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A comprehensive review of weathering patterns and protective materials for stone relics

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Abstract. Stone relics are among the most important cultural heritages as they preserve a trove of cultural information of historical import. Many of these relics have sustained damage due to extensive periods weathering outdoor environment conditions causing different weathering patterns', including cracking, fracture, blistering, efflorescence, peeling, flaking and exfoliation. Among the main environmental factors causing these types of decay are water, acids, temperature fluctuations, soluble salts, and microorganisms. To preserve these stone monuments, Extensive research efforts have been devoted toward protecting these artifacts from environmental deterioration. The present paper reviews the pros and cons as well as future development perspectives of inorganic, organic, inorganic/organic composites and biological protective materials for prevention of stone relics deterioration from physical, chemical, and biological factors, which indicates that inorganic/organic composites possess obvious advantages for preventing water deterioration. Which provide future development perspectives about the protective materials.

1. Introduction

Stone monuments are an essential part of our cultural heritage, representing the legacy of our ancestors and offering insights into past civilizations [1, 2]. These heritages can take various forms, such as ancient buildings, sculptures, and monuments. Most of them are exposed to the natural environment, especially large structures since it is difficult to house them indoors and they must endure in outdoor environments [3, 4]. Hence, they are more vulnerable to deterioration and damage caused by various factors [5], including environmental factors, biological factors, natural disasters, war and conflict, theft and vandalism [6].

With the passage of time, they are constantly eroded and damaged by various factors, with some relics sustaining damage past the point of recognition. The weathering damage of stone relics refers to the process of various physical states and chemical compositions changing due to the effects of environmental temperature, atmospheric pollution, precipitation, soluble salt crystallization and microorganisms [4, 7]. With the rapid development of industry and the aggravation of environmental pollution, the weathering rate of stone relics in recent decades has exceeded that of the past few hundred years [1, 5]. Hence, the conservation of stone cultural heritages is crucial for ensuring their survival and promoting cultural diversity and understanding.

The history of cultural relics conservation can date back to hundreds of years ago, while people recognized the value of preserving their cultural heritage. However, it was not until the 18th century that the concept of cultural heritage conservation emerged as a systematic and scientific discipline [8]. Scientists from around the world recognized the importance of preserving stone relics [9], and different approaches have been employed for stone relics conservation, such as traditional restoration methods and modern conservation technologies. Traditional restoration methods adopt materials and techniques that have been used for centuries, such as the use of lime mortar [10, 11] and traditional painting techniques [12]. Modern conservation technologies include non-invasive conservation technologies, such as protective coatings [13, 14], laser scanning and digital imaging [15].

The conservation approaches performed a vital role for cultural relic protection. However, traditional materials have come shortcoming, for example, high shrinkage, tendency of getting cracked when carbonation. Hence, surface protection of the stone relics is one of the most effective techniques for conservation of stone relics, which can offer a protective coating that can safeguard the relics and enhance their appearance based on the modification [6]. Since the beginning of the 20th century, numerous research has been done about conservation materials of stone relics by conservationists with the progress of green approach of conservation, the selection of protective materials can be assessed that are safer for the cultural relics [16]. In the past decades, the inorganic and organic materials has received more attention based on their particular properties [17]. In comparison to the current accessible review articles, this paper reviewed both the weathering patterns of the stone relics in the world and the corresponding protective materials. The benefits and drawbacks of the protective materials with its suitability for the stone relics protection in combating different weathering factors was securitised, identifying the main weathering factor and appropriate protective materials [18-21].

2. The Weathering Situation and Patterns of Stone relics

The effects of weathering and human activities on stone relics is a complex and ongoing issue that has been a concern for many years. The effect of weathering pattern is also mediated by the composition of the stone. Sandstone is widely used in stone relics, like tombstones, monuments, building, grottoes and all kinds of sculptures, due to their abundance and availability as well as their ease of use [22]. However, their porous structure and relatively loose properties lead to these materials being more vulnerable to rain water, temperature variation, soluble salts and microorganism, and other environmental factors [23], which demonstrate varied weathering patterns.

2.1 The Damage of Triumphal Arch of Galerius in Thessaloniki

Figure 1 depicts the current status of the Triumphal Arch of Galerius in Thessaloniki, Greece, which was built during 298 AD and 305 AD, which depicts the damage sustained by the Triumphal Arc of Galerius as of 2020. Figure 1 (a) show the stone surface covered with black crusts, in Figure 1 (b), the statues details have gradually been eroded, in Figure 1 (c), many parts of the reliefs are vanishing, and in the Figure 1 (d), the details especially the faces of the statues have worn away.

In a nutshell, the Arch has experiences significant deterioration due to weathering in recent years [24].

Figure 1. The Triumphal Arch of Galerius and the statues as of 2020. a) Arch covered in black crust, b) erosion of etchings, c) significant loss of statue details, and d) loss of finer etchings especially on face and hands of statue.

2.2 The Fade of the "Wall-Erotica" artworks in Greek

Nikos Kessanlis is known as one of the most famous figures in Greek and worldwide art scene. The "Wall-Erotica" artworks were created in the end of 20th century by Nikos Kessanlis. However, lots of damages and deterioration of Nikos Kessanlis "Wall-Erotica" can be revealed from Figure 2, such as, the change of black colour to brownish (a), loss of the photosensitized layer (b), various area with losses and blistering and flaking (c), and obvious cracks can be observed in (d). In addition, the colour of the artworks has changed to brownish and yellowish [25].

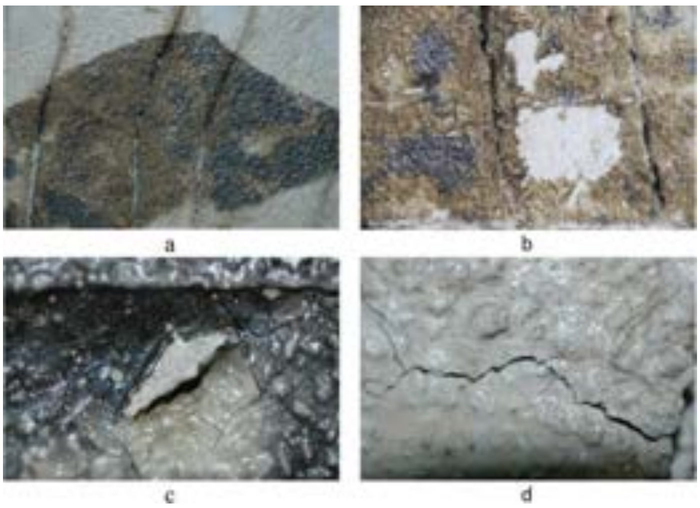

Figure 2. Surface deterioration of the images in Nikos Kessanlis "Wall-Erotica", a) change of black colour to brownish, b) loss of the photosensitized layer, c) blistering, and d) cracking.

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2.3 The Microorganism Accumulation of Iranian Cultural Heritage Monuments

Microorganism is one of the most important factors for corrosion of the stone relics, it can lead to degradation of the stone, because of the secretion of the microorganism like sulphur compounds which can accelerate the decomposing [26]. Moist environment around the stone heritage are beneficial for the growth of moss, lichens, and cyanobacteria. Figure 3 shows the damage on the surface of Iranian stone relics, there is both damage due to weathering such as the cracks and erosion shown in Figure 3 a), which is likely due to wind, rain and temperature fluctuation as well as biological growth damage as shown in Figure 3 b), such as microorganism, algae and lichen accumulation. The first step to conserving these relics would involve cleaning and removing these bio-pollutants [27].

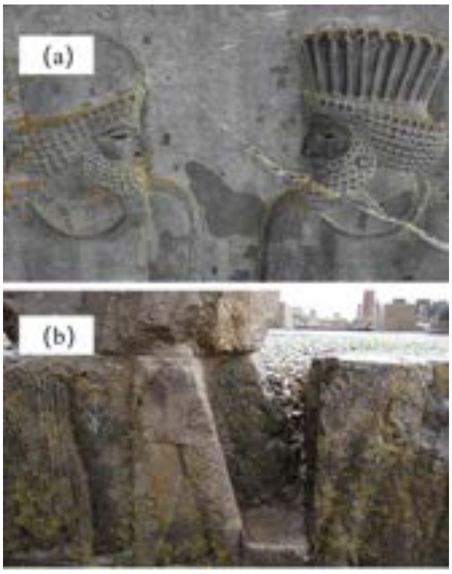

Figure 3. Damage to Iranian cultural heritage monuments: a) erosion, loss of detail and cracking, and b) biological growth of lichen, moss and algae.

2.4 The Graffiti and fade of the Paintings in Cave of Kelawar

Figure 4 shows the paintings in the Gua Kelawar cave, Perak, Malaysia, which were excavated by Callenfels and Nooe (1940) [25]. They can be dated back to a recent period, maybe the product of the Orang Asli (aborigine people) ancestors who lived within the area. From the images we can see that the drawings have faded and there is loss of resolution, some parts of them graffitied.

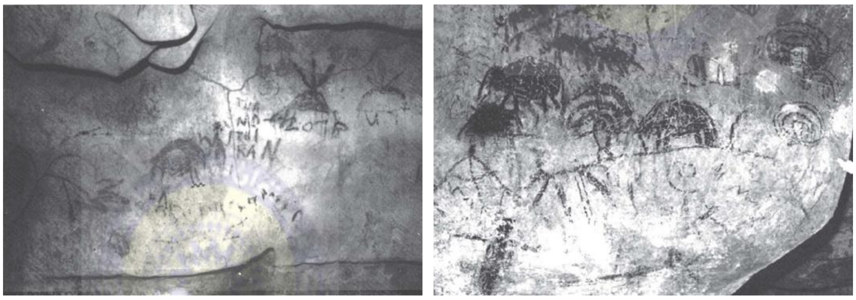

Figure 4. Paintings in the Gua Kelawar cave, Perak, Malaysia.

2.5 The Seepage Erosion of Qingyang North Grottoes

In the northern China, there are numerous stone heritages, which can be damaged by freezing-thawing due to the noticeable variation of temperature between day and night, and the changes in humidity during different seasons. Qingyang is a city in Gansu Province, which is in the northwest of China. Figure 5 shows damage to the North Grottoes of Qingyang. The bottom and interior of the heritage are deteriorated severely by seepage erosion as evidenced by the less distinct and rounded edges of the carvings, in addition, there are lots of transverse pore cracks on the surface of stone after undergoing many of freezing-thawing cycles [28]. The upper and middle part of the cave and Buddha were affected by capillary action, and there can be seen some of the white precipitation. which may indicate salt crystallization. When water from ground sources seep into the pores and cracks of these stone relics, the salt crystals can accumulate and as they crystallize, the expansion puts pressure on the surface causing pitting, flaking and disintegration which may explain the damage observed to the statue in Figure 5b.

Figure 5. Damage to Qingyang North Grottoes in Gansu Province, China: a) visible biological colonization, and b) effect of weathering causing the rounded edges and lack. of definition.

2.6 The Comprehensive Weathering of the Dazu Rock Carvings

Figure 6 illustrates the surface condition of the foundation of Sakyamuni niche, as can be seen from that most of degradation and cracks processes occur on the surface of the stone heritages, that can be attributed to the environment, stone composition and other properties [29]. From Figure 6 it can be observed that the surface weathering is due to multiple factors, namely a) granular disintegration, b) salt efflorescence, c) moss and abscess, d) structural cracking, e) weathering crack, f) water seepage, g) scaling, h) blistering, which are based on the Glossary on Stone Deterioration Patterns published by ICOMOS International Scientific Committee for stone deterioration. The cracking and water seepage are the largest contribution factors to the surface damage [30]. Therefore, it is time to take some effective measures to protect the stone, or risk forever losing cultural heritage sites such as this.

2.7 The Cracking of the Stone relics in Chengde Mountain Resort

Figure 7 shows damage to the Xumifushou Temple located in the Chengde Mountain Resort comprising of a) stone elephants, b) stone arch bridge, c) stone lion, and d) its pedestal constructed more than 250 years ago. Figure 7 a) indicates weathering damage found on the stone elephants - the trunk and legs exhibit substantial cracks after rainwater erosion and multiple freeze-thaw cycles. In Figure 7 b) we can see that the carved balustrades of the stone bridge have been fissured and exfoliated, which may be caused by vandalism and weathering, the lower part of the wall has been corroded due to the long-term soaking by rainwater. Figure 7 c) shows the

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surface exfoliation of the lion body, its claws and foundation which are situated in front of Chengde Mountain Resort gate.

Figure 6. Surface condition of stone relics of that a is Dazu Rock Carvings.

Figure 7. The stone elephant (a), stone bridge (b), stone lion (c) and the pedestal of the stone lion in Xumifushou Temple and Chengde Mountain Resort.

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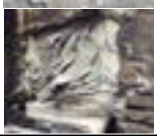
From the statement above, we can conclude the weathering patterns for the stone relics in the Table 1 [31-37]. The damage of the stone relics is usually caused by water and soluble salts. Therefore, water repellence is one of the most important properties of the protective materials [38].

Table 1. The representative weathering patterns of the stone relics

Weathering patterns	Images	Reasons
Vandalism		Anthropic action
Graffiti		Anthropic action
Cracking and fracture		Water erosion and freeze/thaw
Blistering		Soluble salts and capillary water
Efflorescence		Water and soluble salts
Peeling and flaking		Salt crystallization
Exfoliation		Soluble salt and stone structure

3. Analysis of Factors Leading to Stone Relic Deterioration

Although stone always be considered as the most durable material for monuments, the stone heritages are exposed to outdoor for a long time, which leads to deterioration, from both natural and anthropic factors, such as water erosion, salt crystallization, acid deposition, microorganisms, higher plants, and contaminant caused by human activities which can be simplified to physical chemical and biological weathering, and anthropic action [39]. In this section, some of the specific factors will be discussed.

3.1 Water

The deterioration of rock caused by the physical, chemical and mechanical action of water is usually an intricate process, bind of mutual promotion. For example, hydrolysis is mainly manifested in the orthoclase in sandstone, water absorption to form the decomposition process of kaolinite and bauxite [40], as shown in the following Equation (1) and Equation (2).

$$4KAlSi_3O_8 + 6H_2O \rightarrow 4KOH + 8SiO_2 + Al_4Si_4O_{10}(OH)_8 \quad \text{Equation (1)}$$
$$Al_4Si_4O_{10}(OH)_8 + H_2O \rightarrow 2Al_2O_3 \cdot 5H_2O + 4SiO_2 \quad \text{Equation (2)}$$

As water seeps into the pores of the stone, it can cause the surface to become rough and pitted, leading to loss of sharpness and detail. This can make it difficult to read or recognize inscriptions or other elements that are critical to the artifact's historical or cultural significance [41].
Water erosion can also cause discoloration or staining of the surface of stone relics. As water seeps into the pores of the stone, it can dissolve minerals and other materials that cause discoloration or staining of the surface. This can be particularly damaging for artifacts that feature intricate patterns or colours, as discoloration can make these elements difficult to see or appreciate.

To mitigate the negative effects of water erosion on stone relics, it is essential to take proactive measures to protect these artifacts from prolonged exposure to water. This may involve installing protective coverings or sheltering the artifacts from rain or other sources of moisture. Hence, water erosion is a noteworthy risk for stone.

3.2 Acid

Water and gas contaminant can result in acid rain containing sulfur dioxide and nitrogen dioxide which are major culprits for stone corrosion. Acids can react with salts such as calcium carbonate in rocks, which causes irreversible damage to sandstone. The loss of binding can cause the internal structure to be destroyed and the surface of the rock mass to become loose. The surface layer will then eventually be exfoliated from stone. The acid rain reacts with stone material in accordance with the chemical reaction as given in Equation (3):

$$2CaCO_3 + 2SO_2 + O_2 + 4H_2O = 2CaSO_4 \cdot 4H_2O + 2CO_2 \quad \text{Equation (3)}$$

3.3 Temperature Fluctuation

The stone surface temperature is positively correlated with the ambient temperature, and the sandstone daily variable temperature zone is within 0 cm to 50 cm of the surface, and the temperature gradient within the range of 0 cm to 5 cm is the largest [40]. Temperature changes can cause significant damage to stone relics. When temperature fluctuations occur, the expansion and contraction of the stone can cause cracks and fissures. These cracks can weaken the stone, making it more vulnerable to weathering and erosion. This can lead to the gradual deterioration of the relics with time.

In addition, temperature changes can also impact the structural integrity of the site where the stone relics is located. For example, temperature fluctuations can cause the soil around the site to expand and contract, leading to shifting and settling of the foundation. This can cause the site to become unstable, which can put the relic at risk of damage or collapse. The temperature fluctuation also compounds the effect of freeze/thaw when water is present in the inner structure of stone which accelerates the cracking and fracturing process.

Table 2. The common inorganic materials and its properties.

Nos.	Inorganic materials	Advantages	Drawbacks
1	Calcium Hydroxide	low price, good durability, breathable	Lower water resistance and penetration
2	Barium Hydroxide	Good aging resistance, breathable	Lower permeability, transparency
3	Silicates	Good compatible and aging resistance	Poor adhesion, Hard-shell

3.4 Soluble Salt

The effects of soluble salt on stone relics occurs through the process of salt crystallization. This occurs when salt enters the porous structure of the stone and then dissolves in water, creating a concentrated solution. As the water evaporates, the salt begins to crystallize and expand, creating pressure within the stone. This pressure can cause the stone to crack and flake [27].

Soluble salt can also lead to efflorescence, which is the white crystalline deposit that often appears on the surface of the stone. Efflorescence occurs when the salt in the stone reacts with water, and the resulting solution is forced to the surface of the stone as the water evaporates. These deposits can be unsightly and can obscure the details of the stone's surface, making it difficult to appreciate the full beauty and historical significance of the artifact. The presence of salt can accelerate the rate of weathering and erosion of the stone, making it more susceptible to damage from environmental factors such as wind, rain, and pollution [42].

3.5 Microorganism

Although the deterioration of stone relics can be attributed to physical, chemical and biological factors, the effect of microorganisms contributes an estimated 20%-30% to the observed damage to stone structures [43]. This deterioration by microorganism is known as biodeterioration, which refers to biological growth of agents, such as bacteria, moss, fungi, algae and plants, which can cause corrosion or degradation of stone relics through various mechanisms [44].

As stated by Zhu et al, moss is one of the most important factors for deterioration of the stone relics in China, especially in tropical and subtropical regions[44], such as the damage observed in Leshan Giant Buddha in Sichuan province, China, and Angkor temples in Cambodia [45]. Therefore, the corrosion mechanism of microorganisms on stone relics is complex and depends on the type of microorganism, the environmental conditions, and the properties of the stone material. Preventive measures such as regular cleaning, controlling the environmental conditions, and using appropriate conservation techniques can help to slow down the corrosion effects of mosses on stone relics.

4. Conservation Materials of Stone Relics

Coating stone by hydrophobic chemical materials is one of the most effective way to prevent stone relics from deterioration and destruction caused by water [46].

There are various types of conservation materials been studied in the last several decades, and they provided the characteristics of an ideal protective coatings, such as transparency, compatibility with the stone surface, good durability, hydrophobicity, economy and non-toxicity. These coating materials can be categorized: inorganic materials, organic materials, nano materials, inorganic/organic materials and biological materials [6].

4.1 Inorganic Materials

Inorganic materials have been widely used in the conservation of stone relics due to their chemical stability, compatibility with stone, and ability to withstand harsh environmental conditions. The common inorganic materials are showed in Table 2.

4.1.1 Calcium Hydroxide

Calcium hydroxide is an inorganic material commonly used in the consolidation of stone relics [11], which is one of the most important conservation materials used for a long time. Calcium hydroxide solution is used to fill cracks, gaps, and voids in the stone surface, and bond the loose particles by reacting with carbon dioxide from atmosphere, and then creating new chemical bonds in the degraded areas. The reaction equation as follows Equation (4):

$$Ca(OH)_2+CO_2=CaCO_3+H_2O \qquad \text{Equation (4)}$$

Calcium carbonate is highly breathable, which allows moisture to evaporate from the stone surface and prevents the buildup of internal moisture that can lead to stone decay [47]. It is also highly compatible with stone, which minimizes the risk of damage to the stone surface, what is more, it is non-toxic and does not damage the stone surface, making it ideal for use in conservation projects. The example is the Wall paintings from Mayan Classic period were consolidation by calcium hydroxide as shown in Figure 8 [48].

However, there are some readily identifiable disadvantages of the saturated lime water, first is the low solubility of calcium hydroxide in water (the solubility is only 0.17 g at 20^{o}C), secondly, the penetration into the internal of stone is very poor due to the particles size [49]. Hence, the application of the lime water is limited by its properties [50].

4.1.2 Barium Compounds

The barium-based materials were considered for the consolidation of stone in the 19th century. Barium hydroxide applied for stone protection involve a more complex processes than calcium hydroxide discussed above. Barium carbonate produced from barium hydroxide, which has been considered as consolidant because barium hydroxide is more soluble than calcium hydroxide in water, hence more barium hydroxide could penetrate into the inner of stone. Barium compounds has been used for wall painting in Italy with the so-called "Florentine method" by Matteini [51]. However, the application of this consolidant on the surface of stone that was achieved led to negative effects, especially the exfoliation of the surface hardened layer of barium carbonate, the consolidating mechanisms were described by Hansen [52] as Equation (5) and (6).

$$Ba(OH)_2+CO_2=BaCO_3+H_2O \qquad \text{Equation (5)}$$
$$Ba(OH)_2+CaCO_3=BaCO_3+Ca(OH)_2 \qquad \text{Equation (6)}$$

4.1.3 Silicates

Silicates are used as consolidants in stone relics conservation in order to get better compatibility, since most stone cultural sites were built with inorganic materials. They are highly stable and can penetrate the stone surface to form a stable network of minerals that strengthen the stone structure. Silicates are highly resistant to weathering, UV radiation, and acid rain, making them ideal for use in outdoor environments. Over the last decades, different kinds of silicates material were developed which are especially applicable to protection of the sandstone relics in arid regions. For example, Zhang [53] applied the potassium silicates to protection of earthen sites, anti-weathering abilities were improved noticeable, such as the mechanical strength and the aeolian erosion and heavy precipitation, which contributes to the reaction of hydrolysis by K_2SiO_3 and produces the colloidal silicon dioxide [54].

Figure 8. Wall paintings from Mayan Classic period in Calakmul (Mexico). Calcium hydroxide nanoparticles were used for consolidation.

Table 3. Properties of organic materials for stone relics.

Nos.	Organic materials	Advantages	Drawbacks
1	Epoxy	Strong adhesion and high strength	Poor weather resistance and easily change color under ultraviolet radiation
2	Acrylates	Good transparency, stability, and weather resistance	Water resistance and yellowish
3	Organic Fluoride	Good hydrophobicity and self-cleaning properties	Poor adhesion and processability
4	Organic Silicone	Good hydrophobicity and weather resistance	Poor mechanical properties and acid and alkali resistance

Inorganic materials have been widely used in the conservation of stone relics due to their chemical stability, compatibility with stone, and ability to withstand harsh environmental conditions. However, there are some drawbacks which need to be improved, such as water resistance, penetration, permeability and transparency.

4.2 Organic Materials

Organic materials have been widely applied on stone relics conservation due to the excellent properties that differ slightly from those of inorganic materials, such as good compatibility with silicate heritages, super hydrophobicity and good transparency. Table 3 shows the properties of representative organic materials for stone relics conservation [55].

4.2.1 Epoxy

The application of epoxy resins in the conservation of stone relics has been an ongoing topic of research from 1960s [56]. In the end of 20th century, transparent and colorless epoxy resin have been prepared and used for consolidation and as an adhesive in conservation of stone relics [57].

However, there are some drawbacks of epoxy, for example, poor durability, brittleness, cracking resistance, poor anti-UV ageing, fatigue resistance and tendency for yellowing. Therefore, to overcome these shortcomings, modifications of the epoxy are requisite before they can be applied in stone relics protection. Introducing silica-based groups and fluorine-based groups to improve materials properties is the common methods. Xu [58] prepared the hybrid materials of modified epoxy-SiO_2 incorporating poly(dimethylsiloxane) hydroxyl, which impart toughness and flexibility to the epoxy-SiO_2 target to prevent polymers from cracking during curing process, which is important in the design of a hydrophobic material. In 2016, a series of fluorosilicone/acrylic/epoxy polymers were synthesized for stone relics protection by Zhang, and the water resistance and weather resistance were optimized by changing the content of fluorine and silicon [59].

Overall, the research progress of epoxy application on stone relics conservation has been significant, with ongoing efforts to develop new formulations, application techniques, and eco-friendly options. These efforts will continue to improve the effectiveness and sustainability of epoxy for stone relics protection.

4.2.2 Acrylates

Acrylates are a group of synthetic polymers that have been extensively used in the stone relics protection since the 1960s [60]. They are known for several properties, such as penetrability of the porous structure of stone and the ability to consolidate its fragile components, as well as ease of forming films and excellent mechanical properties, transparency, stability, and good adhesion and water-repellent performance when used for protective coatings [61]. Hence, it can provide long-term protection from weathering caused by ultraviolet and water.

One of the most famous in last several decades is Paraloid B72, which is synthesized use methyl acrylate (MA) and ethyl methacrylate (EMA), and it have been extensively studied and application in stone relics protection [16, 62]. However, the durability and hydrophobicity decrease limit its outdoor application for long time [63].

Even if the polyacrylates coatings provide an effective drainage of the water from the coated surface, there are a few of shortcomings when used for a long time as the coatings on outdoor artifacts. The most relevant issue produced by application of acrylates and methacrylic polymers is their durability and irreversibility. Studies have concluded that it is near impossible to remove it from the stone surface once the hydrophobicity begins decreasing [64].

Therefore, the research of acrylate will continue to improve the effectiveness and sustainability of acrylate use in stone relics conservation, such as, silane-modified methacrylic resins and fluorinated acrylate polymers have been studied by many of conservators in recent times.

4.2.3 Acrylates

Organic fluorine has been increasingly used in the protection of stone relics due to good water repellence, as well as ease of producing transparent and durable coatings for stone using this material. Studies on the application of organic fluorine compounds in the preservation of stone relics have concentrated on various essential aspects, such as formulation enhancement to improve penetration and bonding with the stone structures.

In recent years, a series of fluorinated polymers were synthesized. In1990s, Alessandrini [65] studied the effect of side-chain fluorination on the properties of acrylates-based polymers which were characterized by comparing them with un-fluorinated polymers. The results showed that fluorine could increase the hydrophobicity of the products notably. However, some research results showed that acrylate polymers with fluorine atoms in the main chain are more photostable than the fluorine atoms in the polymers' side-chain [66]. Following up on this discovery, partially fluorinated polymers based on acrylates with fluorine atoms in the main chain were synthesized for improving the properties by Mazzola in 2003 [67]. This material showed good properties for potential application of stone preservation. Jiang prepared the crosslinked polyurethane-hexafluorobutyl methacrylate polymers by the macro iniferter-controlled radical polymerization. However, it is difficult to control the molecular weight or molecular weight distribution [68]. In the following years, the conservation effect was studied by testing the physical and chemical properties and fluorine atoms were found to have a positive effect on durability, resistance to degradation and transparency [62, 69]. In particular, 2, 2, 3, 4, 4, 4-Hexafluorobutyl methacrylate (HFMA) is one of the most important fluorinated acrylates due to its high fluorine content. However, the anti-fouling and anti-microorganism properties were not found based on the fluorinated polymer coatings.

Future works need to focus on developing eco-friendly fluorine compound formulations that are free from harmful chemicals and can be safely produced and used in conservation projects.

4.2.4 Organic Silicone

Silicon-based compounds have become widely utilized as coatings. This is attributed to specific properties, such as transparency, corrosion resistance, and hydrophobicity. When applied in a hydrolysed form, silicone materials form Si-O-Si bonds can covalently interact with the surface of stone relics. It is evident that the establishment of a silane film is contingent upon the physical and chemical characteristics of the stone surface. This limitation in comparison to acrylates or fluorinated polymers lies in the dependence of silane film formation on the inherent properties of the stone surface for effective application in relics conservation [64].

Much work has been done to improve the performance of silane coating. Polymers of 3-(trimethoxysilyl)propyl methacrylate was obtained from organic siloxane using sol-gel method, and it was proved that these coating shows good adhesion as a consolidant, due to it is ability to form hydrogen bonds with hydroxyl groups on the stone surface [20]. From the studies conducted by Tang it was found that polysiloxane has exceedingly good hydrophobicity, thermal stability and flexibility [70]. Each siloxane unit can provide two functional groups for reaction, increasing the adhesion with the substrate. It has been reported that siloxanes have been widely studied and applied for stone protection as these materials are well known for hydrophobic coating, able to achieve contact angle values with water up to more than 120°, when in the format of hybrid siloxane or silicone polymers [71].

A hybrid sol was prepared and applied to protect stone relics from weathering based on tetraethoxyorthosilicate (TEOS) precursor by Xu [21] and the contact angle of stone surface with water increased from 58° to 123°. The properties for anti-acid aging of this material were evaluated, which revealed a satisfactory protective effect. Although lots of studies on silicon-based polymer consolidation have been conducted, especially for durability and compatibility, the time and condition of curing of TEOS hydrolysis have been of particular interest in the past decade [72]. Vinyl triethoxysilane is one of the most important reagents for preparation of protection coatings due to the presence of olefin group, which can react with acrylates directly. Recently, many of siloxane-based protective coatings were synthesized and applied for stone relics conservation [13, 14]. However, when applied for the conservation of carbonate rocks, there are lots of drawbacks, for example they cannot effectively prevent the cracking and deterioration of heritages. Therefore, it is necessary to study the interaction mechanism between these materials and stone [73].

4.3 Nano Materials
Nano particles have drawn more attention in recent decades due to their high reactivity, surface area, and tunable characteristics. Some research reports the introduction of nano materials (SiO_2, TiO_2, ZnO, CuO and MgO) in protective coating to improve durability, anti-fouling, self-cleaning and anti-microorganism effects [74, 75]. Various nano coatings have been synthesized in past years which mainly focused on silica nanoparticles and titanium dioxide nanoparticles [76].

4.3.1 Silica Nanoparticles
Nano SiO_2 (silica nanoparticles) is a commonly used nano material in stone relics conservation. The research progress of its application has focused on several key areas.

The study of nano SiO_2 (silica nanoparticles) mainly focus on development of new formulations for stone relics preservation. Researchers have studied the effects of concentration, particle size and surface modification on the performance of nano SiO_2 for protecting stone relics [16]. Different preparation methods, such as sol-gel and hydrothermal synthesis, have also been investigated to produce high-quality nano SiO_2 with desirable properties [14, 20].

Another area of research has focused on the mechanisms of action of nano SiO_2 in protecting stone relics using contact angle measurements or UV resistance testing. Researchers have studied the physical and chemical interactions between nano SiO_2 and stone surfaces, as well as the effects of nano SiO_2 on the microstructure and properties of stone. In particular, nano SiO_2 has been shown to improve the water resistance, mechanical strength, and durability of stone relics [16].

In recent years, there has been considerable research on synthesizing silica-based nanoparticles and acrylate polymers, with particular emphasis on composite materials. Bogdana conducted a study involving the synthesis of a novel silicon-based polymer nanocomposite containing silsesquioxane units using the sol-gel method and the composite produced was successfully employed as a protective coating [20]. Ferri reported a study about sol-gel coating obtained from two siloxanic with different amounts of silica nanoparticles functionalized with 1,1,1-Trimethyl-N-(trimethylsilyl) silanamine where the results indicated that nano materials at a suitable concentration maintained a good static contact angle with water, even up to four months of exposure to atmospheric conditions [71]. A series of nanosilica-based fluorinated polyacrylate composites were synthesized with dodecafluoroheptyl methacrylate (DFMA), acrylate and different amount of nanosilica, which were used as the stone surface protective coatings for cultural relics. The protective properties like mechanical stability, coagulum rate, surface tension of the coatings and the erosion effects undergoing the freeze-thaw accelerated aging were tested, these results showed a positive effect compared tocounterparts without nanosilica [55].

Nano silica as the addition for preventing UV can be used to improve the protection performance of the coatings against UV ageing and provide a high water contact angle. However, further research is needed to understand the mechanisms of degradation and to optimize the formulation and application of nano silica coatings for preparation of the polymer coatings.

4.3.2 Titanium Dioxide Nanoparticles
Titanium dioxide (TiO_2) plays a very important role as the protective materials of stone relics, owing to its ability to prevent the bacterial erosion and improve chemical resistance. In fact, the

low price, non-toxic and self-cleaning action are the valuable properties of TiO_2 relevant for protection of stone relics.

The effects of different parameters have been studied, such as crystalline structure, and surface modification, on the performance of TiO_2 nanoparticles in protecting stone surfaces [64, 73]. Various synthesis methods, such as sol-gel and hydrothermal synthesis, have also been investigated to produce high-quality TiO_2 nanoparticles with desirable properties [4].

Skoulikidis proposed the method to synthesized the protective materials using TiO_2 in 1992 [77]. After that, much research has been done by using TiO_2 nano particles dispersed in the solution or added into acylates polymers. Giovanni et al investigated the inhibition effect of microalgal fouling by TiO_2-based nano compounds applied on the stone surface by spray coating for stone relics [78]. The self-cleaning and depolluting properties of nano TiO_2 protective coatings was evaluated by Enrico, and the results showed that it was effective for protecting stone relics made by limestone from the erosion caused by microalgae [79].

However, the application of the titania is limited for stone surface protection due to cracked coatings formed on the stone which compromise the protection and the film contain titanium dioxide can be easily removed from the stone surface compare with SiO_2 modified materials due to the weak cohesiveness [80]. This can be mitigated by forming composites of TiO_2 particles and acrylates materials which can prevent the loss of TiO_2 particles. However this method limits the fraction of TiO_2 particles which are exposed on the surface of the acrylates coatings, which leads to the decrease for conservation performance due to a reduction in the anti-microbial effect of TiO_2 [81]. In order to overcome this limitation of the TiO_2 nano particles, the nano SiO_2/TiO_2 hybrid fluorinated B-72 hydrophobic coating was prepared by TiO_2 nano particles dispersed into SiO_2-sol and the results shows the effective conservation for relics [62]. Phinho et al synthesized a self-cleaning building material with nano SiO_2/TiO_2, which also proved the valuable role played for consolidant cracking and titania particles loss [80].

4.4 Organic/Inorganic Composites

The ideal protective coating should be durable, hydrophobic, transparent, nontoxic, easy to use and compatible with the substrate, thanks to the water or moisture can cause stone deterioration, while the coating needs to ensure the transpiration of the relics. Hence, multifunctional protective materials are prerequisite for conservation of stone relics [82].

However, each of these material types have inherent drawbacks, be it inorganic, organic or nano materials. For instance, inorganic materials have great anti UV-aging performance, however, their adhesiveness, transparency and compatibility with stone relics are poor. Organic materials including the epoxy resin, acrylate polymer and silicone resins have good weather resistance and transparency, but the poor water resistance except when modified by fluorine and silicates [73].

Thus, the composite material, incorporating both organic and inorganic components, can achieve on-site reinforcement by effectively bridging the interface between the conservation material and the stone substrate. This results from the amalgamation of the benefits associated with both inorganic and organic materials, producing a synergistic effect that significantly improves the protective capabilities and longevity of the coatings [83].

The epoxy-SiO_2-PDMS-OH composites were synthesized by Xu in order to overcome the drawbacks caused by organic materials. A notable reduction of microcracks were obtained by the hybrid materials and the effectiveness of the composites as the preservation coating were effective [58]. Ni analysed the composition, structure and macroscopic/microscopic morphology of the inorganic/organic polymer based epoxy silanes, and the composite protective material was applied to weathered stone samples and the properties for stone protection were evaluated [84]. A sunlight-curable organic/inorganic composite protective coating was prepared by Striani [85], and the protective performance was characterized by applied on a typical Apulian stone substrate.

A TiO_2 modified sol coating material that is able to protect stone relics was prepared by Shu [6], whereby the results suggest that this material has excellent water vapor permeability, acid resistance and weather resistance for protection of stone relics, while there was no examination of hydrophobicity or anti-microorganism effect. Yu synthesized the nano-SiO_2/fluorinated polyacrylate polyurethane hydrophobic composite coating, while mainly studied the UV-aging and hydrophobicity of the coating, the properties of transparency and anti-fouling was not examined [86]. As a further study of the pioneer research, the Paraloid B72 was modified with nano SiO_2 by He, the properties of hydrophobicity, breathability and ultraviolet protection were characterized by spraying the material onto the substrate of fabric, paper and wood. The results shown good UV resistance after 10 days of UV accelerated aging and the maximum contact angle was 165^o which showed good water-repellence [83]. Wang prepared a transparent and hydrophobic organic-inorganic composite coating by modifying the fluorinated Paraloid B72 with methyl-modified silica and titania, which was used for protecting bricks cultural relics from invasion of microorganisms. The mechanism of the material for antibacterial and anti-algae were studied and the results demonstrated that the weathering process can be slowed by coating the brick cultural relics with silica-titania hybrid fluorinated Paraloid B72 effectively [62, 87].

Although various composite materials have been synthesized based on nano silica, titania and fluorocarbon, the ideal conservation performance of the protective materials still need to be improved by changing the components and preparation methods, ensuring to meet the needs of the multifunctional protective coating.

4.5 Biological Materials

Biological materials provide a more environmentally friendly and sustainable alternative properties to traditional conservation materials. Methods such as microbial secreta and enzymes have been explored for their potential to remove biological growth, stains, and pollutants from stone surfaces, as well as to strengthen and protect the stone against weathering.

Some studies have been conducted with materials extracted from plants or organisms or made of amino acids. The bio-film of 1-amino-9,10-anthraquinone conducting films was prepared by electro polymerization for biosensor and corrosion protection [88]. Chitosan was investigated as the green protective coating to inhibit copper corrosion. The chitosan/tripolyphosphate-based coatings have been proved which can prevent biodeterioration for outdoor stone relics [89]. Another example is that the possibility of using fungal species on the surface of heritage that they can produce the oxalic acids useful in converting corrosion components into stable film [64].

However, the research and application of the biological materials are still sporadic and do not establish reliable conservation method, yet deserve to be mentioned and investigated.

5. Conclusion

Stone relics that are immovable are often exposed to various risks that can compromise their integrity, leading to deterioration and a loss of their intrinsic value. This work reviews the weathering patterns of representative stone relics in the world and the advance progress of the common protective materials, determining that water and soluble salt are the most important factors contributing to the deterioration of stone due to the weathering patterns of Vandalism, Graffiti, cracking and fracture, blistering, efflorescence, peeling and flaking, exfoliation, and most of them can be attributed to water. So, to shield these stone relics from water.

Conservators have dedicated substantial efforts to identify the optimal conservation materials to shield stone relics from water. Previous research indicates that inorganic or organic materials are the primary choices, with widespread use observed in Italy, China, India, and America for protective coatings on stone surfaces. However, prolonged exposure has revealed certain drawbacks, such as the development of a yellowish hue and concerns related to aesthetic and mechanical properties.

This work reviews the weathering patterns of representative stone relics in the world and the advance progress of the common protective materials. From the statement above, the water and soluble salt are the most important factors contributing to the deterioration of stone.

Particularly, Nano SiO_2, TiO_2, siloxane show perfect properties for modifying the polyacrylates, however, the synthesis steps increase the complexity. Future research should focus on simplifying the synthesis processes while maintaining or enhancing the multifunctional properties of the coatings. The methodology should be developed for a more precise measurement of hydrophobicity contact angles required, desired penetration into stone porous networks and degree of anti-microbial activity required for long term conservation to guide the fine tuning of future materials produced as stone relic coatings to protect these cultural heritage treasures.

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