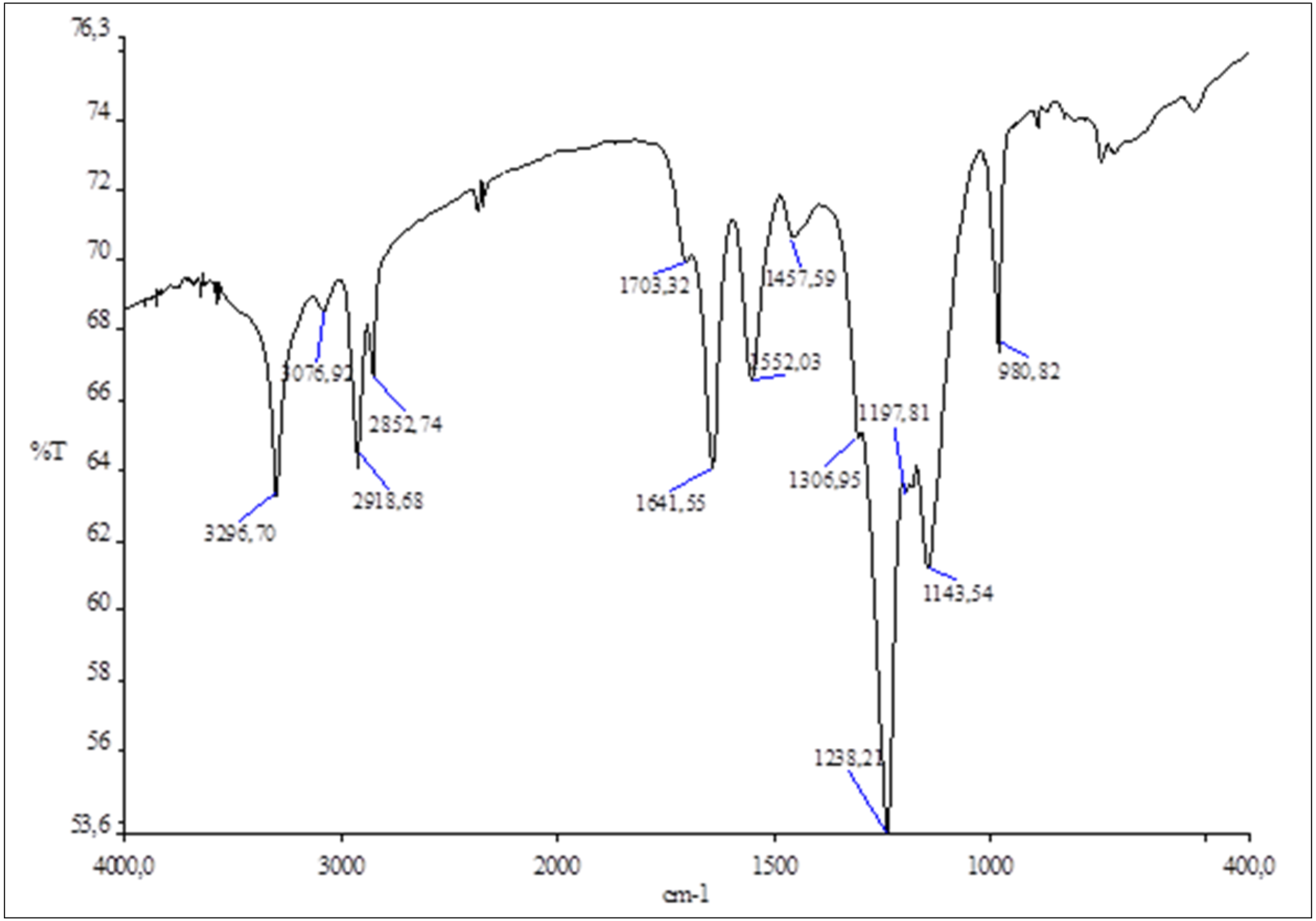
Spectra 8. SubC(1:5) 2^{nd} +Krytox



Spectra 9. SubC (1:2)4th + EG 900 after 45 hours reaction

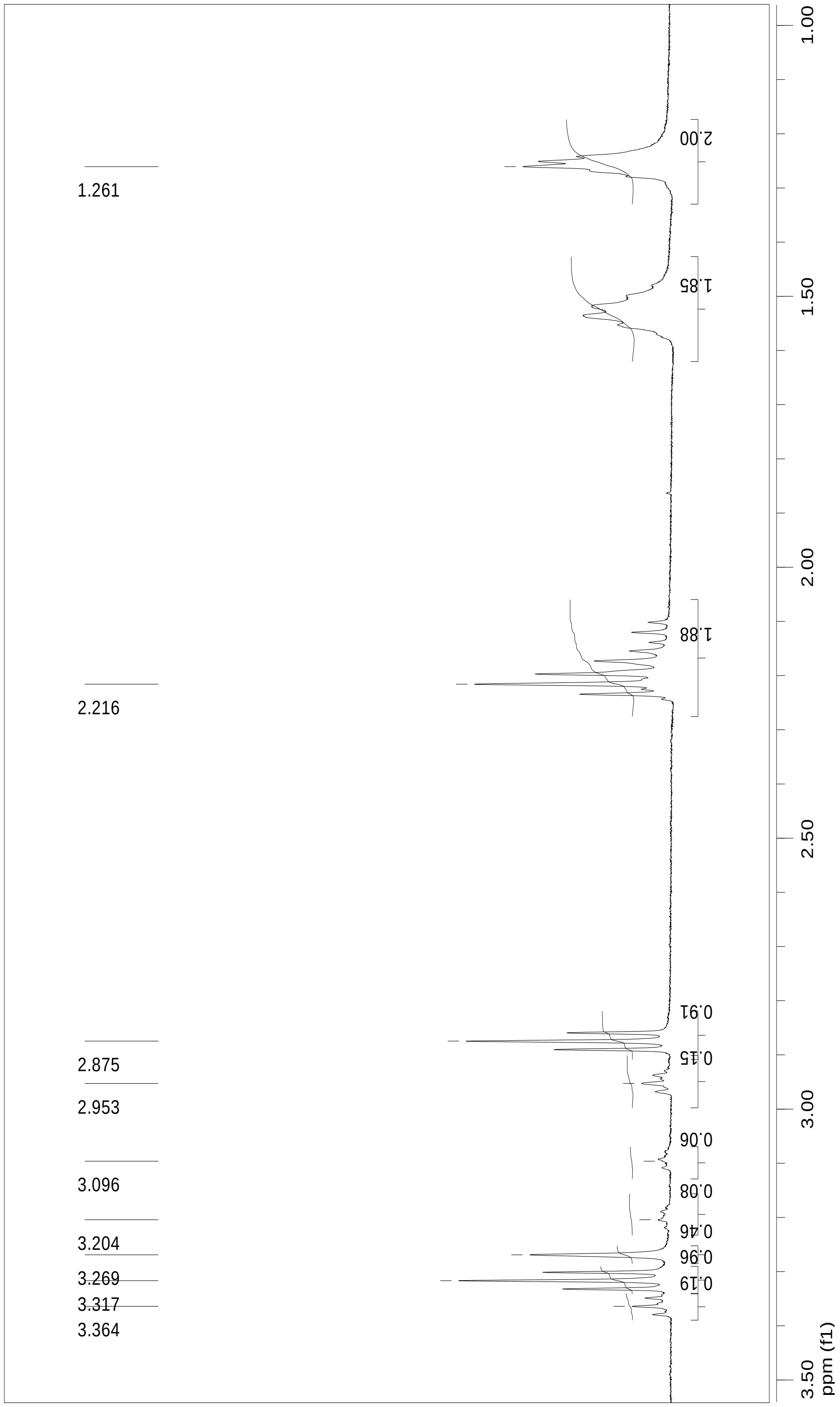


Spectra 10. SubC (1:2) + EG 900 after 3th washing with

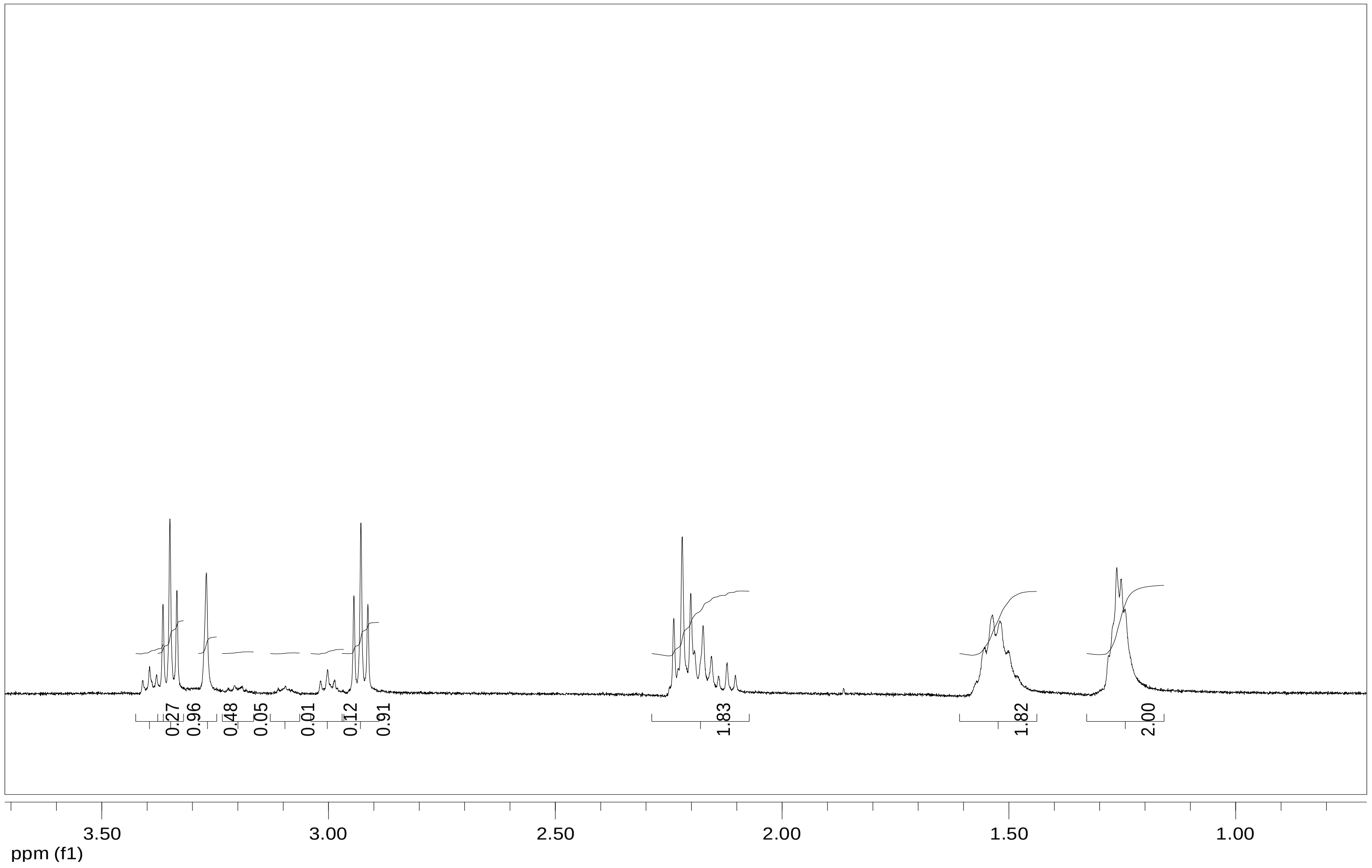


Spectra 11. SubC (1:2) 4th + G900

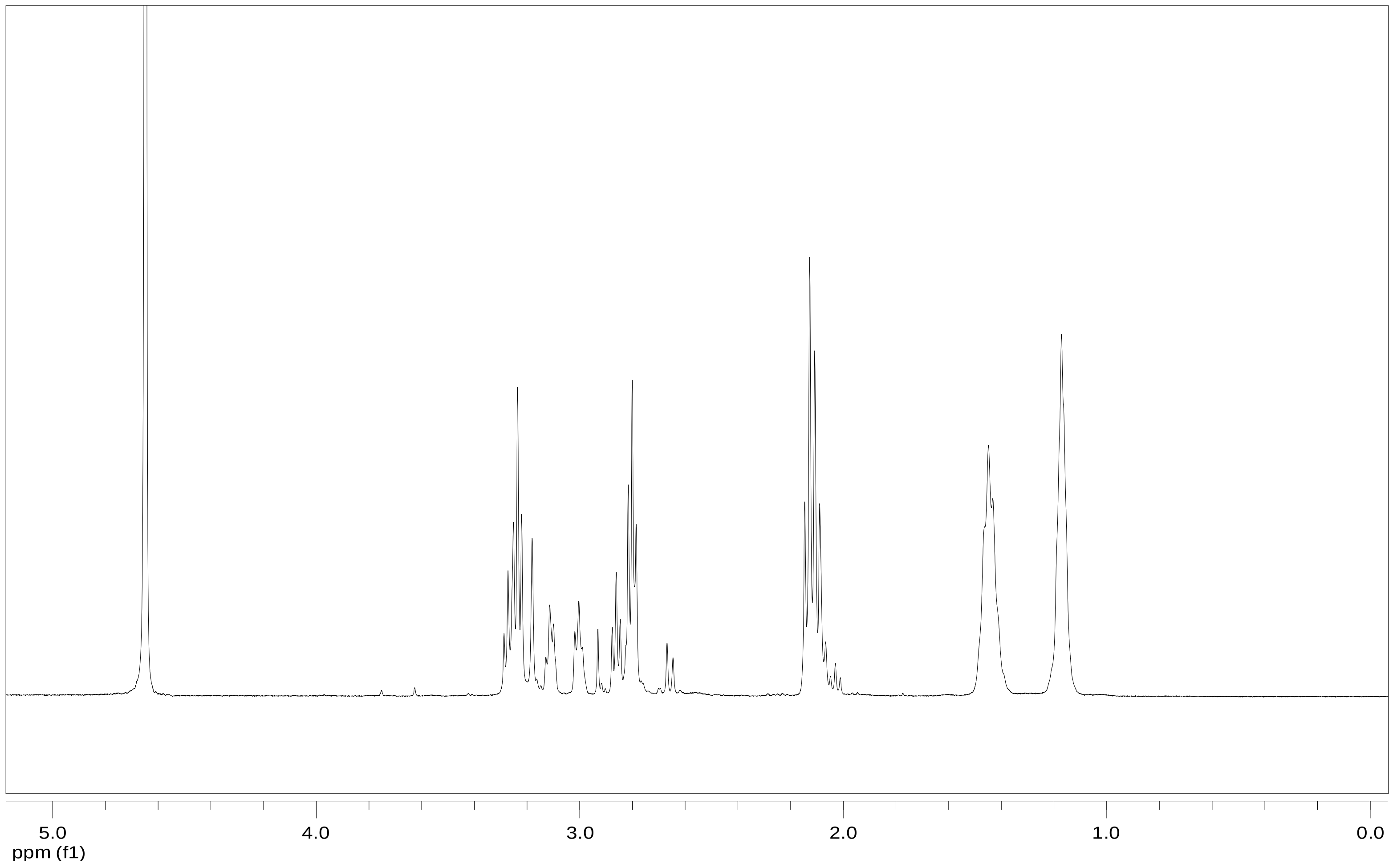
^{1}H NMR Spectra



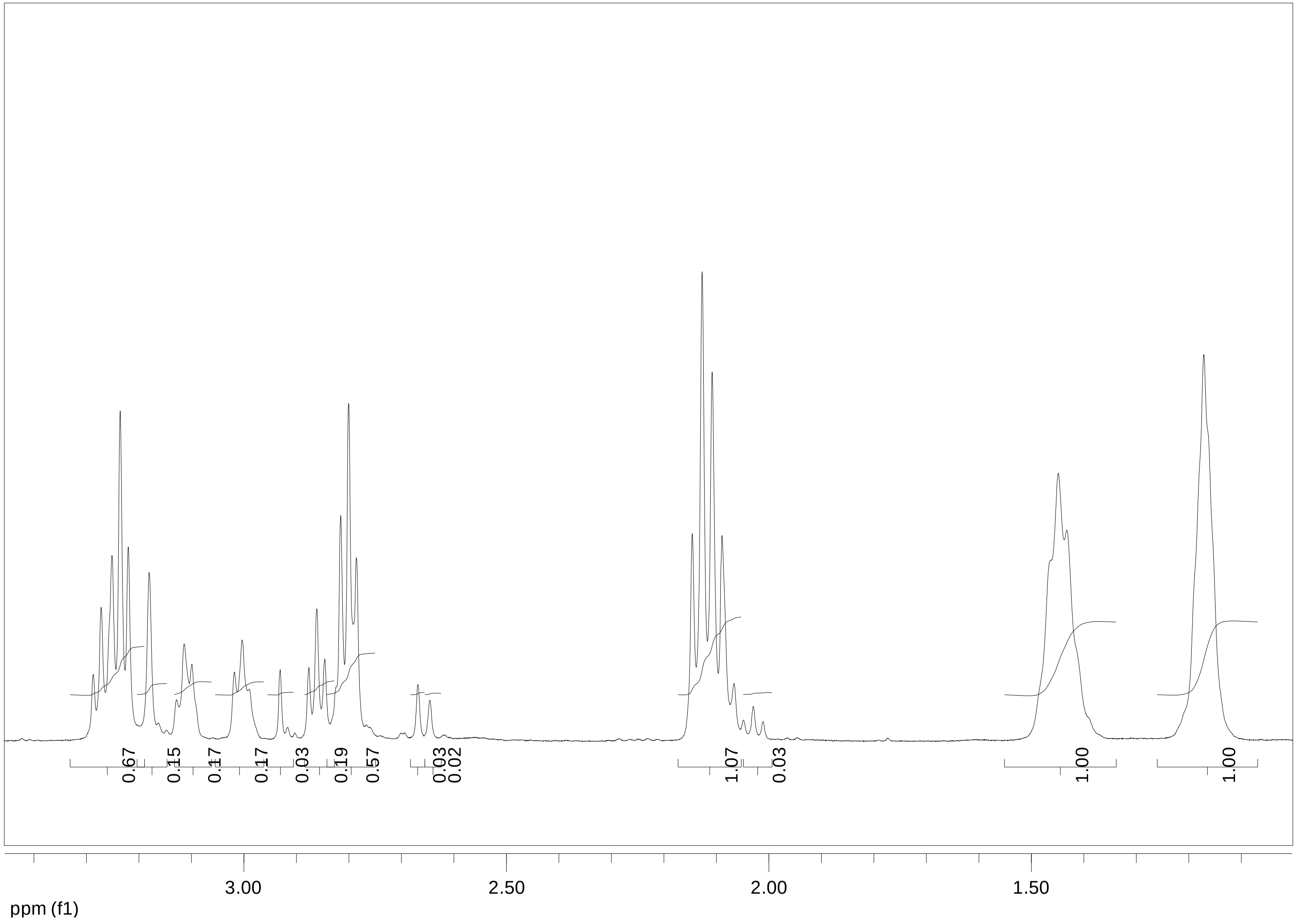
Spectra 12. SubC (1:2) 4th soluble part



Spectra 13. SubC (1:2) 4th insoluble part



Spectra 14. SubC (1:2) 4th soluble fraction with little dispersed material deposited on the tube



Spectra 15. SubC (1:2) 4th soluble fraction with little dispersed material deposited on the tube

Graphics of Contact Angle

DW

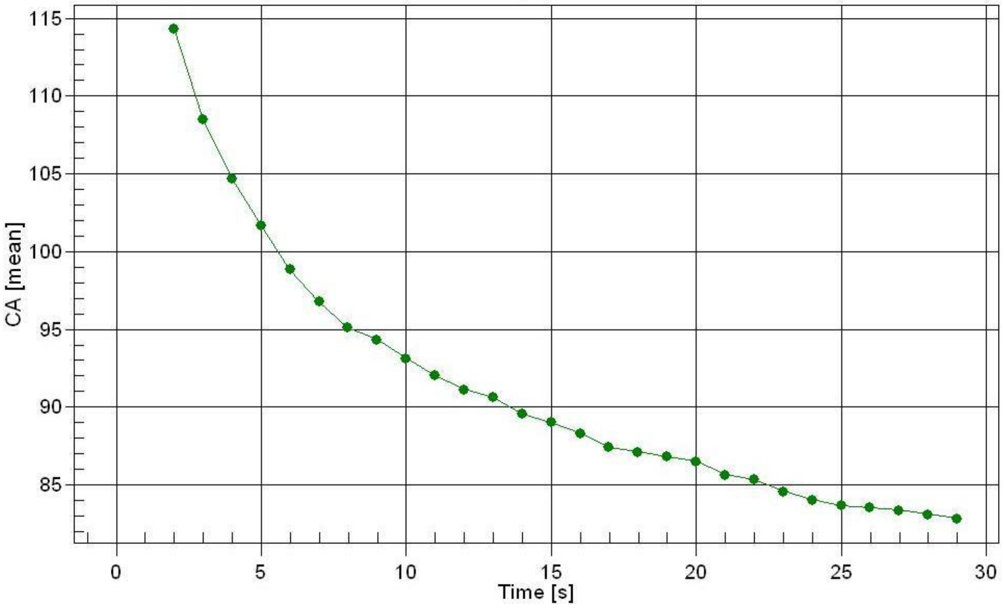


Figure 41. Contact Angle Graphic of DW (untreated) in the 30 seconds

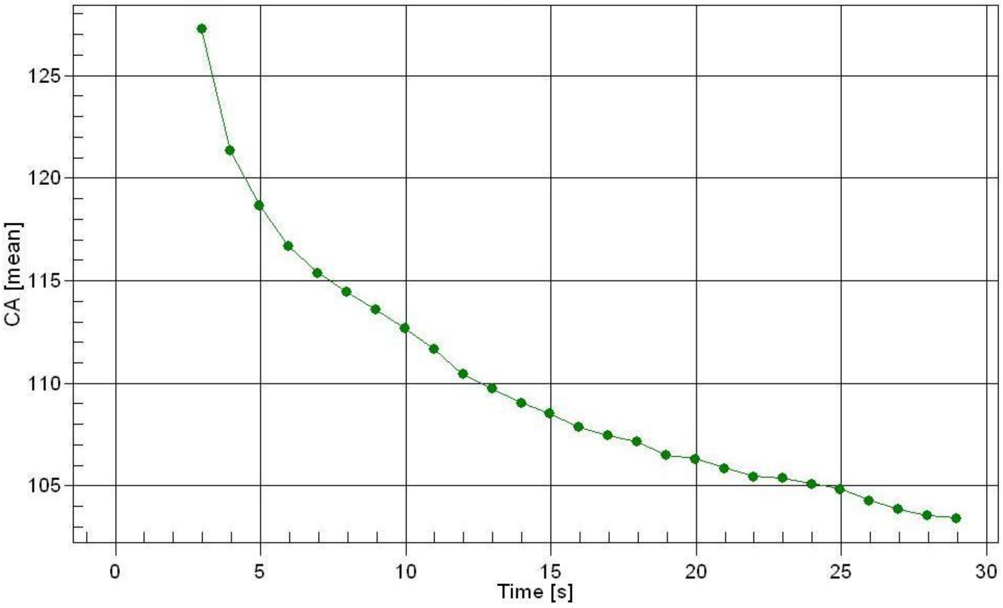


Figure 42. Contact Angle Graphic of DW (treated) in the 30 seconds

MY

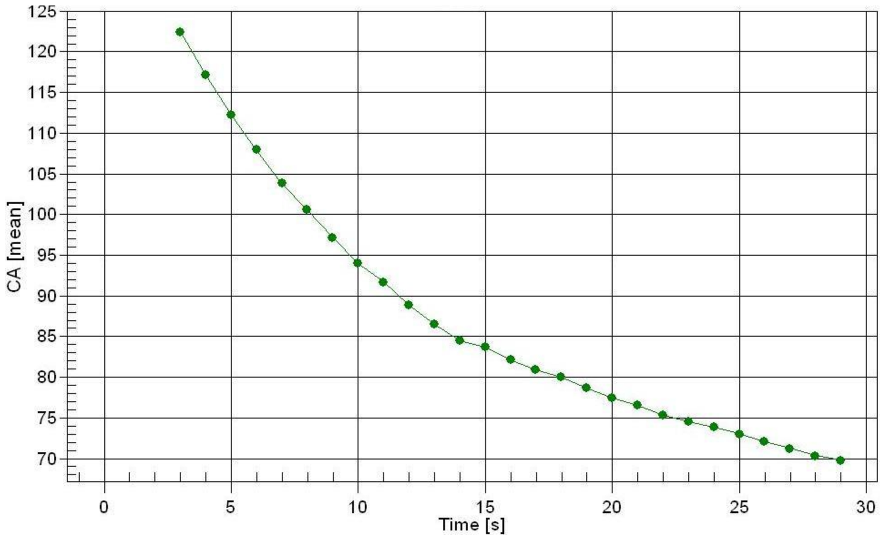


Figure 43. Contact Angle Graphic of MY (untreated) in the 30 seconds

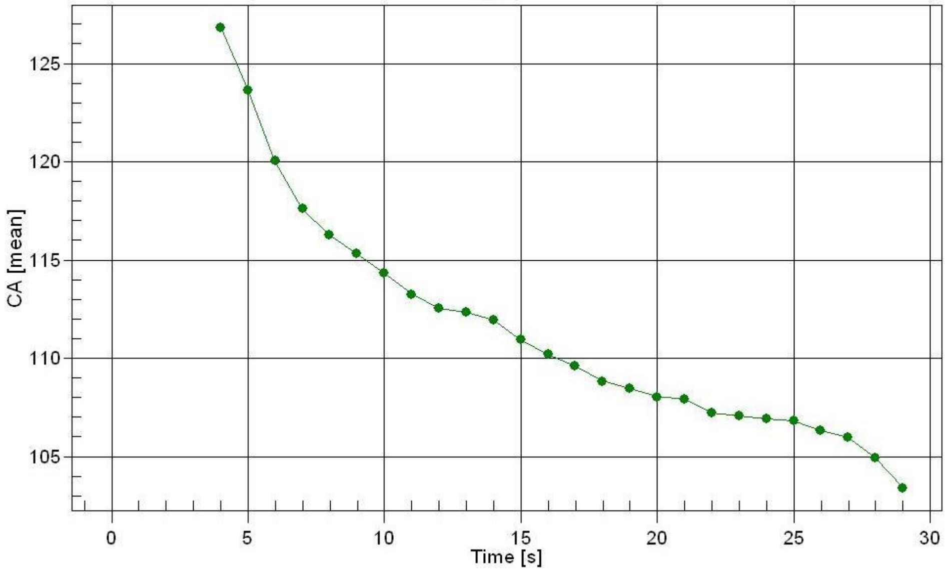


Figure 44. Contact Angle Graphic of MY (treated) in the 30 seconds

EQ

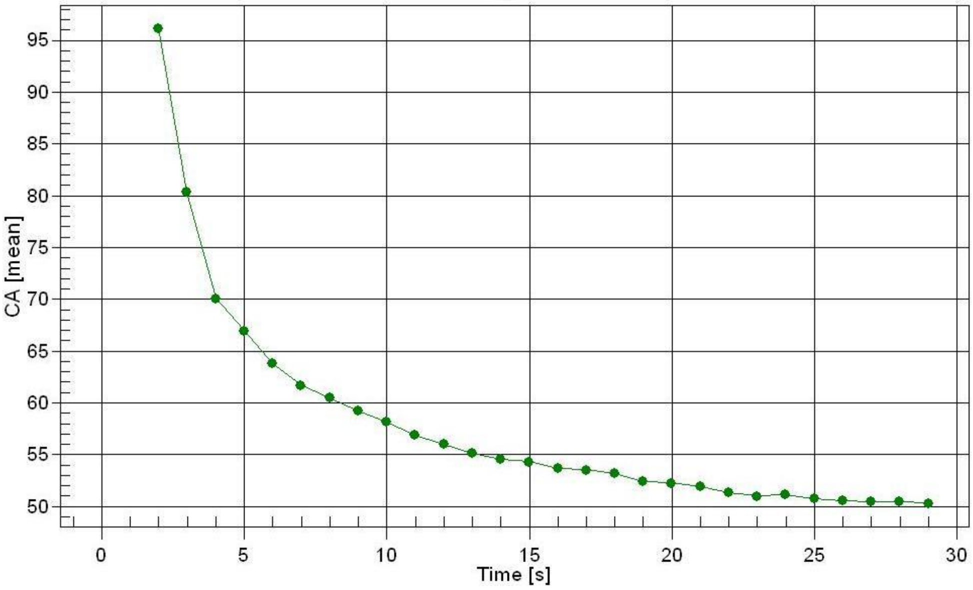


Figure 45. Contact Angle Graphic of EQ (untreated) in the 30 seconds

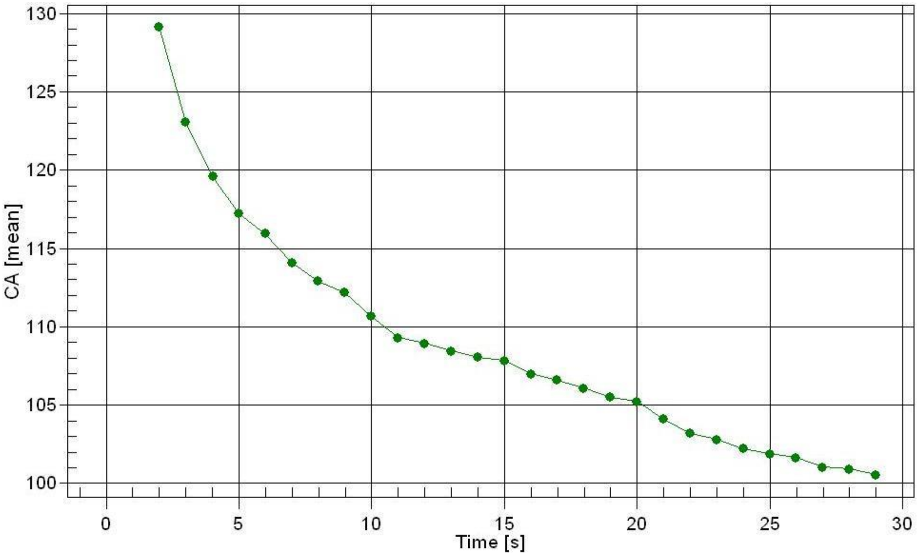


Figure 46. Contact Angle Graphic of EQ (treated) in the 30 seconds

DV

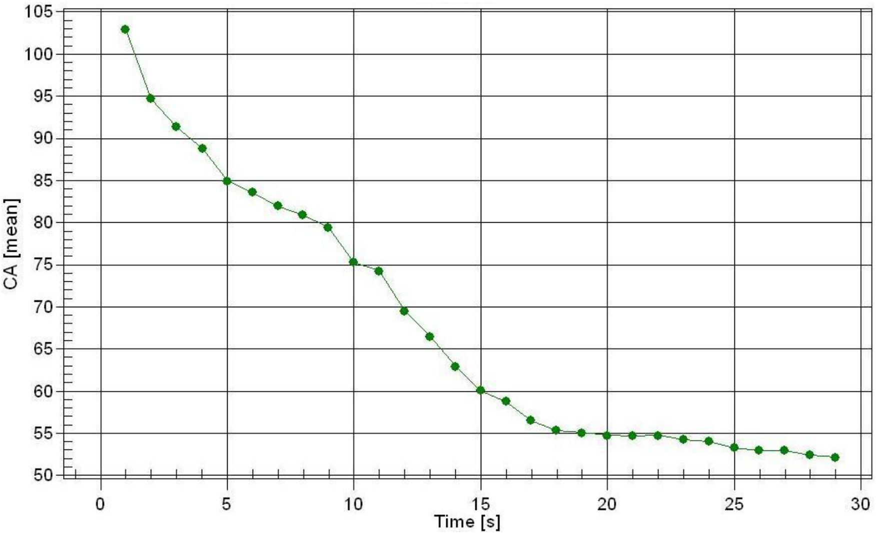


Figure 47. Contact Angle Graphic of DV (untreated) in the 30 seconds

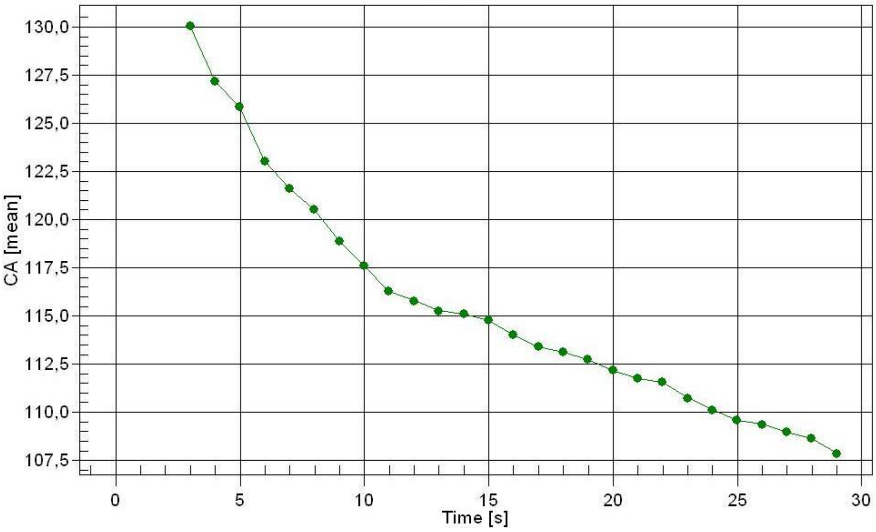


Figure 48. Contact Angle Graphic of DV (treated) in the 30 seconds

DG

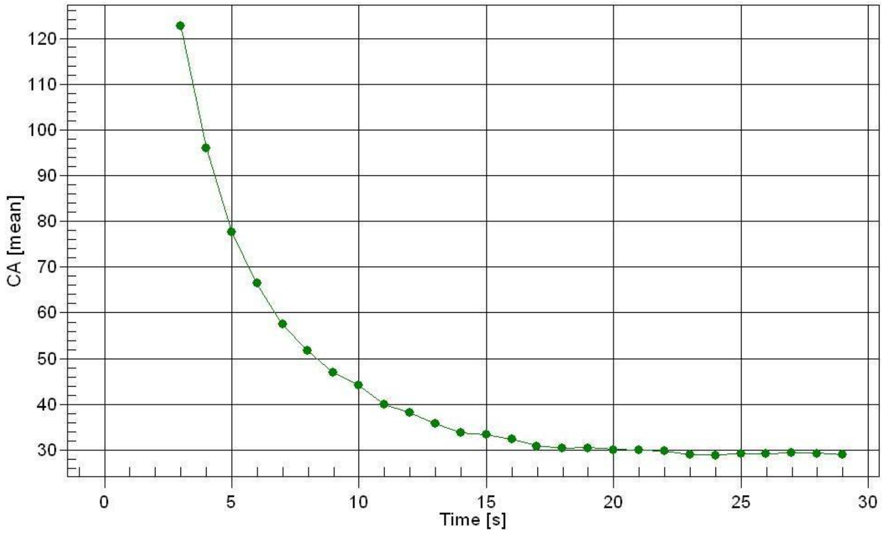


Figure 49. Contact Angle Graphic of DG (untreated) in the 30 seconds

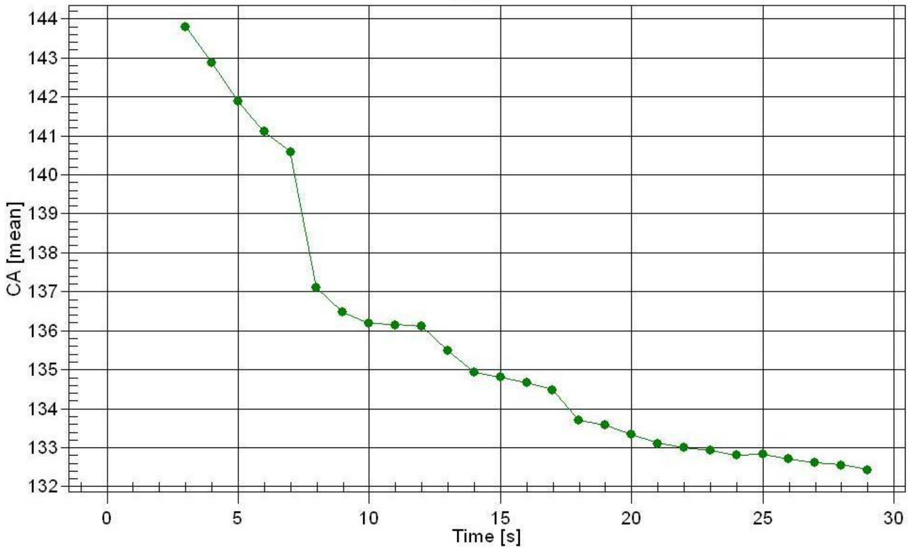


Figure 50. Contact Angle Graphic of DG (treated) in the 30 seconds

BIBLIOGRAFIA

[1] Serdaroğlu,U.,1969**,** *"Temple Decoration and Cultural Identity in the Archaic Greek World"* 1969, AnnEconSocCiv 37:953-*64.*

[2] Berti, F. Peirano D., 2016**, "***Iasos di Caria e il rilancio del suo porto in età bizantina: il ruolo del marmo***"** Hortus Artium Medievalium 22, 2016, pp. 178-189**.**

[3] H. Canol, 2009, *"Conservation Studies and Problems Concerning the Stone Artifacts in Iasos Antiquarium"*, Bollettino dell'associazione Iasos di Caria, 2009, pg.40-45.

[4] M. Camaiti, H. Canol, 2011**,** *"Study of New Conservation Products for The Marble Artefacts of Balik Pazar – Iasos-Caria (Turkey)"*, 5th International Congress on "Science and Technology for the Safeguard of Cultural Heritage in the Mediterranean Basin", Istanbul 22-25 November 2011, pg.138.

[5] M. Camaiti, H. Canol, 2012**,** *"Study of The Superficial Cohesion and Chromatic Changes of Marbles Treated with Polymers and Exposed to Artificial Ageing*", 2nd International Conference in Chemistry for Cultural Heritage, Istanbul July 9-12, 2012, pg.70.

[6] E.N. Caner, BÖKE, H., 1992, *"Occurrence of Calcıum Oxalates on monuments in Anatolia",* Biogeochemistry. Volume 19, Issue 3, pp 129–147.

[7] A.Webster,E. May., 2006**,***"Bioremediation of Weathered-Building Stone Surfaces"* Elsevier, Trends in Biotechnology,Vol.24 No.6 2006,pp 255-260.

[8] Maxwell, I. 1992. "*Stone cleaning: For better or worse?*" An overview. In Stone Cleaning and the Nature, Soiling and Decay Mechanisms of Stone: Proceedings of the International Conference Held in Edinburgh, UK, 14–16 April 1992, ed. R. G. M. Webster, 3–49. London: Donhead Publishing.

[9] MacDonald, J., B. Thomson, and K. Tonge. 1992. "*Chemical cleaning of sandstone: Comparative laboratory studies. In Stone Cleaning and the Nature, Soiling and Decay Mechanisms of Stone"* Proceedings of the International Conference Held in Edinburgh, UK, 14–16 April 1992, ed. R. G. M. Webster, pg. 217‒26. London: Donhead Publishing.

[10] Young, M., and D. Urquhart. 1992. *"Abrasive cleaning of sandstone buildings and monuments: An experimental investigation. In Stone Cleaning and the Nature,Soiling and Decay Mechanisms of Stone"* Proceedings of the International Conference Held in Edinburgh, *UK, 14–16 April 1992,* ed. R. G. M. Webster, 128‒40. London: Donhead Publishing.Andrew, C. M., M. Young, and K. Tonge. 1994. *Stone Cleaning: A Guide for Practitioners*. Aberdeen: Robert Gordon University; Edinburgh: Historic Scotland.

[11] De Witte, E., and M. Dupas. 1992. *"Cleaning poultices based on EDTA"*. In Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, 15–18 June 1992, ed. J. Delgado Rodrigues, F. Henriques, and F. Telmo Jeremias, 1023‒31. Lisbon: Laboratorio Nacional de Engenharia Civil.

[12] Alessandrini, G., L. Toniolo, A. Antonioli, A. Di Silvestro, F. Piacenti, S. Righini Ponticelli, and L. Formica. 1993. "*On the cleaning of deteriorated stone minerals"*. In Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress "Conservation of Stone and Other Materials:Research – Industry – Media," UNESCO Headquarters, Paris, June 29–July 1,1993, ed. M.-J. Thiel, 503‒11. RILEM Proceedings 21. London and New York:E & FN Spon.

[13] Maravelaki, P., G. Biscontin, R. Polloni, W. Cecchetti, and E. Zendri. 1992. "*Investigation on surface alteration of limestone related to cleaning processes*." In Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, 15–18 June 1992, ed. J. Delgado Rodrigues,F. Henriques, and F. Telmo Jeremias, pg. 1093‒101. Lisbon: Laboratorio Nacional de Engenharia Civil.

[14] Friese, P., and A. Protz. 1997. "*Entsalzung mit zwei-seitiger Kompresse*." Bautenschutz + Bausanierung 20 (8): pg.10–13.

[15] Friese, P., A. Protz, and D. Peschl. 1997. **"***Entsalzung: Kompressenputz mit passenden Porenradien*." Bautenschutz + Bausanierung 20 (5): pg.26‒30

[16] Hempel, K. 1976. "*An improved method for the vacuum impregnation of stone*." Studies in Conservation 21 (1): 40‒43.

[17] Kouzeli, K. 1992. "*Black crust removal methods in use: Their effects on Pentelic marble surfaces*." In Proceedings of the 7th International Congress on Deterioration and

Conservation of Stone, Lisbon, 15–18 June 1992, ed. J. Delgado Rodrigues, F. Henriques, and F. Telmo Jeremias, 1147–56. Lisbon: Laboratorio Nacional de Engenharia Civil.

[18] Gauri, K. L., L. Parks, J. Jaynes, and R. Atlas. 1992. "*Removal of sulphated-crust from marble using sulphate-reducing bacteria*." In Stone Cleaning and the Nature, Soiling and Decay Mechanisms of Stone: Proceedings of the International Conference Held in Edinburgh, UK, 14–16 April 1992, ed. R. G. M. Webster,160–65. London: Donhead Publishing.

[19] Gauri, K. L., and A. N. Chowdhury. 1988. "*Experimental studies on conversion of gypsum to calcite by microbes*." In Proceedings of the 6th International Congress on Deterioration and Conservation of Stone, Torun´, 12–14.09.1988, ed. J. Ciabach, 545‒50. Torun´, Poland: Nicolaus Copernicus University.

[20] Gabrielli, N. 1991. "*Mural paintings*." In Science, Technology, and European Cultural Heritage: Proceedings of the European Symposium, Bologna, Italy, 13–16 June 1989, ed. N. S. Baer, C. Sabbioni, and A. I. Sors, pg.168–79. Oxford and Boston: Published for the Commission of the European Communities by Butterworth-Heinemann Publishers.

[21] Domaslowski, W. 1969. "*Consolidation of stone objects with epoxy resins*." Monumentum Vol4: pg. 51–64.

[22] Mirowski, R. 1988. "*A new method of impregnation of stone historical objects.*" In Proceedings of the 6th International Congress on Deterioration and Conservation of Stone, Torun´, 12–14.09.1988, ed. J. Ciabach, 633–40. Torun´,Poland: Nicolaus Copernicus University.

[23] Schoonbrood, J. W. M. 1993. "*Low pressure application technique for stone preservatives*." In Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress "Conservation of Stone and Other Materials: Research—Industry—Media," UNESCO Headquarters, Paris, June 29–July 1, 1993, ed. M.-J. Thiel, 512–18. RILEM Proceedings 21. London and New York: E & FN Spon.

[24] Hempel, K. 1976. "*An improved method for the vacuum impregnation of stone*." Studies in Conservation 21 (1): 40‒43.

[25] Antonelli, V. 1979. "*Il restauro della Porta della Carta in Venezia*." In Deterioramento e conservazione della pietra: Atti del 3º Congresso internazionale, Venezia, 24–27 ottobre 1979, Fondazione "Giorgio Cini," Isola di S. Giorgio Maggiore =Deterioration and Preservation of Stones: Proceedings of the 3rd International Congress, Venice, 24–27 October 1979 = La déterioration et la préservation de la pierre: Actes du 3ème Congrès international, Venise 24–27 octobre 1979,629–44. Padua: Universita degli Studi di Padova, Istituto di Chimica Industriale.

[26] Wheeler, G. S., G. L. Shearer, S. Fleming, L. W. Kelts, A. Vega, and R. J. Koestler. 1991. "*Toward a better understanding of B72 acrylic resin/methyltrimethoxysilane stone consolidants."* In Materials Issues in Art and Archaeology II Symposium, Held April 17–21, 1990, San Francisco, ed. P. B. Vandiver, J. R. Druzik, and G. S. Wheeler, 209‒26. Materials Research Society Symposium Proceedings 185. Pittsburgh: Materials Research Society.

[27] Wheeler, G. S., E. Wolkow, and H. Gafney. 1992. "*Microstructures of B72 acrylic resin/ MTMOS composites***.**" In Materials Issues in Art and Archaeology III Symposium, Held April 27–May 1, 1992, San Francisco, ed. P. B. Vandiver, J. R. Druzik, G.S. Wheeler, and I. C. Freestone, 963–67. Materials Research Society Symposium Proceedings 267. Pittsburgh: Materials Research Society.

[28] Piacenti, F., M. Camaiti, C. Manganelli del Fa, and A. Scala. 1993. "*Fluorinated aggregating materials for stone."* In Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress "Conservation of Stone and Other Materials: Research—Industry—Media," held at UNESCO Headquarters, Paris, June 29–July 1, 1993, ed. M.-J. Thiel, 740‒47. RILEM Proceedings 21. London and New York: E & FN Spon.

[29] Aglietto, M., E. Passaglia, E. Taburoni, F. Ciardelli, C. Botteghi, U. Matteoli, S. Paganelli, R. Arbizzani, and V. Fassina. 1993. *"A new class of fluorinated acrylic polymers: Protective materials for stone."* In 10th Triennial Meeting, ICOM Committee for Conservation, Washington, DC, 22–27 August 1993: Preprints,ed. J. Bridgland, 553‒58. Paris: ICOM Committee for Conservation; Lawrence, KS: Allen Press (distributor).

[30] Fassina, V., R. Arbizzani, C. Botteghi, U. Matteoli, E. Passaglia, and M. Aglietto. 1994. “*Behaviour of 2,2,2-trifluoroethylmethacrylate polymers as stone protective materials.”* In Conservation of Monuments in the Mediterranean Basin: Stone Monuments, Methodologies for the Analysis of Weathering and Conservation; Proceedings of the 3rd International Symposium, Venice, 22–25 June 1994 = La conservazione dei monumenti nel bacino del Mediterraneo: Materiali lapidei e monumenti, metodologie per l’analisi del degrado e la conservazione; Atti del 3°simposio internazionale, Venezia, 22–25 giugno 1994, ed. V. Fassina, H. Ott, andF. Zezza, 911‒23. Venice: Soprintendenza ai beni artistici e storici di Venezia.

[31] Guidetti, V., M. Chiavarini, and P. Parrini. 1992. “*Polyfluorourethanes as stone protectives*.” In Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, 15–18 June 1992, ed. J. Delgado Rodrigues,F. Henriques, and F. Telmo Jeremias, 1279‒88. Lisbon: Laboratorio Nacional de Engenharia Civil.

[32] Biscontin, G., P. Maravelaki, E. Zendri, A. Glisenti, and E. Tondello. 1993. “*Investigation into the interaction between aqueous and organic solvent protection and building materials*.” In Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress “Conservation of Stone and Other Materials: Research – Industry – Media,” UNESCO Headquarters, Paris, June 29–July 1, 1993, ed. M.-J. Thiel, 689‒96. RILEM Proceedings 21. London and New York: E & FN Spon.

[33] Ciabach, J. 1996. “*The effect of water soluble salts on the impregnation of sandstone with silicone microemulsions*.” In Proceedings of the 8th International Congress on Deterioration and Conservation of Stone, Berlin, 30 Sept.–4 Oct. 1996, ed. J. Riederer, 1215–21. Berlin: Moller Druck und Verlag.

[34] Guidetti, V., M. Chiavarini, and P. Parrini. 1992. “*Polyfluorourethanes as stone protectives*.” In Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, 15–18 June 1992, ed. J. Delgado Rodrigues, F. Henriques, and F. Telmo Jeremias, 1279–88. Lisbon: Laboratorio Nacional de Engenharia Civil.

[35] Torraca, Giorgio., 1994, “*Science and conservation: the work of art in the flow of time*.” Special Issue - Art and Science: Studies from the World Academy of Art and Science. World Futures, v40, no. n1-3, 1994 July 15, p129(4) (ISSN: 0260-4027). Gordon and Breach Science Publishers S.A., 1994 July 15.

[36] M. Sanopoulou and J.H. Petropoulos, 1991, "*Relation of Diffusion to Viscoelastic Properties in Glassy Polymer-Swelling Agent System"*, J. Non-Cryst. Solids, 131-133, 827-830.

[37] Agarossi, G., R. Ferrari, and M. Monte. 1990. "*Biocides in the control of biodeterioration*." In The Conservation of Monuments in the Mediterranean Basin: The Influence of Coastal Environment and Salt Spray on Limestone Marble:Proceedings of the 1st International Symposium, Bari, 7–10 June 1989 =La conservazione dei monumenti nel bacino del Mediterraneo: Influenzadell'ambiente costiero e dello spray marino sulla pietra calcarea e sul marmo:Atti del 1o simposio internazionale, Bari, 7–10 giugno 1989, ed. F. Zezza,511–17. Brescia, Italy: Grafo Edizioni.

[38] Anagnostidis, K., C. K. Gehrmann, M. Gross, W. E. Krumbein, S. Lisi, A. Pantazidou, C. E. Urzi, and M. Zagari. 1992. "*Biodeterioration of marbles of the Parthenon and Propylaea, Acropolis, Athens: Associated organisms, decay and treatment suggestions."* In La conservation des monuments dans le bassin méditerranéen: Actes du 2ème Symposium international = The Conservation of Monuments in the Mediterranean Basin: Proceedings of the 2nd International Symposium, ed. D. Decrouez, J. Chamay, and F. Zezza, 305–25. Geneva: Ville de Geneve,Museum d'histoire naturelle, and Musee d'art et d'histoire.

[39] Caneva, G., M. P. Nugari, and O. Salvadori. 1991. "*Biology in the Conservation of Works of Art*." Rome: ICCROM.

[40] Elmer, K., E. Rose, B. Fitzner, Wolfgang E. Krumbein, and T. Warscheid. 1993. "*Sterilisation of cultural objects by ethylene oxide: Application for conservation practice by laboratory-based or mobile treatments*." In Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress "Conservation of Stone and Other Materials: Research—Industry—Media,"UNESCO Headquarters, Paris, June 29–July 1, 1993, ed. M.-J. Thiel, 581–88. RILEM Proceedings 21. London and New York: E & FN Spon.

[41] Bassier, C. 1989. "*Le rayonnement ultra-violet dans la desinfection des materiaux de nature ou d'origine minerale: Exemples d'application = Ultraviolet radiationin the disinfection of materials of a mineral nature or origin: Examples of its application*." In *Patrimoine culturel et altérations biologiques:* Actes des journées d'étude de la S.F.I.I.C, Poitiers, 17 et 18 novembre 1988, 201–6. Champs-sur- Marne: Section francaise de l'Institut international de conservation.

[42] Sorlini, C., D. Falappi, and P. Sardi. 1991. "*Effects of mould growth on Serena stone samples untreated and treated with resin*." In Science, Technology, and European Cultural Heritage: Proceedings of the European Symposium, Bologna, Italy, 13–16 June 1989, ed. N. S. Baer, C. Sabbioni, and A. I. Sors, 632–35. Oxford and Boston: Published for the Commission of the European Communities by Butterworth-Heinemann Publishers.

[43] Koestler, R. J., and E. D. Santoro. 1988. "*Assessment of the Susceptibility to Biodeterioration of Selected Polymers and Resins: Final Report Submitted to the Getty Conservation Institute*." GCI Scientific Program Reports. Bloomfield, NJ: Bloomfield College; Marina del Rey, CA: Getty Conservation Institute, Scientific Program.

[44] Petushkova, Y. P., and A. F. Grishkova. 1990. "*Bacterial degradation of limestone treated with polymers*." In 9th Triennial Meeting, ICOM Committee for Conservation, Dresden, German Democratic Republic, 26–31 August 1990: Preprints, ed. K. Grimstad, 347–49. Los Angeles: ICOM Committee for Conservation; Marina del Rey, CA: Getty Conservation Institute.

[45] Krumbein, W. E., S. E. Diakumaku, K. Petersen, T. Warscheid, and C. Urzi. 1993. "*Interactions of microbes with consolidants and biocides used in the conservation of rocks and mural paintings.*" In Conservation of Stone and Other Materials: Proceedings of the International RILEM/UNESCO Congress "Conservation of Stone and Other Materials: Research—Industry—Media," UNESCO Headquarters, Paris, June 29–July 1, 1993, ed. M.-J. Thiel, 589–96. RILEM Proceedings 21. London and New York: E & FN Spon.

[46] Cappitelli, F., L. Toniolo, A. Sansonetti, D. Gulotta, G. Ranalli, E. Zanardini, and C. Sorlini. 2007b. "*Advantages of using microbial technology over traditional chemical technology in removal of black crusts from stone surfaces of historical monuments*." Applied and Environmental Microbiology 73 (17): 5671–5675.

[47] Cappitelli, F., and C. Sorlini. 2008. "*Microorganisms attack synthetic polymers in items representing our cultural heritage."* Applied and Environmental Microbiology 74 (3): 564–569.

[48] Antonioli, P., G. Zapparoli, P. Abbruscato, C. Sorlini, G. Ranalli, and P. G. Righetti. 2005. "*Art-loving bugs: The resurrection of Spinello Aretino from Pisa's cemetery*." Proteomics 5 (9): 2453−59.

[49] **Camaiti, M., S. Bugani, E. Bernardi, L. Morselli, and M. Matteini**. 2007. "*Effects of atmospheric NOx on biocalcarenite coated with different conservation products*." Applied Geochemistry 22 (6): 1248−54.

[50] O. Chiantore, L. Trossarelli, M. Lazzari.,2000. **"***Photooxidative Degradation of Acrylic and Methacrylic Polymers"***.** Elsevier, Polymer 41 (2000) 1657–1668.

[51] Haeri Jeon, JinHwan Park, MinYoung Shon., 2013, "Corrosion *protection by epoxy coating containing multi-walled carbon nanotubes."* Elsevier Journal of Industrial and Engineering Chemistry 19 (2013) 849–853.

[52] Hamad A. Al-Turaif., 2013, "*Relationship between tensile properties and film formation kinetics of epoxy resin reinforced with Nano fibrillated cellulose."* Elsevier, Progress in Organic Coatings 76 (2013) 477– 481.

[53] Robery Peter Shaw John., 1997, "*Materials for The Repair and Protection of Concrete*." Elsevier, Construction and Building Materials, Vol 11, Nos 5-6, pp.275- 287.

[54] Dessy P., Fantucci A., Galimberti,V. P, Nironi L., 2000, *"Performance and Durability Tests for Plastering Mortars*." 12th International Brick/Block Masonry Conference, Madrid Spain, pp.2067-2081.

[55] Jefferson, D., S. Hanna, B. Martin, and D. M. Jones. 2006, "*Identifying and Sourcing Stone for Historic Building Repair: An Approach to Determining and Obtaining Compatible Replacement Stone*." Technical Advice Note (English Heritage). Swindon, UK: English Heritage.

[56] **Dingelstadt, C., R. Dreesen, J. Thorez, G. Lorenzi, D. Bossiroy, D. Antenucci, and J. Banier.** 2000. *"A petrographical atlas as a decision-tool in replacement and substitution of ornamental stones in historical buildings and monuments*." In Proceedings of the 9th International Congress on Deterioration and Conservation of Stone, Venice, June 19–24, 2000, ed. V. Fassina, vol. 2, 33–41. Amsterdam and New York: Elsevier

[57] Hyslop, E., A. McMillan, D. Cameron, A. Leslie, and G. Lott. 2009, "*Building stone databases in the UK: A practical resource for conservation*." Engineering Geology. DOI: 10.1016/j.enggeo.2009.05.008.

[58] Prikryl, R. 2007, "*Understanding the earth scientist's role in the pre-restoration research of monuments: An overview*" In Building Stone Decay: From Diagnosis to Conservation, ed. R. Prikryl and B. J. Smith, 9–21. Geological Society Special Publication 271. London: Geological Society of London.

[59] Yilmaz, I. 2008, Discussion on the paper entitled, *"Mechanical and physical properties of the Kandira stone, Kandira, Turkey"* by Arman et al., Bull Eng Geol Environ. Bulletin of Engineering Geology and the Environment 67 (2): 289–90. DOI:10.1007/s10064-006-0082-x.

[60] T. Weiss, S. Siegesmund, D. Kirchner, J. Sippel. 2004, *"Insolation weathering and hygric dilatation: two competitive factors in stone degradation"*. Environmental Geology, Volume 46, Issue 3–4, pp 402–413.

[61] Gründer J 1980 "*Über Volumenänderungsvorgänge in überkonsolidierten, diagenetisch verfestigten Tonen und ihre Bedeutung für die Baupraxis"*. Geotechnik 2:60–66 (Essen).

[62] Madsen FT, Müller-Vonmoos M, 1989, *"The swelling behaviour of clays"*. Apply Clay Science, Vol 4, pg.143–156.

[63] **H. Canol,** 2012*"Ancient Marbles from Iasos Of Caria, Mineralogical and Petrographic Characterization and Problems of Conservation"* thesis in Mineralogical and Petrographic Characterization of Natural Artificial Stone, Second Cycle Degree master's in science for the Conservation- Restoration of Cultural Heritage – University of Bologna, A.Y. 2010-2012 – III session (Unpublished Thesis).

[64] Croci, G., and J. Delgado Rodrigues. 2002. **"***Surface and structural stability for the conservation of historic buildings.*" In Science and Technology of the Environment for Sustainable Protection of Cultural Heritage: EC Advanced Study Course. London: University College London.

[65] Sousa, L.M.O., Rio, L.M.S., Calleja, L., Argandona, V.G.R., Rey, A.R., 2005, *"Influence of microfractures and porosity on the physico-mechanical properties and weathering of ornamental granites"*, Eng. Geol., 77 (1–2), pp. 153–168.

[66] Benavente, D., Martínez-Martínez, J., Algozzini G., García Del Cura, M.A., 2006, "*Influence of water transport and pore structure on the durability of porous building stones"*, The 10th IAEG International Congress, Nottingham, United Kingdom, Paper Number 233, pp.6-10.

[67] Ioannou, I., Andreou, A., Tsikouras, B., Hatzipanagiotou, K., 2009, *"Application of the Sharp Front Model to capillary absorption in a vuggy Limestone",* Engineering Geology, 105, pp.20–23.

[68] Sterflinger, K., 2005. *"Black yeasts and meristematic fungi: ecology, diversity and identification"*. In: Rosa, C., Gabor, P. (Eds), Yeast Handbook. Biodiversity and Ecophysiology of Yeasts, vol. 1. Springer, New York, pp. 501–514.

[69] **Sterflinger, K.,** 2010. *"Fungi: Their role in deterioration of cultural heritage"* Elsevier, Fungal Biology Reviews 24, pg.47–55.

[70] Woiter, B., Sand. W., Ahlers. B., Sameluck, F. Meincke, M., Meyer, C. Krause-Kupsch. T. &Bock. E. 1988. **"***Nitrification: the main source for nitrate deposition in building stones"*. In 6th International Congress on Deterioration and Conservation of Stone, ed. J. Ciabach. Nicholas Copernicus University. Press Department. Torun. pp. 24-31.

[71] Ortega, J., J. Hernandez-Marine. M. & Saiz-Jimenez. C, 1991. "*Biodeterioration of building materials by cyanobacteria and algae"*. International Biodeterioration. 28, pg.165-85.

[72] Caneva, G. & Salvadori, O. 1989. "*Biodeterioration of stone"*. In the Deterioration and Conservation of Stone, ed. L. Lazzarini & R. Pieper, UNESCO. Paris, pp. 182-234.

[73] Kuroczkin. J. Bode, K., Petersen, K. & Krumbein, W. E. 1988. "*Some physiological characteristics of fungi isolated from sandstone"*. In 6th International Congress on Deterioration and Conservation of Stone. Supplement.

[74] Silverman, M. P. & Munoz. E. F. 1970. "*Fungal attack on rock: Solubilization and altered infrared spectra"*. Science. 169, 985-7.

[75] Jones. B. & Pemberton. S. G. 1987. "*The role of fungi in the diagenetic alteration of spar calcite"*. Canadian J. Earth Sciences. 24, 903-14.

[76] Koestler, R. J., Charola, A. E., Wypyski, M. & Lee. J. J. 1985. "*Microbiologically induced deterioration of dolomitic and calcitic stone as viewed bv scanning electron microscopy"*. In 5th International Congress on Deterioration and Conservation of Stone. Proceedings. Vol. 2. ed. G. Felix. Presses Polytechniques Romandes. Lausanne. pp. 617-26.

[77] Petersen, K., Grote, G. & Krumbein, W. E. 1988a. "*Bio transfer of metals by fungi isolated from rock*." In 6th International Congress on Deterioration and Conservation of Stone. Supplement. Nicholas Copernicus University. Press Department, Torun, pp. I 11-19.

[78] Petersen, K. Kuroczkin, J. Strelcczyk. A. B. & Krumbein, W. E. 1988b. "*Distribution and effects of fungi on and in sandstone"*. In Biodeterioration 7, ed. D. R. Houghton, R. N. Smith, & H. O. W. Eggins. Elsevier. New York. pp. 123-8.

[79] Realini, M., Sorlini, C. & Bassi. M. 1985**.** "*The Certosa of Pavia: a case of biodeterioration*." In 5th International Congress on Deterioration and Conservation of Stone. Proceedings, Vol. 2, ed. G. Felix. Presses Polytechniques Romandes, Lausanne, pp. 627-32.

[80] P. S. Griffin, N. Indictor, R. J. Koestler.,1991. *The Biodeterioration of Stone: A Review of Deterioration Mechanisms, Conservation Case Histories, and Treatment"* Elsevier, International Biodeterioration 28, pg. 187-207.

[81] Jones, D. & Wilson. M. J. 1985. "*Chemical activity, of lichens on mineral surfaces A-review"*. International Biodetermination Bull. 21, pg. 99-104.

[82] Leysen, L., Roekens, E. and Van Grieken, R. 1989, "*Airpollution- induced chemical decay of a sandy-limestone cathedral in Belgium*." Sci. Total Enuir. 78. 263--287.

[83] Fassina, V. 1978, "*A survey of air pollution and deterioration of stonework in Venice*." Atmospheric Environment 12, 2205-2211.

[84] Zezza, F. and Macri, F. 1995, "*Marine aerosol and stone decay*." Sci. Total Enuir. 167, 123-143.

[85] Moropoulou, A., Theoulakis, P. and Chrysophakis, T. 1995, "*Correlation between stone weathering and environmental factors in marine atmosphere*." Atmospheric Environment 29, 895-903.

[86] Anandi Krishnan, Yi-Hsiu Liu, Paul Cha,Roger Woodward ,David Allara , Erwin A. Vogler,2005. "*An evaluation of methods for contact angle measurement"*. Colloids and Surfaces B: Bio interfaces 43 (2005) pg. 95–98

[87] E.L. Decker, B. Frank, Y. Suo,S. Garoff,1999, "*Physics of contact angle measurement*" Elsevier, Colloids and Surfaces, A: Physicochemical and Engineering Aspects 156 (1999) pg. 177–189