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Evaluation of using Nanocomposite polymers in treatment of ancient Egyptian faience

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Abstract:

Ancient Egyptian faience is a significant object which has enormous technical and historical information about Egyptian civilization. The recently discovered faience is exposed to many deterioration factors, which have a serious impact on its components and its physical and mechanical properties leading to poor structure, broken parts, and separated glazing layer.

The current study aims to stop the continuous undesired effect of the deterioration factors and consolidate the recent discovered fiancé objects by using four different nanocomposite (Nanosilica SiO_2 with Waker OH100 and TEOS as well as nano calcium hydroxide $Ca(OH)_2$). The chosen consolidants (Polymer-nanomaterials) have been applied on simulated Egyptian blue faience object samples depending on an analytical study of recently discovered ancient faience objects at Tepla hill, Egypt using XRD, and SEM_EDX.

Porosity, water absorption, density, compressive strength, colorimetric measurements, water contact angle and Scanning electron microscope (SEM) were used to evaluate the efficiency of the selected consolidants, the result revealed that composite of nanosilica with Waker OH100 and TEOS were provide notable protection for the deteriorated faience.

Keywords: Faience, Polymers, Nanocomposites, Consolidation, protection, ancient, nanomaterial.

1- Introduction

Faience objects had been known by the ancient Egyptians more than 5000 years ago, it is such strong evidence for the development of mechanical engineering in the ancient Egypt [1], the internal components of ancient Egyptians' faience are SiO_2 (92-99%), Na_2O (0.5-3%) and CaO (1-5%) [2]. it has been made by grinding quartz and low percentages of sodium, calcium, potassium, magnesium and copper oxides colors for glazed (raw materials), then adding water for moulding process by hand or mould [3], the glazed surface layer contains basically of silica, lime, soda ,colored mineral oxide[4] and certain percentages of alumina[5], three manufacturing methods were represented; The first glazing method is efflorescence the raw materials of the core are mixed (quartz, alkali, lime and colorant) during drying process, the salts migrate and efflorescence on the surface, so the glaze is thicker when firing the opposite happens at the base and interior wall to slow the drying process) [6]. The second method is cementation glazing method, is self-glazing technique [7] as fellow: the object is placed in the glazing mixture (quartz, alkali, oxide or calcium hydroxide and copper compounds) after the completion of the molding and its drying process, during the firing process a glaze layer of is formed on the surface of the faience under a temperature of 1000°C as a result of different reactions between siliceous surface of the core and the glazing mixture [8]. The third method is application glazing, in this method, the glazing mixture is applied inside saggars using a brush, and when upon firing, the brush marks appear and the thickness of the glaze layer varies on the surface of the faience body along with the finger marks [9], The finally step is firing process, it is considered one of the most important processes and raw materials are burned at temperatures between 800-1000°C [10].

As a result of the impact of harmful environmental factors such as humidity, the glazed traces are exposed to many factors of damage that affect the glazing layers in surface corrosion, exfoliation, cracks and missing parts from the glazed layer additionally, the most common deterioration is discoloration damage to the glaze layer [11] [12] [13], Nanomaterials have been widely used in consolidation processes, either alone or in the form of nanocomposites which produce strong consolidating , repellent to water and resistance to compressive forces with acceptable color change [14]15 [] [16] [17][18] [19].

2- Experimental

2-1Materials

- Wacker OH 100 (Aldrich Co – Dusseldorf Germany).
- TEOS (Nen-Tech Ltd, Brixworth Northants United Kingdom).
- Nano-silica (SiO2) particles (fumed powder, Aldrich) with a 7 nm mean diameter.
- Nano calcium hydroxide $Ca(OH)_2$ with 80 nm mean diameter; was prepared by the researcher.

2. 2. Method

The experimental study relied on three groups of consolidates: The first is polymer solutions; Wacker OH 100 and TEOS, and the second group is Nanocomposites (including silicon-based pervious polymers with nano-silica (SiO2) to Walker OH 100 and TEOS Which is called WN and TN respectively, the third group is Nano calcium hydroxide $Ca(OH)_2$ in ethanol 2g /L that mixture is called NL. All consolidates were applied on experimental colored cupid fiancé samples (3×3cm) which were prepared depending on the result of the analytical study of recent ancients discovered finance remains at Tepla hill, Egypt by XRD and SEM-EDX. The prepared samples were exposed to accelerating thermal/salt artificial ageing before and after application.

Porosity, water absorption, density, compressive strength, colorimetric measurements, water contact angle and Scanning electron microscope (SEM) were used to evaluate the efficiency of the selected consolidants.

- Compressive Strength: MATEST, ASTM C39 | BS 1610 | NF P18-411 | AASHTO T22.
- Colorimetric: BYK-Gardner - spectro-guide with gloss spectrophotometer
- Contact angle: Sessile Drop ADSA-P, its Lines system: 0.1: 1.5 mm/min
- SEM: **JEOL JSM-840a** scanning microscope equipped with a
- backscattered electron detector and energy dispersive X-ray analyzer For the SEM-EDX measurements accelerating voltage was 20 kV and working distance.10 mm.

2.2.1 The experimental samples and the artificial aging:

New colored glazed finance samples were produced by the researcher as small cubes with (3×3×3)cm. which were prepared after identifying the components and the internal ratios of the components of the ancient Egyptian faience through the XRD analysis and SEM-EDX for recent discovered ancient fiancé objects at Tepla hill, Egypt.(Fig no), The new produced samples are subjected to accelerated artificial aging processes in an attempt to find out what damage factors might be exposed to in burial environments, whether before applying consolidants or after It`s an application in order to determine the efficiency and effectiveness of each composite for protecting the ancient faience.

2.2.2 Prepare and produce of the Selected Consolidants

The selected consolidates were prepared using polymers in their product form, unlike the nanocomposites are prepared by adding nano-silica SiO_2 particles to both TEOS and Wacker OH100 substance with a concentration of nanosilica (nanosilicate) in TEOS and Wacker OH100 is 0.5% W/V, the mixture was dispersed well by Ultrasonicator and magnetic stirring for 20 minutes, to produce both nano-composite ;nano-silica with Waker OH100 WN and nano silica with TEOS TN.

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The nano calcium hydroxide (Nanolime) was produced in the laboratory as follows; The Calcium nitrate dihydrate $Ca(NO3)_2.2H_2O$ as a precursor and The alkaline NaOH solution was used as the precipitator, under the condition of continuous stirring at a rate of 1200 rpm at room temperature (30°C), the precipitator was added drop by drop into the aqueous solution of $Ca(NO_3)_2.2H_2O$ for an hour, a white precipitate was obtained. The precipitate was filtered and washed several times with deionized water to remove the excess calcium nitrate dihydrate. The final product was dispersed in ethanol 2g/L which was characterized by TEM with an average size of 80 nm as it is shown in (Fig 2), the mixture was used as NL in the experimental study.

2. 2. 3. Thermal and humidity aging

The samples were subjected to heating in an oven at a temperature of 65 ° C with relative humidity inside the oven for 8 hours and then left at room temperature for 16 hours. This is equivalent to 24 hours a full cycle and this process was repeated several times in a row (60 cycles).

2.2.4. Salt aging

At this stage of aging, a salt solution of sodium chloride was prepared at a concentration of 10%, where the samples are immersed for 10 hours inside the solution, and then they are dried at room temperature for 14 hours, provided that the cycle duration is 24 h and then this cycle is repeated several times in a row (15 cycles), then monitor the change that occurs to these samples. As a result of the aging processes, both with thermal and humidity aging and salt aging, cracks appeared on the glaze layer and salt crystals were seen on the surface.

2.2.5. Application

clean surface of the prepared samples is an important step before the consolidation process, whether nanoparticles or polymers, were applied by a soft brush with two consecutive layers of each selected consolidates, taking into account drying of the first layer

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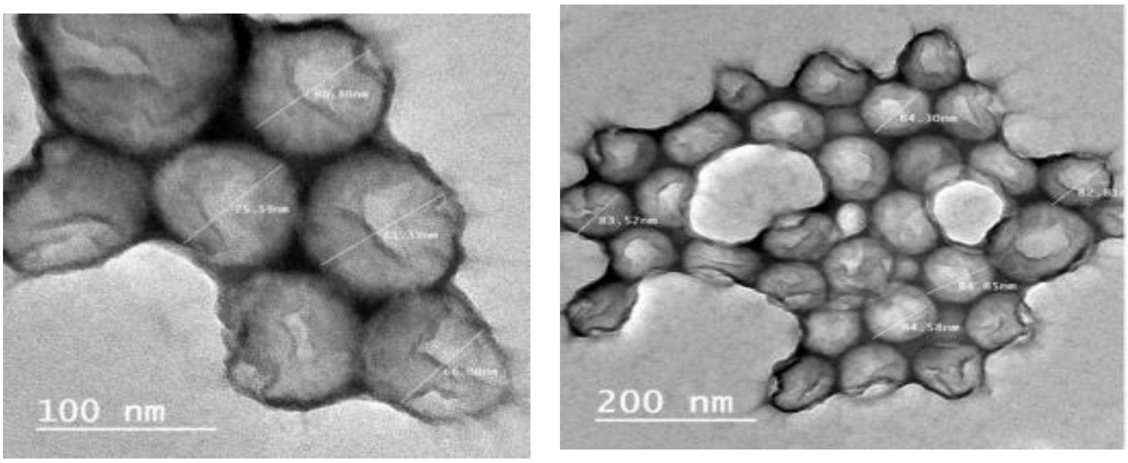
before applying the second. This process was applied at the normal room temperature of 20° and the samples were left for 30 days to ensure the complete polymerization of the polymers and the maximum carbonation for the calcium hydroxide nanoparticle.
several physical and mechanical measurements were performed on the experimental samples after the application and after the artificial ageing to evaluate the effectiveness of the selected consolidates in protecting the ancient Egyptian faience through the results.

Fig. 1: Different aspects of deterioration on shabtis



(A) **(B)**

Fig.2. TEM micrographs of the Nanolime (nano calcium hydroxide) (< 50nm), An image (A, B) shows the shape of calcium hydroxide nanoparticles under the TEM microscope for the produced nano calcium hydroxide with a magnification \ of 100nm and 200 nm enlargement, which confirms the homogeneous particles size around 80nm.

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3. Results and Discussion

3. 1. Physical and Mechanical properties before and after Artificial Aging

3. 1. 1. Porosity and water absorption

The percentage of porosity and water absorption was determined for the treated experimental faience samples and measured after aging for the treated samples with the following steps: Samples are dried for 24 hours in a dedicated drying oven at 105°C, after drying in the oven, samples are weighed to determine their dry weight (W1), For up to 48 hours, the samples are then immersed in water, after which the samples are weighed again to determine the wet weight (W2), to determine the volume, the three dimensions of the samples are measured to calculate the value of (V), as in the following equation:-

* Porosity = $\frac{\mathrm{W2-W1}}{\mathrm{V}} X\ 100 = \cdots \%$.

* Water absorption = $\frac{W2-W1}{W1} X\ 100 = \cdots \%$.

3. 1. 2. Density

Density is the ratio of weight to volume, including pores, and is estimated in gm / cm^3 and can be determined by W/V, the results showed from (Table 1) that the nanomaterials improved the properties of polymers which helped to improve the physical properties of the faience samples, especially after the aging processes of the treated samples, which confirmed the effectiveness of the nanocomposites in protecting the archaeological faience, especially the nanocomposite Wacker OH100 with Nanosilica.

3. 1. 3. Compressive Strength

The measurement of compressive strength of the untreated, treated and treated aged faience sample were carried out using compression testing machine, The dimensions of the samples are

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calculated, their area is measured, then weighed, and then the samples are placed on the testing machine to measure the compressive strength, then the bearing ratios of the samples are recorded, and the pressure is slowly loaded onto the samples until the sample cracks or shatters. (Table 2) It also indicates that the consolidation materials have improved the mechanical properties of the treated faience samples, especially the samples have been treated with nanocomposites WN and TN which showed high resistance to the weathering factors, compared with untreated samples after aging processes, as the pure nanosilica material helped the polymer in the normal state to resist shrinkage and cracking during aging processes and reducing it`s viscosity during aging, also it enhanced its ability to fill the intermediate spaces between grains inside the fiancé, which produced better mechanical properties even after aging,

Wacker OH100 with Nanosilica WN showed the best result with compressive strength ratios.

Consolidaton materials	After treatment			After treatment and aging		
	Porosity %	Water absorption %	Density gm/cm^3	Porosity %	Water absorption %	Density gm/cm^3
Standard (S) untreated sample	**22.50**	**15.08**	**1.42**	**22.50**	**15.08**	**1.42**
Wacker OH100 (W)	**13.7**	**9.19**	**1.49**	**15.42**	**10.68**	**1.44**
TEOS (T)	**15.33**	**10.54**	**1.49**	**18.04**	**12.57**	**1.43**
Wacker OH100 +Nanosilica(WN)	**9.60**	**6.11**	**1.58**	**10.4**	**6.73**	**1.54**
TEOS +Nanosilica (TN)	**10.95**	**6.99**	**1.57**	**12.87**	**8.48**	**1.50**
Nanolime (NL)	**12.13**	**7.85**	**1.54**	**14.6**	**9.84**	**1.48**

Table 1 Average results of the Porosity, Water absorption and Density of the treated faience samples and their results before and after aging.

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Consolidaton materials	compressive strength Kg/ cm^2	
	After treatment	After treatment and aging
Standard (S) untreated samples	129	108
Wacker OH100 (W)	208	196
TEOS (T)	189	175
Wacker OH100 +Nanosilica(WN)	238	235
TEOS + Nanosilica (TN)	229	223
Nanolime (NL)	218	209

Table 2 Average results of the compressive strength test of manufactured and treated faience samples before and after aging.

3.1.4 Colorimetric Measurements

Measuring the value of the color change is one of the most important measurements to know the effectiveness of the consolidating material in maintaining the color of the glaze layer, so the values of the colorimetric of the surface of the glaze layer were measured for all the faience samples, and the color change was measured by Colorimetric measurements in a system called CIE L * a * b * [The color change is calculated through the 20] following equation: -

$\Delta E^* = \sqrt{L^{*2} + a^{*2} + b^{*2}}$ [21]. (Table 3, 4)

Consolidation material	After treatment			After aging			
	ΔL	Δa	Δb	ΔL	Δa	Δb	ΔE
Wacker OH100 (W)	33.70	-18.17	31.23	38.43	-19.49	-27.71	6.04
TEOS (T)	35.86	-18.59	-19.03	37.8	-19.78	-19.92	5.96
Wacker OH 100 + Nanosilica (WN)	37.59	-17.38	-28.85	40.63	-21.52	-31.76	5.93
TEOS + Nano Silica (TN)	36.32	-16.73	-29.83	39.21	-19.92	-26.11	5.68
Nanolime (NL)	39.20	-15.20	-15.13	38.29	-18.49	-16.94	5.30
Standard (S) untreated samples	36.37	-19.84	-31.95	40.98	-25.53	-32.29	9.33

Table 3 Results of comparison of colorimetric measurement of treated samples before and after aging.

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ΔE treated/untreated samples	Wacker OH100 (W)	TEOS (T)	Wacker + Nanosilica (WN)	TEOS + Nanosilica (TN)	Nanolime (NL)	Standard (S) Untreated sample
After aging	5.70	0.85	4.45	2.88	6.89	--
Before aging	6.41	5.96	5.93	5.68	5.30	9.33

Table 4 Evaluate the after and before aging ΔE results of the treated faience samples.

The measurement of the colorimetric showed that the treated samples with nanocomposites of Wacker OH100 + Nanosilica WN and TEOS+ nanolsilica have desirable color change after changing with 4.45 and 2.88 however the pure polymer TEOS achieved the best color change with 0.85. from the result in the table N.4 it is clear that the nanomaterials have improved the colorimetric properties of polymers especially after aging.

3. 1.5 Measuring the angle of water contact (water contact)

The hydrophobicity of the treated samples were evaluated using a device Sessile Drop ADSA-P, its Lines system: 0.1: 1.5 mm/min, Measure system: performed dynamically by using a motor-driven syringe to pump liquid steadily from below the surface, Measure rang: 0: 180°, and Stage operation: dynamic - motor drive, it was clear through the results shown the table No 2 which confirm the efficiency of nanocomposite(WN and TN) to increase hydrophobicity of the sample surface, the contact angle for that treated samples was (131: 127°)(Fig 3), respectively, which confirms the effectiveness of nanomaterials in improving the properties of polymers in repelling water comparing with the water contact angle of the untreated sample (72°). (Table 5).

3. 2. Scanning electron microscope (SEM)

This is considered one of the important stages by conducting a microscopic examination with Zeiss DSM 962 microscope after treatment, the success and depth of diffusion of the consolidants, especially the nanoparticles, and the extent of penetration between

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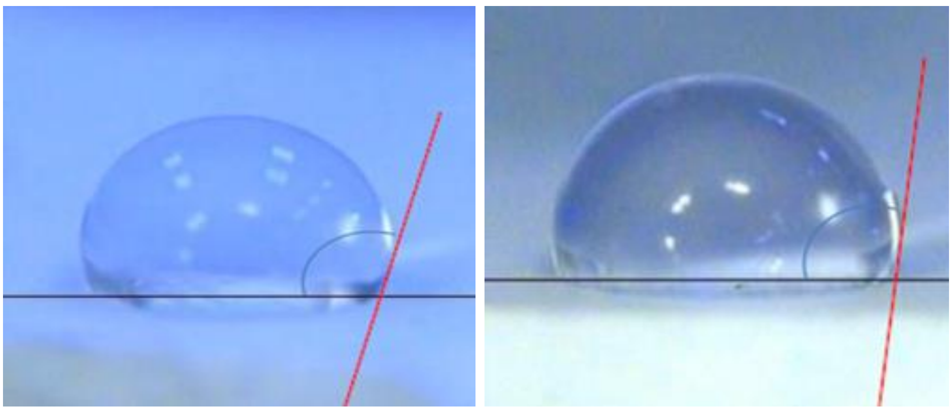
the grains, especially lies in the importance of examining the treated samples also after the aging process to identify the consolidate of their cohesion, in order to determine the effectiveness of the materials in consolidating the faience in the long term. (Figure 4) shows the results of the microscopic examination of the samples treated after aging.

It was notable that the treated samples have interconnected and coherent after the consolidating processes. However, the treated samples with TEOS showed their damage which clearly surface cracks. the examination of the treated samples with Nanolime showed that the material was deposited and formed a white substance of calcium carbonate, the examination of the untreated faience sample showed fine pores and cracks in this glaze layer, as well as being heterogeneous, confirming the clear difference between treated and untreated faience samples to enhance the effectiveness of using the selected nano-composite in consolidation of the faience (Fig 4).

consolidating material /untreated sample	Wacker OH100 (W)	TEOS (T)	Wacker + Nanosilica (WN)	TEOS + Nanosilica (TN)	Nanolime (NL)	Standard (S) Untreated sample
After aging	116	107	131	113	101	--
Before aging	106	95	127	105	93	72

Table 5 Results of comparison of the water contact angle of the treated faience before and after aging with the untreated sample



(A) **(B)**

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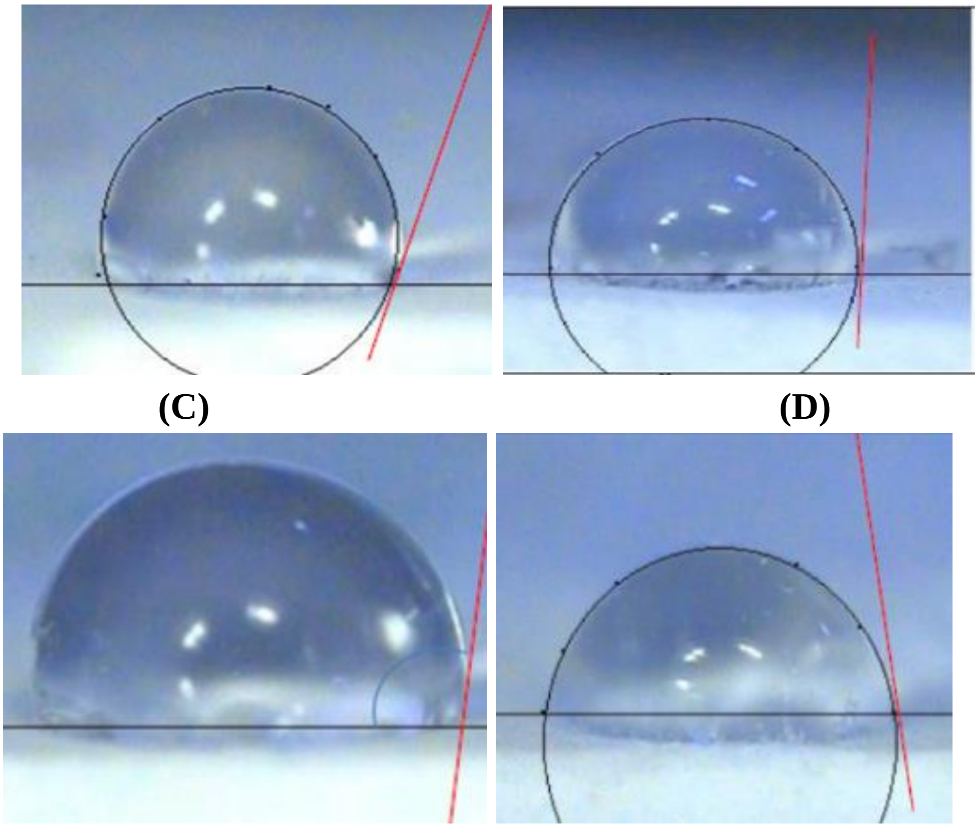

(C) (D)

(E) (F)

Fig 3 The water contact angle values for the treated faience samples after aging (A) Wacker OH100 (106°), (B) TEOS (95°), (C) Wacker OH100+ Nanosilica (127°), (D) Nanolime (93°), (E) TEOS+ Nanosilica (105°) and (F) untreatment sample standard (72°).

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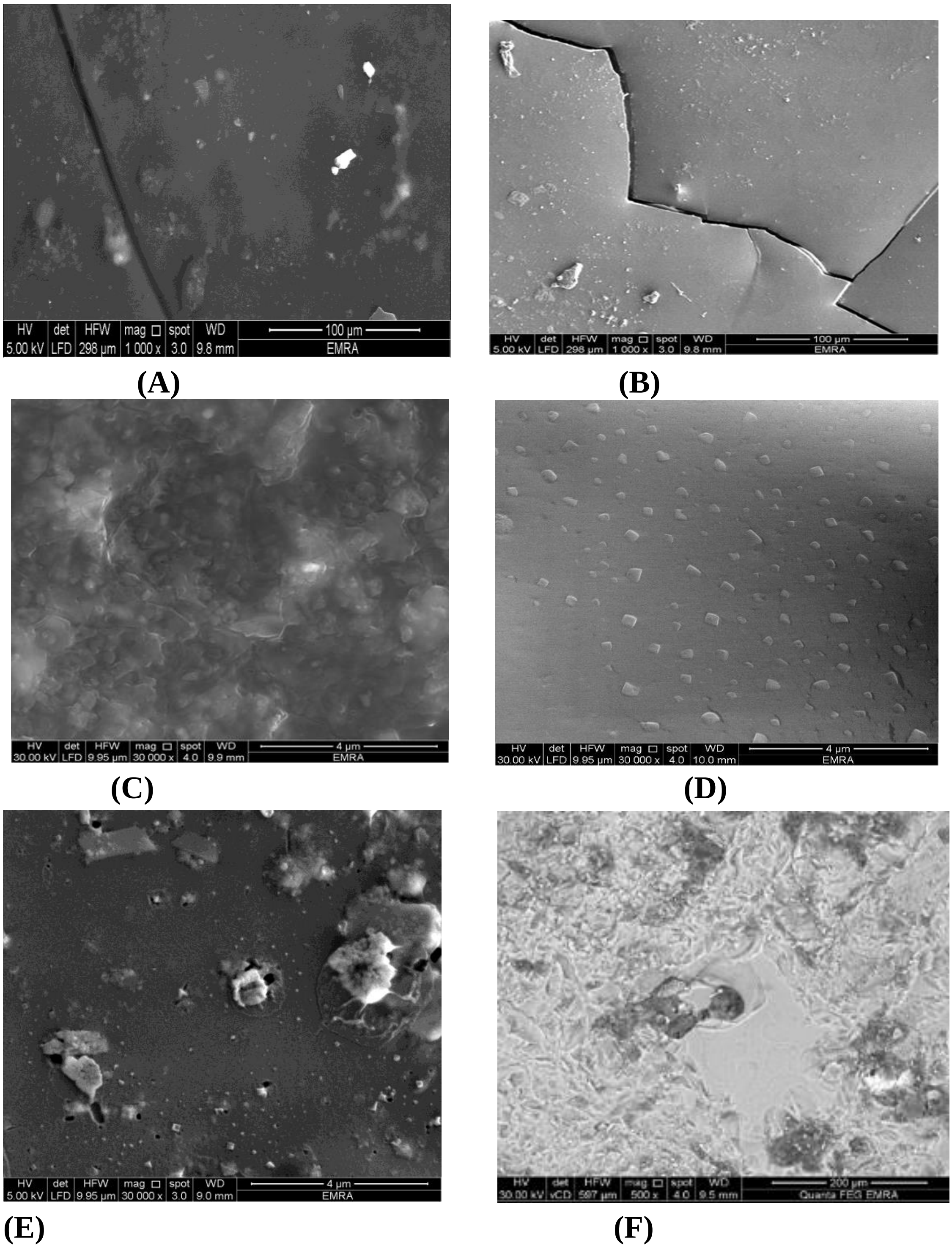

Fig 4 (A-F) SEM micrographs of the treated and untreated faience samples,(A) Wacker OH100, (B) TEOS, (C) Wacker OH100+Nanosilica, (D) TEOS+Nanosilica, (E) Nanolime and (F) untreated sample standard .

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4. Conclusions

This study used simulated experimental samples with the same properties and components of the Egyptian archaeological faience which was recently discovered in Tepla hill, Egypt, after using several analysis methods like SEM-EDX, XRD. In order to evaluate using selected consolidants whether they are polymers in their normal form or nanocomposites mixture or inorganic consolidates, several mechanical and physical measurements were applied after the application and after artificial aging.

The pure polymer TEOS and walker achieved good consolidation with less color change although some surface cracks have appeared, the nano lime improved the mechanical properties of the treated samples, however, a white light layer of the calcium carbonate was deposited on the glazed surface of the treated faience samples. The nanocomposite Waker OH 100 and TEOS with nanosilica WN and TN achieved a significant improvement in the mechanical and physical properties of the treated samples with negligible color change be Average ΔE 3.5. additionally, the hydrophobicity of the treated faience is obviously increased as the contact angle for that treated samples were (131: 127°) for the WN and the TN respectively comparing with 72° for the untreated samples the microscopic investigation ensured the extent and depth of penetration of the nano composite WN and TN with ability to bind the micro structure grains.

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