Egypt. J. Chem. **Vol. 66**, No. 10 pp. 403 - 414 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Enhancing the Performance of SILRES® BS OH 100 as A Consolidant of Archaeological Limestone Using Nano-Hydroxyapatite

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Abstract

This study aims to evaluate the effectiveness of nanohydroxyapatite as a consolidating material for limestone monuments when dispersed in the SILRES® BS OH 100, compared to the polymer in individual form. The current study was applied to one of the stone artifacts displayed at the Obelisk Open Air Museum in El-Matareya, Cairo. Treated samples were subjected to accelerated aging by moisture, temperature and salts to evaluate the stability of the consolidants. Nanohydroxyapatite/ polymer nanocomposite was prepared using in situ emulsion polymerization system. TEM, SEM-EDX, PLM, XRD, colorimetric measurements, water contact angle, porosity, capillary water absorption measurements and compressive strength tests were used to evaluate the consolidants efficiency. The results of thin sections revealed that the studied limestone samples were very fine-grained (micrite) containing microfossils. XRD analysis proved that the archaeological limestone consists mainly of calcite with a small percentage of gypsum, while SEM examination showed the weakness and high porosity ratio of the archaeological limestone samples. However, SEM investigation proved that the samples treated with HAP/ polymer nanocomposite have a homogeneous coverage, and the consolidant was able to fill pores and provide good consolidation. Moreover, the physical and mechanical properties of studied limestone samples were significantly improved as a result of the use of HAP/ polymer nanocomposite after treatment and aging.

*Keywords:*Hydroxyapatite nanoparticles; Consolidation; Limestone monuments; Compressive strength; Colorimetric measurements.

1. Introduction

Iunu "or Onu", as it was called in ancient Egypt which means the city of pillars where a temple of the God "Ra", was established that including many obelisks that appear in the form of columns. Others believe that Heliopolis means in Greek "The house of the sun". One of the stone remains from the temple of Heliopolis is the present study piece, which is a stone block was found and re–used in the 11th century Fatimid wall at the Bab El-Nasr /Gamalya district in historic Cairo. The studied stone artifact dates back to the era of the New Kingdom, Dynasty 19. The inscription contains the name of the God "Amun- of -Ramesses". The birthname cartouche of the king can be read as "Paramessu" instead of "Ramessu". This name is only attested in the Heliopolitan temple of Ramses II for Amun and Mut. This artifact is now on display at the Obelisk Open Air Museum in El-Matareya, Cairo [1, 2] (Figures 1, 2).

Limestone is one of the most famous types of sedimentary rocks, its main chemical composition is calcium carbonate. Limestone monuments suffer from the negative impact of continuous weathering processes. There are many forms of weathering such as deposits, detachment of stone layers, significant reduction in the density of the stone, weakness of the internal structure of stone [3, 4]. Weathering is a complex and continuous natural process that is the result of interactions between stone monument and physical, chemical and biological factors in the environment surrounding the stone substance [5, 6]. Moisture, temperature changes and air pollutants play key role in the mechanics of physiochemical damage

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EJCHEM use only: Received date 07 December 2022; revised date 07 February 2023; accepted date 14 February 2023

DOI: 10.21608/EJCHEM.2023.179271.7276

Fig. 1. El-Mesala (Obelisk) Open Air Museum in El-Matareya, Cairo, Egypt

Fig. 2. (A) The studied archaeological limestone artifact from the temple of Heliopolis before treating, (B) The studied archaeological limestone artifact after treating

to the stone monuments [7].Synthetic polymers have been used as consolidants and water repellent for stone preservation. Silica-based consolidants are the commonly materials which are used for stone consolidation [8, 9]. One of the main problems in these materials is the coating layer thickness limitation, so it tends to form fragile and cracked film inside the stone, due to its shrinkage during drying, so the elasticity of stone surface is lost. [10, 11]. Recently, many researches in the investment of nanomaterials in the treatment and conservation of antiquities have introduced. Nanometer is a billionth of a meter. Nanomaterials have at least one dimension in nanoscale (1–100 nm) [12]. Increasing the surface area of nanomaterials is the most important characteristic that distinguishes these materials from their traditional counterparts, increasing their ability to interact. It is worth noting that the small size of particles with the increasing of surface area has a strong impact on the forces of hydrogen bonds and van der waals and affects the surface tension of these particles, resulting in unique physical properties[13,14]. Moreover, nanomaterials have many advantages such as stability, chemical and biological inactivity, nontoxic, and water repellence properties. Nanomaterials are use as additives to modify the synthetic polymers and enhance their properties [15]. Furthermore, nanomaterials have a great benefit in improving the properties of organic/ inorganic hybrid composite. nanocomposite has at least one component in nanoscale size [16]. Therefore, many studies have paid great attention to invest these polymers and avoid their defects by adding various inorganic oxides in nanoscale into hybrid siloxane or silicon polymers [17]. Eventually, researches have proved that the efficiency of nanomaterials and nanocomposite and their physical, chemical and mechanical properties are better than the traditional ones which have been widely used in stone consolidation for many decades [18]. Inorganic nanomaterials are highly compatible with the stone material so they are commonly used in conservation treatment [19, 20] and thus improve the properties of stone, when are used as consolidants [21]. Many

recent researches have shown the effectiveness of nanomaterials in carbonate stones consolidation such as calcium hydroxide, barium hydroxide, magnesium hydroxide, strontium hydroxide and hydroxyapatite [22, 23]. Several studies have recently emerged to strengthen carbonate stones with phosphate-based consolidants and these studies have reached promising results for these consolidants in terms of efficiency and durability as well as their suitability for carbonate stone material [24]. One of the advantages of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] in strengthening carbonate stones, is improving the mechanical properties of treated stones, increasing the resistance of stones to acid degradation and forming a protective layer with strong bonds on the surface of the treated stone [25]. It is also Characterized by its low melting degree, where its melting degree is 18 times lower than calcite, its crystalline structure is similar to calcite where the cell unit appears in the form of hexagonal, while the cell unit appears for calcite rhombohedral, often described as hexagonal and its lattice parameters are close to calcite, differing from it at a slight rate of only 5%, indicating the harmony between their crystalline structure, which allows for the construction of a new crystal layer with strong long chains associated with the surface of the carbonate stones [26, 27, 28]. But one of the defects that appeared when treated with hydroxyapatite is the formation of a porous layer and incomplete coverage of the stone surface or the presence of cracks due to the increased thickness of the formed layer [29].

In this study, the effectiveness of nanohydroxyapatite will be assessed by adding it to a silicon polymer SILRES® BS OH 100 to form nanocomposite for avoiding each other's defects in their individual state, and compared to the polymer in its individual state. For this purpose, different examinations and tests were carried out to assess the consolidating materials, comparison between untreated, treated and treated aged samples were taken place by using different methods. SEM examination was carried out to assess the depth of penetration of the consolidating materials and surface morphology. To assess the improvement in the mechanical properties of treated stones, the compressive strength test was taken place, the improvement in the physical properties of the treated stones evaluated by porosity and water absorption capillarity tests. Optical appearance was evaluated by colorimetric measurement.

2. Experimental

2.1. Materials and Methods

SILRES® BS OH 100, (Also known as: Wacker OH 100), is a solventless ethyl silicate, it has been used as consolidant since 1960's, it can penetrate into stone then form a glass like silica gel.The product used in the present was supplied by Wacker Silicons, Germany. It's ready to use for consolidation of stones and other building materials. The polymer is commonly used due to its water-repellency properties [30].

2.1.1. Preparation of nanohydroxyapatite

Chemical precipitation method was used for the preparation of the hydroxyapatite nanoparticles solution. The starting materials in this process are calcium chloride ($CaCl_2.2H_2O$) and sodium dihydrogen orthophosphate (NaH_2PO_4). The most preferred method for the synthesis of hydroxyapatite is sonication with magnetic stirring method where there is no foreign elements and water is the only product of this reaction. 0.1M of ($CaCl_2.2H_2O$), 3g of (NaH_2PO_4) were weighed and dissolved in 500 mL of distilled water and stirred vigorously for about 3hr at 50 °C. NH_4OH solution was used to control the pH of the prepared aqueous solution to 11. A homogenous solution was formed followed by aging for 22 – 24 h, and then washed 3 times with distilled water. A milky gelatinous precipitate was formed after centrifugation at 1500 – 25000 rpm for 15 min. The precipitate was dried at 90 °C for 24 h. Using a mortar, the dried powder was crushed to fine powder then calcined at 700 °C to increase the crystallinity of the hydroxyapatite nanoparticles. [31]

2.1.2. Preparation of hydroxyapatite/polymernanocomposite

SILRES® BS OH 100 was dissolved in ethanol in ratio 5:1 to make Wacker solution. 0.25 gm of nanoparticles was dispersed in Wacker solution using ultrasonic sonifier under ultrasonic dose 400 watt in order to produce nano composite where the ratio of nanoparticles in the solution was 3% [32].

2.1.3. Preparation of experimental limestone samples

The experimental limestone samples were cut into small cubes 4×4×4 cm, and cleaned with a soft brush and then washed with distilled water to remove dust stuck in the stones. The samples were dried in an oven at 105 °C for 24 h. Before the application of consolidants, the samples were left for 24 h at 23 ± 2 °C, 50 ± 5% RH [33].

2.1.4. Application of consolidating materials on stone samples

The consolidating materials were applied by brush at room temperature and pressure. The process was repeated three cycles, between each consolidation and the other 48 h. The samples were left after final consolidation to dry for 21 days at room temperature and a controlled relative humidity (RH) 50% in order to complete the polymerization process. Some treated samples were submitted to examination methods, while the others were submitted to the accelerating aging process and then to the examination methods to observe changes in consolidation materials after artificial aging [34, 35].

2.1.5. Thermal aging (wet – dry cycles)

Simulating the environment surrounding the monument is the objective of this test to identify the

impact of changes in temperature and moisture on the treated samples to determine the efficiency and effectiveness of consolidating materials. The treated samples subjected to immersion and drying cycles as follows: 18 h immersion in distilled water, then 6 h in an oven "Herous-Germany" at 105 °C [36] for 10 cycles. The samples were submitted to cycles of immersion in a saturated NaCl solution for 4 h then 28 h of exposure in room temperature (25 °C and 40% RH) followed by 16 h in an oven at 105 °C [37].

2.1.6. Microscopic examination

2.1.6.1.Polarizing microscope (PLM)

Through the examination using the polarized light microscope (PLM), model Olympus BX50, identify some of the manifestations of damage to stone samples such as cracks and very fine cracks, and also identify transformations of the stone minerals, in addition to seeing the mineral deposits that distort the stone such as iron. The examination was carried out in the Egyptian Mineral Resources Authority, Center Laboratories Sector, Giza, Egypt.

2.1.6.2. Scanning electron microscope (SEM)

Scanning electron microscope/ FEI Quanta 3D 200i Edx/ thermofisher pathfinder was used to examine and study the crystalline structure of stone samples, the extent of damage to them, in order to examine the shape and morphology of the layer of consolidating material and the extent of its ability to bind the granules of the stone material then evaluate the ability of consolidants to consolidate and protect the stone [38]. The examination was carried out in the Grand Egyptian Museum, Giza, Egypt.

2.1.6.3.Transmission electron microscope (TEM)

The study and investigation of nanomaterials and nanostructure is needed to discover the properties of nanostructured materials, for achieving this purpose, the efficient characterization instruments were used. TEM has evolved to become an indispensable device in the field of nanotechnology due to its high capabilities in providing structural and chemical information of nanomaterials from length scales to atomic dimensions, which provides the opportunity to understand the properties of nanomaterials and manipulate their behavior [39, 40]. A high-resolution transmission electron microscope (HR-TEM, JEM-1230, Japan) operated at 120 kV was used in this study to investigate the studied nanomaterials and nanostructures. The study was carried out in the transmission electron microscopy laboratory at the National Center for Housing and Building Research, Dokki, Giza, Egypt.

2.1.7. X- Ray diffraction analysis (XRD)

The method of analysis with X-ray diffraction (XRD) is the most important and common method of analysis used in the field of studying archaeological crystalline materials, where it is possible through this method to accurately identify the mineralogical composition of the stone material[41]. XRD analysis was carried out to identify the mineralogical composition of the archaeological limestone and experimental limestone samples, in addition to identifying the mineralogical composition of nanohydroxyapatite. For this study, a Siemens diffractometer (30 kV and 25 mA) with the Kα1 radiation of copper (λ = 1.5406 Å) (2θ = 20 – 60°) was used. The analysis was carried out in the XRD laboratory at the National Center for Housing and Building Research, Dokki, Giza, Egypt.

2.1.8. Colorimetric measurements

Evaluation of color changes of treated and treated aged experimental samples were carried out, to determine the impact of consolidating materials before and after ageing process on the color changes of the stone.The color change rate of samples treated was measured by CIE L*a*b*, a global measure of color change for different samples, which measures the degree of the blade symbolized by the symbol (L*) and tends to be bright white when the color value is 100, The lower this value to zero, the greater the total blackness, the higher the value (a*) it measures red and green and the color is red when the color value is positive, but if it is negative it indicates that the color is green, and the value (b*) indicates yellow and blue, where the color is yellow when the value of the color is positive, but if it is negative it indicates that the color is blue, and the color difference between two samples is specified using the symbol (ΔL*, Δa*,Δb*) and the total color difference is ΔE) according to the following equation:

ΔE= √((ΔL+Δa+Δb)2)[42].

2.1.9. Physical properties measurements

Water is the basis of the occurrence of damage as it is one of the most important physiochemical factors that cause damage to the stone monuments. There are no chemical interactions between the deteriorating factors and the surrounding environment without its presence[43]. Density, porosity and water absorption measurements were carried out according to UNI 10859:2000 [44, 45] for untreated, treated and treated aged samples that were submitted to immersion in distilled water for 24 h after that the samples were taken out and wiped with tissue paper then weighed immediately. The values of density, water absorption and porosity were calculated using these following equations:

1- Density = $\frac{W}{V}$ **(gm/cm^3)**

2- Porosity (%) = $\frac{W2-W1}{V}$

3- Water absorption (%) = $\frac{W2-W1}{W1}$

Where W is the sample weight, V is the sample volume, W1 is the sample weight before immersion in water for 24 h and W2 is the weight after immersion in water. The measurements were carried out in the laboratory of building materials properties at the National Center for Housing and Building Research, Dokki, Giza, Egypt.

2.1.10. Mechanical properties measurements

Compressive strength is one of the most important mechanical properties that should be measured for untreated, treated and treated aged samples. According to ASTM C170-Standared Test Method for Compressive Strength of Dimension Stone, the load – bearing area of each sample was calculated before the test then the samples were put into an Amsler compression - testing machine [46]. The measurements were carried out in the laboratory of building materials properties at the National Center for Housing and Building Research, Dokki, Giza, Egypt.

2.1.11. Static water contact angle measurements

Dueto the fact that the water is the main factor in most of the damage process to stone monuments, it is necessary for reinforcing materials to have a high-water repellent ability. Water hydrophobicity of the untreated, treated and aged samples were evaluated by measuring the static water contact angle. The test was carried out using an electron microscope equipped with special camera model T330, Generated with One Attension Version 2.7 (r5433), Company name: Biolin Scientific, Finland, according to standard UNI EN 15802-2010. The samples were placed on allocated place then a 3µL water drops falls on the surface of the samples using a graduated micro pipette. High resolution image was taken by Canon camera with high quality lenses. Finally, the contact angles were calculated by digital program. The measurement was repeated at least five times for each sample then the average for each sample was recorded [47]. The examination was carried out in Faculty of nanotechnology postgraduate, Sheikh Zayed, Giza, Egypt.

3. Results and Discussion

3.1. X- Ray diffraction analysis (XRD)

XRD analysis was carried out on the samples of archaeological limestones, and those used in the experimental study, as well as, the nano-hydroxyapatite material (HAP) used in the study. With regard to the archaeological stone samples, the results showed that the limestone at the archaeological site consists mainly of calcite grains ($CaCO_3$) with a percentage of 96% and Gypsum ($CaSO_4.2H_2O$) with a percentage of 4%, while the experimental limestone samples consist of 91% Calcite and 7% Ankerite $Ca(Fe^{+2}, Mg)(CO_3)_2$ (Figure 3 A, B). On the other hand, X-ray diffraction patterns of nano HAP were recorded in the angular range 2θ = 20 – 60°represented the XRD of crystalline size of nano HAP whit phase corresponds to ICDD database. The main (h k l) are: (002), (211), (300), (202), (130), (002), (222) and (213) (Figure 3 C). The average crystallite size can be estimated by X-ray diffraction pattern, using the Scherrer equation: [48]

$$d = \frac{0.9\lambda}{\beta \cos \Theta}$$

Where 0.9 is the Scherrer constant, λ is the x-ray diffraction wavelength (λ=1.5406 Å), β is the full width at half maximum (FWHM) of plane (311) and θ is the Bragg angle in degree. The average crystal size of nano HAP was 27-70 nm which was agree with TEM results.

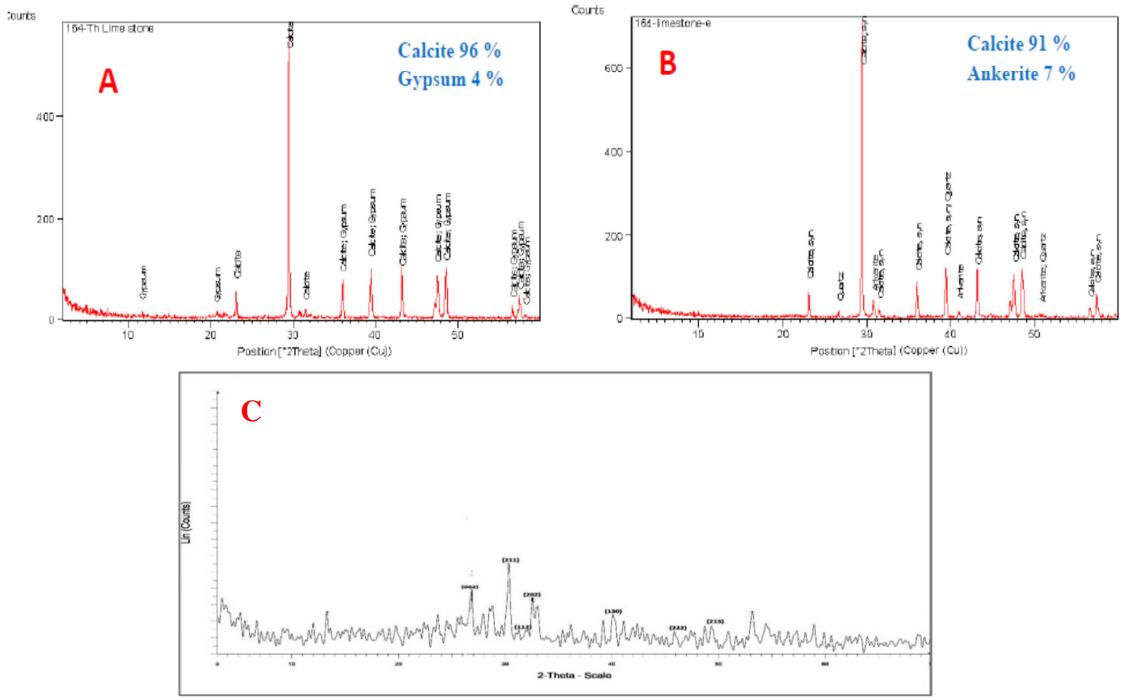

Fig. 3. X-ray diffraction patterns (A) XRD pattern of the archaeological limestone sample, (B) XRD pattern of the experimental limestone sample, (C) XRD pattern of nano HAP

3.2. Transmission electron microscope (TEM)

Microscopic examination by transmission electron microscope (TEM) was performed to confirm the nanostructure of hydroxyapatite nanoparticles. TEM images of HAP nanoparticles (hydroxyapatite/polymer nanocomposites) were shown in Figure 4 A, B. The nanoparticles are comparatively rod-like particles with a mean size ranged from 27- 69 nm.

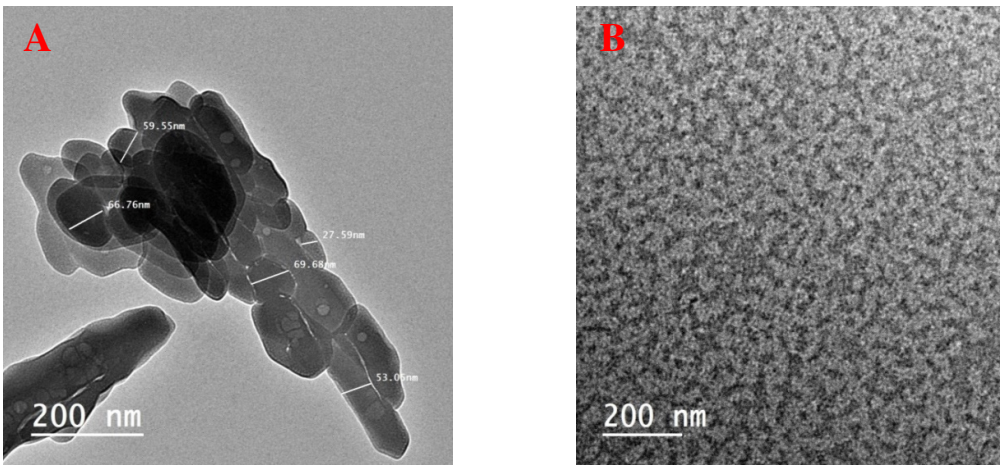

Fig. 4. TEM photomicrographs (A) TEM photomicrograph of the particles size of hydroxyapatite nanoparticles, (B) TEM photomicrograph of hydroxyapatite/ polymer nanocomposite

3.3. Polarizing microscopy of studied samples (PLM)

Thin sections were used to identify the minerals of stone using polarized light microscope (PLM). Figure 5 A, shows the structure of the archaeological limestone sample, which is very fine-grained. Significant number of microfossils are scattered in the matrix. Many pores and voids are present in the sample. The stone is composed mainly of calcite as the essential component associated with rare amounts of dolomite, quartz, gypsum, iron oxides and opaque minerals. Calcite occurs as very fine-grained (micrite), anhedral crystals that represent the matrix of the sample. Dolomite occurs as very fine-grained, subhedral to euhedral crystals admixed with calcite in the matrix. Quartz occurs as very fine to fine-grained, anhedral crystals scattered in the matrix. Iron oxides occur as heavy patches and staining over the essential minerals. Opaque minerals occur as very fine-grained single crystals scattered in the rock matrix. Gypsum occurs as very fine-grained, subhedral crystals filling some pore spaces. Significant number of microfossils and fossil fragments of different shapes are scattered in the matrix of the sample. Some microfossils are filled by recrystallized carbonates. PLM examination of the experimental limestone sample was shown in Figure 5 B. It is clear that is similar to archaeological one. It is very fine-grained and composed mainly of calcite as the essential component associated with minor amount of quartz and rare amounts of iron oxides and opaque minerals. Many microfossils are scattered in the very fine-grained matrix (micrite).

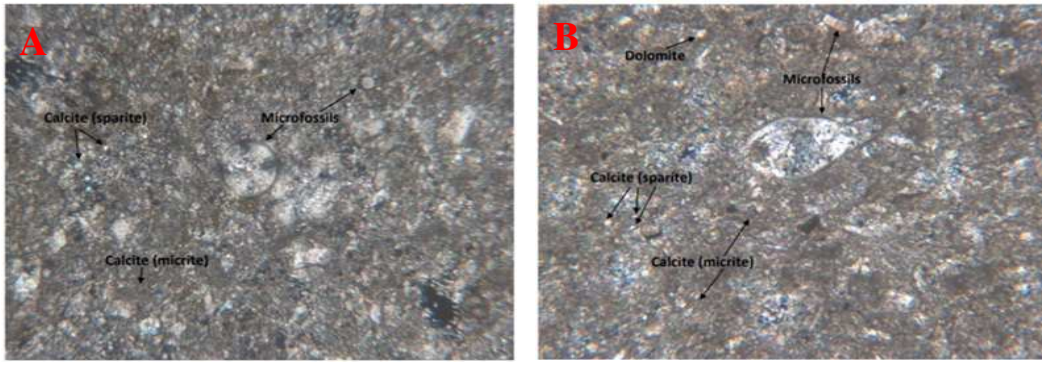

Fig. 5. PLM photomicrographs of studied limestone samples (A) PLM photomicrograph of the archaeological limestone sample, (B) PLM photomicrograph of the experimental limestone sample (63 X, C.N)

3.4. Scanning electron microscopy of studied samples (SEM-EDX)

SEM examination showed a high porosity of limestone and the state of extreme weakness of archaeological stone samples (Figure 6 A) and experimental stone samples (Figure 6 B), and this is evident in the form of cracks, corrosion in the granules, as well as disintegration and separation of the particles**.** SEM examination and EDX elemental analysis showed a great similarity in the components of both archaeological and experimental samples. There were clay deposits represented in aluminum and magnesium, in addition to sand deposits appeared in the sample represented by quartz. Presence of carbon in the samples suggests that the stone contains various fossils. Both samples contain the same chemical elements: Ca, K, Mg, Si, Al, S and C as previously explained (Figure 6 C, D).

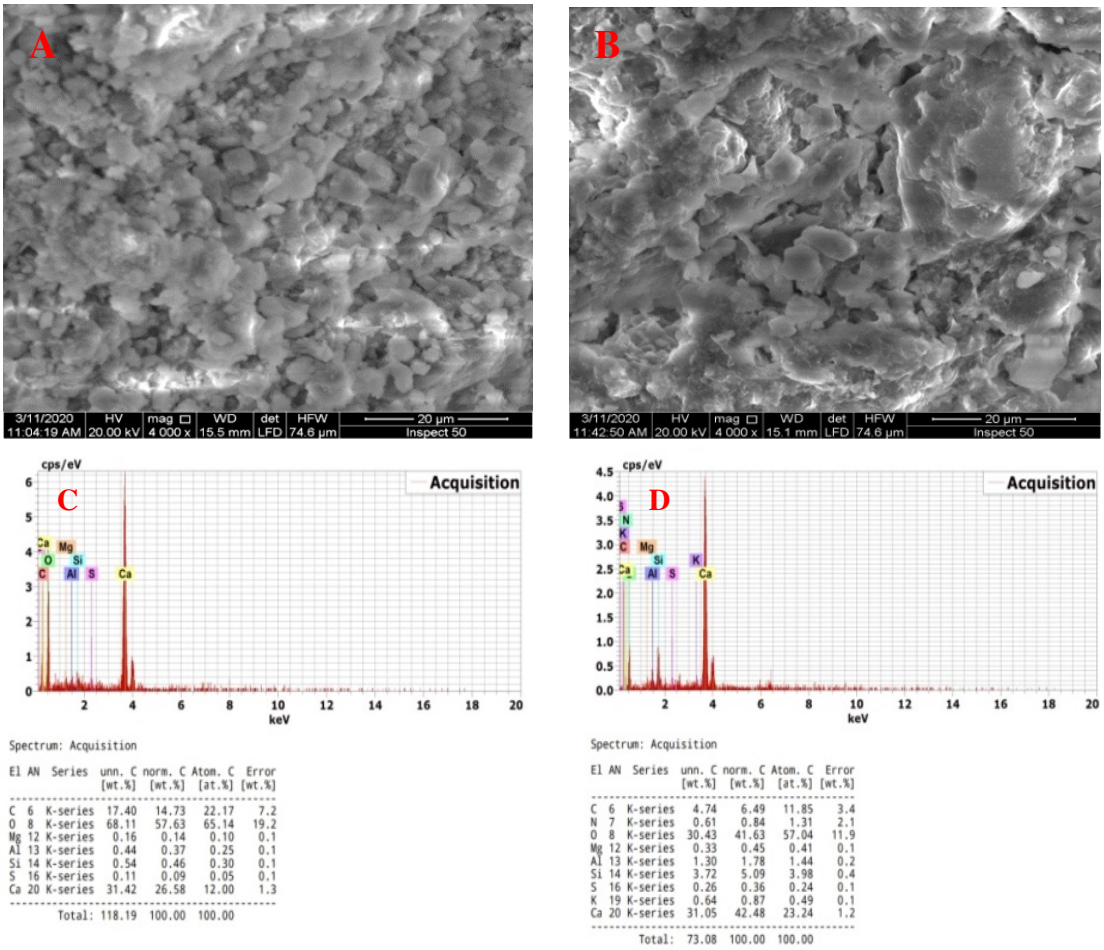

Fig. 6. SEM Photomicrographs and EDX analyses of studied limestone samples (A) SEM photomicrograph of the archaeological limestone sample, (B) SEM photomicrograph of the experimental limestone sample, (C) EDX analysis of the archaeological limestone sample (D) EDX analysis of the experimental limestone sample

Moreover, untreated, treated and treated aged samples were examined by SEM to determine the morphology of the samples surfaces and the extent of penetration of the consolidating materials. SEM photomicrographs of untreated samples showed severe fragileness, granular decay and presence of voids and gaps due to the disappearance of the bonding between granules, which led to poor stone structure (Figure 7 A). Furthermore, SEM examination of the samples treated with pure SILRES® BS OH 100 showed that the consolidant was able to fill some pores, but it could not fill many gaps, cracks and pores, and also showed the failure of the consolidant to reattached the granules of the treated samples (Figure 7 B).

On the contrary, the samples treated with HAP/ polymer nanocomposite showed a homogeneous coverage, the ability of consolidant to fill pores, fine cracks and reattach granules because of the small size of the nanoparticles and their high penetration inside the treated stone (Figure 7 C). After aging process, it was clear that the polymer alone was unable to maintain the stability and homogeneity of the consolidating layer (Figure 7 D) and on the contrary, in case of addition of nanoparticles, the polymer was able to maintain the homogeneity of the consolidating layer and achieve perfect consolidation (Figure 7 E).

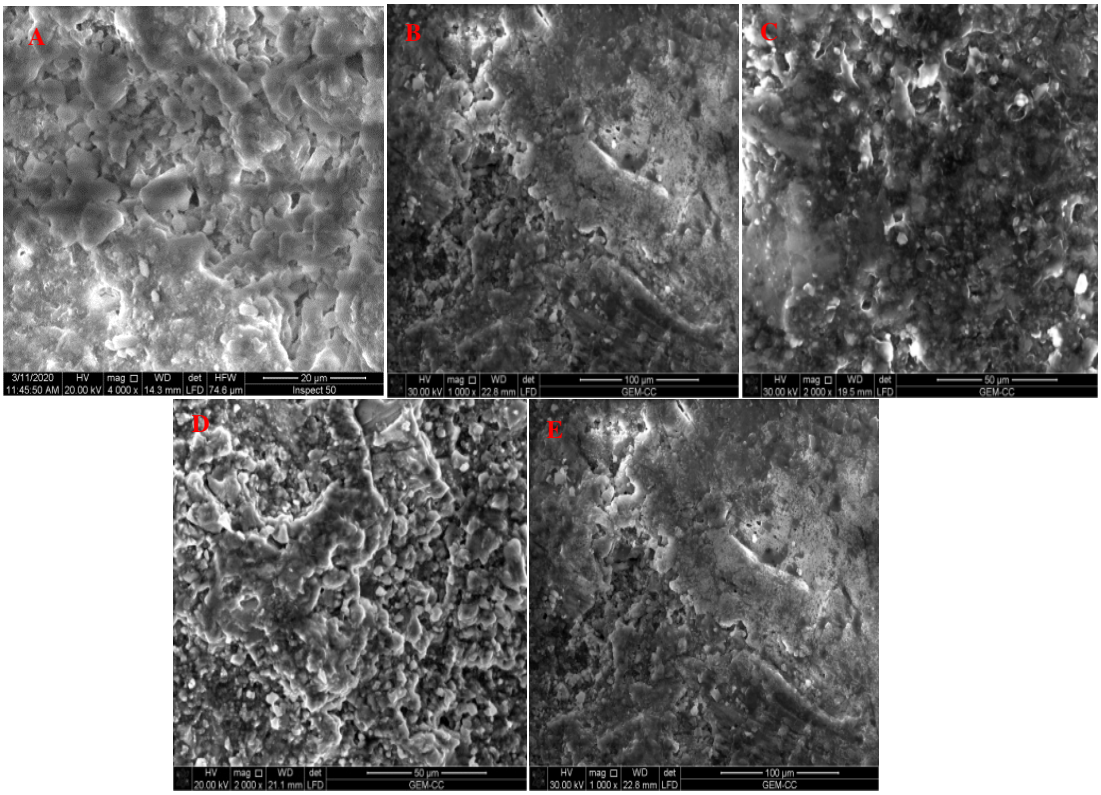

Fig. 7. SEM Photomicrographs of studied samples (A) Untreated samples, (B) Samples treated with pure SILRES® BS OH 100, (C) Samples treated with HAP/ polymer nanocomposite, (D) Samples treated with pure SILRES® BS OH 100 after aging, (E) Sample treated with HAP/ polymer nanocomposite after aging

3.5. Color measurements of studied limestone samples

A devicewas used to identify color changes to determine changes in the aesthetical properties of treated samples in according to the following equation:

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

Where ΔL^*, Δa^* and Δb^* are the difference in the, L^*, a^* and b coordinates (according to CIEL AB color space) of the treated and untreated limestone samples according to the Italian guidelines for the Restoration of Stone monuments the ΔE value must be < 5 [49], after consolidation and aging, an unpretentious color change was observed and all values were in the acceptable limit except the samples which were treated by pure SILRES® BS OH100 after aging. This emphasizes the effectiveness of nanomaterials in reducing the color changes of treated stones. The obtained data are listed in table 1. It is worth noting that the color change that occurs due to the use of traditional polymer is due to several reasons, the most important of which is the large size of the polymer particles, and sometimes the large viscosity, which causes only superficial consolidation without penetration into the inner core of the stone, which leads to darkening the treated stone surface. On the other hand, some traditional polymers cause yellowing of the treated stone surface as a result of exposure to the external atmosphere, especially direct sunlight. Laboratory and field experiments have demonstrated that adding the appropriate nanomaterials to the traditional polymer clearly improves the properties of the polymer, and prevents the discoloration of stone surface.

Table 1. Color measurements of treated and aged samples

Consolidants	Δ (treated and untreated samples)				Δ (aged and untreated samples)			
	ΔL*	Δa*	Δb*	ΔE	ΔL*	Δa*	Δb*	ΔE
Pure SILRES® BS OH 100	-2.90	0.25	1.70	3.37	-4.83	0.48	3.58	6.03
HAP/ polymer nanocomposite	-1.80	0.32	1.31	1.99	-3.61	0.18	2.73	4.53

3.6. Physical properties of studied limestone samples

Measuring density, water absorption and porosity values for untreated, treated and aged samples is necessary to evaluate the efficiency of consolidating materials.The results shown in table 2 proved that the addition of nanoparticles to the polymerreduced water absorption rates, indicating the improving of the physiochemical properties of the polymer, which led to a reduction in the rate of cracking during the drying process of the polymer. The density and porosity of the treated stone with HAP/polymer nanocomposite is also improved.

Table 2. Density, water absorption and porosity values for untreated, treated and aged samples

Consolidants	After treatment			After artificial aging		
	Density gm/cm^3	Porosity (%)	Water absorption (%)	Density gm/c m^3	Porosity (%)	Water absorption (%)
Untreated samples	2.13	22.0	10.3			
Pure SILRES® BS OH 100	2.20	4.0	1.8	2.17	4.1	1.9
HAP/polymer nanocomposite	2.27	3.3	1.4	2.26	3.6	1.6

3.7. Mechanical properties of studied limestone samples

Compressive strength of untreated, treated and aged experimental samples was carried out. The results shown in table 3 proved that the addition of HAP nanoparticles to the silicon polymer increased the values of compressive strength after treatment and aging, indicating that the addition of HAP nanoparticles improved the durability of the polymer toward the artificial aging and enhanced the stone ability to resist the moisture and temperature effects compared to the treated samples with the silicon polymers without nanoparticles.This is due to the role of nanoparticles in reinforcing the polymer and improving their interaction with the grains of stone.

Table 3. Compressive Strength values for untreated, treated and aged samples

Consolidants	Compressive strength Kg/Cm^2		
	Untreated samples	After treatment	After artificial aging
	179.1		
Pure SILRES® BS OH 100		333.4	161.2
HAP/polymer nanocomposite		351.9	279.0

3.8. Static water contact angle measurements

The hydrophobia was evaluated by measuring the contact angle of the treated samples. Table 4 shows the average contact values obtained through the measurement of three drops, the results showed the inability of the polymer in its pure state to make the stone water-repellent, but after the addition of hydroxyapatite nanoparticles, an improvement appeared in the stone's ability to expel water and this ability continued after artificial aging. But neither material has reached the point of superior water resistance.

A contact angle of less than 90° usually indicates that surface wetting is very suitable and the liquid will spread over a large surface while a contact angle of more than 90° means that surface wetting is undesirable and thus reduce the spread of liquid on the surface and form a compact drop but contact angle larger than 150° mean that the consolidant material is super hydrophobic [50, 51].The results of water contact angle measurements for untreated, treated, and aged limestone samples are shown in Table 4 and Figure 8.

Table 4. Values of static water contact angle (θ) for untreated, treated and aged samples

Samples	Static water contact angle θ (± 3°)		
	Untreated sample	After treatment	After artificial aging
	68°		
Samples treated with Pure SILRES® BS OH 100		88.31°	76.10°
Samples treated with HAP/ polymer nanocomposite		110.62°	96.50°

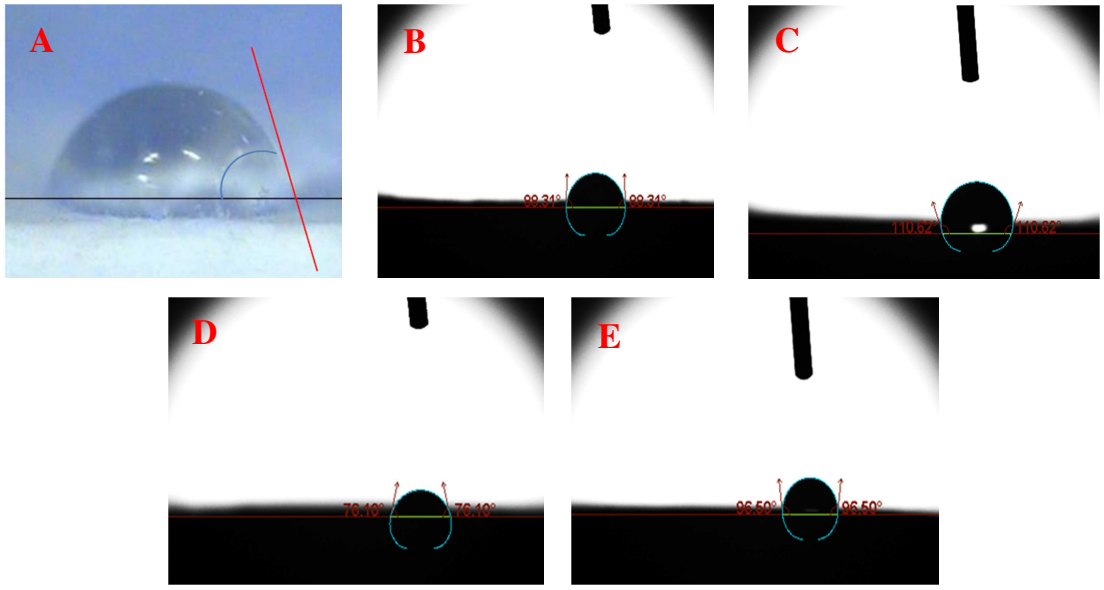

Fig. 8. Images of drops of distilled water on the surface of studied limestone samples for static water contact angle measurements (A) Untreated sample, (B) Sample treated with pure SILRES® BS OH 100, (C) Sample treated with HAP/ polymer nanocomposite, (D) Sample treated with Pure SILRES® BS OH 100 after artificial aging, (E) Sample treated with HAP/ polymer nanocomposite after artificial aging

4. Conclusions

The deterioration of the stone monuments displayed in the outdoor environment is one of the most important problems that need the efforts of researchers to face it. In this study, nanohydroxyapatite was added to the SILRES® BS OH100 in order to improve the physical and mechanical properties of it to use as a consolidant and protective material for limestone monuments. The polarized light microscope showed the mineralogical composition of the experimental stone samples that consist of calcite, quartz, organic materials and rare of iron. The results of SEM showed the weakness and fragility of the experimental samples as well as the degradation of calcite crystals in some areas. The result of TEM confirmed the success of the preparation of nanohydroxyapatite/ polymer nanocomposite by in situ emulsion polymerization system. Samples treated with pure SILRES® BS OH 100 and those treated with hydroxyapatite/polymer nanocomposite were exposed to artificial aging. The results of the colorimetric test showed preference for samples treated with nanohydroxyapatite /polymer nanocomposite after treatment and aging over others treated with pure polymer. The mechanical properties of polymer were enhanced by addition of nanoparticles so improved the interaction with stone grains. Moreover, the addition of nanohydroxyapatite to the polymer enhanced stone resistance to the moisture and temperature effects. The effectiveness of the nanocomposite has been demonstrated by the improvement of the physical, mechanical and water-repellency properties of the treated limestones.

5. Conflicts of interest

The authors declare that there are no conflicts of interest.

6. Acknowledgment

The researchers would like to express their thanks and appreciation to The Arab Academy for Science, Technology and Maritime Transport for their support and sincere efforts. The researchers would also like to extend their sincere thanks and gratitude to the Administration of Restoration of Antiquities of El Matariya and Ain Shams and all its employees for their great efforts.

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