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USING NANOCOMPOSITES IN THE CONSOLIDATION AND PROTECTION OF SANDSTONE

Fatma Mohamed HELMI[1], Yasser Kamal HEFNI[2*]

[1]Conservation Department, Faculty of Archaeology, Cairo University, Egypt.
[2]Conservation Department, Faculty of Archaeology and Tourism Guidance, Misr University for Science & Technology, Egypt.

Abstract

In the last few years, nanoparticles have widely been used in the field of restoration and conservation of artworks. The minimizing of particles size into nanoscale, results in better properties from the large grain size materials of the same chemical composition. In this paper, pure and nanoparticles modified silicon-based polymers, were used to consolidate and protect sandstone samples. Silicon dioxide (SiO_2), and zinc oxide (ZnO) nanoparticles, were added to different types of the silicon-based polymers (Wacker OH 100, Dow Corning MTMOS, Mega Protec 1, Mega Protec 2) in order to improve their physiochemical and mechanical properties, which produced a significant improvement in the ability of the polymers to consolidate and protect the stone. The properties of the treated sandstone samples were evaluated comparatively by visual appraisal, colorimetric measurements, measuring of static contact angle of water droplets on the surface of the samples, total immersion water absorption, compressive strength, and scanning electron microscope. Results demonstrated that the addition of nanoparticles to silicon-based polymers enhanced their capability to consolidate and protect the sandstone samples.

Keywords: *nanoparticles; Silicon dioxide; zinc oxide; hydrophobic; superhydrophobic; nanocomposites.*

Introduction

Sandstone is considered one of the most important types of stones, which was used in the field of arts and architecture in ancient Egypt. In particular, it was used in the construction of numerous ancient Egyptian temples in Upper Egypt, such as Luxor and Karnak temples [1-3]. It was also used in the sculpting of the finest statues, as well as many other important sculptures such as obelisks, columns, coffins and funerary stele.

Unfortunately, due to the high porosity of the sandstone, it is easily affected by water from its different resources such as rain, relative humidity, and groundwater [4]. Water, in any physical state, is considered the major deterioration factor, due to its ability to dissolve the salts and the other soluble components in the stone, in addition to cause cracking in freeze-thaw and wet-dry cycles, as well as its roles as a catalyst in the chemical and microbiological deterioration processes of the stone, that cause diverse deterioration aspects such as granular disintegration, exfoliation, detachment, erosion, as well as cracking, deformation, efflorescence,

* Corresponding author: Yasser.shahin240@yahoo.com

discoloration, different microbiological colonization, and finally loss of the monuments which were carved or constructed from this stone [5-12].

In order to prevent the damage processes of the stones, there is a necessity to treat them with a material has the ability to consolidate their internal structures, as well as protect them from the effects of water by means of water repellent consolidator [13-15].

In the last few years, nanoparticles have widely been used in the fields of restoration and conservation of cultural heritage [16-18]. The minimizing of particles size into nanoscale, results in better properties from the large grain size of the materials of the same chemical composition. The dispersion of nanoparticles in the polymers used in the consolidation and protection processes lead to a significant enhancement of their physiochemical and mechanical properties [19-26].

In this study, we have added silicon dioxide (SiO_2), and zinc oxide (ZnO) nanoparticles to different types of the silicon-based materials (Wacker OH 100, Dow Corning MTMOS, Mega Protec 1, Mega Protec 2) in order to improve their properties and compose suitable nanocomposites to be used in the consolidation and protection of the sandstone samples.

The properties of the treated sandstone samples were evaluated comparatively by using different methods such as visual identification of general appearance of the samples, colorimetric measurements, measuring of static contact angle, total immersion water absorption, compressive strength, scanning electron microscope. The results demonstrated that the addition of nanoparticles into the silicon-based polymers, produced a significant improvement in their efficiency to consolidate and protect the sandstone samples.

Materials and Methods

Materials

The sandstone blocks were collected from the quarry of gebel Ahmar, one of the most important quarries of sandstone in Egypt. The mineralogical composition was determined by X-Ray diffraction analysis, which was performed using Philips Analytical X-Ray Diffractometer (PW1840), using Cu Anode, on a maximum tension of 40KVm, 25mA, Wavelength Alpha1(Å): 1.54056, Wavelength Alpha2(Å): 1.54439, no monochromator.

Four types of pure silicon-based polymers were used in the consolidation and protection of sandstone samples. SiO_2 and ZnO nanoparticles < 50 nanometers (nanotech center, Egypt), were dispersed in the 4 types of the silicon-based polymers (2% w/v) respectively. Dispersions were stirred vigorously for 30 minutes, and then were applied on the samples by brushing.

The materials which have been used in this study were divided into three groups (A, B, C). The materials in group A are: (1) Wacker OH 100 (Wacker Chemie, Germany) ethyl silicate based product; (2) Dow Corning (Sigma-Aldrich, Germany) methyltrimethoxysilane based product; (3) Mega Protec 1 (Intrade chemicals, Egypt) silane and siloxane – water based product; (4) Mega Protec 2 (Intrade chemicals, Egypt) silane and siloxane – organic solvent based product. All the above polymers are ready to use products without any dilution.

Group B includes the same polymers of group A, but all of them contain 2% w/v silica nanoparticles with grain size < 50 nanometers. Group C includes the same polymers of group A, But all of them contain 2% w/v zinc oxide nanoparticles with particle size < 50 nanometers. The grain size of the nanoparticles was determined by means of Jeol JEM-2100 high resolution transmission electron microscope. Figs 1, 2 show TEM micrographs of silica and zinc oxide nanoparticles.

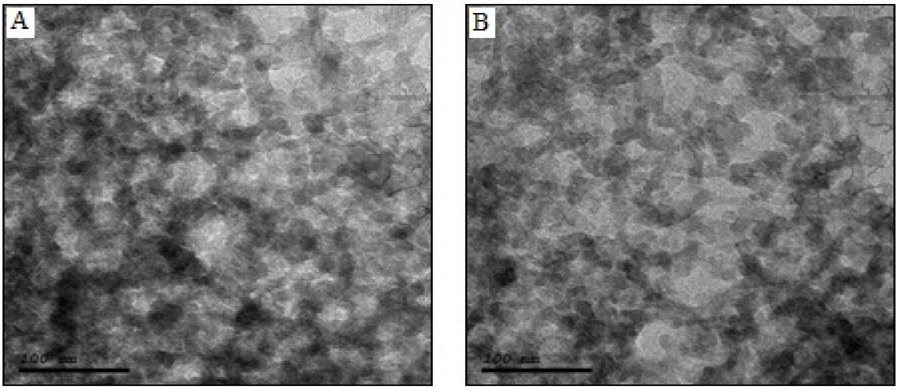


Fig. 1. TEM micrographs of the silica nanoparticles (< 50 nm).

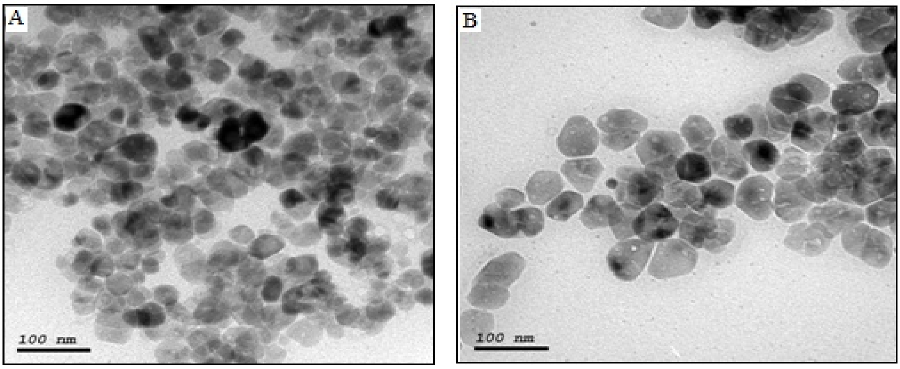


Fig. 2. TEM micrographs of the zinc oxide nanoparticles (< 50 nm).

Procedures of consolidation and protection

In order to preparing the experimental specimens, the sandstone blocks were cut into cubic samples 2.5 cm^3 and 5 cm^3. The cubic samples were washed by distilled water, and dried in an oven at 105°C for at least 24 hours to reach constant weight, and left to cool at room temperature and controlled RH 50%, then weighed again.

The polymers and nanocomposites were applied onto the sandstone samples by brush (three applications). Treated samples were left for 1 month at room temperature and controlled RH 50% to allow the polymerization process to take place. The samples were weighted again, and the polymer uptake was calculated.

Evaluation tests

Firstly, the effect of pure polymers and nanocomposites on the appearance of the treated sandstone samples was evaluated by visual appraisal, and colorimetric analysis. The colorimetric measurements were carried out on the treated and untreated sandstone samples, on homogenous spots, by means of Optimatch 3100, based on the L^*, a^* and b^* coordinates of the CIELAB color space [25-28].

The hydrophobicity of the treated and untreated sandstone samples was evaluated by measuring the static water contact angle. The measurements were carried out by means of custom apparatus made in compliance with standard UNI EN 15802 – 2010 [29]. The specimens were placed on a sample stage and then a 5 μl water drop was applied onto the sample surface using a graduated micro-pipette. High resolution Canon camera with a 18-55 lens was used to capture the images of water droplets on the sandstone samples. The contact angles were finally calculated by software program [30]. Each measurement was repeated at least five times and the average value is quoted in each case.

The water absorption measurements were carried out using the gravimetric method. The sandstone samples were completely immersed in deionized water at room temperature. After 24 hours, the samples were taken out, wiped with tissue paper carefully and weighed immediately. The amount of the absorbed water was calculated using the following equation:

$$\text{Water absorption} = \frac{(W_2 - W_1)}{W_1} \times 100 = \cdots\ \% \qquad (1)$$

Where (W2) is the mass of the sample after immersion in water for 24 hours, and (W1) is the mass of the sample before immersion.

Mechanical properties were determined by testing the compressive strength of the treated and untreated sandstone samples. According to ASTM C 170, the compressive strength test was carried out on three sandstone cubes (5 cm^3) for each treatment and also for the untreated samples [31].

Scanning electron microscope (Model INSPECT S, FEI Company) equipped with a high stability field emission gun and large specimen chamber, was used to examine and evaluate the ability of the polymers and nanocomposites to consolidate and protect the sandstone samples.

Results and Discussion

Mineralogical composition

The charts of X- Ray diffraction (Fig. 3) showed that the sandstone samples consists mainly of Quartz [SiO_2] as a major mineralogical constituent, with trace amounts of Goethite [FeO (OH)] and Hematite [Fe_2O_3]. The results are summarized in Table 1.

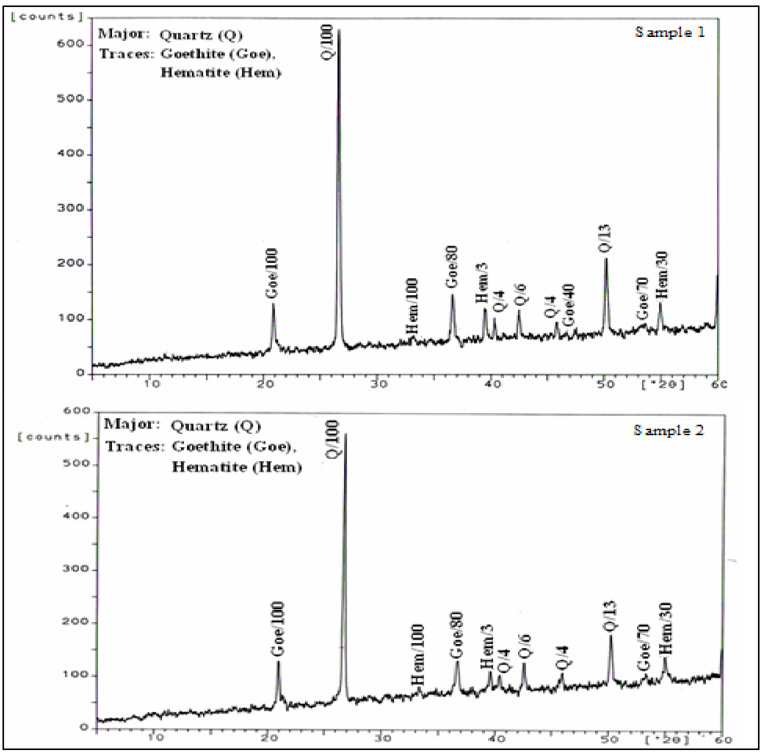


Fig. 3. X-ray diffraction charts of two sandstone samples.

Table 1. Mineralogical composition of the sandstone samples

Composition %	Quartz	Goethite	Hematite
Sample 1	80	12	8
Sample 2	78.5	13.5	8

Polymer uptake

By comparing the values of polymer uptake (Table 2), it was observed that Wacker OH 100 achieved the highest value of polymer uptake for pure polymers. This result can be attributed to the low viscosity of Wacker OH 100, which allows to high penetration inside the stone pores. In addition, it is also clear that the addition of nanoparticles leads to increase in the values of polymer uptake. This may be related to the deposition of nanoparticles in the pores of the sandstone samples [32].

Table 2. Average values of polymer uptake by treated sandstone samples

	Polymer or nanocomposite	Symbol	Polymer or nanocomposite Uptake (%)
Group A	Wacker OH 100	A	4.4 ±0.2
	MTMOS	B	1.5 ±0.1
	Mega (1)	C	1.3 ±0.1
	Mega (2)	D	3.3 ±0.2
Group B	Wacker OH 100 + SiO_2 Nanoparticles	E	5.7 ±0.4
	MTMOS + SiO_2 Nanoparticles	F	2.6 ±0.2
	Mega (1) + SiO_2 Nanoparticles	G	1.9 ±0.2
	Mega (2) + SiO_2 Nanoparticles	H	4.8 ±0.2
Group C	Wacker OH 100 + ZnO Nanoparticles	I	4.8 ±0.5
	MTMOS + ZnO Nanoparticles	J	2.4 ±0.2
	Mega (1) + ZnO Nanoparticles	K	1.9 ±0.2
	Mega (2) + ZnO Nanoparticles	L	3.5 ±0.2

Color alteration

By the visual appraisal of the color difference between the treated and untreated sandstone samples, it was found that Wacker OH 100 and MTMOS didn't have a noticeable effect on the color of the samples. Mega (1) led to a slight change in the color of the treated samples. Also it was found that the addition of silica and zinc oxide nanoparticles to the polymers, didn't affect their transparency, and had no effect on the color of the treated samples. Both pure polymer and nanocomposites of Mega (2) failed in this test, as they led to a significant change in the color of the treated samples. Therefore they were excluded from the rest of the tests.

The chromatic changes ΔE^*_{ab} were also carried out by means of Optimatch 3100, in order to calculate and determine the variation of the aesthetical properties induced by the treatments, according to the following equation:

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

where ΔL^*, Δa^* and Δb^* are the differences in the, L^*, a^* and b^* coordinates (according to CIELAB color space) of the treated and untreated sandstone samples. The ΔE^*_{ab} values obtained from the chromatic measurements of the treated samples confirmed the results of the visual appraisal. Table 3 shows the average values of color variation for the treated sandstone samples.

Table 3. Average values of color variation for the treated sandstone samples.

	Polymer or nanocomposite	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}
Group A	Wacker OH 100	-2.18	0.02	0.99	2.39 ±0.1
	MTMOS	-1.80	1.81	1.54	3.15 ±0.1
	Mega (1)	-5.22	0.70	0.23	5.27 ±0.3
Group B	Wacker OH 100 + SiO_2 Nanoparticles	-2.35	0.49	1.35	2.75 ±0.2
	MTMOS + SiO_2 Nanoparticles	2.07	1.75	2.83	3.92 ±0.1
	Mega (1) + SiO_2 Nanoparticles	-5.13	0.80	0.36	5.20 ±0.2
Group C	Wacker OH 100 + ZnO Nanoparticles	-2.22	0.90	1.45	2.80 ±0.2
	MTMOS + ZnO Nanoparticles	-1.62	2.54	2.15	3.70 ±0.3
	Mega (1) + ZnO Nanoparticles	-5.23	0.51	0.21	5.26 ±0.3

Water repellency or hydrophobicity

The hydrophobicity of the samples was evaluated by measuring of static contact angle of water droplets on the surface of the samples. For the pure polymers, MTMOS achieved the best results in the test of hydrophobicity. This is attributed to its hydrophobic character, resulting from the presence of non polar methyl group connecting to the silicon atoms (the backbone in this polymer). However, Mega (1) had the ability to be water repellent, it was found to be less hydrophobic than MTMOS. Since Wacker OH 100 loses all its organic parts (Ethyl groups) when it reacts with water, it didn't show hydrophobic properties, and had little effect on repelling water droplets.

In a comparison, it was found that the addition of nanoparticles to the polymers led to a significant increase in their hydrophobicity. MTMOS + SiO_2 nanocomposite achieved the best results in the test of hydrophobicity, as it became superhydrophobic material on which the water droplets form almost perfect spheres with contact angle larger than 150º. Moreover, it was found that the type of nanoparticles had no substantial effect on superhydrophobicity, which suggests that this property depends on the nanoscale roughness of the surface that led to trapping of air between the water droplet and the rough surface, which is illustrated in the Cassie-Baxter scenario [33]. Fig 4 shows the average values of static water contact angle for the treated and untreated sandstone samples.

Water absorption

Since the water is considered to be the major deterioration factor, so it is very important that the materials of consolidation and protection are able to reduce water penetration into the stone bulk. By measuring the water absorption values of the samples treated with pure polymers and nanocomposites, it was found that addition of nanoparticles to the polymers led to reduce their water absorption rates. This is attributed to the improving of physiochemical properties of the polymers by nanoparticles, which also led to decreasing the cracking rates during the drying process [34]. Table 4 shows the average values of water absorption for the treated and untreated sandstone samples.

Mechanical properties

The mechanical properties of the treated and untreated sandstone samples were determined by testing the compressive strength. Table 5 shows the average values of compressive strength for treated and untreated sandstone samples. By comparison, it was found that the addition of nanoparticles to the polymers increase their compressive strength values. This may be attributed to the role of nanoparticles in reinforcing the polymers, and also improving their interaction with the stone grains [34].

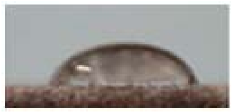
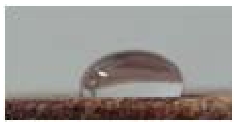
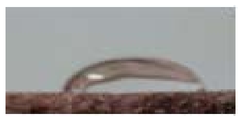
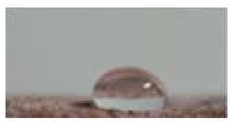
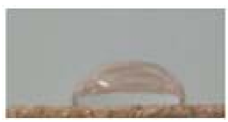
	Polymer or nanocomposite	Symbol	SCA (º)	
	Untreated sample	U	Zero	
	Wacker OH 100	A	37º ± 5º	
Group A	MTMOS	B	104º ± 3º	
	Mega (1)	C	71º ± 2º	
	Wacker OH 100 + SiO_2 Nanoparticles	E	70º ± 7º	
Group B	MTMOS + SiO_2 Nanoparticles	F	153º ± 5º	
	Mega (1) + SiO_2 Nanoparticles	G	110º ± 3º	
	Wacker OH 100 + ZnO Nanoparticles	I	67º ± 9º	
Group C	MTMOS + ZnO Nanoparticles	J	151º ± 8º	
	Mega (1) + ZnO Nanoparticles	K	111º ± 4º	

Fig.4. Average values of static water contact angle for the treated and untreated sandstone samples.

Moreover, it is observed that the results of silica nanoparticles were better than zinc oxide nanoparticles. This can be attributed to the compatibility and homogeneity between silica nanoparticles and the chemical composition of sandstone and silicone polymers.

Table 4. Average values of water absorption for the treated and untreated sandstone samples.

	Polymer or nanocomposite	Symbol	Water absorption %
	Untreated sample	**U**	**9.3** ±0.1
Group A	Wacker OH 100	A	4.9 ±0.2
	MTMOS	B	1.1 ±0.1
	Mega (1)	C	3.6 ±0.1
Group B	Wacker OH 100 + SiO_2 Nanoparticles	E	3.8 ±0.2
	MTMOS + SiO_2 Nanoparticles	F	0.1 ±0.1
	Mega (1) + SiO_2 Nanoparticles	G	1.3 ±0.2
Group C	Wacker OH 100 + ZnO Nanoparticles	I	3.9 ±0.3
	MTMOS + ZnO Nanoparticles	J	0.3 ±0.1
	Mega (1) + ZnO Nanoparticles	K	3.2 ±0.2

Table 5. Average values of compressive strength for treated and untreated sandstone samples.

	Polymer or nanocomposite	Symbol	Compressive strength kg/cm^2
	Untreated sample	**U**	**102** ±5
Group A	Wacker OH 100	A	201 ±7
	MTMOS	B	153 ±5
	Mega (1)	C	123 ±3
Group B	Wacker OH 100 + SiO_2 Nanoparticles	E	227 ±9
	MTMOS + SiO_2 Nanoparticles	F	169 ±7
	Mega (1) + SiO_2 Nanoparticles	G	132 ±3
Group C	Wacker OH 100 + ZnO Nanoparticles	I	212 ±8
	MTMOS + ZnO Nanoparticles	J	160 ±9
	Mega (1) + ZnO Nanoparticles	K	126 ±4

Scanning electron microscope

The examination by scanning electron microscope was used to study the ability of polymers to consolidate and protect the sandstone samples. The untreated sandstone samples appeared to be very fragile, and suffered from granular disintegration. All the polymers used in this study succeeded in covering the grains of the sandstone samples with almost homogenous polymeric networks. Also it was found that the addition of nanoparticles to the polymers improve their interaction with the stone grains, in addition to increase their ability to fill the big pores between the grains. Fig 5 shows SEM micrographs of the treated and untreated sandstone samples.

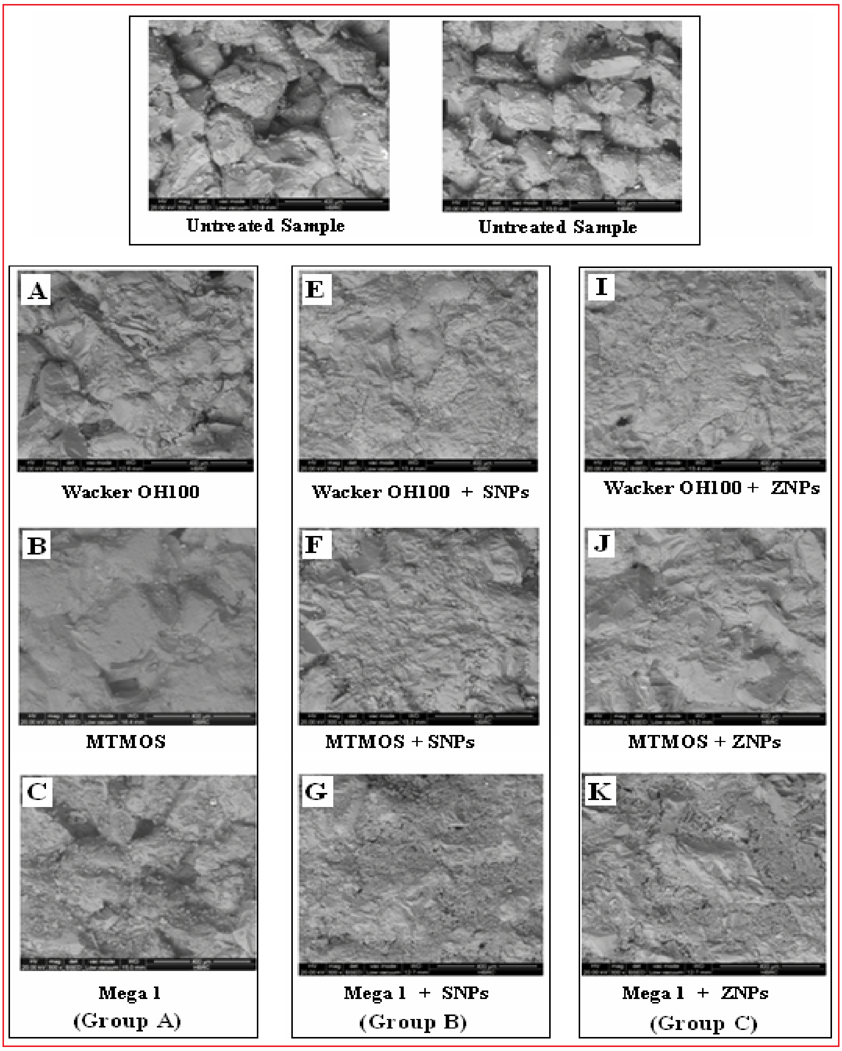


Fig. 5. SEM micrographs of the treated and untreated sandstone samples.

Conclusion

In this study, silicon dioxide (SiO_2), and zinc oxide (ZnO) nanoparticles, were added to different types of the silicon-based polymers (Wacker OH 100, Dow Corning MTMOS, Mega Protec 1, Mega Protec 2) in order to improve their physiochemical and mechanical properties, in order to use them in the consolidation and protection of sandstones. The results showed that the addition of nanoparticles to the silicon-based polymers improved their ability to consolidate and protect the sandstone samples. The samples treated with nanocomposites showed hydrophobic properties better than the samples treated with pure polymers. However the hydrophobicity of samples mainly depends on the nature and chemical composition of polymers, it can be enhanced by the addition of nanoparticles. Also it was found that the type of nanoparticles had no substantial effect on superhydrophobicity, which suggests that this property depends on the surface roughness.

Moreover, the addition of (SiO_2) and (ZnO) nanoparticles enhances the mechanical properties of the polymers. Silica nanoparticles achieved better results than zinc oxide nanoparticles. This can be attributed to the compatibility and homogeneity between silica nanoparticles and the chemical composition of sandstone and silicone polymers.

MTMOS+ Nano-SiO_2 achieved the best results in water repellent properties, and Wacker OH 100 + Nano-SiO_2 achieved the best results in improving the compressive strength. Therefore it is recommended that: (1) MTMOS + Nano-SiO_2 should be used in the consolidation and protection of the sandstone monuments which exposed to water from any of its resources, (2) Wacker OH 100+ Nano-SiO_2 should be used in the consolidation and protection of the fragile sandstone monuments which kept away from water.

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