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Enhancing the Durability of Calcareous Stone Monuments of Ancient Egypt Using $CaCO_3$ Nanoparticles

Mohammad A. Aldoasri [1,*], Sawsan S. Darwish [2], Mahmoud A. Adam [2], Nagib A. Elmarzugi [3] and Sayed M. Ahmed [4]

[1] National Nanotechnology Research Center, King Abdulalziz City for Science and Technology (KACST), P.O. Box 6086, Riyadh 11442, Saudi Arabia
[2] Department of conservation, Faculty of Archaeology, Cairo University, P.O. Box 12613, Giza 12221, Egypt; sawsansd@hotmail.com (S.S.D.); hafezm762000@yahoo.com (M.A.A.)
[3] Faculty of Pharmacy, Tripoli University and National Nanotechnology Project, Biotechnology Research Center, LARST, P.O. Box 13100, Tripoli, Libya; nelmarzugi@gmail.com
[4] Ministry of Antiquities, The grand Egyptian Museum, Giza 12556, Egypt; sayedmansour32@yahoo.com
* Correspondence: aldosari@kacst.edu.sa

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Abstract: The unwanted changes in valuable historic calcareous stone monuments due to exposure to many physical and chemical effects may lead to its deterioration. The growing interest in the field of conservation of stone monuments encourages the development of consolidation and water-repellent materials. The aim of this study is to evaluate the effectiveness of $CaCO_3$ nanoparticles as a consolidation and protection material for calcareous stone monuments, when those nanoparticles used are dispersed in acrylic copolymer; polyethylmethacrylate (EMA)/methylacrylate (MA) (70/30), respectively. Samples were subjected to artificial aging by relative humidity/temperature to show the optimum conditions of durability and the effectiveness of the nano-mixture in improving the physical and mechanical properties of the stone material. The synthesis process of $CaCO_3$ nanoparticles/polymer nanocomposite has been prepared by in situ emulsion polymerization system. The prepared nanocomposites with 0.15 g $CaCO_3$ nanoparticles showed obvious transparency features and represent nanocomposites coating technology with hydrophobic, consolidating and good protection properties. Some tests were performed in order to estimate the superficial consolidating and protective effect of the treatment. The obtained nanocomposites have been characterized by TEM, while the surface morphology before and after treatment and homogeneous distribution of used consolidation materials on stone surface were examined by SEM. Improvement of stone mechanical properties was evaluated by compressive strength tests. Change in water-interaction properties was evaluated by water absorption capillarity measurements, and colorimetric measurements were used to evaluate the optical appearance. Taken together, the results indicate that $CaCO_3$/polymer nanocomposite is a completely compatible, efficient material for the consolidation of artistic and architectural limestone monuments capable of enhancing the durability of limestone toward artificial aging and improving the stone mechanical properties compared to the samples treated with pure acrylic copolymer without Calcium carbonate nanoparticles.

Keywords: calcium carbonate nanoparticles; consolidation; nanocomposites; calcareous stone; TEM; Colorimetric measurements; compressive strength

1. Introduction

Since Ancient Egypt times, local Limestone has been used in Cairo for monument construction. Islamic monuments represent a large and main group of historical monuments in Cairo [1,2]. Generally, due to their prevalently outdoor location, the historical stone buildings dating to Islamic periods in Egypt are subjected to a complex series of weathering and decay factors, such as fluctuation of temperature/humidity, wind erosion, rainwater, hazardous gases and microbes. Limestone blocks that are used in construction in Egypt are very porous stone, with a porosity of up to 14%. The pores are mainly channel type, which allows suction of water by capillary action through the pore structure. This type of lime-based porous material is very sensitive to weathering processes, which affects not only the aesthetic appearance of stones but also causes structural damage [3,4].

The constant exposure to combined action of natural weathering and urban pollution causes several types of damage including physical weathering such as microcracking and disintegration, and chemical weathering such as discoloration and dissolution of component mineral grains [5,6].

The results of this phenomenon (Figure 1) are flaking of the surface layers, powdering, and formation of small blisters with loss of large parts of the artifact and building materials. Additional problems include dissolution of the soluble carbonated components, sulphatation processes, deposition of substances coming from the surrounding environment, granular disintegration, black crust formation, chemical alterations, cracks, erosion, and white stains, which serve to detract from the aesthetic beauty of the structures.

Since at least the early 1960s, acrylic resins have been used for conservation purposes [7,8]. Acrylic polymer has the ability to form a protective layer on the monuments' surface as well as to control the transport of different fluids from the surface to the monument interior [9,10]. In addition, it has good solubility in several solvents, transparency, good adhesive power, and low rigidity at room temperature. Although protection of monuments by using polymeric coatings has created serious challenges for the surface science and technology, the performance of polymer coating after almost twenty years is quite satisfactory [11,12]. The failure of some of these treatments was due to the monument surface deterioration and/or coating-layer/stone interaction. The improper interaction leads to damage of the surface layer and in some cases to remove the coloring and textural details on the monument surface [13–15]. All of these challenges and drawbacks in polymeric materials have attracted the attention of conservation experts to increase the efficacy of the conventional methods to achieve higher consolidation and protection efficiency, and the use of modern techniques of other sciences to overcome these problems.

Nano-technology can be considered a scientific achievement. It has been applied in many fields, such as biomedical, food safety, and environmental applications [16–18]. It has also triggered a huge revolution in electrons, resulting in superior performance in the military field, engineering and water sciences, robotics, biology and medicine, fiber optic communication networks, aerospace technology, advanced materials technology, chemical engineering and precision manufacturing, and is expected to play a major role in social life in the future. Therefore, this technique has received wide attention from scientists and specialists in universities and research institutions from all over the world [19–21]. Conservation science uses the achievements of other sciences, and the time seems ripe to apply the knowledge acquired on nanomaterials in the cultural heritage sector. One important application of nano-materials and technologies is in consolidating or retrofitting degraded materials. This is exploited in cultural heritage conservation, namely in safeguarding quasi-brittle composites and other porous inorganic materials [22,23].

In the last few years, nanocomposites have been frequently applied to restoration and conservation of artworks [24–26]. The minimizing of particle size into nanoscale results in better properties than 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 improve the performance of materials used to improve the durability of stone monuments. Consolidant, protective and hydrophobic polymeric materials have been used in conservation science for several decades [27–30].

Figure 1. Neighboring sewage and its effect on limestone material (Al-zahir baybars mosque).

In the present work, $CaCO_3$ nanoparticles were added as nanometric filler to acrylic polymeric dispersions in order to improve its physical, chemical, mechanical and thermal contraction properties, and compose suitable nanocomposites to be used in the consolidation and protection of the limestone samples. Nano $CaCO_3$ was chosen for its physical, chemical and mechanical properties, such as improved water repellence, increased physical and mechanical properties of the mixed nanocomposites. The presence of nano-$CaCO_3$ may possibly facilitate the mobilization of macromolecular chains and improve the ability of matrix polymer to adapt to deformation and hence to increase the ductility and impact strength of composites. The nanoparticles may also initiate micro-void formations which locally deform the matrix surrounding the particles and initiate mass plastic deformation and, in consequence, increase the toughness and impact energy [31,32].

The selection of the treatment materials concentration was based on many previous studies which presented different strategies for incorporation and dispersion of nanoparticles in polymeric materials.

Mansour (2014) carried out some experiments using various concentrations of nanoparticles mixed with acrylic polymers in order to determine the best concentrations suitable for the conservation of ancient Egypt stone monuments [33]. In addition, many other studies presented different concentrations of $CaCO_3$ nanoparticles and other types of nanoparticles 1%, 3%, 5%, 7%, and 10% of the concentration of the polymeric materials. The best results showed that the proper nano-particles content should be 3–7% of the polymer concentration. The high content of nanoparticles lead to aggregates of nanoparticles and low penetration inside stone structure. When nanoparticles content increased, they tended to form agglomerates that can be described as particles with higher dimensions, smaller surface contact area and smaller effect in the mechanical properties of the matrix [34–36]. The achievement of good dispersion, good penetration in stone material, high physical and mechanical properties seems to be strong with the low content of nanoparticles. In addition, in the field of restoration of ancient Egypt stone monuments, one of the important issues when choosing the concentration of treatment material is porosity and composition of stone material. Thus, due to the high porosity of limestone, the proper concentration of treatment material (5%) will be appropriate.

In order to evaluate the potential use of this $CaCO_3$ in the field of Cultural Heritage, the most important tests were carried out, which is mandatory for Cultural Heritage applications. The properties of the treated limestone samples were evaluated comparatively by using different methods; the selected products were tested under artificial aging. Scanning electron microscopy (SEM) examination is performed to evaluate morphology of the surface and homogeneous distribution of used consolidation materials on stone surface. Improvements in the stone mechanical properties were evaluated by compressive strength test, which is the most important test to evaluate the stone consolidation materials. Changes in water-interaction properties were evaluated by water absorption capillarity measurements and water contact angle measurements, and colorimetric measurements were used to evaluate the optical appearance. The results demonstrated that the addition of nanoparticles into the acrylic-based polymers produced a significant improvement in their efficiency to consolidate and protect the limestone samples.

2. Materials and Methods

2.1. Materials

2.1.1. Experimental Limestone Specimens

The limestone blocks (samples) were collected from the quarry of Mokattam limestone plateau east of Cairo city, one of the most important limestone quarries in Egypt. Most limestone blocks used in construction works of historical monuments in historic Cairo came from the Al-mokattam quarries. The limestone blocks were cut into cuboid samples 3 cm × 3 cm × 3 cm. The samples were washed by distilled water, dried in an oven at 105 °C for at least 24 h to reach constant weight. After that, they were left to cool at the room temperature and controlled RH 50%, then weighed again [37].

2.1.2. Protective Products Treatment

- Paraloid-B72, one of the most largely applied copolymers, is poly ethyl methacrylate (EMA)/methyl acrylate (MA) (70/30, respectively). It was purchased from C T S, Italy. It has been widely used in the treatment of stone artworks and construction materials of historical monuments for consolidation and conservation of such structures [38].
- Nano-powdered $CaCO_3$, Figure 2 (with particle mean diameter <50 nm) were produced by GNM-Get Nano Materials Company—Saint-Cannat, France. Acrylic copolymer was prepared at concentration of (3% w/v) and $CaCO_3$ nanoparticles was dispersed in an aqueous suspension of an acrylic polymer (Polymer 3% w/v, $CaCO_3$ 0.15 g) [11,39]. The interactions between an acrylic copolymer and $CaCO_3$ nanoparticles were investigated in order to establish the reciprocal influence of these two compounds on their peculiar properties.

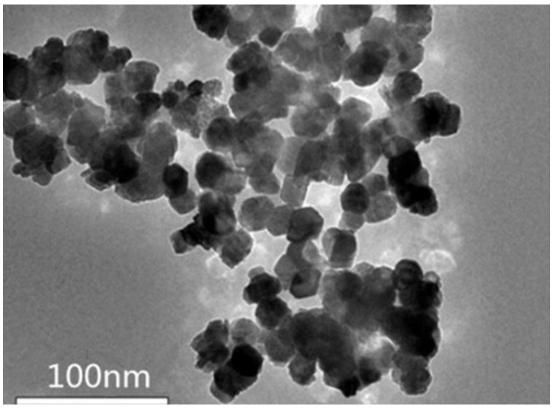


Figure 2. TEM micrograph of the Calcium carbonate nanoparticles (<50 nm) produced and characterized by GNM-Get Nano materials, data sheet supplied by the company.

2.2. Methods

2.2.1. Nanocomposite Preparation by In Situ Emulsion Polymerization System

The $CaCO_3$/polymer nanocomposite has been prepared by different methods as in situ polymerization, which was the first method used to synthesize polymer/nanocomposites based on polyamide 66 [40,41]. The procedure consisted of synthesis of the acrylic polymer with fixed concentration 3% *w*/*v* (solid content 3 g/100 mL), then 0.15 g of $CaCO_3$ nanoparticles was added during the synthesis of the polymer to make the concentration of the nanoparticles in nanocomposites equal to 5% *w*/*v*. The $CaCO_3$ nanoparticle concentration depends on polymer solid content (see Table 1).

Table 1. Concentrations of used consolidation materials.

Treatment Material	$CaCO_3$ Nanoparticles Concentration	$CaCO_3$ Solid Content	Polymer Solid Content	The Obtained Nanocomposite
Paraloid B-72	-	-	3 g	Zero composite
$CaCO_3$ nanoparticles	5%	0.15 g	3 g	$CaCO_3$ nanoparticles/polymer nanocomposites (5%)

The nanocomposite preparation processes were carried out as follows:

The chemicals used in this study, including sodium per sulfate (SPS), sodium bisulphate (SBS) and sodium dodecyl sulfate (SDS) were obtained from Sigma-Aldrich, Munich, Germany. In 250-mL round flask, 3 g monomer, 100 mL deionized water, 0.4 g KOH, 1 g emulsifier sodium dodecyl sulfate (SDS), 0.15 g $CaCO_3$ nanoparticles were added and stirred for 30 min at room temperature. Then the mixture was heated to 80 °C. After that the initiator (SPS/SBS) was added to the mixture under continuous stirring for 3 h. After cooling, the product was precipitated in methanol. The precipitated nanocomposites hybrid was filtered, washed with methanol, and finally dried under vacuum for 24 h at 60 °C.

2.2.2. Procedures of Consolidation and Protection

The pure acrylic polymers and nanocomposites were applied on the limestone samples by brush (three applications). Treated samples were left for 1 month at room temperature and controlled RH 50%. The polymer materials usually need some time, from 15 days to 1 month in order to dry, and this depends on the stone type and the surrounded environmental conditions [42,43]. Some of the treated samples were submitted to investigation methods and the others were submitted to the artificial aging and then to the investigation methods to monitor the changes of protective materials after accelerated aging test.

2.2.3. Microscopic Examination

$CaCO_3$ nanoparticles/polymer nanocomposites obtained were investigated by TEM, Tecnai G20, Super twin, double tilt, Electron accelerating voltage 200 kV using lanthanum hexaboride (LaB6) electron source gun and the diffraction pattern imaging (the examination was carried out in TEM lab, Agriculture research center, Cairo University, Cairo, Egypt).

Thin sections were used for identification of stone minerals by using polarized transmitted light microscopy (PLM), model Nikon opti photo X23 equipped with photo camera S23 under100× magnification in plane-polarized light.

The microstructure of the untreated treated and treated aged samples were observed by SEM, Philips (XL30), equipped with EDX micro-analytical system (the examination was carried out in SEM lab, housing and building national research center, Cairo, Egypt). This examination was performed to detect the element contents of archaeological limestone samples, to determine the morphology of the particles, voids and weathering status of the particles and cracks of coating after treatment with polymer, and to evaluate the distribution, penetration and behavior of the consolidants on untreated and treated samples. Images were acquired in backscattered mode (BSE).

2.2.4. Artificial Aging Test (Wet-Dry Cycles)

This test is aimed at simulating the actual environmental deteriorating conditions and at quantifying the durability of the treatments. The artificial aging test was carried by subjecting the treated samples to frequent changes in temperature and humidity to find the effect of humidity and temperature on the rock by trying to simulate the climatic change from sunny to wet rainy weather. Thus, the treated samples were put in a temperature-controlled oven "Herous-Germany" on special frames. This test consists of 30 cycles of immersion and drying as follows: 18 h of total immersion in distilled water then 6 h in a temperature-controlled oven at 105 °C [44,45].

2.2.5. Colorimetric Measurements

Colorimetric measurements were carried out on untreated, treated and treated aged limestone sample using a CM-2600d Kon-ica Minolta spectrophotometer to assess chromatic variations. Chromatic values are expressed in the CIE L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue) [46,47].

2.2.6. Mechanical Properties

The measurement of compressive strength of the untreated, treated, and treated aged limestone samples were carried out using an Amsler compression-testing machine, with the load applied perpendicular to the bedding plane. According to ASTM C 170, the compressive strength test was carried out on three limestone cubes (3 cm^3) for each treatment material [48], and the average values of compression strength were recorded.

2.2.7. Water contact angle measurements

The hydrophobicity of the untreated and treated aged limestone 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 [49]. The specimens were placed on a sample stage and then a 3 μL water drop was applied onto the sample surface using a graduated micro-pipette. High resolution Canon camera with 18–55 lens was used to capture the images of water droplets on the limestone samples. The contact angles were finally calculated by software program [50]. Each measurement was repeated at least five times and the average value is quoted in each case.

2.2.8. Water Absorption

The water absorption measurements were carried out using the gravimetric method [51]. The water absorption test was carried out on three limestone cubes (3 cm^3) for each treatment material, the limestone samples were completely immersed in deionized water at room temperature. After 24 h, the samples were taken out, carefully wiped with tissue paper and weighed immediately. The amount of the absorbed water was calculated using the following equation (Equation (1)):

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

Equation (1). Calculation of water absorption percentage, where (W_2) is the mass of the sample after immersion in water for 24 h, and (W_1) is the mass of the sample before immersion.

3. Results and Discussion

3.1. Microscope Observations of Historic Limestone Samples

Thin–section analysis a limestone sample was sectioned and mounted on a microscopic slide. Polarizing microscope (PLM) observation of limestone, Figure 3A, showed that the limestone sample consists mainly of fine-grained calcite crystals (marked by blue circle). Disintegration of calcite crystals was inferred from the presence of blurred dispersed points and strong interference of colours between the calcite grains in addition to quartz crystals (marked by red circle), clay minerals (marked by green circle), clay mineral rich iron oxides and high ratio of organic materials (marked by black circle).

SEM investigation of the historic limestone sample, Figure 3B, showed high porosity of limestone and includes high ratio of calcite (Ca), quartz (Q), clay minerals (C.M) and clay minerals rich iron oxides (C.M+) as observed by (PLM). Disintegration of calcite crystals in some areas is due to degradation by physical weathering and salt crystallization. The total EDX analysis of the limestone samples, Figure 3C, showed that calcium (Ca) and Silicon (Si) are the dominant elements, while iron (Fe), potassium (K), Aluminum (Al), Magnesium (Mg) and sulfur (S) were also observed. These patterns indicated that the impurities in the samples are minor, but is expected to play a significant role in deterioration of stone during the weathering process.

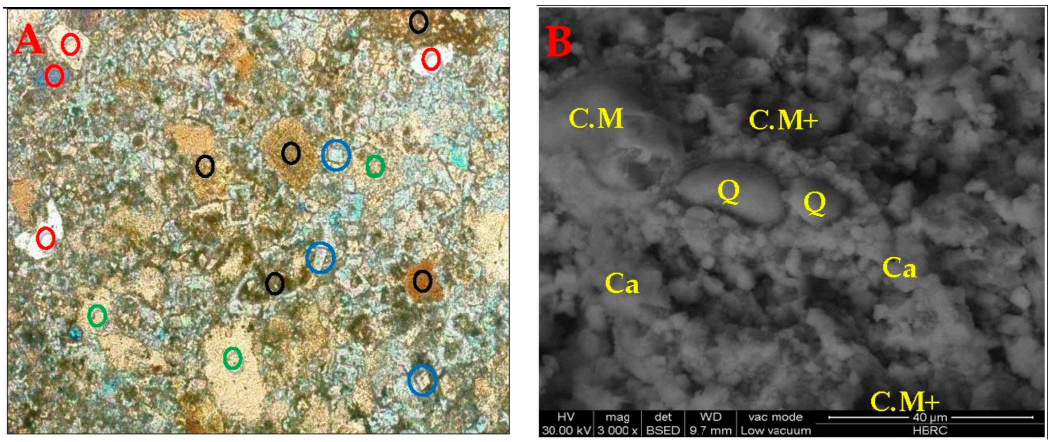
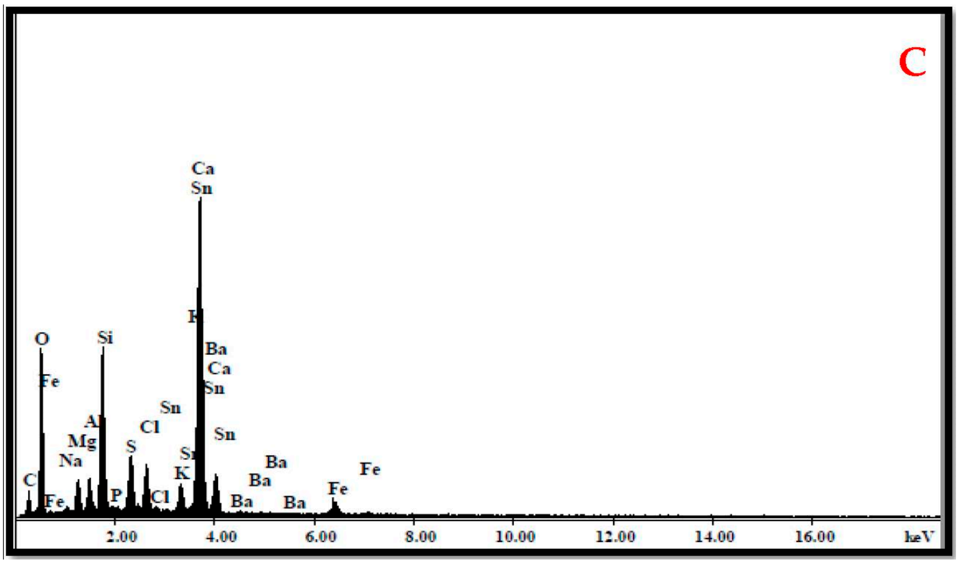


Figure 3. *Cont.*



Element	WT %	AT %	K-Ratio	Z	A	F
CK	15.01	23.48	0.0306	1.0326	0.1975	1.0006
OK	47.24	55.50	0.0786	1.0181	0.1634	1.0002
Nak	1.08	0.88	0.0024	0.9564	0.2294	1.0023
Mgk	2.65	2.05	0.0085	0.9815	0.3264	1.0038
Alk	1.96	1.36	0.0081	0.9537	0.4310	1.0062
Sik	7.87	5.27	0.0427	0.9825	0.5487	1.0053
Pk	0.33	0.20	0.0019	0.9509	0.5797	1.0087
S K	2.64	1.55	0.0182	0.9764	0.6966	1.0117
CLk	2.06	1.09	0.0150	0.9354	0.7636	1.0160
K K	1.34	0.64	0.0115	0.9311	0.8881	1.0365
SnL	0.34	0.05	0.0030	0.7593	1.1538	1.0011
CaK	15.73	7.38	0.1385	0.9528	0.9226	1.0014
BaL	0.25	0.03	0.0020	0.7534	1.0550	1.0022
Fek	1.51	0.51	0.0130	0.8815	0.9756	1.0000
Total	100.00	100.00				

Figure 3. Investigation of historic limestone sample: (**A**) PLM, 100×. The sample consists of calcite crystals (blue circle), quartz crystals (red circle), clay minerals (green circle), clay mineral rich iron oxides and organic materials (black circle). (**B**) SEM image 3000×. The sample includes: calcite (Ca), quartz (Q), clay minerals (C.M) and clay mineral rich iron oxides (C.M+). (**C**) EDX spot analysis from image (**B**).

3.2. Characterization of Obtained Nano-Composites by TEM

The structure and behavior of the prepared nanocomposites was investigated by TEM. The characterization was carried out for the pure acrylic polymer (Poly (EMA/MA), and again after adding the $CaCO_3$ nanoparticles.

TEM images shown in Figure 4A indicated that the pure Poly (EMA/MA) consists of repeated and connected chains in continuous shape (marked with red circle). In Figure 4B is shown the results after adding nanoparticles. The TEM images indicate that the Poly EMA/MA was homogenously interacted with $CaCO_3$ nanoparticles, as there appeared a homogenous dispersion of $CaCO_3$ nanoparticles in the polymer matrix with the formation of $CaCO_3$ nanoparticles/polymer nanocomposites ($CaCO_3$ marked with blue circle). $CaCO_3$ nanoparticles diameter lies in the range from 7 to 13 nm as shown in Figure 4C, no aggregates were observed, and the nanocomposites were successfully prepared by in situ Emulsion Polymerization system.

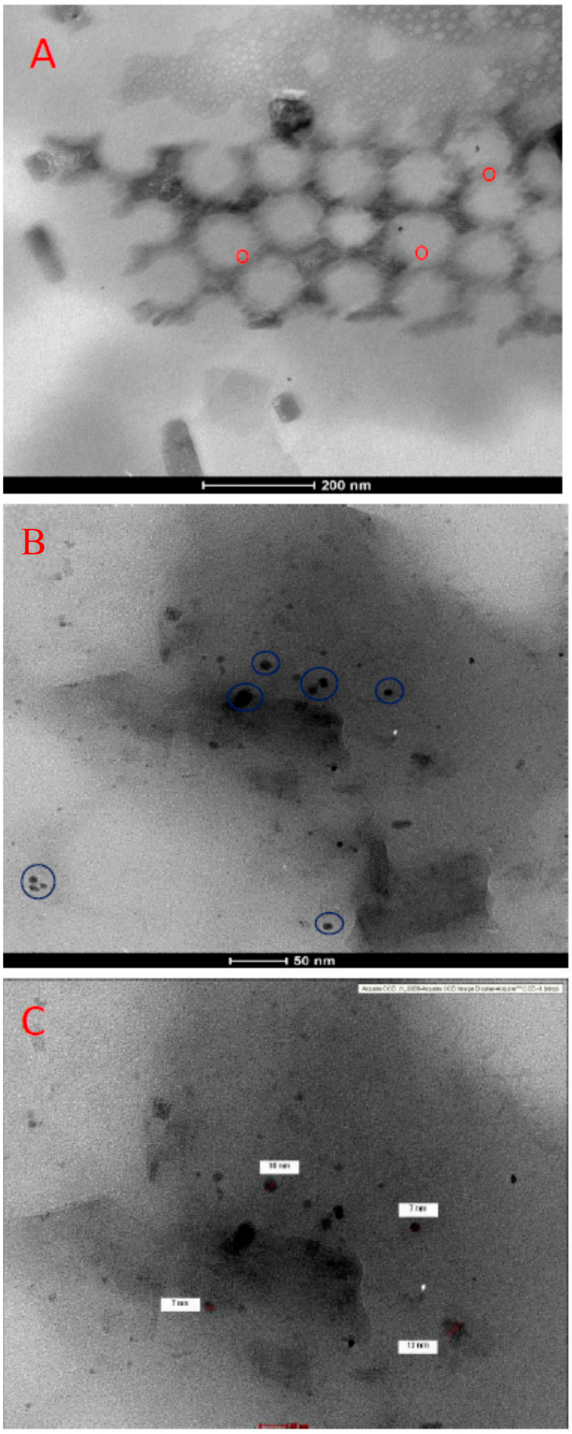


Figure 4. TEM micrographs of the prepared $CaCO_3$ nanoparticles/polymer nanocomposites after synthesis process: (**A**) shows the pure Poly (EMA/MA) and (**B**,**C**) show the homogeneous interaction between $CaCO_3$ nanoparticles and Poly EMA/MA and $CaCO_3$ particle size.

3.3. SEM Microscopy Investigations

Untreated and treated limestone samples were examined and photographed at identical magnifications using Environmental Scanning Electron Microscope (ESEM, Mod. XL30, Philips Company, Amsterdam, The Netherlands). This was done to study the type of coating, film-forming capacity, adherence to material, continuity of treatments, or cracking, in addition to evaluate morphology of the surface and homogeneous distribution of used consolidation materials on stone surface. The SEM micrographs of the untreated experimental limestone sample, (Figure 5A), showed a surface with loose, individual rounded grains and rounded calcite crystals (marked with red circle). The presence of some voids and disintegration was noticed because of dissolving and disappearance of binding materials (marked with yellow circle). As the sample is an experimental sample (new sample), not historic, it was shown under SEM pure and free from impurities and iron oxides.

After treatment, both products used in this study succeeded in covering the grains of the limestone samples with almost homogenous polymeric networks. The SEM examination of the samples treated with Paraloid B-72 showed that the consolidant filled some of the pores and obscured many of particles (marked with blue circle), but material has failed to penetrate to the depth area of stone structure to fill the fine cracks in these areas (marked with yellow circle), and also show that the polymer coating is formed by irregular aggregation of particles (marked with red circle) and there is no formation of a uniformly spread film on the limestone surface (Figure 5B). In contrast, in the samples treated with $CaCO_3$/polymer nanocomposites (Figure 5C), it was found that the addition of nanoparticles to the polymers improves their interaction with the stone grains. In addition to increasing their ability to penetrate to the depth areas and fill the wide pores between the grains, the film shows homogenous and compact distribution (marked with blue circle), with no aggregating particles of the nanocomposite on the limestone surface. This may be due to the fact that the computability between the $CaCO_3$ nanoparticles and limestone composition, and to the unique physical and chemical properties, size and the higher surface area of the nanoparticles.

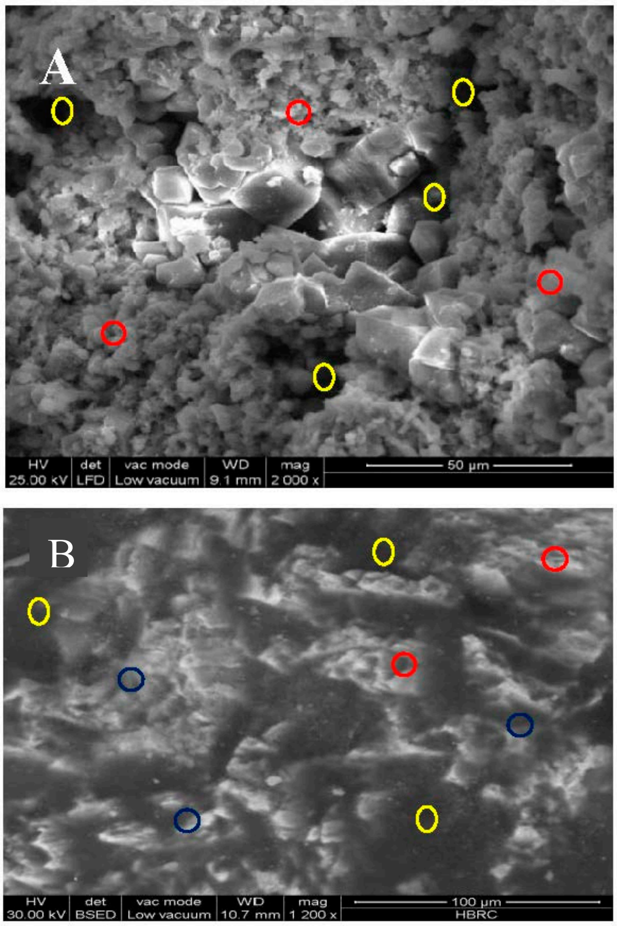


Figure 5. *Cont.*

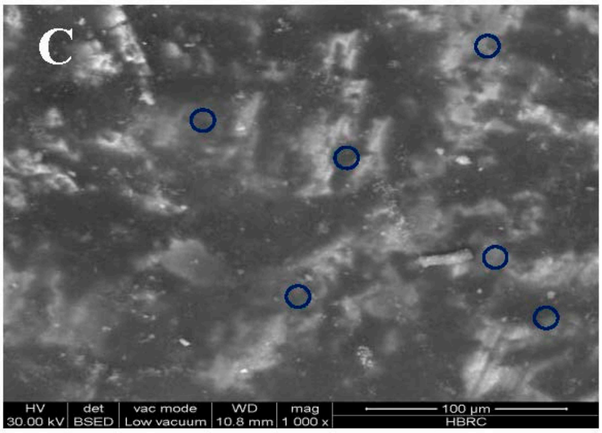


Figure 5. The SEM micrographs of (**A**) untreated experimental limestone sample, and (**B**) Experimental sample treated with pure Poly (EMA/MA) and (**C**) Experimental sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites.

3.4. Colorimetric Measurements

Untreated, treated and aged treated stone surfaces were investigated in order to assess the color variations with respect to untreated samples. The total color change (ΔE) was calculated using the following formula (Equation (2)):

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

Equation (2). Total color change calculation, where ΔL*, Δa* and Δb* are the differences in the L*, a* and b* coordinates (according to CIE LAB color space) of the treated and untreated limestone samples, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue). Such parameters are important for aesthetic reasons. According to Italian guidelines for the restoration of stone buildings, the ΔE value must be <5 [52]. In order to preserve the original color of surfaces, other authors stated that this threshold value should be <10. ΔE scale in stone materials conservation is as follows [53].

- $\Delta E < 0.2$: no perceptible difference
- $0.2 < \Delta E < 0.5$: very small difference
- $0.5 < \Delta E < 2$: small difference
- $2 < \Delta E < 3$: fairly perceptible difference
- $3 < \Delta E < 6$: perceptible difference
- $6 < \Delta E < 12$: strong difference
- $\Delta E > 12$: different colours

After treatment and aging by RH/Temperature, negligible color variations were observed, and all values were in acceptable limit (ΔE value < 5), confirming the suitability of the product for restoring purposes. The obtained data were fully listed in Table 2.

The results in Table 2 showed that the total color change ΔE for the samples treated with nano composite were lower than that for the samples treated with control coating. After aging, however, it was observed that ΔE value in samples treated with the nano composite became higher as compared to the control coating, with all values still in the acceptable range.

Table 2. Color measurement in treated and treated aged limestone samples.

Applied Treatment Materials	Δ (Treated and Untreated Samples)				Δ (Artificial Aged and Untreated Samples)			
	ΔL*	Δa*	Δb*	ΔE	ΔL*	Δa*	Δb*	ΔE
The samples treated with Paraloid B72	−1.08	−0.38	0.79	1.39	2.03	0.41	0.66	2.17
The samples treated with $CaCO_3$/Polymer nanocomposites	−1.21	−0.34	0.33	1.30	2.73	0.51	0.52	2.83

3.5. Mechanical Properties before and after Artificial Aging

The mechanical properties of the untreated, treated, and treated aged limestone samples were determined by testing the compressive strength. Table 3 shows the average values of compressive strength for treated and untreated limestone samples. The results showed that the addition of $CaCO_3$ nanoparticles to acrylic polymer increases the compressive strength values after treatment and subjected to the artificial aging by RH/Temperature with significant and acceptable ratio from the conservation point of view. It was clear that adding of $CaCO_3$ nanoparticles enhanced the durability of stone toward artificial aging and improved resistance to RH/temperature compared to the samples treated with the acrylic polymer without $CaCO_3$ nanoparticles. This may be attributed to the role of nanoparticles in reinforcing the polymers, and also improving their interaction with the stone grains [54]. Note that the tests were carried out on untreated samples only before artificial aging, because after aging, no values could be reported because the material was too weak.

Table 3. Average values of compressive strength for untreated, treated and treated aged limestone samples (plus sign means that there is improvement in the mechanical properties).

Samples	Compressive Strength for Treated Samples					
	Before Artificial Aging			After Artificial Aging		
	Average Value (MPa)	Change (%)	Standard Deviation	Average Value (MPa)	Change (%)	Standard Deviation
Untreated samples	20.594	0.00	0.228	nd *	nd	nd
Samples treated with Paraloid B72	22.555	+9.52	0.233	21.084	+2.38	0.738
Samples treated with $CaCO_3$/Polymer nanocomposites	23.046	+11.90	0.154	22.065	+7.14	0.466

* nd = not detected because after aging, no values could be reported for untreated sample. The material was too weak.

3.6. Contact Angle Measurements

The hydrophobicity of the samples was evaluated by measuring static contact angles of water droplets on the surfaces of the samples. The results in Table 4 reported the contact angle θ for the different treatments on the investigated stones. θ is an average value obtained by measurements on three drops [55]. In comparison, the treatment with Pure Paraloid B72 had the ability to be water repellent, but it was found to be less hydrophobic than Paraloid B72 after adding $CaCO_3$ nanoparticles. $CaCO_3$/polymer nanocomposite achieved the best values of the contact angle after treatment and artificial aging, but these values did not reach the point of super hydrophobicity. A contact angle less than 90° (low contact angle) usually indicates that wetting of the surface is very favorable, and the fluid will spread over a large area of the surface. Contact angles greater than 90° (high contact angle) generally means that wetting of the surface is unfavorable, so the fluid will minimize contact with the surface and form a compact liquid droplet [56]. The water droplets form almost perfect spheres with contact angle less than 150°. There is a small increase in the surface hydrophobicity after treatment by pure Paraloid B72 and by adding $CaCO_3$ nanoparticles. However, the results are satisfactory and in acceptable limit in stone conservation field because the main purpose is to obtain reduction in water absorption ratios. This was confirmed in water absorption test, where it was found that the type of nanoparticles had no substantial effect on super hydrophobicity. The surface wettability is not usually governed by the chemical composition of materials but is more likely related to the surface topographic structure, which suggested 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 [57,58]. Figure 6 shows the average values of static water contact angle for the treated and untreated limestone samples.

Table 4. Values of static water contact angle θ (○) for the treated and untreated Limestone samples.

Samples	Contact Angle Measurement for Treated Samples θ (±3°)	
	Before Artificial Aging	**After Artificial Aging**
Untreated samples	nd *	nd
Samples treated with Paraloid B72	104°	71°
Samples treated with $CaCO_3$/Polymer nanocomposites	110°	108°

* nd = not detected i.e., no values could be reported for untreated samples before and after aging because the water spreads over the surface. This means good wettability.

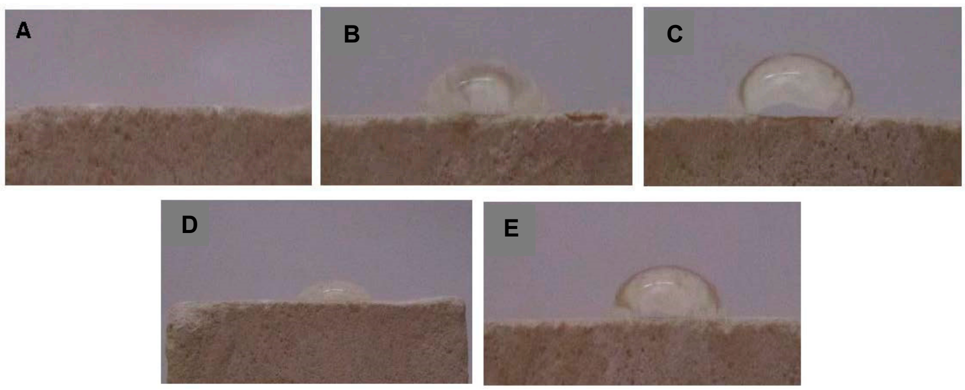


Figure 6. Drops of distilled water on the surface of the limestone for static contact angle measurement (**A**) Untreated samples, and (**B**) the sample treated with pure Paraloid B72, and (**C**) Sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites, and (**D**) Sample treated with pure Paraloid b72 after artificial aging, and (**E**) Sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites after artificial aging.

3.7. Water Absorption

To evaluate the protective efficacy of the water repellent treatments, the UNI 10921:2001 norm was used [59]. Evaluation of the efficacy of water repellent treatments applied on stone materials of cultural and artistic interest requires the measurement of the capillary water absorption. Since the water is considered to be the major deterioration factor, 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 decrease the cracking rates during the drying process. Note that the test was carried out on untreated samples only before artificial aging, because after aging no values could be reported because the material was too weak. In addition, reduction ratio in water absorption value before and after treatment is significant as the important point to reduce the water penetration inside stone does not prevent the water penetration at all. Table 5 shows the average values of water absorption for the untreated, treated and treated aged limestone samples. (Negative sign mean that there is reduction in water absorption ratio).

Table 5. Average values of water absorption for treated and treated aged lime stone samples.

Samples	Water Absorption for Treated Samples					
	Before Artificial Aging			After Artificial Aging		
	Average Value (%)	Change (%)	Standard Deviation	Average Value (%)	Change (%)	Standard Deviation
Untreated samples	3.030	0.0	0.19	nd *	nd	nd
The samples treated with Paraloid B72	1.481	−51.12	0.083	2.255	−25.58	0.033
The samples treated with $CaCO_3$/Polymer nanocomposites	0.769	−74.62	0.016	1.515	−50.00	0.093

* nd = not detected because after aging no values could be reported for untreated sample. The material was too weak.

4. Conclusions

The protection of stones from harmful surrounding conditions by nanocomposites is one of the possible techniques that have been tested. In this study, Calcium carbonate nanoparticles ($CaCO_3$) were added to acrylic-based polymer (EMA/MA) in order to improve its physiochemical and mechanical properties and to use it in the consolidation and protection of limestone monuments. The results of mineralogical composition showed that the sample consists of calcite, quartz, clay minerals, iron oxides and organic materials. SEM results showed the high porosity of limestone in addition to disintegration of calcite crystals in some areas due to degradation by physical weathering and salt crystallization. The results of experimental study showed that the addition of nanoparticles to the acrylic polymer improved its ability to consolidate and protect the limestone samples. The characterization by TEM indicated that $CaCO_3$/polymer nanocomposites were successfully prepared by in situ emulsion polymerization system. Samples treated with pure polymer and $CaCO_3$ nanoparticles/polymer nanocomposites were tested under artificial aging. The result obtained by colorimetric test and hydrophobic measurements showed that the samples treated with nanocomposites were better than the samples treated with pure polymer. Moreover, the addition of ($CaCO_3$) nanoparticles enhanced the mechanical properties of the polymer and improved its interaction with the stone grains. This can be attributed to the compatibility and homogeneity between calcium carbonate nanoparticles and the chemical composition of limestone. In terms of multifunctional features, hydrophobic and photoactive, the consolidation by $CaCO_3$ nanoparticles/polymer nanocomposites seems to give the best performance for limestone monuments. The polymer containing $CaCO_3$ nanoparticles could significantly reduce the water absorption rates inside stone bulk in addition to enhancing the stone durability as compared to those treated with polymer without the nanoparticles. Thus, as mentioned in the introduction, this work presented a novel study about improvement of consolidation and protection material used in consolidation of ancient Egypt stone monuments. The study confirmed that the preparation of nanocomposites by in situ emulsion polymerization method is suitable for the application in conservation of stone monuments.

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