LONG-TERM PROTECTION EFFICIENCY OF
BIODEGRADABLE POLYMER TREATMENTS ON
LIMESTONE

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ABSTRACT

LONG-TERM PROTECTION EFFICIENCY OF BIODEGRADABLE POLYMER TREATMENTS ON LIMESTONE

Synthetic polymers can be replaced by biodegradable ones as adhesive, water repellents and consolidants in stone conservation to preserve historic buildings from further deterioration. In this study, the long-term stabilities of two biodegradable polymers, polyhydroxybutyrate (PHB) and poly-l-lactide (PLA) and an acrylic polymer (Paraloid B72), which are commonly used in conservation works of artefacts, were evaluated on limestone through an UV lamp-weathering chamber. Chemical and morphological changes induced by accelerated weathering test were followed by Fourier Transform Infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) analysis. The protection efficiencies of the polymers were determined by following the changes in the color, capillary water absorption and static contact angle on the limestone surfaces in accordance with CEN standards developed by the European Committee of Standardization (CEN) for conservation of cultural property.

PHB, PLA and Paraloid B72 coatings significantly increased hydrophobicity, decreased capillary water absorption and caused negligible change in the color of the limestone. All polymers showed chemical, physical and optical changes under accelerated weathering conditions. Paraloid B72 decomposed by the reduction of molecular weight, decomposition of ester group and formation of gamma lactones and hydro peroxides. PHB and PLA decomposed with formation of CO₂ and hydro peroxide, hydrolysis of ester groups and reduction of the molecular weight. Chemical changes cause to etching, holes, voids, cracks and slight color differentiations on the coatings by chain scission, breaking of polymer bonds and formation of volatile gaseous products. Protection efficiencies of the PLA and PHB polymers almost same as that of the widely used acrylic polymer Paraloid B72. However, PLA and PHB seem to be promising polymers as protective agents due to their reversibility and biodegradability, low chromatic changes, good hydrophobic behavior and good stability to weathering in reducing the effects of outdoor exposure on limestone surfaces.
ÖZET

BIO BOZUNUR POLİMERLERİN KİREÇ TAŞI ÜZERİNDEKİ UZUN SÜRELİ KORUMA ETKİSİ

Bio bozunur polimerler, tarihi yapıları bozulmaları karşı korumak için taş korumada yapıştırıcı, su itici ve birleştirmici olarak kullanılan sentetik polimerlere alternatif olabilirler. Bu çalışmada, iki bio bozunur polimerin, polihidroksibütirat (PHB) ve poli-l-laktidin (PLA) ve tarihi eserlerin korunmasında yaygın olarak kullanılan bir akrilik polimerin (Paraloid B72) uzun vadeli dayanıklılıkları UV-lambalı-yaşlandırma test cihazında, kireçtaşları üzerinde değerlendirilmiştir. Hızlandırılmış yaşlandırma testi sonucunda oluşan kimyasal ve morfolojik değişiklikler, Fourier Dönüşümlü Kızılötesi spektroskopisi (FT-IR) ve Taramalı Elektron Mikroskobu (SEM) analizleri ile izlenmiştir. Polimerlerin koruma etkinlikleri, kültürel mirasın korunması için Avrupa Standardizasyon Komitesi (CEN) tarafından geliştirilen CEN standartlarına uygun olarak kireçtaş yüzeylerinde renk, kılcal su emilimi, statik temas açısı ve su buharı geçirgenliğindeki değişiklikler izlenerek belirlenmiştir.

PHB, PLA ve Paraloid B72 kaplamalarının; kireç taşının hidrofobikliğini önemli ölçüde artırdığı, kılcal su emiliminin azalttiği ve kireçtaş renginde önemli bir değişikliğe neden olmadığı tespit edilmiştir. Tüm polimerler, hızlandırılmış yaşlandırma koşulları altında kimyasal, fiziksel ve optik değişiklikler göstermiştir. Paraloid B72, moleküller ağırlığının azalması, ester grubunun ayrışması ve gama laktonlarının ve hidro peroksitlerin oluşumu ile bozulmuştur. PHB ve PLA ise CO₂ ve hidro peroksit oluşumu, ester gruplarının hidrolizi ve moleküller ağırlığının azalması ile bozulmuştur. Kimyasal değişiklikler, zincir kırılması, polimer bağlarının kırmış olması ve uçtuğ gaz ürünlerinin oluşumu ile kaplamalarda aşınmaya, deliklere, boşluklara, çatlaklara ve hafif renk farklaşmalarına neden olmuştur. PLA ve PHB polimerlerinin koruma etkinlikleri, yaygın olarak kullanılan akrilik polimer Paraloid B72 ile aynıdır. Bununla birlikte, PLA ve PHB’nin, geri dönüştürülebilirliği, biyolojik olarak parçalananabilirliği, düşük kromatik değişimleri, iyi hidrofobik davranışları ve dış hava koşullarına maruz kalan kireç taşı yüzeyindeki dayanıklılıklarının iyi olması nedeniyle koruyucu maddeler olarak ümit verici olduklarını görülmüştür.
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CHAPTER 1

INTRODUCTION

Stone-built cultural heritage is one of the most important cultural assets that should be conserved with its architectural and material characteristics.

Over the past decades, natural and synthetic polymers have been used to protect stone-built cultural heritage from water damage. Starch, plant gum and resins, glue or albumin, beeswax and fats were widely used natural materials until late nineteenth century (Horie 1988; Masschelein-Kleiner 1985). Different resins and waxes were started to be used after technology and trade developed. Starting with the 19th century, first synthetic polymer cellulose nitrate (Posse 1969) and other cellulose derivatives were used in conservation works (Scott, and Britain 1921; Jenkinson 1924). Then, polyvinyl acetate (PVAC) was used in 1929 (Carmen 1986). From the early twentieth century with the rise of chemical industries many synthetic materials were produced. During 1930s, acrylic polymers became commercially available and they had been considered as promising material for stone conservation. Paraloid B72 was produced by Rohm&Haas in 1930 which is the most widely used synthetic polymer by conservators. Alkoxyamines and epoxies have also been used as stone consolidants over the past 20 years (Wheeler 2005; Cavalletti et al. 1985; Selwitz 1992). In the last decade, with the development of technology, nanomaterials and bio-polymers were started to test in different conservation applications.

ICOMOS Charter “Principles for the Analysis, Conservation and Structural Restoration of Architectural Heritage” stressed preventive maintenance, keeping interventions to a minimum and importance of reversible intervention. The conservation material should be transparent and lead to none or negligible changes in the appearance of the original material. They should be reversible to be removed after many years without any damage to the substrate. They should not modify the original artefact (e.g., patinas, crusts and corrosion layers), as far as they do not threaten conservation and legibility of the object. Also, they should have long stability and efficiency over time. They should be easily applied and removed with eco-friendly operations (Horie 1988; ICOMOS 2003).

The polymers used in the conservation work should be reversible, compatible, water repellent, removable, re-treatable, breathable to allow the passage of water vapor,
not cause any color variation on the object, easy to apply and resist against weathering (Horie 1988; ICOMOS 2003).

In this study, the long-term stability of two biodegradable polymers, polyhydroxybutyrate (PHB) and poly-1-lactide (PLA), and an acrylic polymer (Paraloid B72), which is commonly used in conservation works of artefacts, were evaluated on limestone using a UV lamp-weathering chamber (up to 104 days) for future protection studies. Chemical and morphological changes induced by an accelerated weathering test were examined by Fourier Transform Infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) analyses. Protection efficiency of the polymers was determined by the changes in color, capillary water absorption, static contact angle on limestone.

In the introduction part of the thesis, a brief knowledge about natural and synthetic polymers, their use and related researches for stone conservation has been given. In the following chapters, preparation of limestone samples, preparation of polymer solutions, coatings of samples, aging of coated samples, evaluation of chemical and morphological changes of polymers, evaluation and discussion of the protection performances of polymer coatings were given.

### 1.1. Polymers

Polymers are materials consist of repeating chains of molecules that can be linear, branched chains or three-dimensional networks. When the units of polymer are identical it is called homo-polymer, when the units are varying, it is called copolymer. The major characteristic of a polymer is its chemical structure and molar mass distribution pattern (molecular weight). The chemical structure of a polymer includes the nature of repeating units and end groups, the composition of possible branches and cross links and the nature of defects in structural sequence. The molar mass distribution provides information about the average molecular size (van Krevelen, and te Nijenhuis 2009).

The physical properties of a polymer depend on; its chain length, side groups, branching and linking. It becomes strong when its chain is long. Straight and unbranched chains can pack together more closely than highly branched chains, making polymers more crystalline and stronger. If polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt. Also, percentage of crystallinity in a polymer is very important to determine its properties. The more crystalline the polymer, it becomes the stronger and less flexible (Horie 1988).
Polymers can be classified based on their origin of source, structure, molecular forces and mode of polymerization (Figure 1). In this section, characteristics of natural polymers, synthetic polymers and semi-synthetic polymers were shortly defined based on their origin of source (Misra 1993, Young, and Lovell 2011).

**Figure 1.** Polymer classification based on their origin of source

### 1.1.1. Biodegradable Polymers

Biodegradable polymers are produced by living organisms or chemically by natural sources that are also called biopolymers. They degrade by physical, chemical or biological process that causes to the loss of functionality of the polymer and the loss of its molar mass (Domb et al. 1997). Biodegradation is an enzymatic action produced by living organisms (biological activity) under ultraviolet light, heat and water. During biodegradation, oxidation and hydrolysis take place and macro and molecular scale changes observed. At macro scale, cracking, breakage, fragmentation etc. are observed. At molecular scale, change of the amount of carbonyl groups and the shortening of the polymer chains may be causing loss of the mechanical properties, such as tensile strength, toughness and flexural strength (Bastioli 2011; Avérous, and Pollet 2012).

Biodegradable polymers can be classified as agro-polymers and bio polyesters. Agro polymers are as polysaccharides and proteins, which are directly derived from biomass. Bio polyesters are derived from microorganisms or synthetically made with natural and synthetic monomers (Chamy, and Rosenkranz 2013). They have similar characteristics of conventional plastics and have been used in a wide range of applications from medicine to agricultural industry and packaging due to their harmless effect to environment.

Among agro-polymers, polysaccharides are polymeric carbohydrates molecules composed of long chains of monosaccharide units bound together by glycoside linkages,
and on hydrolysis give the constituent monosaccharides or oligosaccharides. They range in structure from linear to highly branch. They are mainly starch, cellulose, chitin, lignin, etc.

Starch is a polysaccharide composed of glucose units linked by glycosidic bonds. It is obtained from green plants and mostly used in human diet. It is also used as an adhesive in the paper making process, to produce beer, whisky and biofuel (Vijn and Smeeckens 1999; Zeeman, Kossmann, and Smith 2010).

Cellulose is a polysaccharide with linear chain. Cellulose is a widely found naturally occurring reproducible polymer. It is obtained from green plants, algae and oomycetes. Cotton, flax, dry wood and dried hemp contain 90 %, 40-60 %, 57 % cellulose respectively. It is used in the production of paperboard and paper (Kamide and Kamide 2005).

Chitin is a modified polysaccharide with long-chain and contains nitrogen. Chitin obtained from cell walls in fungi, the exoskeletons of arthropods and insects, the radula of mollusks, cephalopod beaks and the scales of fish and lissamphibians. Chitin is used in medicine, industry and biotechnology (Tang et al. 2015).

Lignin is a polysaccharide with cross-linked chain and obtained from woody plants. Lignin and cellulose are built up the cell wall of a plant. Lignin is used for making papers, adhesive binders, resins and coatings, foams, films, paints, plastics, foods and beverages (Belgacem and Gandini 2008).

Proteins are naturally occurring polymers produced by amino acids. A protein is also called polypeptide. Polypeptides are bonded together in a chain and formed a part of a protein molecule (DNA(deoxyribonucleic acid), RNA(ribonucleic acid) and zein etc). Zein is a plant protein that found in corn which belongs to a family of prolamins and composed of high amounts (>50 %) of hydrophobic amino acids, such as proline, glutamine and asparagine (Elzoghby, Samy, and Elgindy 2012).

Biodegradable polyesters can be grouped as polymers produced by micro-organisms (Polyhydroxyalkanoates (PHA)) and produced synthetically from natural (Agro sources) (polylactic acid (PLA)) or synthetic (fossil sources) monomers (Avérous and Pollet 2012). Biodegradable polyesters are used in pharmaceutics, tissue engineering and food packaging industry (Bastioli 2011; Avérous, and Pollet 2012). The most widely used biodegradable polyesters that are obtained from renewable sources are Polyhydroxyalkanoates (PHAs) and polylactic acid (PLA).
**Polyhydroxyalkanoates (PHAs)**

Polyhydroxyalkanoates (PHAs) are naturally occurring polyester that accumulates in bacterial cells as a carbon energy storage (Murthy, Wilson, and Sy 2012). They are generally biodegradable and thermo-processable making them attractive in applications both conventional medical devices and tissue engineering. PHAs are suitable for short-term packaging, and also considered as bio-compatible in contact with living tissues and can be used for biomedical applications (drug encapsulation, tissue engineering, etc.). The polyhydroxybutyrate (PHB), homopolymer, is the main biopolymer of the PHA family. It is a highly crystalline polyester (above 50 %) with a high melting point, Tm=173°C-180°C compared to the other biodegradable polyesters (Domb et al. 1997). The Tg is around 5°C and dissolve in chloroform (Vayer, Vital, and Sinturel 2017). It is nontoxic and less sticky material in melted conditions. These properties make PHB a good candidate to use in wide range of applications as packaging, agriculture, leisure, fast-food, hygiene as well as medicine and biomedical (Khosravi-Darani 2015; Swain et al. 2017).

**Poly-L-Lactide (PLA)**

Poly-l-lactide or polylactic acid (PLA) is mostly used biodegradable material which is a thermoplastic aliphatic polyester derived from lactic acid by renewable sources such as corn starch, cassava roots or sugarcane. Lactic acid is obtained by fermentation of carbohydrates by lactic bacteria (Lactobacillus or fungi) (Garlotta 2002; Wee, Kim, and Ryu 2006; Avérous and Pollet 2012; Spiridon et al. 2015). PLA is a hydrophobic polymer due to the presence of –CH3 side groups. PLA has been started to use in cosmetics, biomedical, agricultural, food, and environmental field in recent years due to high moisture barrier property compared to the conventional polymers (Luckachan and Pillai 2011). PLA are manufactured by biological and chemical from sugar beet, sugar cane, corn, potatoes, and other biomasses. It ranges from amorphous glassy polymer to semi-crystalline and highly crystalline polymer. It has a Tg= 60°C and Tm=130-180°C (Lunt and Shafer 2000). PLA is soluble in chlorinated solvents and degrades in the environment by carbon dioxide and water.

### 1.1.2. Semi-Synthetic Polymers

Semi-synthetic polymers are modified by chemical reactions and obtained from natural polymers. They are vulcanized rubber, cellulose acetate etc. Vulcanized rubber is a natural elastomer that is made more durable by a biochemical process that hardens the
rubber. Vulcanized rubber is stronger than non-vulcanized rubber because its bonds are made of crosslinks at an atomic level. They are used in the construction of rubber hoses, shoe soles, tires, bowling balls, bouncing balls, hockey discs, toys, erasers and tool nozzles (Mourey, and Schunk 1992).

Cellulose acetate, the acetate ester of cellulose, is the earliest synthetic material obtained with cotton or wood pulp cellulose. It is used as a film base in photography, as a component in some coatings, and as a frame material for eyeglasses. It is also used as a synthetic fiber in the manufacture of cigarette filters and playing cards. In photographic film, cellulose acetate replaced nitrate film in the 1950s, being far less flammable and cheaper to produce (Carter 1924).

1.1.3. Synthetic Polymers

Synthetic polymers are artificially produced from petroleum oil. The first synthetic polymer was produced by John Wesley Hyatt in 1869 (Quye 1995). Synthetic polymers have low density, low coefficient of friction, good corrosion resistance, good molding ability, low mechanical properties and poor temperature resistance. They are economical and produced in different colors of transparent. Synthetic polymers are widely used in everyday life such as agriculture, food, automobile, textile, construction industry, medical appliances, etc. Synthetic polymers can be classified as thermoplastics, thermosets, elastomers and synthetic fibers (Amoroso, and Fassina 1983).

Thermoplastics soften when heated and become firm again when cooled. They can be remolded and recycled without affecting physical properties of the material (Olabisi 1997). The properties of the thermoplastics depend on the regularity of the arrangement of the molecular chains. If they are lined up in a regular way, they are strong, hard materials. If they are more irregular, or there are more side-chains on the molecules, they are more flexible. It is resistant to moisture and most of the chemicals. They are polyethylene, polystyrene, polyurethane, polyesters, cyanoacrylates, epoxies acrylics etc.

Polyethylene is a thermoplastic produced from ethane monomer having two carbon atoms and linked by two hydrogen atoms. These bonds are broken when polyethene is subjected to high temperature and pressure. Polyethene is flexible at room temperature and can be sealed by heat (Young, and Lovell 2011).

Polystyrene is a thermoplastic and composed of styrene monomer (Young and Lovell 2011). It is naturally transparent, but can be colored with colorants. Polystyrene is in a solid (glassy) state at room temperature but flows if heated above about 100° C. It
becomes rigid again when cooled. It is a rather poor barrier to oxygen and water vapor and has a relatively low melting point. Polystyrene is most widely used thermoplastic for protective packaging, containers, lids, bottles, trays, tumblers, disposable cutlery and in the making of models. Polystyrene is increasingly abundant as a form of litter in the outdoor environment, particularly along shores and waterways, especially in its foam form, and also in increasing quantities in the Pacific Ocean (Kwon et al. 2014).

Polyurethane is another group of thermoplastic polymers. They are similar to nylons but formed by reacting alcohols with isocyanates and have an amine linkage with an additional oxygen atom in the chain. These polymers are often softer and more elastic than nylons and are used as a substitute for rubber and in elastic and lycra.

Polyester is mostly used thermoplastics polymer, it can be a thermoplastic or thermoset depending on its chemical structure. Polyesters are widely used as fibers for clothes and also for many drinks’ bottles. They are also used to make thin films for applications such as video tape (Nixon, Cahill, and Jolanki 2012).

Cyanoacrylate is an acrylic resin that rapidly polymerizes in the presence of water (specifically hydroxide ions), forming long, strong chains, joining the bonded surfaces. Cyanoacrylates include methyl 2-cyanoacrylate, ethyl-2-cyanoacrylate, n-butyl cyanoacrylate and 2-octyl cyanoacrylate. They used as adhesives with industrial, medical, and household uses.

Acrylics polymers are thermoplastics or thermosetting plastics produced from acrylic acid that dissolved in organic solvents (Penzel, Haberkorn, and Heilig 1999). They consist of small monomers linked together to form long chain-like polymers which provides reversibility. The monomers are esters of acrylic and meth-acrylic acid. They are good adhesives and stable against oxygen and UV radiation (Tabasso 1996; Pepi 2008). However, they are easy to crosslink with high UV irradiation and temperature in respect to the glass transition temperature (Horie 1988; Laurenzi Tabasso and Santamaria 1985).

Paraloid B72, a co-polymer of methacrylate and ethyl methacrylate, is widely used acrylic polymer which was produced in 1930 by Rohm&Haas. It has good solubility in several solvents such as ketones and chlorinated hydrocarbons. It is transparent and has good adhesive properties. Paraloid B72 has low Tg (~40°C) which resulted in low rigidity at room temperature.

Thermosets soften when they are exposed to heat and they can be molded, but then harden permanently. They will decompose when reheated (Prime 2009). It resists to water, and acid in long-term. Epoxies become liquid to solid and then reach to final
hardness in time similar to other thermoset plastics. Epoxies are a widely used in range of applications, including metal coatings, use in electronics/electrical components/LEDs, high tension electrical insulators, paint brush manufacturing, fiber-reinforced plastic materials and structural adhesives.

Elastomers are elastic polymers that deforms under stress and return to its original shape when the stress is removed. Rubbers are the most widely used elastomers. Most elastomers are thermosets and used mainly for the manufacture of tires, tubes, hoses, belts, matting, gloves, toy balloons, rubber bands, pencil erasers, and adhesives.

1.2. Evaluation of Acrylic and Biodegradable Polymers Treatments for Stone Conservation

The conservation treatments of stones include the diagnosis of the deterioration and establishment of criteria for treatment (Gauri and Bandyopadhyay 1999). The treatment criteria depend on the results of the laboratory and field experiments. The treatment should be reversible, cause minimum change in color and gloss of the substrate, decrease the surface tension and prevent wetting of the surface, reduce the absorption of liquid water, minimize the change of water vapor permeability of the substrate, produce no harmful by-products after its application, and maintain its physical and chemical stability against weathering.

Determination of the best polymer treatment for stone conservation became an important subject in the second half of the 20th century. The extensive studies were carried out and a great source of information provided for conservators and conservation scientist. In the following section, the results of some recent studies carried out with acrylics and biodegradable ones will be given.

1.2.1. Acrylics Treatments for Stone Conservation

Acrylic polymers extensively used in stone conservation to preserve monuments from further deterioration. Paraloid B72, an acrylic polymer, is widely used as adhesive, water repellent and consolidant in the conservation work of several movable or immovable artefacts (Melo et al. 1999). It acts as a waterproof coating but loses its efficiency and removability in time due to polymer decomposition (Melo et al. 1999). The surface discoloration resulting from Paraloid B72 coating is not acceptable for the
conservation of cultural heritage (Kaplan et al. 2019). On the other hand, Paraloid B72 increases the water repellency (hydrophobicity) of stone surfaces while hydrophobicity decreases due to the weathering effects.

Paraloid B72 penetrates into the pores of stones producing a uniform surface and, due to outdoor conditions, it is subjected to weathering through UV light exposure, which causes degradation by chain scissions, photoinduced crystallization and cross linking (Favaro et al. 2006; Nyquist, and Potts 1961; Yousif, and Haddad 2013; Wojciechowski et al. 2015; Nguyen et al. 2018; Rabek 1995; Allen et al. 1997; Chiantore, and Lazzari 2001; Miliani et al. 2002; Bracci and Melo 2003; Sadat-Shojai, and Ershad-Langroudi 2009; Doehne, and Price 2010; Scalarone, Lazzari, and Chiantore 2012). UV irradiation leads to color changes and loss of surface hydrophobicity depending on the relative intensity of the radiation (Melo et al. 1999; Favaro et al. 2006).

Acrylic polymers have long-term durability and water protection efficiency which were evaluated by accelerated ageing test by several studies. The main characteristics of the study are shortly given in the Table 1.

Melo et al. 1999 tested the durability of acrylic polymers (Homo-polymers PMMA, PEMA, PIBMA co-polymer P(EMA-MA), PMA and Paraloid B72) on different substrates (dolomite, marble and potassium bromide disk) after aging under UV irradiation (Table 1). Their durability was evaluated by the changes in color, capillary water absorption, and static contact angle on the studied samples. Yellowing with PMA, Paraloid B72 and P(EMA-MA) and discoloration with PIBMA and PEMA were determined after 650 hours ageing due to polymer loss during ageing (Table 2). Complete fragmentation observed with all samples and cross linking takes place at the beginning of UV radiation. The water protection efficacy was completely lost after 650 hours ageing in all polymer which was in agreement with the total loss of polymer (Table 3).

Chiantore, and Lazzari 2001 also investigated photo-oxidative stability of acrylic and meth-acrylic resins under artificial solar light irradiation (Table 1). Structural and molecular changes of polymers were followed by FT-IR and UV-Vis spectroscopy and size exclusion chromatography. Chain scissions and coupling of macro radicals were detected with all polymers. This was resulted in weight loss and molecular weight distribution change.

Toniolo et al. 2002 evaluated the protection efficiency of Paraloid B72 coating on marble surfaces with accelerated ageing test up to 1500 hours and compared with fluorinated acrylic co-polymers (Table 1). After ageing test, FTIR spectroscopy and size exclusion chromatography (SEC) analyses were carried out to determine the photo
stability of the polymers. Also, water repellency, water capillary absorption, water vapor permeability and colorimetric tests were carried out according to Italian protocol. During UV ageing, ΔE* values decreased and after 1500 hours of ageing (Table 2), Paraloid B72 completely lost its hydrophobicity (Table 3). Fluorinated Paraloid B72 appears to be capable of maintaining its efficiency at least partially, even after UV ageing.

Bracci and Melo 2003 evaluated coating life time of Paraloid B72 and homopolymers PMMA, PEMA, and the co-polymer P(EMA-MA) on dolomitic stone and marble under artificial ageing up to 4000 hours and natural ageing with color measurements, Fourier transform infrared analysis (FT-IR), size exclusion chromatography (SEC) and capillary water absorption tests (Table 1). Structural changes were observed after 500 hours of irradiation due to cross-linking and chain scissions. It was noted that Paraloid-B72 is fairly well maintained its water protection efficiency (P.E) up to 2500h ageing, and after 4000h it decreases to 35 %. PMA completely lost its P.E after 2000h, PEMA still retains 60 % and loss after 2500 hours (Table 3). Outdoor ageing of PB72 for 12 months does not seem to affect noticeably the protection efficiency, however, after 42 months reduced to 60 %. For all polymers any relevant color changes were observed (Table 2).

Favaro et al. 2006 tested protection efficiency and photo-oxidative weathering of Paraloid B72, Paraloid B67 and a silicon-based product Dri-Film 104 on marble surfaces and their thin films under aging test (Table 1). Their performances and weathering were evaluated by colorimetric and ultrasonic measurements, removability tests and by Fourier transform infrared analysis, NMR and size exclusion chromatography. Results of the analysis showed that Paraloid B72 had better color variations (ΔE’ < 10) after accelerated ageing test than Paraloid B67 and Dri-Film104 (Table 2). Structural changes were related with the color changes. After 500 hours of ageing, polymer samples were remained soluble.

Favaro et al. 2007 tested protection efficiency of the acrylic silicone mixture of Bologna Cocktail (Paraloid B72 and Dri Film 104) on Carrara marbles exposing to photo-oxidative weathering and saline solution (Table 1). Chemical changes were evaluated by FT-IR, NMR and SEC analysis. Protection performances were determined by removability of polymers, ultrasonic and colorimetric measurements. Molecular changes have been identified in both components of BC applied on marble specimens after artificial ageing. The photo-oxidative deterioration of BC mixture is enhanced applied as thin film and limited as thick coating and on marble. This was explained to the low penetration of O₂ into the bulk of the coating, the photo-oxidative phenomena being
almost confined to the uppermost surface of the polymer. Similar to the Paraloid B72, BC mainly leads to chain cross-linking and scissions, with the formation of intermolecular and terminal double bonds and oxidized species, such as gamma-lactones.

Tsakalof et al. 2007 evaluated the protection efficiency of five synthetics (siloxane/acrylic polymer (Bayer LF), methylsiloxane (Rhodorsil 224), mixture of silanes and siloxanes (Wacker 290), functionalized perfluorinated polyether (Akeogard P) on marble, travertine, sandstone and brick with water contact angle, water vapor permeability and water absorption by capillarity measurements. Results showed that siloxane/acrylic polymer was found to be most suitable coating for all types of stones, except brick (Table 2). However, when color alterations are ignored functionalized perfluorinated polyether has the optimal properties for protection of marble of Drama. Methylsiloxane was estimated most suitable for marble of Thassos, porous stone of Kilkis and sandstone of Turkey (Table 3).

Karatasios et al. 2009 investigated inorganic consolidants, acrylic emulsions and silane-based materials as consolidation materials on marly limestones. The effects of consolidation application monitored by color, porosity and pores size distribution, water absorption by capillarity, mechanical and durability tests. Results showed that Rhodorsil caused darkness on the stone surface while calcium hydroxide attributed a yellowish hue to the stones. Funcosil and Hydrogrund had the lowest effect on the appearance of the stones. Water absorption coefficient was reduced, and total surface areas were increased with all treatments. The reduction of water absorption coefficient has been attributed to the modification of pore size distribution and the static contact angle values. The water drop could be measured with the samples treated by Hydrogrund, Funcosil and Rhodorsil. Rhodorsil exhibited the best hydrophobic properties, followed by Hydrogrund, while Funcosil exhibited a very poor hydrophobic behavior. Considering strength characteristics, Rhodorsil RC-80 and Funcosil-Steinfestiger 100 exhibited the best performance, while concerning the tensile strength Funcosil attributed greater enhancement than Rhodorsil.

Ferreira Pinto and Delgado Rodrigues 2012 tested ethyl silicate (TEOS), acrylic (Paraloid B72), and epoxy resins (cycloaliphatic epoxy resin) as consolidants on limestones and dolostones. Their micro drilling resistance, the absorption of products, depth of the applied polymer, bending strength and surface hardness were determined. The results showed that, same consolidation product could be resulted in different strengthening actions, different amounts of absorbed polymer, when applied on the stone by different methods. Also, the consolidation mainly depends on the stone properties.
El-Gohary 2015 investigated the consolidation efficiency of ethyl silicates-based materials (Tegovakon V, Rhodorsil RC 80, Rhodorsil RC 70 and Eliosil W119) on sandstone. The weight change, depth of penetration, chromatic variation, physio-mechanical and SEM analysis were conducted (Table 2). According to analysis, the type of consolidants significantly changed the physio-mechanical properties of stone. Tegovakon V, Rhodorsil RC 80, Rhodorsil RC 70 were exhibited better performances than Eliosil W119. Qualitative analysis showed that the protective efficiency of ethyl silicate depended on the composition of stone, present condition and the control of external environment. According to results, Tegovakon V improved the stone properties and it could be said that it was the most suitable consolidants than the RC 80 and RC 70. On the other hand, Eliosil W119 caused chemical reaction with the stone cement material.

Farmakalidis et al. 2016 tested Paraloid B72 as a consolidant in painting conservation and compared with Primal AC33, Ketone Resin N and Laropal A81 under accelerated ageing up to 432 hours (Table 1). The changes were monitored by SEM, FT-IR, UV –Vis spectroscopy and Spectro-colorimetry. Results showed that acrylic polymers (Paraloid B72 and Primal AC33) exhibited higher photo stability. Paraloid B72 was more stable after accelerated ageing with small chemical structural changes. It showed slight yellowing and reduction in solubility (Table 2).

Sabatini et al. 2018 synthesized fluorine-based meth acrylic monomers in order to overcome the problems related with the use of widely employed acrylic polymers especially Paraloid B72. The long-term behavior of these polymers estimated by accelerated ageing tests under UV irradiation and monitored by SEC, FT-IR, and biodegradation assay (Table 1). Their macromolecular structures, molecular weights, thermal features and water repellency were determined. Results of the analysis showed that meth acrylic and fluorinated monomers enhanced durability and hydrophobicity of the stone than acrylic polymers (Table 3).

According to studies, acrylics especially Paraloid B72 is widely used adhesive by conservators in stone conservation. Paraloid B72 is capable to be stable against weathering cycles. However, it has poor penetration when applied on marbles and also porous stones and it modifies the color of the stone surface. The water protection efficiency of the surface treated with Paraloid 72 was also decreased with drying and wetting cycles, which is similar with any building stone that exposed to weathering cycles. This has been attributed to hydrolytic processes of the ester side groups when the polymer in contact with water for several hours.
Table 1. Weathering conditions and the findings of the previous studies on acrylic treatments

<table>
<thead>
<tr>
<th>Study</th>
<th>Coating material</th>
<th>Substrate</th>
<th>Weathering conditions</th>
<th>Finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Melo et al. 1999)</td>
<td>Homo-methacrylic and co-polymers and Paraloid B 72</td>
<td>Dolomite</td>
<td>Irradiation, in a climatic chamber, 35 mW/cm² (RH=50 %; T=25°C) up to 700 hours.</td>
<td>Total elimination of the polymer</td>
</tr>
<tr>
<td>(Lazzari and Chiantore 2000)</td>
<td>Paraloid B44, B82, B48N, B66, B67, PMMA, PEMA, PBMA</td>
<td>Thin film</td>
<td>Photo-ageing in Suntest CPS + apparatus equipped with a Xenon light source, wavelength&lt;295 nm irradiation: 765 W/m², max temp: 45°C</td>
<td>B72 and B82 showed neither cracking nor other optical variations</td>
</tr>
<tr>
<td>(Chiantore and Lazzari 2001)</td>
<td>Paraloid B-66, B-67, B-72, B-82</td>
<td>Thin film</td>
<td>Photo-oxidative weathering in Suntest CPS + apparatus equipped with a 1500 W Xenon lamp light source and a cutoff filter for wavelengths &lt;295 nm. Irradiation: 750 W/m². Max temp: 45 °C, up to 3000 hours.</td>
<td>Fluorinated methacrylate’s exhibited worse protection efficiency than B72</td>
</tr>
<tr>
<td>(Tomolo et al. 2002)</td>
<td>Fluorinated methacrylates and Paraloid B 72</td>
<td>Marble</td>
<td>In SolarBox, irradiation: at 700 W/m² (total irradiance=10,080 MJ/m²), up to 4000 hours.</td>
<td>Loss in efficiency, loss in removability,</td>
</tr>
<tr>
<td>(Bracci and Melo 2003)</td>
<td>Paraloid B 72 PMA</td>
<td>Marble</td>
<td>Photo-oxidative weathering in Xenon Weatherometer, irradiation: 0.35 W/m², wavelength 340 nm, temperature: 40°C, relative humidity: 40 %</td>
<td>Limited removability. Lead to color changes. Loss of consolidation efficiency</td>
</tr>
<tr>
<td>(Favaro et al. 2006)</td>
<td>Paraloid B-72, Paraloid B 67 DRI-Film 104 (silicone based)</td>
<td>Marble</td>
<td>Photo-oxidative weathering in Xenon Weatherometer, irradiation: 0.35 W/m², wavelength 340 nm, temperature: 40°C, relative humidity: 40 %. Accelerated ageing (Sunset CPS+) with a xenon arc lamp, wavelength &lt;295 nm, temperature: 50°C</td>
<td>Lost stability. Less removable than Paraloid B72</td>
</tr>
<tr>
<td>(Favaro et al. 2007)</td>
<td>Bologna Cocktail (BG)</td>
<td>Marble</td>
<td>Ageing cycles in climatic chamber, the 1st step (30 cycle’s × 6.15 h of temperature in 5°C, step, followed by 30 cycle’s × 6.15 h of temperature in 95°C). The 2nd step is composed of alternative cycles of moisture (30 cycle’s × 6.15 h of 15 % and 30 cycle’s × 6.15 h of moisture in 85 %) up to 369 hours.</td>
<td>UVB 340 UVeVIS lamp of typical irradiance 0.7 W/m² per nm at 340 nm. 60 C 40 % RH</td>
</tr>
<tr>
<td>(Torrisi 2008)</td>
<td></td>
<td>Marble</td>
<td>Accelerated thermal ageing, in a laboratory oven, at 100 ± 2°C, for 432 hours.</td>
<td>Lost durability</td>
</tr>
<tr>
<td>(El-Gohary 2015)</td>
<td>Ethyl Silicate, Elosil w119, Tegovakon, RC 70, RC 80</td>
<td>Sandstone</td>
<td>Accelerated ageing tests, (ultra Vitalux lamp), wavelength 315-400nm for UVA and 280-315 UVB (UNI 10925:2001), up to 100 hours.</td>
<td>More durable than Paraloid B72</td>
</tr>
<tr>
<td>(Farmakalidis et al. 2016)</td>
<td>Paraloid B72, ketone resin, Laropal,</td>
<td>Painting</td>
<td>Accelerated ageing tests, (ultra Vitalux lamp), wavelength 315-400nm for UVA and 280-315 UVB (UNI 10925:2001), up to 100 hours.</td>
<td>More durable than Paraloid B72</td>
</tr>
<tr>
<td>(Sabatini et al. 2018)</td>
<td>Flourinated methacrylates and Paraloid B72</td>
<td>Marble</td>
<td>Photo-oxidative weathering in Xenon Weatherometer, irradiation: 0.35 W/m², wavelength 340 nm, temperature: 40°C, relative humidity: 40 %</td>
<td>Fluorinated methacrylate’s exhibited worse protection efficiency than B72</td>
</tr>
</tbody>
</table>
Table 2. Color differences of acrylic treatments on stone

<table>
<thead>
<tr>
<th>Study</th>
<th>Substrate</th>
<th>Coating Material</th>
<th>Color difference ΔE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Melo et al. 1999)</td>
<td>Dolomite</td>
<td>Homo-methacrylic polymers (PMMA, PEMA, PIBMA)</td>
<td>Discoloration and Yellowness</td>
</tr>
<tr>
<td></td>
<td>Marble</td>
<td>Co-polymer (PEMA-MA)</td>
<td>Paraloid B72</td>
</tr>
<tr>
<td></td>
<td>Potassium Bromide Disk</td>
<td>PMA</td>
<td>ΔL* = -1.94 a.u.v: 0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ΔL* = -2.45 a.u.v: 0.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ΔL* = -1.52 a.u.v: 0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ΔL* = -2.12 a.u.v: 0.04</td>
</tr>
<tr>
<td>(Tioniolo et al. 2002)</td>
<td>Marble</td>
<td>Paraloid B72</td>
<td>ΔE* = 14 a.u.v: 6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TFEM/MA</td>
<td>ΔE* = 19 a.u.v: 17</td>
</tr>
<tr>
<td>(Favaro et al. 2006)</td>
<td>Carrara marble</td>
<td>DRI-Film 104 (silicone based)</td>
<td>ΔE* = 17 a.u.v: 13</td>
</tr>
<tr>
<td></td>
<td>Proconesium marble</td>
<td>Paraloid B-72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Paraloid B-67</td>
<td></td>
</tr>
<tr>
<td>(Cultrone and Madkour 2013)</td>
<td>Ceramic</td>
<td>Paraloid B72</td>
<td>10.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tegavakon</td>
<td>6.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silo 111</td>
<td>0.67</td>
</tr>
<tr>
<td>(Farkakali dis et al. 2016)</td>
<td>Painting 432 hours Thermal ageing</td>
<td>Paraloid B72</td>
<td>ΔE* = 2.58</td>
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<tr>
<td></td>
<td></td>
<td>Primal AC33</td>
<td>ΔE* = 1.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ketone Resin N</td>
<td>ΔE* = 3.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Laropal A81</td>
<td>ΔE* = 2.21</td>
</tr>
<tr>
<td>(El-Gohary 2015)</td>
<td>Sandstone</td>
<td>Ethyl silicate based consolidants</td>
<td>Darkness observed visually</td>
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<td></td>
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</tbody>
</table>

Table 3. Water protection efficiency of acrylic treatments on stone

<table>
<thead>
<tr>
<th>Study</th>
<th>Substrate</th>
<th>Coating Material</th>
<th>Weathering Conditions</th>
<th>Protection Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Paraloid B-72</td>
<td>650 hours UV irradiation</td>
<td>WCA (Δω)</td>
</tr>
<tr>
<td>(Melo et al. 1999)</td>
<td>Dolomitic white marble</td>
<td>Paraloid B-72</td>
<td></td>
<td>96 % a.u.v:2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P(MA-EMA)</td>
<td></td>
<td>96 % a.u.v:4%</td>
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<td></td>
<td></td>
<td>PMA</td>
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<td>PEMA</td>
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<td></td>
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<td>PMMA</td>
<td></td>
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<td></td>
<td></td>
<td>PIIMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Tioniolo et al. 2002)</td>
<td>Marble</td>
<td>Paraloid B72</td>
<td></td>
<td>a.u.v: 100% reduction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TFEM/MA</td>
<td></td>
<td>ICr=0.59 a.u.v: IC=0.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HFIM/EM/MA</td>
<td></td>
<td>ICr=0.64 a.u.v: IC=1.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>XFDI/DF/HFIM/EM/MA</td>
<td></td>
<td>a.u.v: 0% reduction</td>
</tr>
<tr>
<td>(Tsakalof et al. 2007)</td>
<td>Marble</td>
<td>Travertine</td>
<td>no UV</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sandstone</td>
<td>no UV</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Brick</td>
<td>no UV</td>
<td></td>
</tr>
<tr>
<td>(Karatasios et al. 2009)</td>
<td>Limestone</td>
<td>no UV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.2.2. Biodegradable Polymer Treatments for Stone Conservation

Biodegradable polymers were evaluated as a stone protection material in a few studies with their reversibility and eco-friendly properties. Their compatibility, protection efficiency and long-term durability on stone surfaces were determined by surface color measurements, water contact angle, water absorption by capillarity, water vapor permeability tests.

Their long-term durability and water protection efficiency were evaluated by accelerated ageing test. The protection performances of fluoro-functionalized PLA, homo-polymers and co-polymers of PLA and polyhydroxyalkanoates were investigated on different types stone surfaces.

Ocak et al. 2009 investigated the protection efficiency of biodegradable polymers (zein, chitosan, polyhydroxybutyrate (PHB), and poly-L-lactide (PLA) against SO₂ in the polluted environment on marble samples (Table 4). Their water vapor permeability, water absorption by capillary forces, surface wettability, and color alterations were determined. Results showed that hydrophobicity, water capillary absorption and polymer structure are important factors affecting protection efficiency (Table 5, Table 6). PLA exhibited promising surface protection efficiency and reduced the gypsum formation on marble surface in the polluted environment.

Giuntoli et al. 2012 evaluated and compared water protection efficiency of fluoro-functionalized poly-lactic acid and Paraloid B72 on marble samples. According to analysis, PLA based polymers exhibited higher photochemical and thermal stability, negligible short and long-term color changes and water repellence properties (Table 4, Table 5, Table 6). Also, PLA became an advantageous material as its higher eco-compatibility and solubility and lower cost of the coating material.

Giuntoli et al. 2012 tested the protection performance of the fluoro-functionalized PLA as potential protective coating for stone conservation. Their performance was tested on marble samples under accelerated ageing conditions up to 750 hours in terms of weight loss, solubility, molecular weight changes (Table 4). Also, colorimetric changes and capillary absorption tests by color differences were determined (Table 5, Table 6). Fluoro-functionalized PLAs showed a reduction of the amount of water absorbed by capillarity with respect to the un-fluorinated PLAs. FT-IR spectra generally remained qualitatively unchanged. After different ageing time, polymers were still soluble in chloroform. GPC data evidenced only slight reduction of weight average molar mass. The weight of polymer slightly decreased during ageing and lower color variations were observed.
Polymer remained still completely soluble in chloroform at different ageing times (250, 500, and 1000 hours).

Sacchi et al. 2012 tested the performance of homo-polymers and co-polymers of lactic acid as protective material on marbles under accelerated thermo-hygrometric and UV irradiation conditions up to 1000 hours (Table 4). The durability of polymers was evaluated with water absorption and color measurements (Table 5, Table 6). Results showed that treatment with fluorinated polymers showed higher enhancement in terms of water protection efficiency with respect to un-fluorinated poly-lactic acid. Also, water protection efficiency was maintained after thermo-hygrometric cycles. After UV irradiation, reduction was seen in the water protection efficiency with the marbles with lower porosity due to the detachment of polymer. In terms of color changes ageing decreased the ΔE values of treated marbles.

Pinho and Pedna 2014 prepared fluorinated PLA-SiO₂ nanocomposites and tested on marble samples. The effectiveness of the coating evaluated by water contact angle, water absorption by capillarity, water vapor permeability and color measurements (Table 5, Table 6).

Also, reversibility of the coatings was investigated. Morphological and surface composition changes was determined by SEM-EDS analysis. According to the results of analysis, fluorinated PLA-SiO₂ nanocomposites produced a hydrophobic behavior with addition of SiO₂, the hydrophobic behavior resulted by the reduction of surface energy and increment of surface roughness.

On the other hand, the water absorption by capillarity and water vapor permeability tests verified the hydrophobic behavior of the coating. Also, coating material did not significantly change the surface color of the stone. Furthermore, coatings were easily removed from the stone surface.

Ocak et al. 2015 evaluated the protection performance of biodegradable polymer (poly-L-lactide) and montmorillonite clay (MMT) against air pollution on marble surfaces with surface roughness, wettability, water vapor permeability, capillary water absorption and color measurements. Results showed that coatings did not alter the surface color of the marble (Table 5). On the other hand, coatings significantly improved the hydrophobicity of the stone surface and also inhibition of sulfation reaction under acidic environment (Table 6).

Pedna et al. 2015 synthesized co-polymers of lactic acid and evaluated their protective performances on marble samples. Their stability was evaluated through accelerated ageing test up to 1000 hours with FT-IR, H-NMR, GPC, DSC, solubility and
weight loss tests, chromatic and water absorption by capillary measurements. All polymer coatings showed reduction in weight after 1000 hours (1-2 %). After ageing all the coatings remained soluble. Chain scissions and de-polymerization were predominant degradation mechanisms. Also, their molecular weights decreased after ageing. Fluorinated polymers showed higher stability (Table 4). All treatments reduced the lightness of the stones as they showed a darker aspect (Table 5).

The results showed, total color change value was under the limit of accepted value for the conservation of cultural heritage with all treatments except pol (SALD) and poly (SALDF). The protection efficiency of fluorinated polymers remained almost constant. Their hydrophobic properties slightly lower than PLA (Table 6). Results showed that polymers showed low degradation, good stability to photo-oxidative conditions and negligible color changes determined after 1000 hours exposure.

Pedna et al. 2016 evaluated fluorinated PLA–SiO₂ bio-nanocomposites on both stone and glass surfaces. The effectiveness of the coating was determined by water contact angle measurements. The chemical bonds were analyzed by FT-IR, morphological changes were examined by Scanning Electron Microscope, the compositional analysis was conducted by TEM. The topography of the coated glass surfaces was monitored by AFM. As a result, the fluorinated and SiO₂ mixed polylactide showed good hydrophobic behavior as a coating material (Table 6). The hydrophobicity was improved by the addition of SiO₂ to the polylactide. On the other hand, fluorinated and SiO₂ added PLA composites produced homogenous surfaces and do not alter the surface color of the stone (Table 5). Also, the coating was compatible with the stone properties in terms of permeability. In addition, the coating was easily removed from the stone by chloroform.

Andreotti, Franzoni, and Fabbri 2018 tested the performance of PHAs based materials and two commercially available protective materials (Sol-SIL and Emul-SIL) on different stones in terms of capillary water absorption, static, dynamic contact angles, water vapor diffusion, color changes and surface morphology (Table 6).

Also accelerated ageing tests were carried out with solar light to evaluate the protection efficiency of the coating (Table 4). After seven days of accelerated ageing a drastic decrease observed for PHB and PHBVV, while commercial products exhibited limited decrease in the contact angle. The water absorption by capillarity values of PHB and PHBVV provided better values on sand stone while the hydrophobicity was lost on limestone samples.
Table 4. Weathering conditions and the findings of the previous studies on biodegradable polymer treatments on stone

<table>
<thead>
<tr>
<th>Study</th>
<th>Coating Material</th>
<th>Weathering Conditions</th>
<th>Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Giuntoli et al. 2012)</td>
<td>Fluoro-Functionalized poly lactic acids</td>
<td>Artificial ageing in Solar Box (Xenon-arc lamp), wavelength &lt;290 nm, irradiance: 550 W/m², black standard temperature (BST) at 65±2°C (ISO 1134/2004).</td>
<td>Durable, negligible color changes, high water repellence, removable</td>
</tr>
<tr>
<td>(Sacchi et al. 2012)</td>
<td>PLA and modified PLA’s</td>
<td>Artificial ageing in solar box, irradiance: 500 W/m², up to 1000 hours, (UNI EN 10951:2001), Thermal ageing in Climatic Chamber with thermos-hygrometric cycles</td>
<td>Enhanced water repellency</td>
</tr>
<tr>
<td>(Giuntoli et al. 2014)</td>
<td>Series of end-capped PLA polymers</td>
<td>Photochemical ageing in Solar Box (Xenon-arc lamp) wavelength &lt;290 nm, irradiance 550 W/m², black standard temperature (BST) at 65±2°C, (ISO 1134/2004).</td>
<td>Good stability, negligible color changes</td>
</tr>
<tr>
<td>(Pedna et al. 2015)</td>
<td>Co-polymers of Lactic Acid</td>
<td>Photochemical ageing in Solar Box (Xenon-arc lamp) wavelength &lt;290 nm, irradiance: 550 W/m², black standard temperature (BST) at 65±2, (ISO 1134/2004).</td>
<td>Negligible color changes, good durability, flexible</td>
</tr>
<tr>
<td>(Andreotti, Franzoni, and Fabbri 2018)</td>
<td>PHB and PHBVV</td>
<td>Accelerated ageing in Climatic Chamber, (solar light radiation), irradiation: 1.2 W/m², temperature: 40°C, relative humidity; 60%.</td>
<td>Negligible color changes, good water vapor permeability</td>
</tr>
</tbody>
</table>

Table 5. Color differences of biodegradable polymer treatment on stones

<table>
<thead>
<tr>
<th>Study</th>
<th>Substrate</th>
<th>Coating Material</th>
<th>Color difference ΔE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ocak et al. 2009)</td>
<td>Marble</td>
<td>PHB</td>
<td>ΔE*=3.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LMW-PLA</td>
<td>ΔE*=0.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HMW-PLA</td>
<td>ΔE*=0.38</td>
</tr>
<tr>
<td>(Giuntoli, Rossi, et al. 2012)</td>
<td>White dolomitic marble 750 hours</td>
<td>Fluoro-Functionalized PLA</td>
<td>ΔE*=4.61 a.u.v: 4.62</td>
</tr>
<tr>
<td>(Sacchi et al. 2012)</td>
<td>Marble 1000 hours</td>
<td>PLA</td>
<td>ΔE*=1.2 a.u.v: 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-FLD</td>
<td>ΔE*=1.8 a.u.v: 0</td>
</tr>
<tr>
<td>(Pinho and Pedna 2014)</td>
<td>Macael Marble</td>
<td>PLA</td>
<td>ΔE*=1.43 ± 0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLDA/FLK</td>
<td>ΔE*=2.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-S20</td>
<td>ΔE*=2.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-S80</td>
<td>ΔE*=2.41</td>
</tr>
<tr>
<td>(Ocak et al. 2015)</td>
<td>Marble</td>
<td>PLA</td>
<td>ΔE*=1.87 ± 0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLAD/MMT2</td>
<td>ΔE*=2.99 ± 0.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLAD/MMT5</td>
<td>ΔE*=4.93 ± 0.96</td>
</tr>
<tr>
<td>(Pedna et al. 2015)</td>
<td>Calcitic White Marble</td>
<td>PLA</td>
<td>ΔE*=1.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>poly(PMGLY)</td>
<td>ΔE*=2.55 a.u.v: 14.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a.u.v: ΔE*=12.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>poly(PMGLY)-F</td>
<td>ΔE*=2.97 a.u.v: 2.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a.u.v: ΔE*=2.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>poly(SALD)</td>
<td>ΔE*=3.11 a.u.v: 7.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>poly(SALD)-F</td>
<td>ΔE*=3.84 a.u.v: 2.25</td>
</tr>
<tr>
<td>(Pedna et al. 2016)</td>
<td>Marble</td>
<td>PF-S0 PLA SiO₂ fluorinated</td>
<td>ΔE*=-2.20 ± 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PF-S20 PLA SiO₂ fluorinated</td>
<td>ΔE*=-2.35 ± 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PF-S80 PLA SiO₂ fluorinated</td>
<td>ΔE*=-2.41 ± 0.09</td>
</tr>
<tr>
<td>(Andreotti et al. 2018)</td>
<td>Sandstone</td>
<td>PHB</td>
<td>ΔE*=&lt;2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Limestone</td>
<td>ΔE*=4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Marble</td>
<td>ΔE*=&lt;1</td>
</tr>
</tbody>
</table>
### Table 6. Water protection efficiency of biodegradable polymer treatment on stones

<table>
<thead>
<tr>
<th>Study</th>
<th>Substrate</th>
<th>Coating Material</th>
<th>Weathering Conditions</th>
<th>Protection Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>WCA (Δμ)</td>
<td>WAC (ΔQ)</td>
</tr>
<tr>
<td>(Oćak et al. 2009)</td>
<td>Marble</td>
<td>PHB</td>
<td>86°</td>
<td>68 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HMWPLA</td>
<td>99°</td>
<td>71 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LMWPLA</td>
<td>93°</td>
<td>81 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zein</td>
<td>49°</td>
<td>27 % reduction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chitosan</td>
<td>52°</td>
<td>200% reduction</td>
</tr>
<tr>
<td>(Sacchi et al. 2012)</td>
<td>Marble</td>
<td>PLGA</td>
<td>1000 hours UV irradiation</td>
<td>22%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLLA-FLK</td>
<td>750 hours UV irradiation</td>
<td>80%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLLA</td>
<td>65%</td>
<td></td>
</tr>
<tr>
<td>(Giantoli et al. 2012)</td>
<td>White dolomitic Marble</td>
<td>Fluoro-Functionalized poly lactic acids</td>
<td>750 hours UV irradiation</td>
<td>37%</td>
</tr>
<tr>
<td>(Pinho and Pedna 2014)</td>
<td>Macael marble</td>
<td>Untreated marble</td>
<td>No UV</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLDA-FLK</td>
<td>91°</td>
<td>87 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-S20</td>
<td>105°</td>
<td>90 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-S80</td>
<td>137°</td>
<td>98 %</td>
</tr>
<tr>
<td>(Oćak et al. 2015)</td>
<td>Marble</td>
<td>PLA</td>
<td>96±2.51°</td>
<td>46±1.8 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLA/MMT2</td>
<td>-</td>
<td>65±4.8 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLA/MMT5</td>
<td>108±2.49°</td>
<td>66±4.5 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLA/MMT7</td>
<td>105±2.61°</td>
<td>59±5.4 %</td>
</tr>
<tr>
<td>(Pedna et al. 2015)</td>
<td>Calcitic White Marble</td>
<td>PLA</td>
<td>37%</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PLA-F</td>
<td>78%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly(PMGLY)</td>
<td>67%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly(PMGLY)-F</td>
<td>94%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly(SALD)</td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly(SALD)-F</td>
<td>85%</td>
<td></td>
</tr>
<tr>
<td>(Pedna et al. 2016)</td>
<td>Marble</td>
<td>untreated</td>
<td>54°</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PF-S0</td>
<td>91°</td>
<td>87 %±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PF-S20</td>
<td>105°</td>
<td>90 %±0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PF-S80</td>
<td>140°</td>
<td>98 %±0.04</td>
</tr>
<tr>
<td>(Andreotti, Franzoni, and Fabbri 2018)</td>
<td>Sandstone</td>
<td>PHB</td>
<td>15 to 95 to 6</td>
<td>84 %</td>
</tr>
<tr>
<td></td>
<td>Limestone</td>
<td></td>
<td>0 to 108 to 6</td>
<td>0 %</td>
</tr>
<tr>
<td></td>
<td>Marble</td>
<td></td>
<td>40 to 80 to 21</td>
<td>-</td>
</tr>
</tbody>
</table>

### 1.2.3. General Remarks on Paraloid B72 and Biodegradable Polymers as Protective Substances on Stone

The studies showed that Paraloid B72 easily dissolves in solvents and applied on stone surfaces. Paraloid B72 increased the hydrophobicity of the stone surfaces. However, after long exposure to UV light, humidity and temperature Paraloid B72 lost protection efficiency. Also, Paraloid B72 became insoluble and unable to be removed from the stone surface. In addition, UV light leads to color changes on stone surface which is above the
acceptable value for the conservation of cultural heritage (Melo et al. 1999; Alessandrini et al. 2000; Favaro et al. 2006).

On the other hand, biodegradable polymers were also increased the hydrophobicity of the stone surfaces. Also they reduced the effects of gases present in polluted air such as SO₂ on the stone surface (Ocak et al. 2009; Sacchi et al. 2012; Pedna et al. 2016). However, similar with the Paraloid B72, biodegradable polymers lost their protection efficiency after long exposure to UV light, humidity and temperature. In contrast with the Paraloid B72, biodegradable polymers remained soluble and removable from the stone surface after long exposure to weathering conditions. Also, biodegradable polymers exhibited negligible color variations which are under the acceptable value for the conservation of cultural heritage. Among all the evaluated biodegradable polymers, PLA exhibited higher photo-stability and water protection efficiency and lower color variations (Giuntoli, Rosi, et al. 2012; Giuntoli, Frediani, et al. 2012; Pedna et al. 2015). While, PHB caused negligible color changes but provided a good water protection efficiency (Andreotti, Franzoni, and Fabbri 2018).

Eventually, synthetic polymers are long lasting in environment against physical, chemical and biological degradation. However, they have negative effect on safety, health and environment. They are non-biodegradable that they cannot be decomposed by bacteria or another microorganism. This will cause disposal problems as the polymer will not decay like other organic garbage. Therefore, an increasing attention is given to look for innovative and environment friendly materials. Even in the field of conservation, sustainability should also be considered to convey the cultural heritage to future generations. Therefore, conservation process should include environmental, economic and social sustainability. In this scope, the use of bio polyesters (biodegradable polymers) in the field of Conservation of Cultural Heritage to reduce or avoid possible future damages to environment is important which makes the biodegradable polymers as potential candidates for synthetic polymers.

1.3. Aims and Scope of the Study

The majority of built cultural heritage are stone monuments. Stone monuments are precious and vulnerable to any weathering conditions and their conservation should meet different requirements. Thus, stone conservation is one of the most important subjects in conservation studies to convey built cultural heritage for the future generations
with an environmentally friendly approach. In this context, the use of eco-friendly materials is started to be considered as an alternative material in the last decades.

This study aims to investigate the use of biodegradable polymers as alternative surface coating material to acrylic polymers. In this scope, PLA and PHB which are high molecular weight biodegradable polymers, and Paraloid B72, which is a commonly used material in the conservation of built cultural heritage, were chosen as coating materials. The chosen substrate was limestone, a sedimentary rock which has been the major source of architectural and statuary stone (Gauri, and Bandyopadhyay 1999). The durability and protection efficiency of Paraloid B72, PLA and PHB were determined under same conditions by accelerated weathering test with the combination of UV light, heat and moisture in accordance with European standard test method.
CHAPTER 2

METHOD

In this study, the long-term protection efficiencies of two biodegradable polymers, polyhydroxybutyrate (PHB) and poly-l-lactide (PLA) and an acrylic polymer (Paraloid B72), which is commonly used in conservation works of artefacts, were evaluated on limestone using a UV lamp-weathering chamber (up to 104 days) for future protection studies. The protection efficiencies of polymers were evaluated by color measurements, capillary water absorption and static contact angle and water absorption by capillarity measurements. Tests were conducted according to the norms of European Committee for Standardization (CEN). Their chemical and morphological changes were monitored by Fourier Transform Infrared (FT-IR) and Scanning Electron Microscope analyses (SEM). Flow chart of methodology is given in the Figure 2.

![Flow chart of methodology](image)

Figure 2. Flow chart for the methodology

2.1. Preparation of Limestone Samples

In this study the protection efficiency of biodegradable polymer coatings was investigated on limestone samples. Limestone is a sedimentary rock and has been the major source of architectural and statuary stone (Gauri, and Bandyopadhyay 1999). The chosen limestone was less dense (2.2 g/cm³) and a porous stone (11.3 %). Limestone is mainly composed of CaCO₃ and has traces of quartz, alumina, magnesium and iron oxides. It contains high amounts of amorphous silica from diatoms (Böke et al. 2008).
The limestone samples were prepared by cutting limestone pieces into rectangular plates 1.5cm×2.5cm×1.5mm using a Buehler Isometry cutting instrument and polished with 400-grit silicon carbide powder. The samples were then cleaned ultrasonically in deionized water and dried at 60°C.

2.2. Polymers Used in Limestone Coating

In this study, polyhydroxybutyrate (PHB) and poly-l-lactide (PLA), and an acrylic polymer (Paraloid B72) were used on limestone as coating materials. The biodegradable polymers were poly(L-lactide) PURASORB PL 65 (PLA) (Corbion, Netherlands) and Polyhydroxybutyrate (PHB) (Good fellow) and the synthetic polymer was Paraloid B72 (ZAG Kimya). Based on the recent studies of the protection efficiencies of biodegradable polymers on calcareous stones under the effect of acidic deposition (Ocak et al. 2009), PLA and PHB possessing higher molecular weight were chosen for their better protection performances. They are semi crystalline and have good water barrier properties. Both have the density around 1.2 (g cm⁻³). In addition, PHB has high melting point (175-180°C) and is a water insoluble biodegradable polymer similar to petroleum based synthetic polymers. PLA is also biodegradable, thermoplastic, aliphatic polyester derived from renewable resources. The properties of PLA are determined by the molecular architecture and the molecular weight while the melting temperature is in the range of 130-180°C.

2.3. Preparation of Polymer Solutions

Polymer solutions were prepared without any purification as 5 % (weight/volume). The PLA solution was prepared by dissolving PLA in chloroform with magnetic stirring at room temperature for 4 hours. The PHB solution was prepared by dissolving PHB in chloroform at 60°-70°C by a reflux system for approximately 2-3 hours. The Paraloid B72 solution was prepared by dissolving Paraloid B72 in acetone with magnetic stirring at room temperature for approximately 1-2 hours.

2.4. Coatings of Limestone Samples

Each polymer solution was applied onto a limestone sample by a dip-coating apparatus (Noma dipper) at room temperature with a 100 mm/min immersion rate and
150 mm/min retraction rate. After coating, the samples were left in an oven to volatilize the solvent at 40°C for several hours until they reached a constant weight. The film thicknesses of biodegradable polymers (PHB and PLA) and synthetic polymer (Paraloid B72) determined by SEM analysis were approximately 30µm and 50µm, respectively. The four coated parallel samples were weathered in an accelerated weathering chamber and used in evaluating the protection performances of coatings.

2.5. Preparation of Thin Polymer Films

The effects of accelerated weathering conditions on the chemical properties of the polymers were determined by FT-IR analysis on thin polymer films. Thin films were prepared by casting each polymer from solution. The polymer solutions were poured into petri dishes and left under a hood for 24 hours to volatilize the solvent. The formed films were then left under vacuum at 60°C for 24 hours.

2.6. Accelerated Weathering Tests

Accelerated weathering tests were carried out to evaluate the long-term protection efficiency of polymer coatings in a short time and to estimate long-term serviceability under expected conditions of use. Accelerated weathering tests were carried out in the test chamber (QUV/se Q Lab chamber) equipped with 4 UVA-340 lamps (wavelength from 365nm to 295nm) at up to 80°C temperature and 100 % relative humidity.

The weathering conditions were determined in accordance with the European Standard titled “Plastics - Methods of exposure to laboratory light sources - Part 3: Fluorescent UV lamps” (ISO 4892-2 2013).

The samples were exposed to 8 hours of UV irradiance of 0.76 (W/m²) at 60°C followed by 4 hours of condensation without irradiation at 50°C for 10 cycles up to 2500 hours (104 days). Almost 500 hours of irritation under UV exposure may correspond to 60 months of exposure to atmospheric weathering when water protection efficiency results of Paraloid B 72 coated stones have been considered (Bracci and Melo 2003). The effects of accelerated weathering conditions on the chemical properties of the polymers were determined by FT-IR analysis on thin polymer films. The long-term protection efficiencies of polymers were evaluated by color measurements, capillary water absorption and static contact angle and water absorption by capillarity measurements.
2.7. Evaluation of Chemical and Morphological Changes of Polymers

The chemical and morphological changes on polymer films during weathering were monitored by Fourier Transform Infrared (FT-IR) and Scanning Electron Microscope analyses (SEM).

2.7.1. Determination of Chemical Changes by Fourier Transform Infrared Analysis (FT-IR)

The chemical changes on the polymer films were determined by recording the FT-IR spectrum of the films at the specified time intervals of the weathering test. For the Paraloid B72, 7 measurements were taken between at 0, 25, 125, 250, 500, 750 1000 hours due to dissolution of the total Paraloid B72. For PLA and PHB, 10 measurements were taken at 0, 25, 125, 250, 500, 1000, 1500, 2000, 2250, 2500 hours. Spectral measurements were conducted by a Spectrum BX II FT-IR spectrometer (Perkin Elmer) operated in absorbance mode and spectra were collected with the use of 4 cm⁻¹ resolution in the range of 400 to 4000 cm⁻¹.

The chemical changes on the surface of the polymer films were monitored by calculating the absorption band area of each polymer during weathering. The band areas were first normalized by dividing each band value by the band value that did not change significantly (internal standard) due to the apparent randomness of the data. The C-H stretching band at 2988 cm⁻¹ were chosen for Paraloid B72, PHB and PLA, respectively, as internal standard (Agarwal, Koelling, and Chalmers 1998; Scalarone, Lazzari, and Chiantore 2012). Calculation of the percent change of normalized peak areas was based on the average area for virgin polymer bands and the area of the weathered polymer bands (Eqn. 1) (Copinet et al. 2004; Furukawa et al. 2005).

\[
\text{% change in area} = 100 \times \frac{\text{Av} - \text{Aw}}{\text{Av}}
\]

(2.1)

where Av and Ad are the area under peak bands for virgin and weathered sample, respectively.
The FT-IR results were expressed as a percentage increase or decrease in the peak area after completion of each exposure cycle. Values above zero indicate decrease in the peak areas, while values below zero indicate increase in the peak areas. A one-tailed paired sample t-test analysis was performed on the band areas to determine whether the final values for areas were statistically different from the original ones.

2.7.2. Determination of Morphological Changes by Scanning Electron Microscopy Analysis (SEM)

Morphological changes of coated limestones and thicknesses of all the polymers on limestone samples were examined before and after weathering test by Scanning Electron Microscope analysis with a FEI QUANTA 250 FEG equipped with an EDX detector (Oxford Azteck).

In the analysis, samples were fixed onto aluminum stubs through carbon adhesive disks and coated with gold to ensure conductivity. Images were collected at different magnitudes by secondary electron detector at a voltage of 3kV. Analyses were carried out at room temperature.

2.8. Determination of Removability of Paraloid B72 After Accelerated Weathering Test

The removability of Paraloid B72 was evaluated to estimate the degree of cross-linking degree by extraction with acetone on 2500 hours weathered limestone samples. The limestone samples were treated in acetone for 24 hours at 23±2°C and 50±3 % relative humidity and the acetone was evaporated. Then, solubility reduction of Paraloid B72 was determined by calculating the % differences of CO₂ and CaO contents of uncoated and Paraloid B72 removed limestone surfaces through SEM-EDX analysis. The removability of PHB and PLA were not tested due to their removability properties.

2.9. Evaluation of the Protection Performances of Polymer Coatings

The long-term protection efficiency of biodegradable polymer coatings (4 parallel samples) were estimated by recording color, capillary water absorption and static contact
angle of the coated samples after each cycle of weathering test. Seven cycles were evaluated in 2500 hours of weathering tests.

2.9.1. Color Measurements

The color change of coated samples was examined with a colorimetric measurement instrument (Avantes) by Avasoft 6.2. Measurements were conducted on the surface with 4mm diameter spot size, D65 daylight illuminant and 10° observer. Measurements were performed at 23±2°C and 50±3 % relative humidity in accordance with CEN standard for conservation of cultural property (UNI EN 15886 2010). For four parallel samples, three measurements were taken on different positions of the surface of each sample. Color coordinates were determined as CIELAB (CIE L*a*b*) values. L* is the lightness (ranging from black to white), a* and b* are the chromatic coordinates (a*: green to red; b*: blue to yellow). Color differences of coated samples were calculated by the following equation (Eqn. 2). The results were expressed as ΔE* values and uncoated limestone slabs were used as reference.

\[ \Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \]  

(2.2)

2.9.2. Measurements of Water Absorption by Capillarity

The amount of water absorbed by capillarity forces were determined by measuring the amount of water that is absorbed by capillarity through the stone surface when it is in contact with water (UNI EN 15801 2010). Measurements were conducted with each coated limestone plate at 23±2°C and 50±3 % relative humidity before and after each period of weathering test in accordance with European Standard.

A dry bedding layer (with filter paper) was placed on the bottom of the vessel. Water was added until the paper was saturated (not exceed the upper surface of the papers) and water level was kept constant during the test (Figure 3).

Before the analysis, samples were dried to a constant weight in an oven at 40°C and kept in a desiccator until the temperature reached 23°C. Each pre-conditioned sample was weighed (m₀) with an analytical balance and, samples were placed on the bedding layer. They were weighed at predefined time intervals (0 sec, 1 sec, 3 sec, 5 sec, 10 sec,
30 min, 60 min, 120 min) until the difference between two successive weighing was not greater than the 1% of the mass of the water absorbed by the specimen.

![Diagram of water absorption](image)

Figure 3. Illustrated drawing of water absorption by capillarity measurements

The water protection efficiency of treated limestones was calculated as percentage change of the amount of absorbed water of coated and weathered limestones (Eqn. 3) (Toniolo et al. 2002).

\[
E\%\ (\text{Protection Efficiency}) = \frac{(Q_i (c) - Q_i (w))}{Q_i (c)} \times 100
\]  

(2.3)

where \( Q_i (c) \) is the amount of absorbed water before weathering and \( Q_i (w) \) is the amount of absorbed water after weathering.

### 2.9.3. Static Contact Angle Measurements

Surface wetting properties of coated limestone samples were investigated by measuring the static contact angle of a water drop on sample surfaces with a Goniometer (Attension Theta). Measurements were conducted at 23±2°C and 50±3 % relative humidity in accordance with European Standard (UNI EN 15802 2010).

For measurement, each polymer coated limestone plate was dried to a constant weight in an oven at 40°C and then kept in a desiccator until the temperature reached 23°C. A micro-pipette filled with deionized water was used to deposit the drop on the sample surface slowly (Figure 4). The measurement was carried out after the deposition of the drop. Six measurements were taken on each sample for four parallel samples to ensure reliable values.
2.9.4. Water Vapor Permeability Measurements

Water vapor permeability of coated limestone samples were determined by measuring the mass of water vapor flow through the limestone by wet cup method in accordance with European Standard test methods (UNI EN 15803 2010).

For the measurement, each polymer coated limestone plate was dried to a constant weight in an oven at 40°C and then kept in a desiccator until the temperature reached 23°C. Cylindrical PVC test cups were filled with water minimum 15mm and air space between sample and water is at least 15mm (Figure 5).

Each pre-conditioned coated limestone plate was weighed (m0) with an analytical balance and, samples were sealed to the cups and placed in a climate-controlled chamber at 23°C and 50 ± 3 % relative humidity. After that, cups were weighed until they reached a constant mass in 24 hours time intervals. The percent reduction of the water vapor permeability (Wp) is obtained with the following equation;
\[ W_p = \frac{G}{A \times \Delta p_v} \]  

(2.4)

G is the mass of water vapor transferred through the sample per time. A is the test surface in m², \( \Delta p_v \) is the water vapor pressure difference across the sample.
CHAPTER 3

RESULTS AND DISCUSSION

Protection efficiencies of poly-lactic acid (PLA), polyhydroxybutyrate (PHB) and Paraloid B72 coatings on limestone were evaluated by accelerated weathering test under combination of UV light, heat and moisture in accordance with CEN standard. Chemical and morphological changes, surface color variations and water protection efficiency of biodegradable polymers on limestone were monitored during accelerated weathering conditions in comparison with a commercially available and a commonly used acrylic polymer in stone conservation.

Weathering induced by accelerated aging test were examined by Fourier Transform Infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) analyses respectively. The chromatic variations of polymer surfaces monitored by color measurements and water protective efficiency of polymer surfaces were determined by water contact angle, water absorption by capillarity and water vapor permeability measurements. The results of the analysis and the discussions are given in this section.

3.1. Coating Thicknesses of the Polymer Films

The uncoated limestone has a slightly rough surface with the presence of small and large grain-sized calcite crystals with diatoms distributed randomly through the stone (Figure 6).

Limestone was coated by each polymer solution using a dip-coating apparatus (Noma dipper) at room temperature with a 100 mm/min immersion rate and 150 mm/min retraction rate. Polymer coatings made the limestone surface smoother and homogeneous, when comparing to the uncoated one.

Paraloid B72 produced a uniform flat surface with 8-10 μm layer thickness on the limestone while PHB produced a coralloid surface with 10-15 μm layer thickness and with pores of mostly smaller than 2 microns. The PLA coating had a surface with 10-15 μm layer thickness and very fine pores approximately 8 microns in size, which were regularly distributed and interconnected with each other (Figure 6).
Figure 6. SEM images of uncoated and coated limestone surfaces
3.1.1. Surface Color of Uncoated and Coated Limestone

Color stability of coated stone surfaces is an important factor used in the selection of polymers in the protection and preservation of stones. A polymer used as coating material on stone surfaces should not significantly change surface color. The acceptable total color change ($\Delta E^*$) should be lower than 5, the standard accepted by the International Conservation Community of Historic Monuments and Buildings (Illescas and Mosquera 2012), whereas the human eye perception threshold is lower than 3 (Berns, Billmeyer, and Saltzman 2000; De Rosario et al. 2015).

In this study, the effects of coatings on the color of the limestone were determined using a Handheld Reflection Spectrophotometer by taking three measurements on different positions of uncoated and coated limestone surface. Color values were indicated by L* (lightness= black to white), a* (green to red) and b* (blue to yellow) in Figure 7. Also, color changes after coating with polymers were indicated by $\Delta L^*$, $\Delta a^*$, $\Delta b^*$ and $\Delta E^*$ (total color change) values in Figure 8.

The L*, a* and b* values of uncoated limestone were 62.5, 0.4 and 5.1 respectively. The L* value of Paraloid B72 coated limestone were lower than the uncoated limestone. However, the a* (green to red) and b* values (blue to yellow) were higher than uncoated limestone (Figure 7). The total color change ($\Delta E^*$) of Paraloid B72 coated limestone was 8.01 (Figure 8) which is higher than the value (5) reported by the International Conservation Community of Historic Monuments and Buildings. These results indicate that the surface of the limestone surface was slightly darkened after coating with Paraloid B72 and it caused yellowness on the limestone surface while considering L* and b* values. Changes in the surface color of the limestone may be due to the a-methyl group in the ester group of Paraloid B72 (Melo et al. 1999; Lazzari and Chiantore 2000; Chiantore and Lazzari 2001; Favaro et al. 2006; Giuntoli et al. 2014). Similar color changes were also observed with the acrylic polymers on marble surfaces caused darkness which was resulted by the lower lightness values ($\Delta L^*\sim-2$) of the coated stone surface (Toniolo et al. 2002). In addition, the acrylic polymers caused yellowing on the marble surfaces (Melo et al. 1999).

The L* value of PHB coated limestones was higher than the uncoated limestone. The a* and b* values of PHB coated limestone was found to be lower than the uncoated limestone (Figure 7). The $\Delta E^*$ value of PHB coated limestones was 2.72 which was lower than the threshold for human eye perception value (<3) (Figure 8). Color compatibility of PHB was evaluated by Andreotti et al (2018) and results showed that
PHB exhibited lower ΔE* on sandstone, limestone and marble samples respectively (Andreotti, Franzoni, and Fabbri 2018).

The L* and a* values of PLA coated limestones were lower than the uncoated limestone. The b* value of PLA coated limestones was higher than the uncoated limestone (Figure 7). The ΔE* value of PLA was 3.15 which is near the threshold for human eye perception value (<3) (Figure 8). However, it can be said that PLA caused negligible color change on limestone surface due to high crystallization of PLA which forming a film with a low visible light-absorbing property (Auras, Harte, and Selke 2004). Similar results were obtained with PLA coated stones as the L* value of the surface decreased which resulted in darkening of the stone surface (Giuntoli, Frediani, et al. 2012; Sacchi et al. 2012).

As a result, the highest L* value was determined in Paraloid B72 coated limestones, and PHB and PLA coated limestones showed values close to L* value of uncoated limestones. It was also determined that, on the uncoated and coated limestone surfaces, the a* values were insignificant, but the b* value indicating the yellowness of the surface was higher with Paraloid B72 and lower with PHB coated limestones. Consequently, considering ΔL*, Δb* and ΔE* values in the total color change values
graph in Figure 8, it is seen that Paraloid B72 causes the highest color change values on limestone surface. The PHB and PLA coated limestones showed lower color change values near the human eye perception value (<3). Eventually, it can be said that PHB and PLA are suitable polymer coatings when considering color compatibility for the conservation of stones.

![Figure 8. Color change values of polymer coated limestones (ΔL*, Δa*, Δb* and ΔE*)](image)

### 3.2. Water Protection Efficiency of Coatings on Limestone

Water protection efficiency for coatings on limestone samples were determined using water absorption by capillary, static contact angle and water vapor permeability measurements.

### 3.2.1. Water Absorption Capacity of Uncoated and Coated Limestone

Water absorption capacity of uncoated and polymer coated limestone were determined by measuring the amount of water that is absorbed by capillarity (Qi) through the stone surface when it is in contact with water. In addition to that, water protection efficiency of coated limestones was calculated as percentage change of the amount of absorbed water of uncoated and coated limestone (Figure 9).
The amount of absorbed water of uncoated limestone was found as 0.16 kg/m² (Q1) due to the higher interconnectivity of the pores in the uncoated limestone. Polymer coatings decreased the water absorption capacity of limestone by reducing its pore connectivity (Figure 9) (Cultrone and Madkour 2013).

After coating with Paraloid B72, the amount of water absorbed by the limestone drastically decreased from 0.16 kg/m² to 0.03 kg/m² which showed that Paraloid B72 provided 81 % protection efficiency.

PHB coatings decreased insignificantly the amount of absorbed water providing 39 % protection efficiency. Similar water protection efficiencies of PHB on limestone and marble were also found in studies carried out by Andreotti, Franzoni, and Fabbri 2018 and Ocak et al. 2009.

Higher reduction was seen on the PLA coated limestone by providing the highest protective shield against water as 91 %. Similar results were obtained with PLA as a coating material on marble samples between 80 % and 90 % (Yılmaz Ocak et al. 2009; Yılmaz Ocak et al. 2015; Giuntoli, Rosi, et al. 2012; Pinho, and Pedna 2014).

These results indicated that PLA and Paraloid B72 coatings provided higher protection than that of PHB coatings (Figure 9).

![Figure 9. Water absorption by capillarity values uncoated and coated limestones and water protection efficiencies of polymers](image-url)

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3.2.2. Hydrophobicity of Uncoated and Coated Limestone

Hydrophobicity of uncoated and coated limestone samples were investigated by measuring the static contact angle of a water drop on sample surface with a Goniometer meter (Attension Theta).

The ideal polymer coatings should increase the contact angle of stone greater than 90° (Buergo and González 2001). Hydrophobicity of a surface directly related with the surface roughness (microstructure) and chemical heterogeneities of the stone and the coverage of the stone by polymer and the amount of polymer absorbed by the stone (Torrissi 2008). Polymer coatings reduce the surface roughness, chemical heterogeneity, surface free energy and minimize the contact area between water droplets, air and treatment surface.

In this study, the water contact angle of limestone was determined as 30°, indicating the hydrophilicity of limestone surface. Polymer treatment increased the contact angle of limestone. Paraloid B72 and PHB treatments increased the contact angle to 80° and 92°, respectively, which was a borderline case and would almost be accepted as hydrophobic (Figure 10).

![Contact Angle Chart](image)

Figure 10. Water contact angle values of uncoated and coated limestone surfaces
The highest contact angle value was obtained on PLA coated limestones around 125°, which was above the borderline of hydrophobicity (Figure 10). The hydrophobicity of a surface directly related with the surface free energy (or coating material) and surface roughness (microstructure) (Shen et al. 2015). PLA coating significantly increased the surface hydrophobicity, by increasing the surface roughness more than those of Paraloid B72 and PHB (Figure 11). PHB produced a coralloid surface with pores (2 microns) on the limestone and reduced the surface free energy more than Paraloid B72 (Figure 11).

Contact angle measurements showed that PLA and PHB coatings significantly increased the hydrophobicity of limestone surfaces. However, Paraloid B72 coatings did not provide a significant hydrophobic surface on the limestone.

![Uncoated Limestone](image1)

![Coated (0 h)](image2)

![PARALOID B72](image3)

![PHB](image4)

![PLA](image5)

Figure 11. SEM images of uncoated and coated limestones and their contact angle values

### 3.2.3. Water Vapor Permeability of Uncoated and Coated Limestone

Water vapor permeability of coated limestone samples were determined by measuring the mass of water vapor flow through the limestone by wet cup method (EN 15803, 2010).

The water vapor permeability of uncoated limestone was 1.7E-05 g/(m×s×Pa). All the polymer coatings reduced the water vapor permeability of limestone (Figure 12). The reduction in water vapor permeability of coated limestones were calculated as 81±3.26
%, 77±6.22 % and 90±3.53 % with Paraloid B72, PHB and PLA respectively. These drastic reductions can be related with the higher water-repellent character of the polymer coatings (Toniolo et al. 2002).

Figure 12. Water vapor permeability and reduction of water vapor permeability values of uncoated and coated limestones

3.3. Long-term Durability of Polymer Coatings on Limestone Surface

Accelerated weathering tests were carried with polymer coated limestone and polymer films up to 2500 hours in order to determine the long-term durability of polymer coatings on limestone surface. Long term stability of coatings was estimated by monitoring the chemical and morphological changes on coated limestones and polymer films by FT-IR and SEM analysis. Parallel with the chemical stability of coatings, the long-term durability of polymer coatings on limestones was estimated by recording color, capillary water absorption, static contact angle and water vapor permeability at specified time intervals between 0, 250, 500, 1000, 1500, 1750, 2000 and 2500 hours of weathering tests. The results of the analysis were given in the next section.

Long term stability of Paraloid B72, PHB and PLA films were determined with Fourier transform-infrared (FT-IR) spectroscopy by following the chemical changes of polymer films after predefined time intervals of weathering test up to 2500 hours.

The chemical changes were recorded by calculating the areas of absorption bands on the FT-IR spectra. Due to apparent randomness of the data, the band areas were normalized by dividing each band value by the band value that did not change
significantly (internal standard). The C-H stretching band at 2988 cm⁻¹ were chosen as internal standard (Wojciechowski et al. 2015; Pinho and Pedna 2014). The results were expressed as a percentage increase or decrease in the areas after completion of each exposure cycle. A one-tailed paired sample t-test analysis was performed on the band areas to determine whether the final values for areas were statistically different from the original ones.

3.3.1. Paraloid B72

The FT-IR spectrum of virgin Paraloid B72 showed the characteristic bands of –OH stretching at 3750-3250 cm⁻¹, C-H stretching at 2982 cm⁻¹, -C=O ester carbonyl stretching at 1730 cm⁻¹, -C-H deformation at 1475-1450 cm⁻¹, -C-O- ester stretching at 1365-1024 cm⁻¹ and -C-C stretching at around 860 cm⁻¹ (Figure 13) (Lazzari and Chiantore 2000; Melo et al. 1999). Peak band assignments and corresponding positions of Paraloid B72 were given in the Figure 13 and Table 7.

![FT-IR spectrum of virgin Paraloid B72](image)

Figure 13. FT-IR spectrum of virgin Paraloid B72
Table 7. Peak band assignments for Paraloid B72 spectra

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Peak position, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH stretching</td>
<td>3750-3250</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>2982</td>
</tr>
<tr>
<td>-C=O ester carbonyl stretching</td>
<td>1730</td>
</tr>
<tr>
<td>-C-H deformation</td>
<td>1475-1450</td>
</tr>
<tr>
<td>-C-O ester stretching</td>
<td>1365, 1024</td>
</tr>
<tr>
<td>-C-C stretching</td>
<td>860</td>
</tr>
</tbody>
</table>

The FT-IR spectra of virgin and weathered Paraloid B72 films were compared after 1000 hours weathering test. Results of the analysis showed that the degradation of Paraloid B72 started after 25 hours of weathering until 1000 hours as reduction and broadening at -C=O ester stretching bands (1730 cm\(^{-1}\), 1360 cm\(^{-1}\)), -C-H deformation bands (1470-1450 cm\(^{-1}\)), and -C-C stretching band (988 cm\(^{-1}\)). In addition, -OH stretching bands (3750-3250 cm\(^{-1}\)) increased and a new weak band formed at around 1645 cm\(^{-1}\) (C=C) (Figure 14).

![Figure 14. FT-IR spectrum of the virgin and weathered Paraloid B72 samples](image-url)
The degradation process could be summarized as follows: First, initial oxidation starts with the addition of oxygen to the radicals of abstraction of tertiary hydrogen of methacrylate units by UV-irradiation. Then decomposition of carboxyl lead to the formation of ketones which resulted in a decrease at carbonyl groups especially carbonyl ester band. Then, a chain scission occurred and hydroperoxides formed and resulted in an increase of the hydroxyl bands which indicates hydrophobic behavior of the coating. Also, hydroperoxides caused formation of gamma lactones at the end of the process. The formation of gamma lactones resulted the decreasing and broadening of carbonyl peak.

And overall decrease of the main absorption bands during the UV treatment because of the decrease in molecular weight of the Paraloid B72 (Figure 15).

Figure 15. The degradation process of Paraloid B72 after 1000 hours of weathering

Statistical analysis confirmed that the mean peak area for 25 hour-weathered Paraloid B72 were found to be significantly lower (5% statistical significance level) compared to the mean peak area of virgin Paraloid B72 (Table 8).
Table 8. Results of the one-tailed paired sample welch approximation t-test with peak mean areas of polymer spectra of virgin and weathered samples

<table>
<thead>
<tr>
<th></th>
<th>Paraloid B72</th>
<th>PHB</th>
<th>PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Mean (% change)</td>
<td>180.2</td>
<td>49</td>
<td>78.7</td>
</tr>
<tr>
<td>T-Test (P Value)</td>
<td>0.07**</td>
<td>0.06**</td>
<td>0.39***</td>
</tr>
<tr>
<td>Null Hypothesis</td>
<td>1000h and 0h peak values are identical</td>
<td>Reject the null hypothesis: 2500h and 0h peak values are identical</td>
<td>Reject the null hypothesis: 2500h values are identical</td>
</tr>
<tr>
<td>Result</td>
<td>1000h values are significantly lower</td>
<td>2500h values are significantly lower</td>
<td>2500h values are significantly lower</td>
</tr>
</tbody>
</table>

*denotes significance at 10 %, **5 %, ***1 %

The observed chemical changes on FT-IR spectra were expressed as a percentage increase or decrease in the peak area after completion of each exposure cycle (Table 9, Figure 16). The variations observed due to chemical changes at the absorption bands after 25 hours of weathering until 1000 hours of weathering was summarized as follows:

- The absorption bands of hydroxyl groups between 3750 and 3250 cm\(^{-1}\) (OH-) increased.
- The absorption band of carbonyl at around 1730 cm\(^{-1}\) (-C=O ester stretching) decreased.
- The absorption bands between 1470-1450 cm\(^{-1}\) (-C-H deformation) decreased.
- The absorption bands of carbonyl at 1365 cm\(^{-1}\) (-C-O ester stretching) decreased.
- The absorption band at 988 cm\(^{-1}\) (-C-C stretching) decreased.

Table 9. % changes in the absorption band areas of the Paraloid B72 (“↑” symbol presented the increase of the band area, “↓” symbol presented the decrease of the band area)

<table>
<thead>
<tr>
<th></th>
<th>3750-3250 cm(^{-1})</th>
<th>1730 cm(^{-1})</th>
<th>1470-1450 cm(^{-1})</th>
<th>1365 cm(^{-1})</th>
<th>988 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 hours</td>
<td>↑ 50</td>
<td>↓ 73</td>
<td>↓ 62</td>
<td>↓ 20</td>
<td>↓ 66</td>
</tr>
<tr>
<td>125 hours</td>
<td>↑ 56</td>
<td>↓ 79</td>
<td>↓ 78</td>
<td>↓ 81</td>
<td>↓ 85</td>
</tr>
<tr>
<td>250 hours</td>
<td>↑ 89</td>
<td>↓ 94</td>
<td>↓ 96</td>
<td>↓ 99</td>
<td>↓ 98</td>
</tr>
<tr>
<td>375 hours</td>
<td>↑ 52</td>
<td>↓ 99</td>
<td>↓ 99</td>
<td>↓ 100</td>
<td>↓ 100</td>
</tr>
<tr>
<td>500 hours</td>
<td>↑ 194</td>
<td>↓ 81</td>
<td>↓ 82</td>
<td>↓ 82</td>
<td>↓ 90</td>
</tr>
<tr>
<td>1000 hours</td>
<td>↑ 178</td>
<td>↓ 96</td>
<td>↓ 96</td>
<td>↓ 100</td>
<td>↓ 99</td>
</tr>
</tbody>
</table>
Figure 16. % changes in the absorption band areas of the Paraloid B72 peaks after the normalization to –C–H stretching at 2988 cm\(^{-1}\) during accelerated weathering tests.

Results of the FT-IR analysis showed that after 25 hours of weathering the hydroxyl group bands started to increase rapidly due to the formation of carboxylic acid and hydroperoxides, which may also attribute to the chain scission and the formation of tertiary hydroperoxides and their oxidation. The oxidation of hydroperoxides resulted in an extensive hydrogen bonding showed that Paraloid B72 absorb molecular water. This means that polymer film started to lose hydrophobicity and also its water protection efficiency was lost which also proven by similar studies (Agarwal, Koelling, and Chalmers 1998; Melo et al. 1999; Lazzari and Chiantore 2000; Chiantore and Lazzari 2001; Copinet et al. 2004; Sadi, Fechine, and Demarquette 2010; Rasselet et al. 2014; Olewnik-Kruszkowska et al. 2015; Pedna et al. 2015, 2016).

In addition, at the beginning of weathering tests carbonyl group bands (-C=O and -C-O ester stretching) were broadened and decreased which could be related with the hydrolysis of ester linkages. The hydrolysis of ester linkages resulted in the decrease of average molecular weight and breaking down of long macro molecular chains according to similar studies which tested the durability of Paraloid B72 under accelerated weathering conditions. In various accelerated-aging conditions, weathering of Paraloid B72 was given in Table 1.
Also, the formation of weak band around 1645 cm\(^{-1}\) (C=C) could be the product of the formation of small fragments and was followed by molar mass decrease by chain scissions causing the polymer to acquire a yellowish hue according to similar studies (Chiantore and Lazzari 2001; Gardette et al. 2011; Rasselet et al. 2014; Olewnik-Kruszkowska et al. 2015). However this band was formed at different time intervals with different studies such as after 1000 hours weathering by Melo et al. 1999 and after 1500 hours weathering by Favar et al. 2006.

All the FT-IR analysis results indicated that Paraloid B72 was degraded by hydrolysis of ester linkages and breaking down of long macromolecular chains. Accordingly, Paraloid B72 began to absorb more water, lost it hydrophobicity and acquired a yellowish hue after 1000 hours accelerated weathering.

### 3.3.2. Polyhydroxybutyrate (PHB)

The FT-IR spectrum of virgin PHB showed the characteristic bands of –OH stretching at 3430 cm\(^{-1}\), –C-H stretching at 2973 cm\(^{-1}\), –C=O ester stretching at 1730 cm\(^{-1}\), C-H deformation at 1450–1350 cm\(^{-1}\), C–O– stretching ester at 1277–1054 cm\(^{-1}\) and -C-C- stretching at 978 cm\(^{-1}\) (Copinet et al. 2004; Furukawa et al. 2005). Peak band assignments and corresponding positions are given in Figure 17 and Table 10.
Table 10. Peak band assignments for PHB spectra

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Peak position, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH stretching</td>
<td>3430</td>
</tr>
<tr>
<td>-C-H stretching</td>
<td>2973</td>
</tr>
<tr>
<td>-C=O ester stretching</td>
<td>1730</td>
</tr>
<tr>
<td>-C-H deformation</td>
<td>1450-1350</td>
</tr>
<tr>
<td>C-O- stretching</td>
<td>1277-1054</td>
</tr>
<tr>
<td>-C-C stretching</td>
<td>980</td>
</tr>
</tbody>
</table>

The chemical changes were observed at the absorption bands of PHB after 1000 hours (Figure 18). Results of the analysis showed that the degradation of PHB started after 1000 hours weathering at -OH stretching band (3440 cm\(^{-1}\)), -C=O ester stretching bands (1730 cm-1377 cm\(^{-1}\)), -C-H deformation band (1452 cm\(^{-1}\)), and -C-C stretching band (978 cm\(^{-1}\)). In addition, a new weak band formed at around 1845 cm\(^{-1}\) (C=O-) and the CO\(_2\) region at 2200 cm\(^{-1}\) was increased.

![Figure 18. FT-IR spectrum of the virgin and weathered PHB samples](image-url)
The degradation process of PHB similar to the Norrish type 1 reaction, where radicals are formed in the presence of UV-irradiation (Wei and McDonald 2016). These free radicals initiated the chain cleavage and the carbonyl group converted to a carbon dioxide molecule.

As a result, a decrease in carbonyl peaks observed in the FT-IR spectra. And also, CO₂ gradually increased due to UV-irradiation. In addition, due to presence of water, hydrolysis of ester groups occurred, and acids are generated. This acidic environment caused a decrease in the carbonyl groups. The decrease of OH⁻ band which is associated with hydrogen bonded (-OH) groups indicated that a hydrophilic material had been created, due to the disappearance of hydrophilic OH⁻ group (Figure 19).

![Degradation process of PHB](image)

Figure 19. Degradation process of PHB

One-tailed paired sample t-test analysis confirmed the statistical significance of the difference between the mean peak areas at 0 and 2500 hours weathered PHB were found to be significantly lower (1 % statistical significance level) compared to mean peak area of virgin PHB (Table 8).
The observed chemical changes on FT-IR spectra were expressed as a percentage increase or decrease in the peak area after completion of each exposure cycle (Figure 20, Table 11). The variations observed due to chemical changes at the absorption bands after 1000 hours weathering was summarized as follows;

- The hydroxyl group bands (-OH) at around 3440 cm⁻¹ decreased.
- The absorption band of ester carbonyl band (–C=O) at 1730 cm⁻¹ decreased.
- The absorption band at 1452 cm⁻¹ (-C-H deformation) decreased.
- The absorption bands of carbonyl at 1377 cm⁻¹ (-C-O ester stretching) decreased.
- The stretching band (–C-C) at 978 cm⁻¹ decreased.

Results of the FT-IR analysis showed that, starting with 1000 hours of weathering hydroxyl group bands were decreased which may be related to thermal decomposition of tertiary hydroperoxides (Melo et al. 1999; Lazzari, and Chiantore 2000; Copinet et al. 2004; Sadi, Fechine, and Demarquette 2010; Pedna et al. 2015). The decrement of these bands indicated that a hydrophilic material had been created, due to the disappearance of hydrophilic -OH group (Copinet et al. 2004).

The carbonyl group bands were broadened and decreased due to the hydrolysis of ester linkages which may be related with the decrease in the average molecular weight and breaking down of long macro molecular chains (Agarwal, Koelling, and Chalmers 1998; Wei, and McDonald 2016).

The formation of weak band around 1845 cm⁻¹ (-C=O) could be the acetic anhydride formation which resulted in decrement of strength of the polymer (Gardette et al. 2011; Rasselet et al. 2014; Olewnik-Kruszkowska et al. 2015).

Furthermore, decrease in –C-C stretching at 978 cm⁻¹ may related with the change in the degree of crystallinity of the polymer, leading to a decrease in density, stiffness and strength of the polymer film (Agarwal, Koelling, and Chalmers 1998; Rasselet et al. 2014).

Consequently, PHB was degraded by thermal decomposition of tertiary hydroperoxides, hydrolysis of ester linkages and breaking down of long macromolecular chains, formation of acetic anhydride. Accordingly, it can be said that PHB began to lose its hydrophobicity after 250 hours accelerated weathering and became more fragile.
Figure 20. % changes in the absorption band areas of the PHB peaks after the normalization to –C–H stretching at 2988 cm⁻¹ during accelerated weathering tests.

Table 11. % changes in the absorption band areas of the PHB (“↑” symbol presented the increase of the band area, “↓” symbol presented the decrease of the band area)
3.3.3. Poly-Lactic Acid (PLA)

The FT-IR spectrum of virgin PLA showed the characteristic bands of -OH stretching at 3723-3636 cm\(^{-1}\), -C–H stretching at 2988 cm\(^{-1}\), -C=O ester stretching at 1771 cm\(^{-1}\), -CH- deformation at 1450-1350 cm\(^{-1}\), -C-O- ester stretching at 1277-1055 cm\(^{-1}\) and -C-C- stretching at 872 cm\(^{-1}\) (Meaurio, López-Rodríguez, and Sarasua 2006; Rasselet et al. 2014). Peak band assignments and corresponding positions were given in the Figure 21 and Table 12.

![FT-IR spectrum of PLA before weathering](image)

Figure 21. FT-IR spectrum of PLA before weathering

The chemical changes were observed at the absorption bands of PHB after 1000 hours (Figure 22). Results of the analysis showed that the degradation of PLA started after 1000 hours at -C=O ester stretching band (1730 cm\(^{-1}\), 377 cm\(^{-1}\)), -C-H deformation band (1452 cm\(^{-1}\)), -C-C stretching band (978 cm\(^{-1}\)) and they gradually broaden and decreased until 2500 hours of weathering. In addition, the CO\(_2\) region at 2200 cm\(^{-1}\) was increased.
Table 12. Peak band assignments for PLA spectra

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Peak position, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH stretching</td>
<td>3468-3626</td>
</tr>
<tr>
<td>-C-H stretching</td>
<td>2988</td>
</tr>
<tr>
<td>-C=O ester stretching</td>
<td>1750</td>
</tr>
<tr>
<td>-C-H deformation</td>
<td>1455, 1383-1360</td>
</tr>
<tr>
<td>-C-O ester stretching</td>
<td>1266-1054</td>
</tr>
<tr>
<td>-C-C- stretching</td>
<td>873</td>
</tr>
</tbody>
</table>

Figure 22. FT-IR spectrum of the virgin and weathered PLA samples

The initial oxidation of the PLA started with the hydrogen abstraction on the polymeric backbone at the tertiary carbon of the ester function leading to macroradicals. This radical reacts with oxygen, and lead to a peroxy radical that gives hydroperoxide by abstraction of a labile hydrogen atom which propagates the chain reaction oxidation. This hydroperoxide caused an increase at the hydroxyl bands which resulted in a hydrophobic material. The formed hydroperoxides can decompose and lead to the formation of alkoxy
and hydroxyl radicals. This macroradicals (alkoxy) is the key intermediate in the reaction and decompose by β-scission. Finally, major degradation mechanism during the ageing of PLA under irradiation is the formation of anhydrides at 1845 (C=O) and an overall decrease at carbonyl groups due to the decrement of PLA molecular weight.

To conclude, PLA degrade up to half elimination of the coating from the stone surface starting with the 1000 h of ageing. Furthermore, hydroxyl group bands increased because of the molecular water absorption of PLA, whereas carbonyl group bands decreased due to the formation of gamma lactones and anhydrides formed due to UV-irradiation (Figure 23).

![Figure 23. The degradation process of PLA](image)

One-tailed paired sample t-test analysis confirmed the statistical significance of the difference between the mean peak areas at 0 and 2500 hours weathered PLA were found to be significantly lower (1 % statistical significance level) compared to mean peak area of virgin PLA (Table 8). The observed chemical changes on FT-IR spectra were expressed as a percentage increase or decrease in the peak area after completion of each exposure cycle (Figure 24, Table 13).
The variations observed due to chemical changes at the absorption bands after 1000 hours weathering was summarized as follows:

- The hydroxyl group bands (-OH) at around 3723-3363 cm\(^{-1}\) increased.
- The absorption band of ester carbonyl band (–C=O) at 1771 cm\(^{-1}\) decreased.
- The absorption band at 1454 cm\(^{-1}\) (-C-H deformation) decreased.
- The absorption bands of carbonyl at 1350 cm\(^{-1}\) (-C-O ester stretching) decreased.
- The stretching band (–C-C) at 872 cm\(^{-1}\) decreased.

![Graph showing the percentage change in absorption band areas of PLA peaks](image)

Figure 24. % changes in the absorption band areas of the PLA peaks after the normalization to –C–H stretching at 2988 cm\(^{-1}\) during accelerated weathering tests.

Results of the FT-IR analysis, a negligible increase was seen at the hydroxyl group bands of PLA during weathering test. In addition to that, the decrease of carbonyl group bands was lower which means that the hydrolysis of ester linkages didn’t significantly take place after weathering and as a result the decrease in average molecular weight and breaking down of long macro molecular chains slower considering the PHB.
Table 13. % changes in the absorption band areas of the PLA (“↑” symbol presented the increase of the band area, “↓” symbol presented the decrease of the band area)

<table>
<thead>
<tr>
<th></th>
<th>3723-3363 cm⁻¹</th>
<th>1771 cm⁻¹</th>
<th>1454 cm⁻¹</th>
<th>1350 cm⁻¹</th>
<th>872 cm⁻¹</th>
</tr>
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<tbody>
<tr>
<td>25 hours</td>
<td>↑ 76</td>
<td>↓ 28</td>
<td>↓ 31</td>
<td>↑ 9</td>
<td>↑ 48</td>
</tr>
<tr>
<td>125 hours</td>
<td>↑ 17</td>
<td>↑ 2</td>
<td>↓ 7</td>
<td>↑ 1</td>
<td>↓ 12</td>
</tr>
<tr>
<td>250 hours</td>
<td>↑ 12</td>
<td>0</td>
<td>↓ 5</td>
<td>↓ 5</td>
<td>↑ 14</td>
</tr>
<tr>
<td>375 hours</td>
<td>↑ 3</td>
<td>0</td>
<td>0</td>
<td>↑ 16</td>
<td>↑ 3</td>
</tr>
<tr>
<td>500 hours</td>
<td>↑ 4</td>
<td>↑ 3</td>
<td>↓ 2</td>
<td>↑ 7</td>
<td>↑ 19</td>
</tr>
<tr>
<td>1000 hours</td>
<td>↑ 31</td>
<td>↑ 5</td>
<td>↓ 2</td>
<td>0</td>
<td>↑ 28</td>
</tr>
<tr>
<td>1500 hours</td>
<td>↑ 6</td>
<td>↓ 56</td>
<td>↓ 67</td>
<td>↑ 5</td>
<td>↓ 32</td>
</tr>
<tr>
<td>2000 hours</td>
<td>↑ 80</td>
<td>↓ 51</td>
<td>↓ 51</td>
<td>↓ 59</td>
<td>↑ 2</td>
</tr>
<tr>
<td>2250 hours</td>
<td>↑ 89</td>
<td>↓ 20</td>
<td>↓ 12</td>
<td>↓ 76</td>
<td>↓ 4</td>
</tr>
<tr>
<td>2500 hours</td>
<td>↓ 19</td>
<td>↓ 90</td>
<td>↓ 92</td>
<td>↓ 75</td>
<td>↓ 82</td>
</tr>
</tbody>
</table>

In contrast with the PHB and Paraloid B72, the increase of -C-C stretching band related with the change in the degree of crystallinity of the polymer, leading to an increase in density, stiffness and strength. This may relate with the increased temperature, improving physical characteristics of the polymer (60°) (Pedna et al. 2015).

Furthermore, the formation of a weak band around at 1845 cm⁻¹ (C=O-) may attributed to the lactic acid impurities and the -C=O stretching of lactic acid’s anhydride, originated by solid state reaction of monomeric lactic acid residue and/or slight depolymerization processes in the PLA chain.

Similar result was detected by FT-IR after 90 hours of weathering (Giuntoli, Frediani, et al. 2012; Giuntoli, Rosi, et al. 2012; Pedna et al. 2015). In addition, the formation of a new band in the CO₂ region at 2200 cm⁻¹ may be the related with the UV irradiation (Lim, and Kim 2016).

According to the results of FT-IR analysis, it was determined that the degradation of PLA was slower than the PHB and Paraloid B72. After 2500 hours weathering PLA still protected its hydrophobicity and breaking down of long macro molecular chains process didn’t significantly take place.
3.3.4. Morphological Changes of Polymer

The morphological changes on the Paraloid B72, PHB and PLA coated limestones were investigated after 2500 hours weathering test with Scanning Electron Microscopy analysis (SEM). After weathering tests all polymer coatings showed signs of chemical changes that caused surface damages (Figure 25).

Figure 25. SEM images of Paraloid B72, PHB and PLA coated limestones before and after weathering (2500 hrs).
The weathered Paraloid B72 coated limestones became slightly rough due to the surface erosion and etching (material removal) (Figure 26). The surface erosion originated from mainly thermo-degradation and UV irradiation by breaking down long macro molecular chains (Ghosh, Pal, and Ray 2013, Hidalgo Schulz et al. 2018). Breaking down of long macro molecular chains resulted in etching (Vesel and Semenič 2012).

In addition, solubility reduction of Paraloid B72 was investigated by removing the polymer on limestone surface with acetone and calculating the % differences of CO₂ and CaO contents of uncoated and Paraloid B72 removed limestone surfaces through SEM-EDX analysis. SEM-EDX analysis indicated that between 4-9 % solubility reduction of Paraloid B72 was observed possibly due to the effect of fast and extensive breaking down of the long ester groups (Figure 27) (Lazzari, and Chiantore 2000).

![Figure 26. SEM images of Paraloid B72 coated limestones before and after weathering](image)

![Figure 27. SEM images of uncoated (a) and Paraloid B 72 removed limestone (b) surfaces and their % oxide compositions.](image)
After 2500 hours the surface of the weathered PHB coated limestones became like a sponge, number of the pores were increased, and the mean diameter of the pores decreased from 2 μm to 1.01 μm. Erosion, etching, cracks, holes and voids were observed on the PHB coated limestone surface (Figure 28). The surface of the PHB coated limestone became rougher by thermos-degradation and UV-irradiation (Hidalgo Schulz et al. 2018). Thermo-degradation mainly occurred by breaking down long macro molecular chains of the polymer (Ghosh, Pal, and Ray 2013).

Figure 28. SEM images of PHB coated limestones after 2500 hours weathering test
Etching resulted from the abstraction of a hydrogen atom and the formation of free radicals which leads to chain cleavage and low molecular weight (Vesel, and Semenić 2012). In addition, cracks showed that the crystallinity of the polymer increased with the hydrolytic degradation. The increased crystallinity reduced the permeability and PHB became brittle (Sadi, Fechine, and Demarquette 2010). As a result, the degradation of PHB began with surface erosion and cracks, showed that the degradation process of PHB was thermos-degradation and polymer film partially detached from the limestone surface after 2500 hours weathering.

Also, calcite crystals detected in the pores of the PHB coated limestones surface. Crystals were composed of 84.05 % CaO, 11.30 % SiO₂ and 4.65 MgO % while limestone composed of 56.6 % CaO, 26.5 % SiO₂ (Figure 29).

![Before Weathering](image1). ![After Weathering (2500hrs)](image2)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Oxide %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>4.65</td>
</tr>
<tr>
<td>SiO₂</td>
<td>11.30</td>
</tr>
<tr>
<td>CaO</td>
<td>84.05</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 29. SEM images of PHB coated limestone samples before and after weathering test and EDX analysis of calcite crystals
Figure 30. SEM images of PLA coated limestones after 2500 hours weathering test

Considering PLA coated limestones after 2500 hours weathering, PLA gradually detached from the limestone surface and irregular crazes, cracks and etching were indicated on the surface (Figure 30).

The PLA is generally stable to hydrolysis from 20 to 45° C and absorbs a small amount of water, starting to absorb more water over these temperatures. (Gaurav, Rafael, and Paul 2006). Irregular crazes and cracks indicate that the PLA became brittle by the hydrolysis of the ester linkages with the absorbed water and absorbed water accelerated the fragmentation of the polymer matrix (Ndazi, and Karlsson 2011; Dong et al. 2013).
Etching related with the breaking down of long macromolecular chains and low molecular weight (Vesel, and Semenič 2012). Detachment of PLA from the limestone surface related with the erosion of the surface due to UV light, heat and moisture. In addition, the hydrolysis of the PLA increased the crystallinity of the polymer and resulted in the overall opacity of the polymer (Delcourt et al. 2004). According to the results, the degradation of PLA began with surface erosion and cracks, indicating that the PLA is hydrolytically degraded.

3.3.5. Surface Color Changes

The L*, a* and b* values of uncoated limestone were 62.5, 0.4 and 5.1 respectively. After coating with Paraloid B72 limestone surface was slightly darkened and surface became yellow considering significantly lower L* and higher b* values (Table 14). During weathering test, the L* values of Paraloid B72 coated limestones were fluctuated and follow a linear trend (Table 14).

A* value of Paraloid B72 coated limestone was lower than the uncoated limestone. During weathering test, a* values were fluctuated but the trend was slightly downward (Table 14).

Coating with Paraloid B72 caused a yellow color on limestone surface, however, b* values tend to be decreased during weathering test (Figure 31). Similar result was obtained by Melo et al. 1999 after photodegradation of Paraloid B72 coated marble. Also, no yellowing was measured with Paraloid B72 coated marbles evaluated by Toniolo et al (2002).

The total color change (ΔE*) of Paraloid B72 coated limestone was 8.01. After 2500 hours weathering ΔE* value of Paraloid B72 coated limestone was decreased to 5.69 which was near the accepted value (5) for the conservation of cultural heritage reported by the International Conservation Community of Historic Monuments and Buildings (Figure 31). Similar results were obtained by Favaro et al. 2006 with Paraloid B72 on marble surfaces (Figure 32). According to the study, Paraloid B72 caused color changes as ΔE*~14 on marble surface and after 2000 hours of weathering as ΔE*~7.

Paraloid B72 caused changes in the surface color of different stones due to the a-methyl group in the ester group of Paraloid B72. However, color values tend to decrease which may be related with the polymer loss and reorganization of the polymer film due to exposition to accelerated weathering conditions (Pedna et al. 2015) (Figure 32).
Table 14. CIELAB (L*, a* and b*) color values of uncoated, coated and weathered limestone samples

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th></th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B72 PHB</td>
<td>PLA</td>
<td>B72 PHB</td>
<td>PLA</td>
<td>B72 PHB</td>
<td>PLA</td>
</tr>
<tr>
<td>uncoated</td>
<td>62.5±0.8</td>
<td>60.6</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>8.1</td>
</tr>
<tr>
<td>coated</td>
<td>±1.2</td>
<td>±1.9</td>
<td>±0.1</td>
<td>±0.3</td>
<td>±0.1</td>
<td>±0.9</td>
</tr>
<tr>
<td>250 hrs</td>
<td>±1.3</td>
<td>±1.2</td>
<td>±0.1</td>
<td>±0.1</td>
<td>±0.1</td>
<td>±1.0</td>
</tr>
<tr>
<td>500 hrs</td>
<td>±1.9</td>
<td>±0.9</td>
<td>±0.0</td>
<td>±0.0</td>
<td>±0.0</td>
<td>±1.0</td>
</tr>
<tr>
<td>1000 hrs</td>
<td>±1.6</td>
<td>±1.7</td>
<td>±0.1</td>
<td>±0.1</td>
<td>±0.1</td>
<td>±0.7</td>
</tr>
<tr>
<td>1500 hrs</td>
<td>±2.1</td>
<td>±0.4</td>
<td>±0.3</td>
<td>±0.4</td>
<td>±0.5</td>
<td>±0.5</td>
</tr>
<tr>
<td>1750 hrs</td>
<td>±3.7</td>
<td>±0.16</td>
<td>±0.2</td>
<td>±0.1</td>
<td>±0.2</td>
<td>±1.81</td>
</tr>
<tr>
<td>2000 hrs</td>
<td>±1.0</td>
<td>±0.53</td>
<td>±0.0</td>
<td>±0.2</td>
<td>±0.0</td>
<td>±0.39</td>
</tr>
<tr>
<td>2250 hrs</td>
<td>±2.3</td>
<td>±0.08</td>
<td>±0.3</td>
<td>±0.1</td>
<td>±0.1</td>
<td>±2.67</td>
</tr>
<tr>
<td>2500 hrs</td>
<td>±0.72</td>
<td>±0.59</td>
<td>±0.0</td>
<td>±0.0</td>
<td>±0.13</td>
<td>±2.74</td>
</tr>
</tbody>
</table>

After coating with PHB, limestone surface became slightly whitish considering the higher L* value of the coated limestone. The a* and b* values of PHB coated limestone was lower which exhibited that the PHB didn’t cause a yellow color on the limestone surface.

During weathering test L* value increased as weathering progressed (Table 14). After 2500 hours weathering the higher L* value indicated that PHB caused a bright color on the limestone surface due to the discoloration of PHB caused by photodegradation: resulted in more opaque and whitish surface (Hidalgo Schulz et al. 2018). The lower a* and b* values also tend to be decreased during weathering test and after 2500 hours weathering a* and b* values of PHB coated limestone were found to be lower than the coated limestone.

The ΔE* value of PHB coated limestones was 2.72 which was lower than the threshold for human eye perception value (<3). However, after 2500 hours weathering test the ΔE* value of PHB coated limestones increased to 8.44 which was higher than the acceptable total color change value (<5) for the conservation of cultural heritage. The higher ΔE* value may relate with the increased L* value of the weathered limestone (Figure 31).

After coating with PLA, limestone surface became slightly darkened surface became yellow considering slightly lower L* and higher b* values (Table 14). During
weathering test $L^*$ value of PLA coated limestones slightly increased as weathering progressed, similar trend was seen detected by Giuntoli, Frediani, et al. (2012) and this may relate by the reorganization of the polymer and exposition to accelerated weathering (During UV irradiation at 60). As a result, the surface of the polymer coating became smooth which enhanced the brightness (Frediani et al. 2010). In addition to that, the reduction of $\Delta L^*$, together with the protective efficiency of PLA, may attributed to the detachment of the polymer film from the limestone surface.

During weathering test the $a^*$ values of PLA coated limestones fluctuated and showed negligible variations. The $b^*$ values were also fluctuated and slightly decreased (Table 14). Similar results were obtained by Giuntoli, Frediani, et al. 2012 as the PLA coated stone samples exhibited negligible variations. however, after weathering test $b^*$ value was slightly decreased. This variation showed that weathering did not cause yellowing on the stone surface.

After 2500 hours of UV irradiation PLA still exhibited low color changes which were not detectable by human eye (Giuntoli, Frediani, et al. 2012). Similar results were obtained by coating marble surfaces with PLA against SO$_2$ reaction in the atmosphere. Results showed that $\Delta E^*$ value of PLA coated marble was 1.43$\pm$0.6 which was under limits of conservation of cultural heritage (Ocak et al. 2015) (Figure 32).

![Figure 31. Total color change values ($\Delta E^*$) of coatings during accelerated weathering tests](image-url)
Figure 32. Total color change values (ΔE*) of Paraloid B72, PHB and PLA as coating on limestone before and after accelerated weathering (% values presented the changes of ΔE* values after weathering).

### 3.3.6. Water Protection Efficiency of Coatings on Limestone

Water protection efficiency for coatings on limestone samples were monitored using water absorption by capillary, static contact angle and water vapor permeability measurements during and after accelerated weathering test.

#### 3.3.6.1. Water Absorption Capacity of Weathered Limestone

After coating with Paraloid B72, the amount of water absorbed by the limestone drastically decreased from 0.16 kg/m² to 0.03 kg/m² showed that Paraloid B72 provided 81% protection efficiency. However, the amount of absorbed water increased as the weathering progressed. After 1000 hours of weathering Paraloid B72 coated limestone started to absorb more water than the uncoated limestone (Figure 33). As a result, the
The protection efficiency of Paraloid B72 was lost (Figure 34) due to the hydrolytic degradation of the polymer which showed that Paraloid B72 started absorb higher amounts of water (Ndazi and Karlsson 2011).

Figure 33. The amount of absorbed water per m$^2$ ($Q_i$) vs time of uncoated, Paraloid B72 coated and weathered limestone samples

Figure 34. Protection efficiency (%) Paraloid B72 on limestone samples

Similarly, the efficiency of Paraloid B72 decreased during ageing and lost its efficiency after 1000 hours of weathering when the coated stone absorbed more water than the untreated one (Toniolo et al. 2002). The protection efficiency of Paraloid B72 was also evaluated as a coating material on stone surfaces showed that the protection
efficiency of the polymer was lost after 650 hours of irradiation due to the totally loss of polymer from the stone surface (Melo et al. 1999) (Figure 41).

After coating with PHB, the amount of water absorbed by the limestone decreased from 0.16 kg/m² to 0.10 kg/m² which provided a less protective shield than Paraloid B72 against water as 39 % (Figure 35, Figure 36). During weathering, the amount of water absorbed by the PHB coated limestones exhibited a slight decrease indicated that accelerated weathering didn’t significantly resulted in hydrolytic degradation of PHB coated limestones. Similarly PHB was evaluated by Andreotti, Franzoni, and Fabbri (2018) after accelerated weathering test and its was observed that protection efficiency of the polymer slightly decreased on limestone samples (Figure 41).

![Graph](image1)

Figure 35. The amount of absorbed water per m² (Qi) vs time of uncoated, PHB coated and weathered stone samples

![Graph](image2)

Figure 36. Protection efficiency (%) PHB on limestone samples
After coating with PLA, the amount of water absorbed by the limestone drastically decreased from 0.16 kg/m$^2$ to 0.01 kg/m$^2$ which was showed that PLA provided 91 % protection efficiency (Figure 37, Figure 38). During weathering, the amount of water absorbed by the PLA coated limestones exhibited an increasing trend. After 1500 hours of weathering the amount of absorbed water higher than the uncoated limestone which may explain by the detachment of the polymer film from the surface after 1500 hours of weathering.

The water absorption capacity of PLA was evaluated on marble samples after 1000 hours of UV irradiation and the protection efficiency of PLA was decreased 22 % to 18 % (Sacchi et al. 2012) (Figure 41).

![Figure 37](image1.png)

Figure 37. The amount of absorbed water per m$^2$ (Qi) vs time of uncoated, PLA coated and weathered limestone samples

![Figure 38](image2.png)

Figure 38. Protection efficiency (%) PLA on limestone samples
Results of the analysis indicated that PLA and Paraloid B72 provided higher protection against water than that of PHB (Figure 39, Figure 40). However, after 2500 hours accelerated weathering test PLA and Paraloid B72 started to absorb more water than PHB and lost their protection efficiency against water. In contrast with this PHB couldn’t provide a significant protection efficiency like PLA and PHB, while it remained stable against 2500 hours weathering.

Figure 39. The amount of absorbed water per m² (Qi) vs time of uncoated, coated and weathered limestone samples

Figure 40. Protection efficiency (%) of water absorption by capillarity of the coatings during accelerated weathering tests
Figure 41. The water absorption by capillarity values of Paraloid B72, PHB and PLA as coating on limestone before and after accelerated weathering (% values presented the reduction in contact angle values after weathering).

3.3.6.2. Hydrophobicity of Weathered Limestone

The water contact angle of limestone was determined as 30° and Paraloid B72 treatment increased the contact angle to 80° which was under the borderline of being hydrophobic. During weathering test, Paraloid B72 coated limestones showed slight variation and at the end of the weathering test the contact angle value reduced to 79° (Figure 42). This slight variation could be explained with the less degradation of Paraloid B72 observed on SEM images (Figure 45).

Similarly, Paraloid B72 was tested on marble surfaces by Toniolo et al. 2002. Results showed that Paraloid B72 lost its hydrophobicity after 1500 hours of accelerated weathering as the water started to absorb rapidly through the Paraloid B72 coated marble surface (Figure 47).
Figure 42. The water contact angle values of Paraloid B72 coated limestones during weathering

PHB treatment increased the contact angle value of limestone to 92° which was a near the borderline of being hydrophobic. The contact angle value decreased to 72° as the weathering progressed (Figure 43) due to the hydrolytic degradation determined by FT-IR analysis and also altered surface morphology of the PHB by SEM analysis. In addition, hydrophobicity of the surface decreased with the increase of surface free energy (Spiridon et al. 2015).

Figure 43. The water contact angle values of PHB coated limestones during weathering
The contact angle values of PHB coated sandstone, limestone and marble were evaluated after accelerated weathering test. Results showed that a drastic decrease was observed with all PHB coated stones on sandstone samples contact angle decreased 95° to 6° and on marble samples decreased 80° to 20° while a complete absorption of water was seen with PHB coated limestone as the contact angle decreased 108° to 0° (Figure 47) (Andreotti et al, 2018).

PLA treatment increased the contact angle of limestone to 118° which was above the borderline of being hydrophobic. However, after 1500 hours of weathering the contact angle value decreased below to hydrophobicity line showed that the surface became hydrophilic. After 2500 hours weathering the contact angle drastically decreased to 66° due to the hydrolytic degradation of PLA and the degradation of the surface morphology (Figure 44). Also this reduction related with the increase of surface free energy (Spiridon et al. 2015). Similar results were obtained by Spiridon et al. 2015 as the contact angle values of PLA showed a significant decrease after UV irradiation (Figure 47).

![Figure 44. The water contact angle values of PLA coated limestones during weathering](attachment:image.png)

After accelerated weathering, contact angles of all the polymer coatings reduced which is directly related with the surface topography of the polymer (Figure 45, Figure 46). In accordance with this SEM analysis showed that the surface morphology of polymer coatings degraded by etching, irregular crazes, cracks, holes and voids that resulted in the reduction of surface hydrophobicity. In addition to that, lower variation
was observed with the Paraloid B72 coated limestones before and after weathering test (Figure 45, Figure 46).

Figure 45. SEM images of the coated and weathered limestone samples and their contact angle values
Figure 46. Water drops over uncoated, coated and weathered limestones

Figure 47. The contact angle values of Paraloid B72, PHB and PLA as coating on limestone before and after accelerated weathering (% values presented the reduction in contact angle values after weathering).
3.3.6.3. Water Vapor Permeability of Weathered Limestone

All the polymer coatings drastically reduced the water vapor permeability of limestone. During accelerated weathering test there were no significance variations among the coated and weathered limestones (Figure 48).

The calculated reduction in water vapor permeability values of weathered limestones were 75 %, 74 % and 65 % with Paraloid B72, PHB and PLA respectively. Lower reduction of water vapor permeability related with the fact that both sides of the limestone samples were coated.

![Graph showing water vapor permeability reduction](image)

Figure 48. Reduction of water vapor permeability of polymers (δp reduction (%) = ((δpB-δpA)/δpB) × 100)

The reduction of water repellency mainly attributed to changes in the morphology of polymer coatings as etching, irregular crazes, cracks, holes and voids. In addition, the hydrophobicity and absorption capacity of the polymer coatings directly related with the permeability of the coating, as the similar results were obtained by absorption capacity and contact angle measurements (Figure 49).
Figure 49. Water vapor permeability values of Paraloid B72, PHB and PLA as coating on limestone before and after accelerated weathering (% values presented the reduction of water vapor permeability values after weathering.
CHAPTER 4

CONCLUSION

Protection efficiency and long-term stability of two biodegradable polymers; polyhydroxybutyrate (PHB) and poly-l-lactide (PLA) and an acrylic polymer (Paraloid B72) were evaluated on limestone samples under accelerated weathering conditions.

Paraloid B72, PHB and PLA coatings caused negligible changes in the surface, significantly increased hydrophobicity, decreased capillary water absorption and water vapor permeability of the limestone.

Paraloid B72 caused the highest color change whereas PHB and PLA coated limestones showed lower color change values near the human eye perception value.

Paraloid B72 drastically decreased the amount of water absorbed by the limestone and provided higher protection efficiency than PHB. Highest reduction was seen on the PLA coated limestone. Paraloid B72 and PHB treatments increased the contact angle to a borderline case which is almost accepted as hydrophobic. The highest contact angle value was obtained on PLA coated limestones which was above the borderline of hydrophobicity. All the polymers coatings drastically reduced the water vapor permeability of limestone due to the higher water-repellent character of the polymer coatings.

After accelerated weathering test, all the polymers deteriorated to some extent by exposure to UV light and the combination of high humidity and temperature. Paraloid B72 was degraded by hydrolysis of ester linkages and breaking down of long macromolecular chains. Accordingly, Paraloid B72 began to absorb more water, lost it hydrophobicity and acquired a yellowish hue. PHB was degraded by thermal decomposition of tertiary hydroperoxides, hydrolysis of ester linkages and breaking down of long macromolecular chains, formation of acetic anhydride. Accordingly, it can be said that PHB began to lose its hydrophobicity and became more fragile. PLA degraded up to half elimination of the coating from the stone surface starting with the 1000 hours of ageing. Furthermore, hydroxyl group bands increased because of the molecular water absorption of PLA, whereas carbonyl group bands decreased due to the formation of gamma lactones and anhydrides formed due to UV-irradiation.

After weathering, the surface of Paraloid B72 coated limestones became slightly rough due to the surface erosion and etching (material removal). Paraloid B72 was
became insoluble from the limestone surface after accelerated weathering tests. The surface degradation of PHB coated limestones began with surface erosion and cracks, showed that the degradation process of PHB was thermos-degradation and polymer film partially detached from the limestone surface after accelerated weathering. Considering PLA coated limestones after accelerated weathering, the degradation of PLA began with surface erosion and cracks, indicating that the PLA is hydrolytically degraded.

After accelerated weathering total color change (ΔE*) value of Paraloid B72 coated limestone was decreased below to the accepted value for the conservation of cultural heritage reported by the International Conservation Community of Historic Monuments and Buildings. After accelerated weathering tests the ΔE* value of PHB coated limestones increased above the accepted value while PLA coated limestone decreased below the accepted value.

After accelerated weathering test, PLA and Paraloid B72 started to absorb more water than PHB and lost their protection efficiency against water. However, PHB couldn’t provide a significant protection efficiency like PLA and Paraloid B72 after coating. After accelerated weathering test, contact angles of all polymer coatings reduced which is directly related with the surface topography of the polymer. The surface morphology of PLA and PHB coatings degraded by etching, irregular crazes, cracks, holes and voids, this resulted in the reduction of surface hydrophobicity. The surface morphology of Paraloid B72 coated limestone became slightly rough due to the surface erosion and etching (material removal). During accelerated weathering test there were no significance variations among the water vapor permeability values of coated and weathered limestones.

Eventually, it can be said that PLA is a suitable polymer coating than Paraloid B72 and PHB in terms of color compatibility of the limestone. While considering the protection efficiency of a coating material, PLA and Paraloid B72 coatings provided higher protection than PHB. In terms of long-term stability of a coating material, the chemical degradation of PLA was slower than the PHB and Paraloid B72, while lower surface degradation was observed on Paraloid B72. In addition, Paraloid B72 became insoluble after accelerated weathering while it is seen that PHB and PLA started to be easily removable from the limestone surface, when examined with naked eye. Even under these conditions, PLA still protected its hydrophobicity and breaking down of long macro molecular chains process didn’t significantly take place. Moreover, still the lower color change was observed on the PLA coated limestones, this makes it a suitable coating
material according to International Conservation Community of Historic Monuments and Buildings.

This study indicated that PLA is a promising alternative biodegradable protective agent by its reversibility and biodegradability, color compatibility, good hydrophobic behavior and good stability to weathering in reducing the effects of outdoor exposure on limestone surfaces.
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