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SUSTAINABLE BIOPOLYMERS FOR PROTECTION OF MARBLE STATUE'S HEAD FROM GRAECO ROMAN PERIOD (CASE STUDY)

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ABSTRACT

Polylactic acid (PLA), Chitosan, and Poly hydroxyalkanoate (PHA) were chosen from among the numerous types of biopolymers as coating agents to examine their efficacy in reducing the impact of air pollutants to the formation of black crust on head of marble statue dating back to the Graeco-Roman period, this head is currently on display at the Grand Egyptian Museum in Cairo (GEM No. 65068). In this study two types of samples used, first category specimens were taken from the lower part of the statue's head to characterize the crust and substrate,. According to results, which are obtained from Scanning Electron Microscope (SEM-EDX) analysis, Micro-Raman spectroscopy, and X-ray diffraction (XRD) analysis, Calcite ($CaCO_3$) is the main component in marble samples, and Gypsum ($CaSO_4 \cdot 2H_2O$) is a common component in the black crust. Second category were an experimental marble samples used to evaluate the protection efficiency of biopolymers. After application, the surface morphology, color change, and water static contact angle of the experimental marble samples were assessed. Finally, the samples were aged artificially to see how resistant they were to solar, ultraviolet, and acidic deterioration. In terms of polylactic acid efficacy, promising results were found due to their properties as hydrophobic behavior, it achieved the highest water static contact angle without affecting color measurements, and then applied in the protection of the marble statue's head.

KEYWORDS: Black encrustation, Biopolymers, Coating, Protection, Hydrophobic, Hydrophilic, Marble, Chitosan, Polylactic

1. INTRODUCTION

Alexandria was a showcase for Ancient Egypt's whole cultural and archaeological history during the Graeco-Roman period, including its Ptolemaic heritage, and it was home to a great number of perfect sculpting ateliers capable of producing masterpieces. As a result, Alexandria's rich sculptural legacy was preserved in the Graeco-Roman Museum, which now has over 4,000 pieces (Savopoulos, 2012; Bianchi, 1984). In the museum garden, an astounding collection of marble sculptures were on show in the open air. One of these important artefacts from the Graeco-Roman period is the marble statue's head, which is now housed in the Grand Egyptian Museum (GEM No.65068). The artefact is deteriorating in several ways, the most visible of which is a black encrustation on the surface. The majority of marble monuments have been harmed by a variety of factors, some of which are related to the stone's essential components (mineralogical and chemical composition) (Böke and Gauri, 2003), or stone structure. Conditions of use and installation procedures, as well as the surrounding climatic conditions (temperature, humidity, pollutants) are all factors that must be considered (Siedel and Siegesmund, 2014; Gauri et al., 2017) and various deterioration factors, whether internal or external, play together to tense the damage circle. Atmospheric pollution which increased recently with industrial activates (Böke et al., 2002; Alimbenia et al., 2000) SO_2 is the main pollution agent that recognized to be responsible for superficial crust on marble, with various thickness and morphologies generally known as well attached black crust on stone substrate (Giustetto et al., 2020; Torok and Rozgonyi, 2004; Frank-Kamenetskaya et al., 2009). At risk antiquities are vulnerable heritage entities and a combined interdisciplinary approach is vital for protection (Sideris et al., 2017).

Current protective coatings, such as silanes and siloxanes, waxes, and acrylic polymers, have demonstrated some limits (Ocaka, 2009; Manodius et al., 2009) Because of their properties as renewable, retreatable, and removable polymers, biopolymers have recently been examined as alternative protective agents. (Auras et al., 2004). These properties are considerably important for the sustainability of authenticity of monuments (Belchior and Dos Santos Rosa, 2017; Ocaka et al., 2014; Sacchi et al., 2012; Zong-Ming and Cheng-Yang, 2006).

Three major bio polymer groups were employed and tested in this study as a coating agent for reducing gypsum formation on marble surfaces in laboratory conditions. The first group of biopolymers known as good gas barrier polymers is chitosan, which is one of the most abundant biopolymers found in nature and is produced from chitin in the major structural component of invertebrates' (krill, crab shrimps, etc.) and arthropods' exoskeletons (insects and some fungi). Chitosan has good film forming characteristics without the addition of any extracts, as well as good carbon dioxide and oxygen permeability, as well as good mechanical properties (Srinivas, 2007). Furthermore, recommended as cleaning agents for unwanted materials on the artwork surface, with the goal of addressing specific cleaning concerns (Cavallaro et al., 2019). In addition, chitosan-based coatings can be used to protect copper alloys against corrosion by acting as corrosion inhibitors (Assaretti et al., 2021). Second group biopolymer is polylactic acid (PLA). PLA is a thermoplastic, aliphatic polyester derived from renewable resources, as sugarcanes or corn starch. The properties of PLA are depending on the molecular weight and, the degradation behaviour depends on the crystallinity which directly affect the free volume and the glass temperature. (Tg) of the polymer, and slower diffusion of water vapour and SO_2 gas. So, it could be noted that increasing the MW of the coating agent may delay polymer degradation, this is because in general, molecular weight increases the strength, toughness and chemical stress crack resistance increase (Passaretti et al., 2021; Snetkov et al., 2020). The third group biopolymer is Poly hydroxyalkanoate (PHA). PHA is a type of thermoplastic linear polyesters that are synthesized as high molecular weight polymer chains by numerous bacterial strains supplied with renewable carbon sources such as sugars and agricultural wastes (Khanna and Srivastava, 2020). The stability of PLA, PHA and Chitosan on marble were assessed under same circumstances by accelerated aging tests with the combination of UV light, heat, moisture, and acidic atmosphere. Protection efficacy of the biopolymers were evaluated by the changes in color, static water contact angle and surface morphology. Other methods have been used as well for marble investigation for conservation (Ahmad,2020; Hqiarat et al., 2019; Abdel Rahim et al., 2020).

Figure 1. Marble statue's head artefact, and its deterioration aspects, (A) black encrustation, (B) epoxy resin, (C) gypsum base.

2. MATERIALS AND METHODS

2.1. Materials

In this study, samples are divided in two categories: first, specimens collected from the lower part of the statue head to characterize the crust; second marble samples used to evaluate the protection efficiency of biopolymers. These specimens were collected from rectangular Carrara marble plates, then cut into cubes in 3*3*3 cm, ultrasonically cleaned in deionized water and dried, and then immersed into the biopolymers solutions. Three types of biopolymers were used, Chitosan (deacetylated chitin) dissolved in 25 ml. (v/v) acetic acid solution, PH 6.5 (Sigma Aldrich), Poly hydroxylalkanoates (PHA) dissolved in chloroform solution, and polylactic acid (PLA) dissolved in chloroform (Purac company). Biopolymers possessing higher molecular weight were chosen for their better protection performance due to its durability, and PLA and PHA have good water barrier properties in High molecular weight. The mixtures were stirred with magnetic stirrer for 6 hours to obtain a homogeneous 3% concentration solutions.

2.2. Methods

The following characterization tools were used:

Polarizing Microscope Optical observations under plane polarized light were per-formed by using a Zeiss AxioLab polarizing microscope to petrographic study.

X-Ray Diffraction Analysis (XRD) used with a Rigaku MiniFlex 600 device for mineralogy analysis. The measurement parameters were as follows: recording range 3–70° 2θ, CuKα anode, generator settings 40 kV and 15 mA, angle 3^{o}-65^{o}, step size 0.02^{o}, time per step 5.0 second. XRAYAN software was used to identify the XRD patterns. All the X-rayed samples were powdered to identify the mineralogical components of the substrate and crust.

Raman Spectroscopy (SENTERR Raman Microscope Bruker), with a 532-nm diode laser (with a maximum power of 10 mw), with integration time 2000ms, used to deter-mine the phase composition of deterioration product of crust and the substrate, while spectrum identification was conducted using in-house spectral libraries. The gypsum was measured with resolution 1.5 cm^{-1} in area that ended at 1400 cm^{-1}, while calcium carbonate was measured at resolution 4 cm^{-1} that ended at 4000 cm^{-1} (Marszałek, 2015)

Scanning Electron Microscope (SEM)

Philips (XL30), equipped with EDX micro-analytical system images collected at different magnitudes at a voltage of 3 kV in back scattered mode (BSE). The samples were coated with Carbon and 10 kV voltage was used. Cross section samples were prepared on Historical samples to identify mineralogical changes

of host rock and altered rock surfaces. Also experimental specimens were utilised to get detailed information and morphology of the surface biopolymers coated on unpolished specimens.

X–Ray Fluorescence Analysis (XRF) portable x-ray fluorescence Nitron type, model XLT3 Golded x-ray analyzer was used for elemental study of crust.

Fourier Transform Infrared Spectroscopy Analysis (FTIR) was carried out Thermo Nicolet iS10 FT-IR Spectrometer in reflectance mode with KBr pallet, spectral range 400 - 4000 cm^{-1}, with 20 scans and resolution 4 cm^{-1}.was used to determine the chemical structure and the type of functional groups of each biopolymer.

Color Measurements for measuring of the samples, Konica Minolta spectrophotometer CM-700d was used. An integrating range with a diameter of 3 mm is involved in this portable device. It has a spectral sensitivity of 400 to 700 nm and works in the d/8 illumination-viewing geometry. Each color measurement was repeated three times in different places, with the average being recorded. The lower ΔE values show the lesser color changes of coating moreover more coating stability according to the following equation:

$$\Delta E = \sqrt{(\Delta a^*) + (\Delta a^*) + (\Delta L^*)^2}$$

Color coordinates were determined as CIELAB (CIE L*a*b*) values. The total color change that is permitted (ΔE*) should be lower than 5. The International Conservation Community of Historic Monuments and Buildings accepts this standard (Gómez-Polo et al.,2016; Illescas and Mosquera,2012).

2.2.1. Treatment Procedure and Accelerated Artificial Aging

The performance of biopolymers after application on marble specimens was evalu-ated by using color variation, static water contact angle, scanning electron microscope. The durability of testing biopolymers on marble specimens was evaluated after submit-ting treated and untreated marble specimens to accelerate weathering tests acidic and rel-ative humidity chamber equipped with SO_2 source, relative humidity 100% and U.V. radi-ation with 2 UVA-340 lamps (wavelength from 365 nm to 295 nm) for 480 h. to achieve in-fluence on marble surface, heating aging using oven at 105°C temperature for 320 h.

3. RESULTS

3.1. Stone Characterization

Thin section of marble sample covered with black crust was investigated under a polarizing microscope, it was found that two layers of black crust were formed, the outer layer contains lamellar gypsum chips, black micro particles, and soil-dust deposition, the inner layer has a lower thickness, in direct contact with the marble surface, and is characterized by the presence of micro-to crypto crystalline Gypsum as a result of the sulphation mechanics. Another thin section of marble sample was exanimated, shows fine-grained crystals of calcite with isotropic fabric and grain boundary shapes from straight to curved in mosaic texture (see Fig. 2). SEM–EDX photographs show detailed information about to obtain detailed information about the morphology of the crust, thickness, and chemical composition of both layers' marble and crust which vary in thickness from 85 to 125 µm as shown in (Fig. 3,4,5).

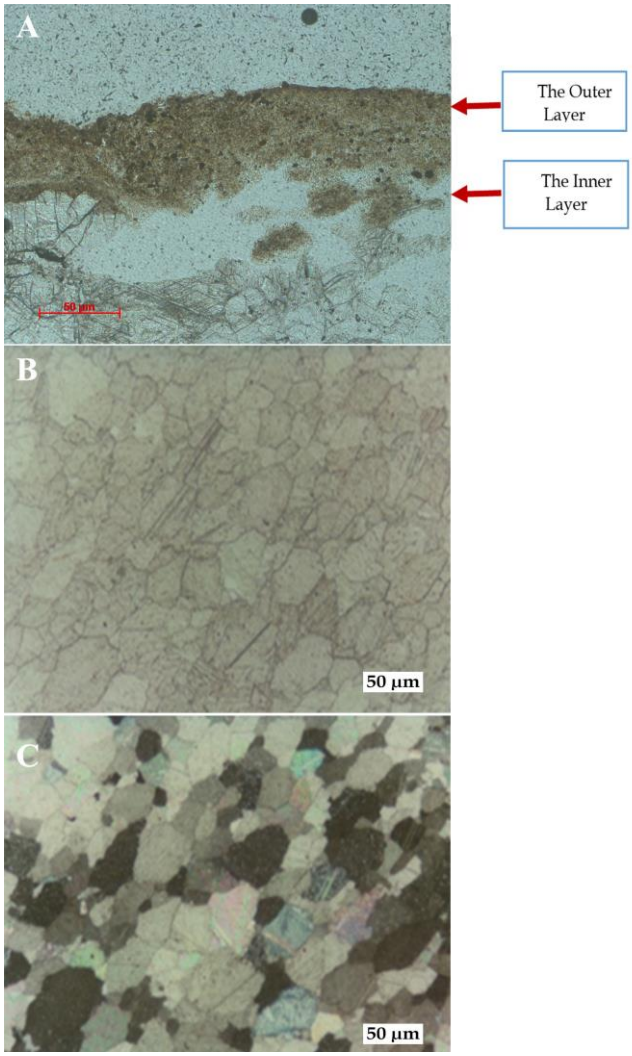


Figure 2. Petrographic images (PLM) showing (A) black weathering crust, (B) the calcite crystals of marble under crossed polarized light (PL), (C) under crossed Nicols (CN).

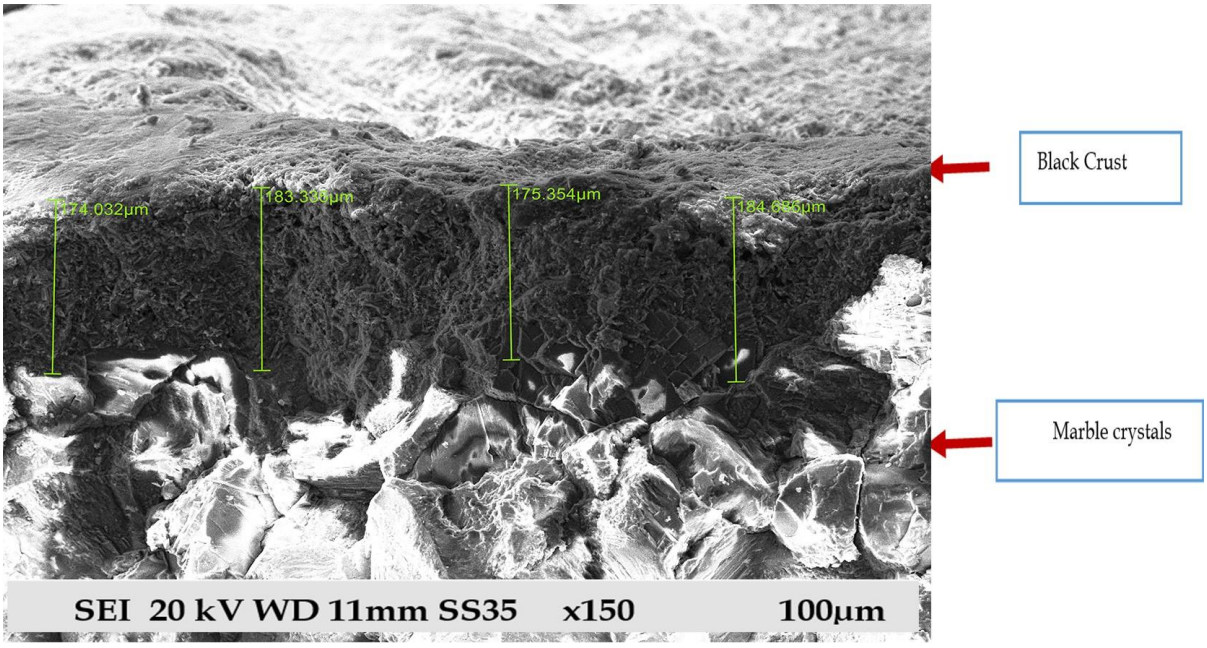
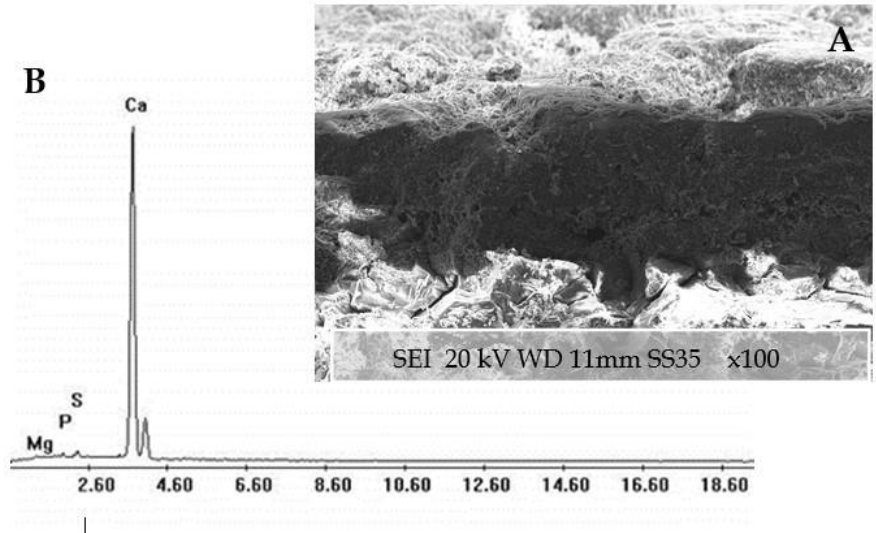


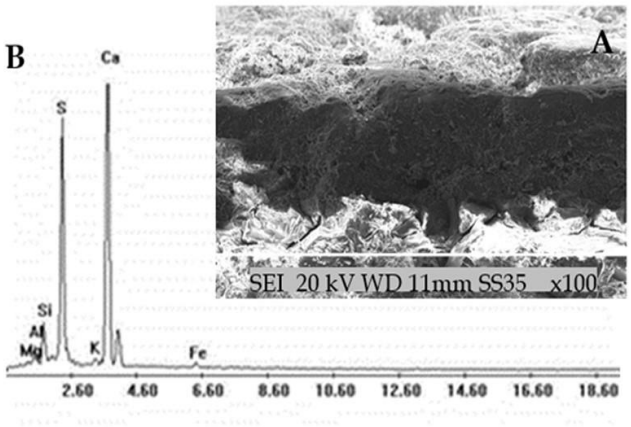
Figure 3. SEM photomicrograph of a polished cross- section of marble surface covered with black



C

Element	Wt %	At%	X-Ratio	Z	A	F
Mg K	1.42	2.31	0.0048	0.0206	0.3321	1.0044
P K	0.43	0.55	0.0032	0.9868	0.7282	1.0316
S K	1.43	1.77	0.0125	1.0126	0.8133	1.0546
Ca K	96.71	95.37	0.9560	0.9994	0.9891	1.0000
Total	100.00	100.00				

Figure 4. SEM photomicrograph of marble, (A) marble crystals, (B) EDX spectrum of marble, (C) percentage of chemical composition of marble crystals.

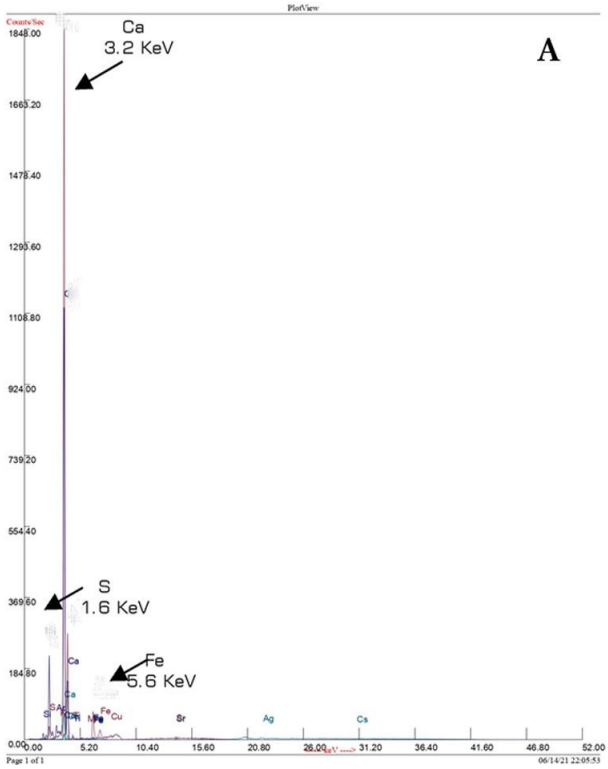


C

Element	Wt %	At%	X-Ratio	Z	A	F
Mg K	0.90	1.34	0.0036	1.0178	0.3947	1.0074
Al K	2.56	3.43	0.0136	0.9883	0.5299	1.0133
Si K	5.33	6.84	0.0354	1.0175	0.6394	1.0207
S K	30.55	34.37	0.2513	1.0099	0.7972	1.0216
K K	1.27	1.17	0.0104	0.9726	0.7847	1.0749
Ca K	57.08	51.37	0.4757	0.9952	0.8369	1.0007
Fe K	2.31	1.49	0.0187	0.9120	0.8870	1.0000
Total	100.00	100.00				

Figure 5. SEM photomicrograph of black encrustation, (A) thickness of crust, (B) EDX spectrum of black crust, (C) percentage of chemical composition of black crust.

Portable x-ray fluorescence pXRF data confirmed the previous EDX results of the marble samples that black crust consists of percentage of S: 23 %, Ca : 69%, Cl: 5 %, Fe :3% as shown in (Fig.6).



B

Element	%
Ca	69
S	23
Fe	3
Cl	5

Figure 6. Figure 6. XRF photomicrograph of black encrustation, (A) XRF spectrum, Ca at 3.2 KeV, S at 1.6 KeV , Fe at 5.6 KeV (B) percentage of chemical composition.

Micro-Raman spectroscopy allowed to identify primary minerals of the rock substrate. Calcite (Cal.) ($CaCO_3$) have been present as main components identified from the symmetric stretching band of the Carbonate group (CO_3^{2-}) at 1085 cm^{-1} also minor bands at 712 and 282 cm^{-1} as shown in (Fig. 7), and Gypsum (Gp.) ($CaSO_4 \cdot 2H_2O$) as a common secondary mineral of the black crust on the marble surface. From its main band at 1010 cm^{-1} (symmetric stretching) of the sulphate group (SO_4^{2-}) and, in some spectra, also minor bands at 416 and 492 cm^{-1} (Fig. 8).

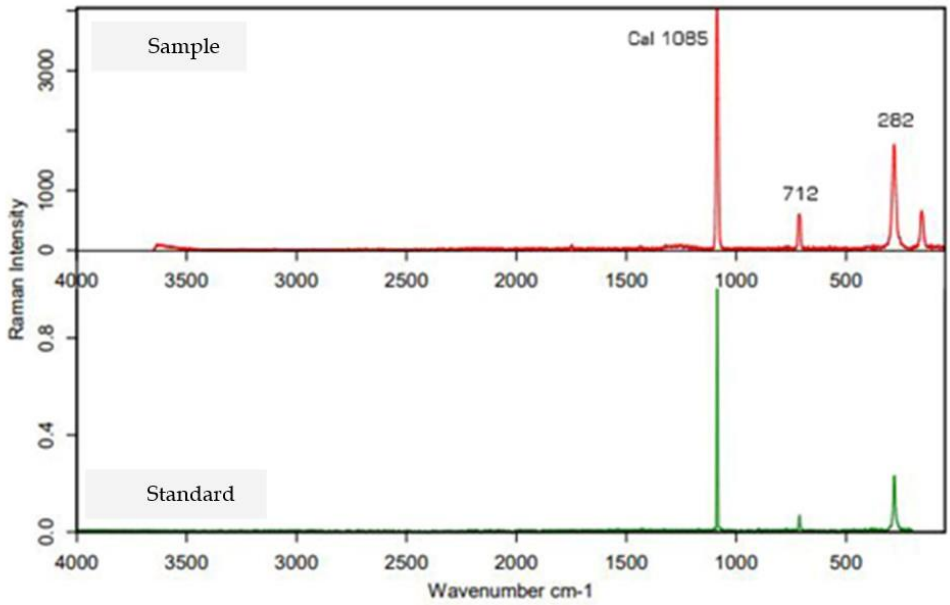


Figure 7. Raman spectra of components of marble calcite – the essential mineral of the stone (Cal, main band st. 1085 cm^{-1} of CO_3)

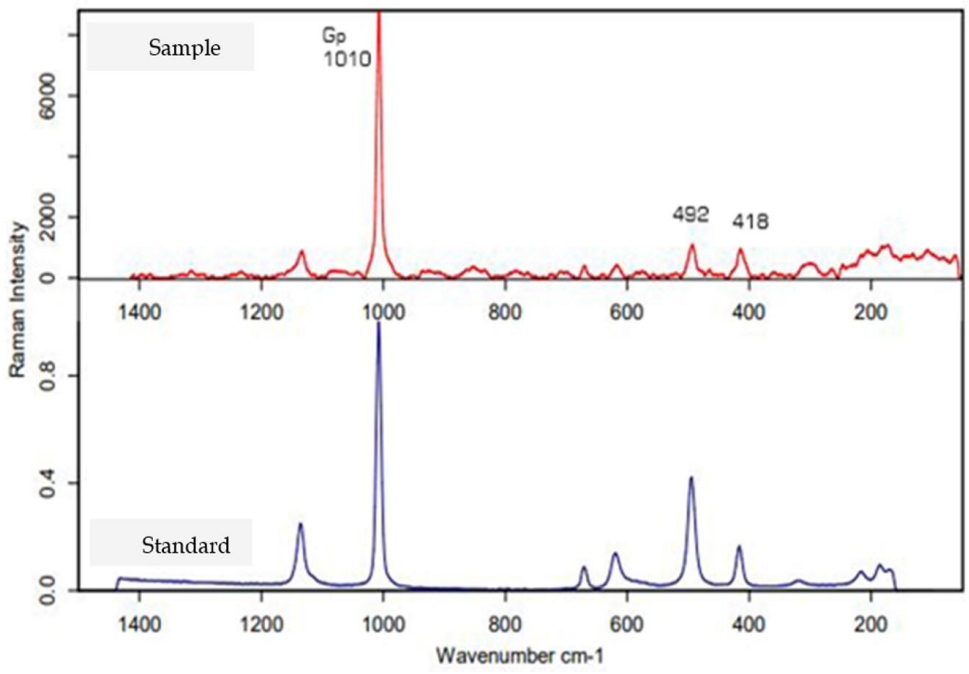


Figure 8. Raman spectra of components of the black crust) gypsum (Gp, main st. band 1010 cm^{-1} of SO_4).

The XRD analyses of samples of the marble statue's head confirms a considerable amount of gypsum in the black crust and also Calcite within the natural components of the marble sample without the crust as shown in (Fig. 9).

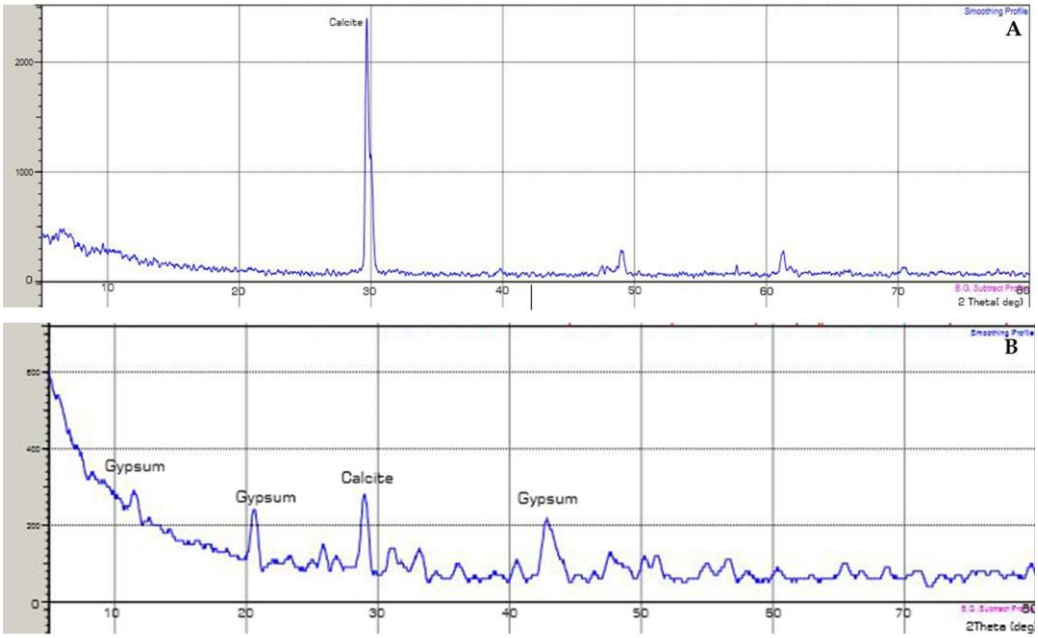


Figure 9. XRD Patterns of the statue (A) Pattern of marble substrate, (B) Pattern of crust.

3.2. *Biopolymers Characterization*

Fourier-transform infrared spectrometry spectrums of three biopolymers are shown in Fig.10 in PHA and PLA the peaks showing the presence of ester group, methylene group, and a hydroxyl group. The characteristic peaks observed in PHA were 3435 cm^{-1} (terminal OH group), 2974 cm^{-1} (methylene C-H group), and 1724 cm^{-1} (ester carbonyl C=O group), in case of PLA peaks were observed at 3421 cm^{-1} (terminal OH group),2993 cm^{-1} (methylene C-H group), and 1759 cm^{-1} (ester carbonyl C=O group) (Shamala, 2009; Chieng et al., 2014). In Chitosan we can observe the spectrum in region 3441 cm^{-1} and 2881 cm^{-1} corresponds to N-H and O-H stretching the presence of band 1604 cm^{-1} confirmed with C=O stretching of amide. The absorption band in 2992 cm^{-1} attributed to C-H stretching, these bands are characteristics of polysaccharide (Hajji, 2014) as shown in (Fig. 10).

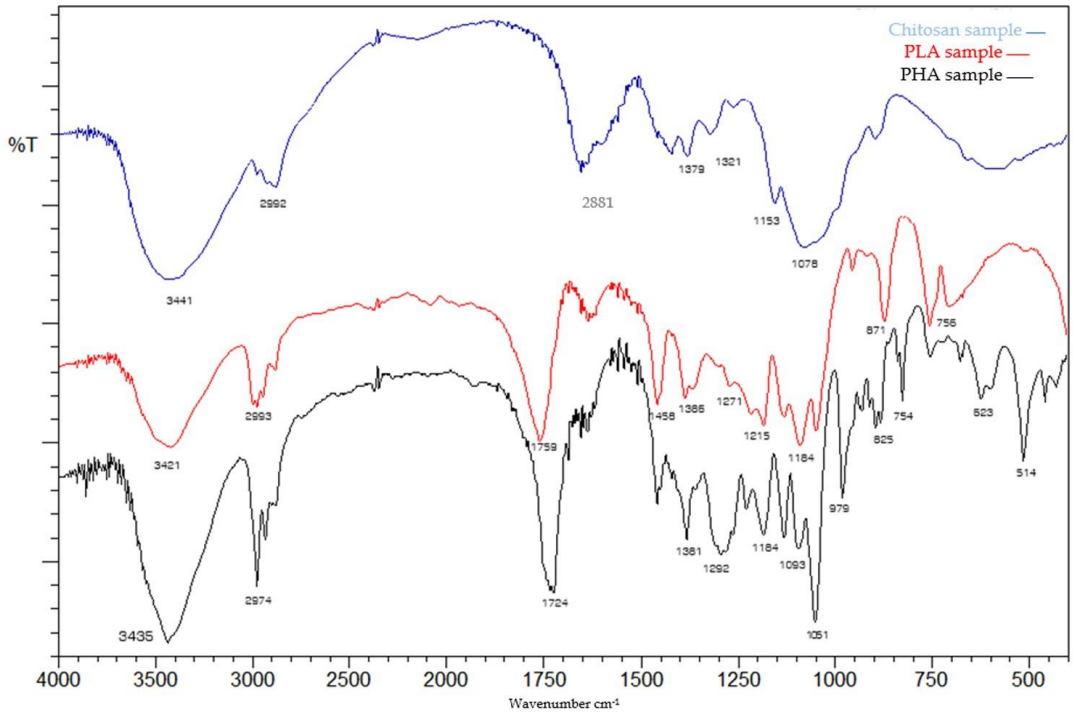


Figure 10. FTIR spectroscopy spectral analysis of the biopolymers

3.3. Coating Morphology

Application of biopolymers on the surface of the stone samples has a significant impact on the surface morphology, which was investigated using a scanning electron microscope. The SEM images of the stone coated and uncoated before and after aging are shown in the (Fig. 11), and this indicates that sample without any protective coating layer has numerous cracks and pores on the surface. It reduced in other coated specimens, it was seen that PLA and PHA coated samples have completely covered with film and have appropriate resistance for weathering cycles. On the other hand chitosan coated samples lost their stability after aging cycles as seen some of the coated film was detached with appearance of black crust. SEM analysis indicated resistance of PLA coated marble samples to weathering tests.

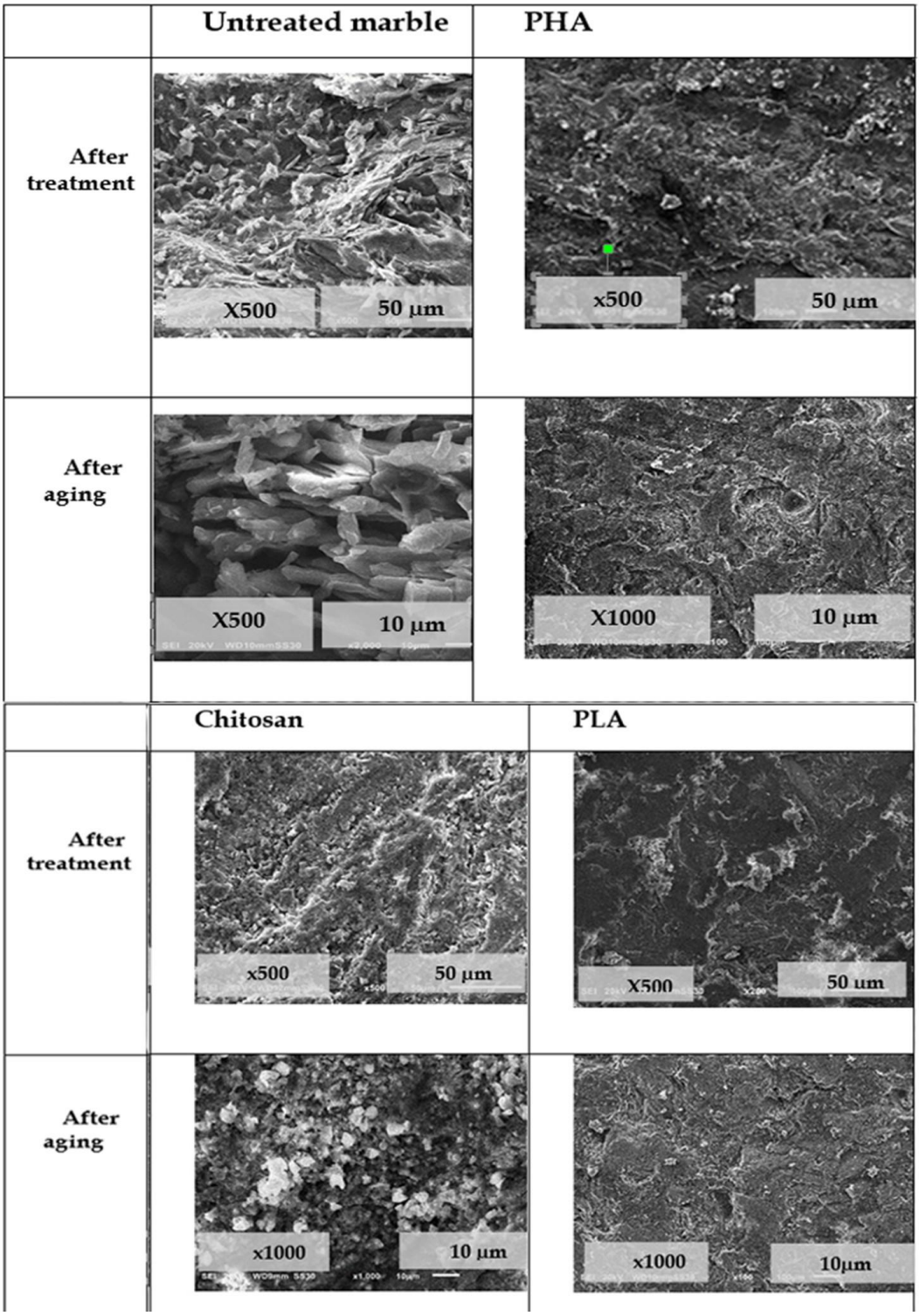


Figure. 11. SEM images of the marble samples before and after weathering analysis.

3.4. Evaluation of Color

The surface color stability is an important characteristic to consider when evaluating the protective coating in artefacts. Each biopolymer's color changes were tested in three times on different places with taking the average, and the total color difference (E) as a color change surface color and displayed higher color stability throughout weathering studies. Parameter was determined before and after ageing cycles, as shown in Table 1.

Table 1. Coating colorimetry before and after ageing

Polymer type	Colorimetric measurements after application				Colorimetric measurements after aging			
	ΔL*	Δa*	Δb*	ΔE	ΔL*	Δa*	Δb*	ΔE
Chitosan	-3.80	-0.09	5.82	4.52	-4.57	-0.02	-0.78	4.11
	-6.10	0.20	0.69	3.08	-1.50	-0.50	-1.81	3.43
	-4.50	0.02	1.90	1.90	0.67	0.06	0.49	5.34
polylactic acid	-6.10	0.20	0.69	3.08	-6.10	0.20	0.69	1.35
	-4.50	0.02	1.90	1.90	-4.50	0.02	1.90	1.97
	-1.86	-0.24	1.60	0.58	-1.86	-0.24	1.60	2.45
Poly hydroxyl alkanoate	-5.05	-0.10	1.77	3.61	0.10	-0.32	-1.58	3.30
	-1.54	-0.34	2.99	2.47	-1.42	-0.36	-2.05	1.75
	-3.86	-0.22	1.19	2.72	0.27	-0.27	-2.94	5.91

Even after accelerated weathering tests, the average of total color change (ΔE*) of PLA before and after weathering cycles is 1.85 and 1.92, respectively, and the average of total col-or change (ΔE*) of PHA before and after weathering cycles is 2.93 and 3.05, respectively.

Thus, PLA, and PHA treated marble specimens were near the threshold for human eye perception (< 3) (De Rosario et al., 2015). Whereas the average of ΔE* value of Chitosan before and after weathering cycles are 4.09 and 4.89, respectively, so coated marble specimens was higher than the acceptable total color change value for cultural heritage conservation. According to color measurements, PLA did not significantly affect the stone's color.

3.5. Measurements of the Static Water Contact Angle

By measuring the static contact angle of a water drop on sample surfaces, the hydro-phobicity of coated marble samples was examined. To ensure values, three measurements were made on each sample for three specimens. The water contact angle of untreated marble was found to be 34°, indicating that the marble surface is hydrophilic. The use of biopolymers improves the contact angle of marble coated samples with PHA, and PLA. The CA was significantly increased to 105° and 95°, respectively, indicating an increase in surface hydrophobicity and roughness. On the other hand, the CA of Chitosan coated marble samples remained hydrophilic at 45°. After weathering tests, the CA of PLA, PHA, and Chitosan coated marble reduced, with PLA coating decreasing to 95° but still almost being accepted as hydrophobic, PHA decreasing the hydrophobicity line after weathering ageing to 78°, and Chitosan decreasing to 22° (Figs. 12, 13). As a result, the following equation was used to assess the CA reduction percentage (CARP) of the samples:

$$\mathrm{CARP} = \left(\frac{\mathrm{CA\ before} - \mathrm{CA\ after}}{\mathrm{CA\ before}}\right) \times 100$$

It can be deduced that a lower CARP indicates higher coating durability and resistance to weathering. Table 2 shows CA and CARP values.

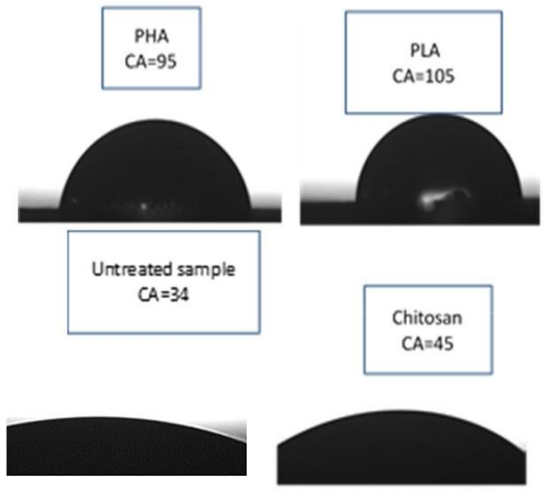


Fig.12 .CA analysis of treated and untreated marble samples before aging cycles

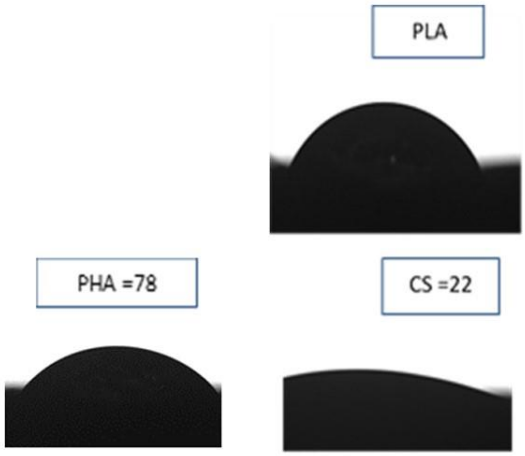


Fig.13. CA analysis of treated and untreated marble samples after aging cycles.

Table 2. Hydrophobicity and durability of the coatings.

Polymer	PLA		PHA		CS	
	After	Before	After	Before	After	Before
CA (°)	105	95	95	78	45	22
CARP (%)	9.5		17.89		51.11	

4. DISCUSSION

First and foremost, the analyses of the sampled surfaces revealed that the black crust was formed up of components and layers of varying thickness within the same object, which could be due to the non-homogeneous distribution of the alteration products (Ma etal., 2014). Multiple factors influence the formation of crust and the resulting stone damage. On and below the stone surface, sulphate formation and calcite precipitation can occur. Several factors influence the location of such processes, including the substrate, exposure, and pollution levels. Gypsum growth and diffusion on marble substrate have been widely in-vestigated using SEM-EDX analysis, Micro-Raman spectroscopy, and XRD analysis, the primary minerals of the marble is Calcite ($CaCO_3$), and Gypsum ($CaSO_4 \cdot 2H_2O$) is a com-mon secondary mineral of the black crust withsmall amounts of Fe, and Al (Maravelaki-Kalaitzaki. 2005) as a result of exposure of marble statue to atmospheric Sulphur dioxide (SO_2) and, moisture in the Garden of the Graeco-Roman Museum in Alexandria.

To reduce the formation of black encrustation on marble surfaces, we tested the effects of polylactic acid, poly hydroxyalkonates, and chitosan polymers on SO_2–reaction on coated marble surfaces. After ageing cycles, the degradation of polymers and the formation of gypsum crystals on marble surfaces were monitored using a scanning electron micro-scope (SEM). Uncoated marble was found to be mostly fine calcite, according to SEM scans. Calcite crystals are changed into prismatic gypsum crystals after SO_2 exposure. Even though chitosan has an excellent gas barrier property, increasing micro-holes and cracks were detected on chitosan coated samples due to the quick breakdown of polymer films. (Despond, 2001), and high amount of gypsum formation on coated marble surfaces, it can be claimed that the use of chitosan as coating material was not effective in inhibiting the marble–SO_2 reaction. The poor protection efficiency of Chitosan on coated specimens was confirmed with the color measurements, the results showed that the average color change (ΔE*) of PLA and PHA before and after weathering cycles of treated marble specimens were near the threshold of human eye perception (< 3) Whereas the average ΔE* value of Chitosan before and after weathering cycles was higher than the acceptable total color change value for cultural heritage. So, PLA did not significantly affect the stone's surface color and displayed higher color stability throughout weathering studies (Al-Dosari, 2017).

Contact angle measurements results showed that the surface of marble coated with this polymer still hydrophilic. On the other hand, PLA and PHA reduced gypsum formation on marble surfaces after ageing cycles especially after exposure to SO_2 reaction. The results showed that PHA and PLA polymers behaved as protective films on marble surfaces against the effects of SO_2 gas. Better performance was obtained from PLA due to its lower degradation rate than that of PHA. In addition to lower degradation rate, the highest contact angle was also observed indicating that the lower vapor–solid interaction. However, gypsum crystals were rarely observed on the degraded PLA coated marble. The protection efficiency polymers could be differing in results according to molecular weight and crystallinity which directly affect on the free volume and the glass temperature (Tg) of the polymer, it could be noted that the increase in MW of coating agent could delay the degradation of the polymer.

5. CONCLUSION

The application of polymers from a monomer produced starting from renewable re-sources in the field of Cultural Heritage represents an attracting alternative to traditional petrochemical-based materials. Overall, the application of biopolymers for stone protection is still in the preliminary stage, and few materials have been used in the real case of stone restoration. Three types of biopolymers have been investigated as protective coatings on marble surfaces in the

laboratory conditions Polylactic acid (PLA), Poly hydroxyl alkanets (PHA), and Chitosan (CS).

The appropriate biopolymer coating was chosen based on the results of the biopolymer coating after treatment and after accelerated ageing cycles on marble samples.

Polylactic acid (PLA), Poly hydroxyl alkanets (PHA), and Chitosan (CS) were selected. The results reveal that, depending on its properties, Polylactic acid (PLA) was the most effective one among the all tried biopolymers. The structural variances in the polymer affected the protection potential, PLA can be used for protection of the historical marble surfaces in the polluted atmosphere to inhibit SO_2-Calcium Carbonate reaction due to their hydrophobic behaviour, it achieved the highest water static contact angle without affecting color measurements, finally this biopolymer offers properties as replicability and reversibility offering the possibility of new application on the marble surfaces.

AUTHOR CONTRIBUTIONS

Conceptualization, E.T.; writing—original draft preparation, E.T.; methodology, E.T. and F.H ; writing—review and editing, F.H. and Y. M. ; supervision, F.H. and Y. M. All authors have read and agreed to the published version of the manuscript.

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