doi:10.20944/preprints201803.0055.v1

Performance of Clay, SiO_2, $Ca(OH)_2$ and $CaCO_3$ - Polymeric Nanocomposites for Conservation and Preservation of Limestone Artworks

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

Abstract: Environmental deterioration factors are constantly increasing, causing unwanted aesthetic changes to stone artworks due to exposure to various physical and chemical deterioration factors. Inorganic nanoparticle-filled polymer composites have extended their multiple functionalities to various applications, including cultural heritage conservation. Therefore, this study has examined the effects of clay, SiO_2, $Ca(OH)_2$ and $CaCO_3$ nanomaterials in the enhancement of the physicomechanical properties of limestone monuments, the aim of the present work being to evaluate comparatively the effectiveness of nanoparticles as consolidation and protection material for limestone artworks. The nanoparticles were added to an acrylic-based copolymer (polyethylmethacrylate (EMA)/methylacrylate (MA) (70/30), in order to improve its physiochemical and mechanical properties, and produced a significant improvement in the ability of the polymers to consolidate and protect the stone. The synthesis process of nanoparticles/polymer nanocomposite has been prepared by an in situ emulsion polymerization system. The nanocomposites contained poly (EMA/MA) with a solid content of 3% [poly (EMA/MA)] in the absence and presence of 5% nanoparticles (0.15 g nanoparticles). Samples were subjected to artificial aging by relative humidity/temperature and acid/salt crystallization weathering 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. To ensure that the treatment had no negative effects on the physical characteristics of the limestone, the properties of the treated limestone samples were evaluated comparatively before and after artificial aging by the conduct of microstructural (phase morphology studied by means of scanning electron microscopy) and aesthetic (colour and lightness measured by spectrophotometry) analyses. Also used were measurement of static contact angle of water droplets on the surface of the samples, total immersion water absorption, compressive strength, and abrasion resistance test. Results demonstrated that the addition of nanoparticles to an acrylic-based polymer enhanced its capability to consolidate and protect the limestone samples.

Keywords: Polymeric nanocomposites; limestone artworks; cultural heritage conservation; consolidation; colorimetric measurements.

1. Introduction.

Limestone is one of the most famous and important types of stone material and has been used in the field of arts and architecture heritage throughout history. [1, 2]. But due to exposure to various environmental deterioration factors, it is easily affected and prone to degradation phenomena, aesthetic, and functional. Historical limestone artifacts suffer various forms of degradation, the most common being: detachment of plaster or masonry substrates, wall decorations, cracks in the substrate, migration and crystallization of salts on stone surface, air pollution in the presence of humidity and temperature variations, and the action of microorganisms that thrive the microclimatic conditions of humidity, temperature, light and air pollution, that cause diverse deterioration aspects such as granular disintegration, exfoliation, erosion, deformation, efflorescence, discoloration, and finally loss of the monuments which were carved or constructed from this stone [3-6].

During recent decades, polymers, mainly acrylic and vinyl resins, have been widely used to consolidate and protect lime-based porous materials used in the artistic/ architectural field (lime-based wall paintings, calcareous stones) [7, 8]. Unfortunately in the last few years, although the performance of polymeric materials for consolidating and protecting of stone monuments has been quite satisfactory [9, 10], they can now be considered one of sources of degradation, which is a basic disadvantage to their use in conservation treatments on lime-based materials, 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 removal of the coloring and textural details on the monument surface [11–13].

The challenges and drawbacks in conventional polymeric materials have attracted the attention of conservation experts to increase the efficacy of the conventional methods to achieve higher consolidation and protection efficiency. Therefore, conservation science uses the achievements of other sciences such as physics, chemistry, geology, biological and engineering to overcome these problems [14], Colloids and materials science are providing effective tools for achieving several tasks related to the durable and compatible conservation of different artistic substrates, minimizing drawbacks and negative effects [15, 16].

Nano-technology has received wide attention from scientists and specialists in universities and research institutions all over the world, Nanomaterials are components of emerging technologies that have numerous applications in electrical engineering, chemistry, material science, and medicine. [17- 20]. In the last decade, nanomaterials have been widely used in the fields of the restoration and conservation of cultural heritage [21, 22]. And application of nanomaterials to the conservation of artistic and architectural heritage has aroused great interest amongst scientists, conservators and archaeologists; the minimizing of particle size into the 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 leads to a significant enhancement of their physiochemical and mechanical properties [23-25].

In our previous study [26], we carried out a fully experimental study 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 an acrylic copolymer, polyethylmethacrylate (EMA)/methylacrylate (MA) (70/30), and the role of the obtained $CaCO_3$/polymer nanocomposite for enhancing the durability of limestone monuments. This study focused only on $CaCO_3$ nanoparticles. The current work is a continuation of the previous study, but in the present work we carried out a comparative study to evaluate the effectiveness of some different types of nanomaterials (clay, SiO_2, $Ca(OH)_2$ and $CaCO_3$) for enhancement of the physicomechanical properties of limestone monuments, when those nanoparticles used are dispersed as nanometric filler in acrylic copolymer; polyethylmethacrylate (EMA)/methylacrylate (MA) (70/30), respectively, in order to improve their physical, chemical, mechanical and thermal contraction properties, and to determine what are the best material for use in the consolidation and protection of the limestone samples.

Nano $CaCO_3$ and Nano $Ca(OH)_2$ were chosen for their higher physical-chemical and physico-mechanical compatibility with the original materials as well as better durability and reversibility, in addition to their ability to penetrate deep into damaged zones without limitations due to the particle size , and high purity and defined composition [27 -29]. Nano clay of the smectite family, montmorillonite, is, because of its ability to thicken by swelling, suitable layer charge density, and low cost nowadays the most widely used clay as a nano-filler. Clay-polymer nanocomposites (PCNs) are compounds in which clay as a layered silicate is dispersed in nanoscale size in a polymer matrix [30]. Recently, these have attracted significant academic and industrial interest due to their excellent properties, such as high-dimensional stability, heat deflection temperature, reduced gas permeability, optical clarity, flame retardancy and enhanced mechanical properties [31, 32]. In addition to that, clay nanosized-layer-filled polymers can exhibit dramatic improvements in mechanical and thermal properties at low clay contents because of the strong synergistic effects between the polymer and the silicate platelets on both the molecular and nanometric scales [33]. Application of silica nanoparticles as fillers in the preparation of nanocomposite of polymers has drawn much attention, due to the increased demand for new materials with improved thermal, mechanical, physical, and chemical properties [34]. This is in addition to the ability of silica nanoparticles as consolidation material to control the deterioration action of silica and calcite as binding materials in stone structure, and improvement in the physicomechanical properties of treated stone [35, 36].

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 calcareous stone monuments [37]. In addition, many other studies presented different concentrations of the used nanoparticles: 0.5%, 1%, 3%, 5%, 7%, and 10% of the concentration of the polymeric materials. The best results showed that the proper nano-particle content should be 3–7% of the polymer concentration. The high content of nanoparticles leads to aggregates of nanoparticles and low penetration inside stone structure. When the proportion of nanoparticles 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 [38, 39]. The achievement of good dispersion, good penetration in stone material, high physical and mechanical properties seems to be stronger with a lower nanonparticle content. In addition, 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.

The properties of the treated limestone samples were evaluated comparatively by different methods; the selected products were tested under artificial aging. Scanning electron microscopy (SEM) examination is performed to evaluate morphology of the surface and the homogeneous distribution of consolidation materials used on stone surfaces. 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 to acrylic-based polymers produced a significant improvement in their efficiency in the consolidation and protection of the limestone samples.

2. Materials and Methods

2.1. Materials

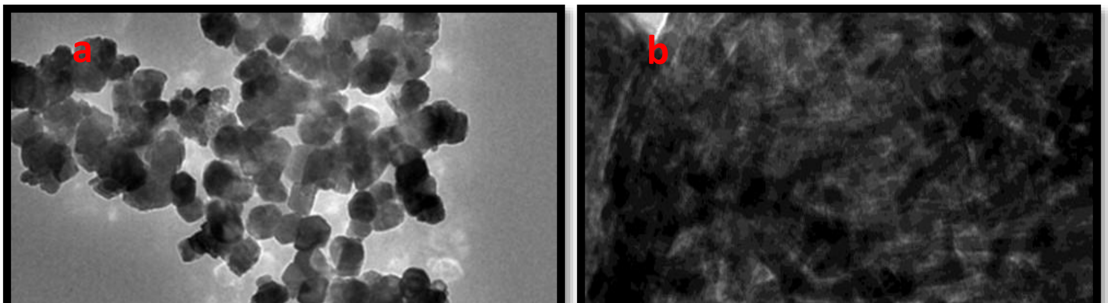
2.1.1. Experimental Limestone Specimens

The experimental limestone blocks were cut into cuboid samples 3 cm × 3 cm × 3 cm. The samples were washed in 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 room temperature and controlled RH 50%, then weighed again [40].

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, Rome, Italy. It has been widely used in the treatment of stone artworks and construction materials of historical monuments for the consolidation and conservation of such structures [41].

- Nano-powdered Clay, SiO_2, $CaCO_3$, and $Ca(OH)_2$, Figure 1 (with particle mean diameter <50 nm) were produced by Nanografi Nanoteknoloji Company—Ankara, Turkey. Acrylic copolymer was prepared at a concentration of (3% *w*/*v*) and the nanoparticles were dispersed in an aqueous suspension of an acrylic polymer (Polymer 3% *w*/*v*, nanoparticles 0.15 g) [42, 43]. The nanocomposites contained poly (EMA/MA) with a solid content of 3% [poly (EMA/MA)] in the absence and presence of 5% nanoparticles (0.15 g nanoparticles).



c

d

Figure 1. TEM micrograph of (a) Calcium carbonate nanoparticles, and (b) $Ca(OH)_2$ nanoparticles, and (c) Clay nanoparticles, and (d)SiO_2 nanoparticles (<50 nm) produced by Nanografi Nanoteknoloji Company, data sheet supplied by the company.

2.2. Methods

2.2.1. Nanocomposite Preparation by In Situ Emulsion Polymerization System

The nanoparticles/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 [44, 45]. The procedure consisted of a synthesis of the acrylic polymer with a fixed concentration of 3% *w/v* (solid content 3 g/100 ml), then 0.15 g of nanoparticles was added during the synthesis of the polymer to make the concentration of the nanoparticles in nanocomposites equal to 5% *w/v*. The nanoparticle concentration depends on polymer solid content (see Table 1).

Table 1. Concentrations of used consolidation materials.

Treatment Material	**Nanoparticle Concentration**	**Nanoparticle Solid Content**	**Polymer Solid Content**	**The Obtained Nanocomposite**
Paraloid B-72	-	-	3 g	Zero composite
$Ca(OH)_2$ nanoparticles	5%	0.15 g	3 g	$Ca(OH)_2$ nanoparticles/polymer nanocomposites (5%)
$CaCO_3$ nanoparticles	5%	0.15 g	3 g	$CaCO_3$ nanoparticles/polymer nanocomposites (5%)
Clay nanoparticles	5%	0.15 g	3 g	Clay nanoparticles/polymer nanocomposites (5%)
SiO_2 nanoparticles	5%	0.15 g	3 g	SiO_2 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 a 250-mL round flask, 3g monomer, 100 ml deionized water, 0.4g KOH, 1g emulsifier sodium dodecyl sulfate (SDS), 0.15g 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 3h. After cooling, the product was precipitated in methanol. The precipitated nanocomposite hybrid was filtered, washed with methanol, and finally dried under vacuum for 24h at 60°C.

2.2.2. Procedures of Consolidation and Protection

The pure acrylic polymers and nanocomposites were applied to 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 surrounding environmental conditions [46, 47]. The samples were weighed again, and the polymer uptake was calculated, then some of the treated samples were submitted to investigation methods and the others were subjected to artificial aging and then to the investigation methods to monitor the changes of protective materials after the accelerated aging test.

2.2.3. Microscopic Examination

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 centre, Cairo, Egypt). This examination was performed to detect the elemental 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 behaviour of the consolidants on untreated and treated samples. Images were acquired in backscattered mode (BSE).

Identification of the mineral composition of the samples was conducted by X-ray diffraction patterns, using A "Philips" X-ray diffractometer (PW 3071) (CuKα 40 kV, 30 mA). The scanned 2-theta range was 5 to 60 degrees.

2.2.4. Artificial Aging

Artificial aging aims to simulate the actual environmental deteriorating conditions and to quantify the durability of the treatments. Two types of weathering-mentioned below were conducted sequentially and termed as "artificial aging".

2.2.4.1. Thermal 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: 18h of total immersion in distilled water then 6h in a temperature-controlled oven at 105°C [48, 49].

2.2.4.2 Salt Crystallization Weathering.

The samples were subjected to cycles of immersion in a saturated Na_2SO_4 solution for 4h followed by 28h of exposure to air in normal room conditions (25°C and 40% R.H.) then 16 h in an oven at 105°C [50, 51].

2.2.5. Colorimetric Measurements

Colorimetric measurements were carried out on untreated, treated and treated aged limestone sample using a CM-2600d Konica 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) [52, 53].

2.2.6. Mechanical Properties

2.2.6.1. Compressive strength test

The measurement of compressive strength of the untreated, treated, and treated aged limestone samples was 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 ($3cm^3$) for each treatment material [54], and the average values of compression strength were recorded.

2.2.6.2. Abrasion Resistance Test

The wide wheel abrasion (WWA) test is among the most widely used standard test methods for determining the abrasion resistance of natural stones. Limestone samples that belong to the calcareous metamorphic type were tested for their abrasion resistance as well as physico-mechanical properties. Care was taken to select samples free of cracks and visible signs of weathering. The abrasion resistance of rocks was mainly controlled by their mineralogical and micro vs. macro textural characteristics. After precisely dimensioning the stone samples, according to the related testing procedures, the abrasion resistance of the considered stone types was determined in the laboratory, by using the wide wheel abrasion test apparatus, in accordance with the procedures described in EN 14157 Standard (2004) (Natural Stones—Determination of Abrasion Resistance) [55].

Wide wheel abrasion (WWA) tests were applied on samples with dimensions of 10 cm x15 cm x 3 cm. Samples used in WWA tests were dried at 105 °C for 24 h until they reached a constant weight. The abrasive powder storage hopper was filled with dry powder and placed between the sample and an abrasive rotating disk (Figure 2). While the abrasive disk rotated at 75 cycles per minute, it was ensured that the flow of abrasivity was uninterrupted. Two surfaces of each sample were exposed to the test. At the end of the test, the surface with traces of abrasion was examined under a loupe and the borders of the abrasion area were depicted, as suggested in EN 14157 (2004). Following this step, three measurements were obtained from each abrasion surface, with a 0.01 mm precision digital caliper, and recorded. In the WWA experiments, it was important that the sample surfaces be smooth and parallel to each other, and before starting the experiments, the calibration of the apparatus was checked against a reference sample of “Boulonnaise Marble” [56].

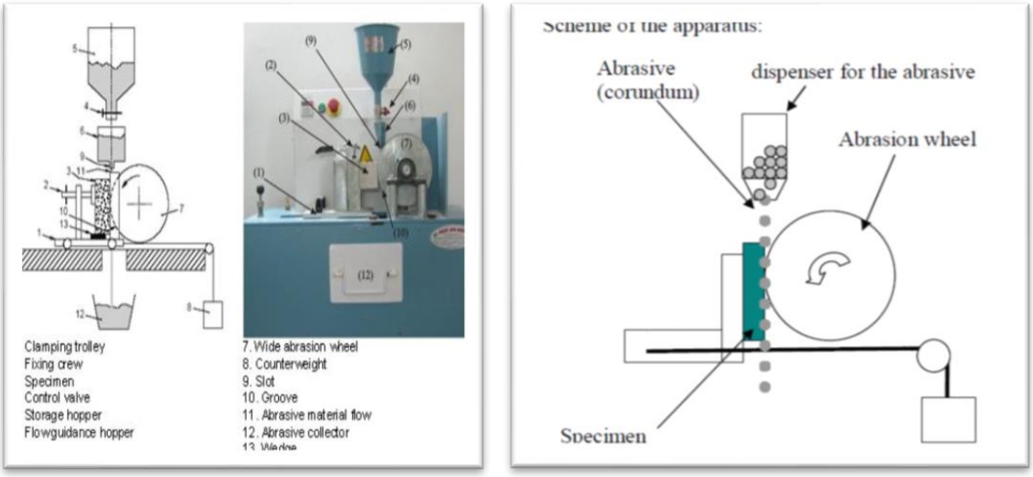


Figure 2. Wide wheel abrasion test device.

Figure 3. Limestone sample inside Wide wheel abrasion disk (the test was carried out in ceramic and stone tests lab, housing and building national research centre, Cairo, Egypt).

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 a piece of apparatus custom-made in compliance with standard UNI EN 15802–2010 [57]. The specimens were placed on a sample stage and then a 3 μl water drop was applied to the sample surface using a graduated micro-pipette. A 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 [58]. 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 [59]. The water absorption test was carried out on three limestone cubes ($3cm^3$) for each treatment material, the limestone samples were completely immersed in deionized water at room temperature. After 24h, 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)):

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

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

3. Results and Discussion

3.1. Characterization of Studied Historic Limestone Samples.

The investigation of historic limestone samples, which were carefully assembled from fallen fragments at some archaeological sites is shown in Figure 4A. The total EDX analysis of the limestone sample showed that calcium (Ca) is the dominant element, while chloride (Cl), sodium (Na), silicon (Si), aluminium (Al), iron (Fe), potassium (K), magnesium (Mg), lead (Pb), and palladium (Pd) were also observed. These patterns indicated that the impurities in the samples are minor, but is expected that they will play a significant role in the deterioration of stone during the weathering process. The XRD analysis (Figure 4B) showed that the limestone sample consists mainly of fine calcite crystals as a major mineralogical constituent, with trace amounts of halite.

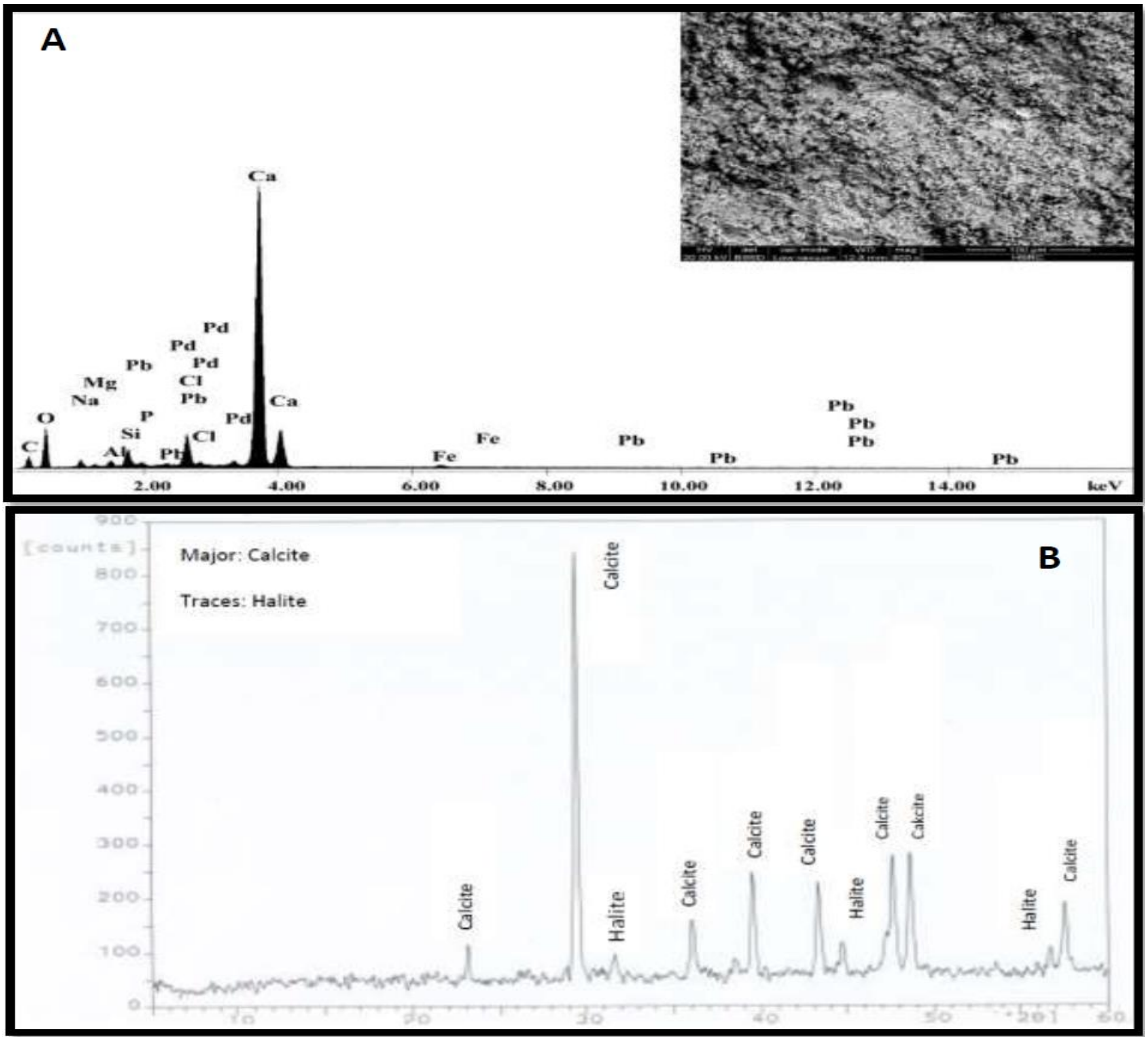


Figure 4. Investigation of historic limestone sample: (**A**) Energy dispersive X-ray (EDX) spot analysis of historic limestone sample; (**B**) XRD pattern of historic limestone sample.

3.2. *Polymer uptake.*

By comparing the values of polymer uptake, it was observed that, the treatment by $Ca(OH)_2$ /polymer nanocomposites achieved the highest value of polymer uptake. This result can be attributed to the higher physical-chemical and physical-mechanical compatibility with the original materials as well as better durability and reversibility, it has the great advantage of achieving a deeper penetration of the dispersion, better stability and avoiding the formation of white glazing on the treated surface. In addition to providing the treatment, the material can act as a binder giving the decayed material a more cohesive texture and increasing the interaction between the stone grains. It is also clear that the addition of nanoparticles leads to an increase in the values of polymer uptake. This may be related to the deposition of nanoparticles in the pores of the limestone samples [60, 61]. Completed data, as listed in Tables 2

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

Consolidation materials	Polymer or nanocomposite uptake (%)	
	Before Artificial Aging	**After Artificial Aging**
Samples treated with Paraloid B72	0.26	0.21
Samples treated with $CaCO_3$/Polymer nanocomposites	0.30	0.25
The samples treated with $Ca(OH)_2$/Polymer nanocomposites	0.32	0.28
The samples treated with Clay/Polymer nanocomposites	0.30	0.24
The samples treated with SiO_2/Polymer nanocomposites	0. 27	0.22

3.3. SEM Microscopy Investigations.

Untreated, treated and treated aged limestone samples were examined and photographed at identical magnifications using an 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, and in addition to evaluate the morphology of the surface and the homogeneous distribution of used consolidation materials on stone surface. The SEM images of the samples are shown in Figure. 5A-5k. 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 a red circle). The presence of some voids and disintegration was noticed because the binding materials dissolved and disappeared (marked with a 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. Approximately all the polymers used in this study succeeded in covering the grains of the limestone samples with almost homogenous polymeric networks. After treatment, 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 in some areas 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).

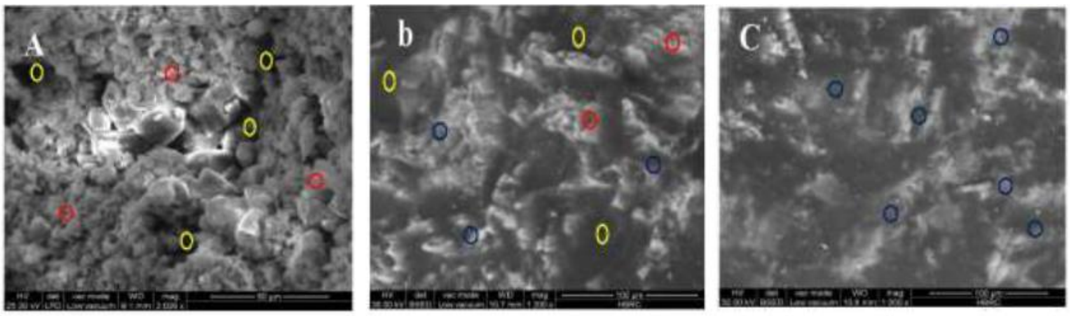


Figure 5. The SEM micrographs of (**A**) Untreated samples, and (**B**) Experimental sample treated with pure Paraloid B72, and (**C**) Experimental Sample treated with $CaCO_3$nanoparticles/polymer nanocomposites, and (**d**) Experimental Sample treated with $Ca(OH)_2$ nanoparticles/polymer nanocomposites, and **(e)** Experimental Sample treated with Clay nanoparticles/polymer nanocomposites, and **(F)** Experimental Sample treated with SiO_2 nanoparticles/polymer nanocomposites. **(g)** Experimental Sample treated with pure Paraloid b72 after artificial aging, and (**H**) Experimental Sample treated with $Ca(OH)_2$ nanoparticles/polymer nanocomposites after artificial aging, and **(I)** Experimental Sample treated with Clay nanoparticles/polymer nanocomposites after artificial aging, and **(J)** Experimental Sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites after artificial aging, and **(K)** Experimental Sample treated with SiO_2 nanoparticles/polymer nanocomposites after artificial aging.

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). A small aggregation of film coating in some areas was noticed but without any effect on film uniformity (marked with red circle). The samples treated with $Ca(OH)_2$ /polymer nanocomposites (Figure 5d), showed a homogeneous coating of the particles and formation of a uniformly spread film on the limestone surface more than the coating with Paraloid B-72 without nanoparticles and $CaCO_3$/polymer nanocomposites; no visible cracks are seen in the film coating, with no aggregating particles of the nanocomposite on the limestone surface (marked with blue circle). This may be due to the fact that the computability between the $CaCO_3$ and $Ca(OH)_2$ nanoparticles and limestone composition, and to the unique physical and chemical properties, size and the higher surface area of the nanoparticles. The samples treated with clay/polymer nanocomposites (Figure 5e), also show a homogeneous and uniform coating on limestone surface, and the treatment material succeeded in penetrating to the depth areas (marked with a blue circle); this is due to the excellent properties of clay, as a layered silicate is dispersed in nanoscale size in a polymer matrix. The samples treated with SiO_2/polymer nanocomposites (Figure 5f), SiO_2 nanoparticles managed to increase the ability of the polymer to fill the big pores between the grains (marked with a blue circle); this is due to the ability of silica nanoparticles as consolidation material to control the deterioration action of silica and calcite as binding materials in the stone structure.

After artificial thermal aging, small changes were observed in samples treated with all products; the film uniformity and homogeneity was affected as a result of aging, which was illustrated further in samples treated with Paraliod B-72 (figure 5g), and the addition of nanoparticles to the polymer matrix improve the stability of the microstructure of the product under the effect of the artificial thermal aging. By comparison, from the SEM results, it is observed that $Ca(OH)_2$ nanoparticles are the best nanomaterial, which filled the polymer matrix, increased the polymer ability to penetrate into stone pores and formed homogeneous coating. This is due to the calcium hydroxide nanoparticles having acquired a considerable relevance due to their potentialities as consolidant product, achieving a deeper penetration of the dispersion, better stability and avoiding the formation of white glazing on the treated surface. In building stones, this treatment reinforces the texture and re-aggregates powdery surfaces. Furthermore, when compared to other consolidating compounds, such as polymeric resins, nano-dispersions of $Ca(OH)_2$ show higher physical-chemical and physical-mechanical compatibility with the original materials as well as better durability and reversibility, without limitation of penetration due to the particle size or mobilisation of soluble salts[62- 63].

3.4. Colorimetric Measurements

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

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

Equation (2). Total colour change calculation, where ΔL^*, Δa^* and Δb^* are the differences in the L^*, a^* and b^* coordinates (according to CIE LAB colour 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 [64]. In order to preserve the original colour of surfaces, other authors stated that this threshold value should be <10. ΔE scale in stone materials conservation is as follows [65].

- $\Delta E < 0.2$: 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 colour variations were observed, there is a change in ΔE value before and after treatment and after artificial aging, but all values were within the acceptable limit (ΔE value < 5), confirming the suitability of the product for restoring purposes. The obtained data were fully listed in Table 3.

The results in Table 3 showed that, 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 3. 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**
The samples treated with $Ca(OH)_2$/Polymer nanocomposites	1.41	-0.60	-2.42	**2.86**	-0.94	0.43	3.79	**3.93**
The samples treated with Clay/Polymer nanocomposites	1.68	-0.22	-1.09	**2.01**	-2.17	0.40	1.36	**2.59**
The samples treated with SiO_2/Polymer nanocomposites	0.16	-0.06	-0.29	**0.33**	-4.77	-0.52	0.11	**4.80**

3.5. Mechanical Properties

3.5.1. Compressive strength test before and after artificial aging

The mechanical measurements of the untreated, treated, and treated aged limestone samples were determined by testing the compressive strength. Table 4 shows the average values of compressive strength for treated and untreated limestone 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 [66].

Moreover, it is observed that the results of $Ca(OH)_2$ nanoparticles and clay nanoparticles gave the highest values of compressive strength after treatment and after being subjected to the artificial aging by RH/Temperature with significant and acceptable ratio from the conservation point of view. This can be attributed to the effect of the carbonation process on $Ca(OH)_2$ particles in limestone samples, high reactivity and fast reactions in the treated zones and high compatibility with $CaCO_3$-based substrates[67], and the chemical composition of clay, as layered silicates, nanosized-layer-filled polymers can exhibit dramatic improvements in mechanical and thermal properties at low clay contents because of the strong synergistic effects between the polymer and the silicate platelets on both the molecular and nanometric scales [68]. 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 4. 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 %**	**Average Value (MPa)**	**Change %**
Untreated samples	20.594	0.00	nd*	nd
Samples treated with Paraloid B72	22.555	+9.52	21.084	+2.38
Samples treated with $CaCO_3$/Polymer nanocomposites	23.046	+11.90	22.065	+7.14
The samples treated with $Ca(OH)_2$/Polymer nanocomposites	24.121	+17.12	23.886	+15.98
The samples treated with Clay/Polymer nanocomposites	23.231	+12.80	22.765	+10.55
The samples treated with SiO_2/Polymer nanocomposites	22.911	+11.25	22.033	+6.98

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

3.5.2. Abrasion resistance test before and after artificial aging

The results of the abrasion resistance test are expressed by the width of the resulting groove in mm. According to the European standard of abrasion resistance test for the stone materials, EN 14157 (2004), the stone surface abrasion values should be not more than 24. Table 5 shows the average values for the abrasion resistance of experimental limestone samples, before and after treatment, and after thermal aging. The results confirmed the abrasion resistance test result and revealed that the addition of $Ca(OH)_2$ and clay nanoparticles to the polymer matrix gave the best results in abrasion resistance values due to the excellent chemical and physico-mechanical properties of those materials as mentioned before. After artificial thermal aging, the surface resistance of samples treated with polymer/nanocomposites was not affected too much and still gave better results than the untreated samples and the samples treated with polymer without the inclusion of nanoparticles as shown in Figure 6. This may be attributed to the role of nanoparticles in enhancing the durability of the stone surface and also improving the interaction with the stone grains.

Table 5. Results of the wide wheel abrasion test.

Samples	**Wide Wheel Abrasion Values (mm)**	
	Before Artificial Aging	**After Artificial Aging**
Untreated samples	19.5	nd*

Samples treated with Paraloid B72	17.5	18
Samples treated with $CaCO_3$/Polymer nanocomposites	16.5	16.8
The samples treated with $Ca(OH)_2$/Polymer nanocomposites	15.7	15.9
The samples treated with Clay/Polymer nanocomposites	16.2	16.5
The samples treated with SiO_2/Polymer nanocomposites	17	17.5

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

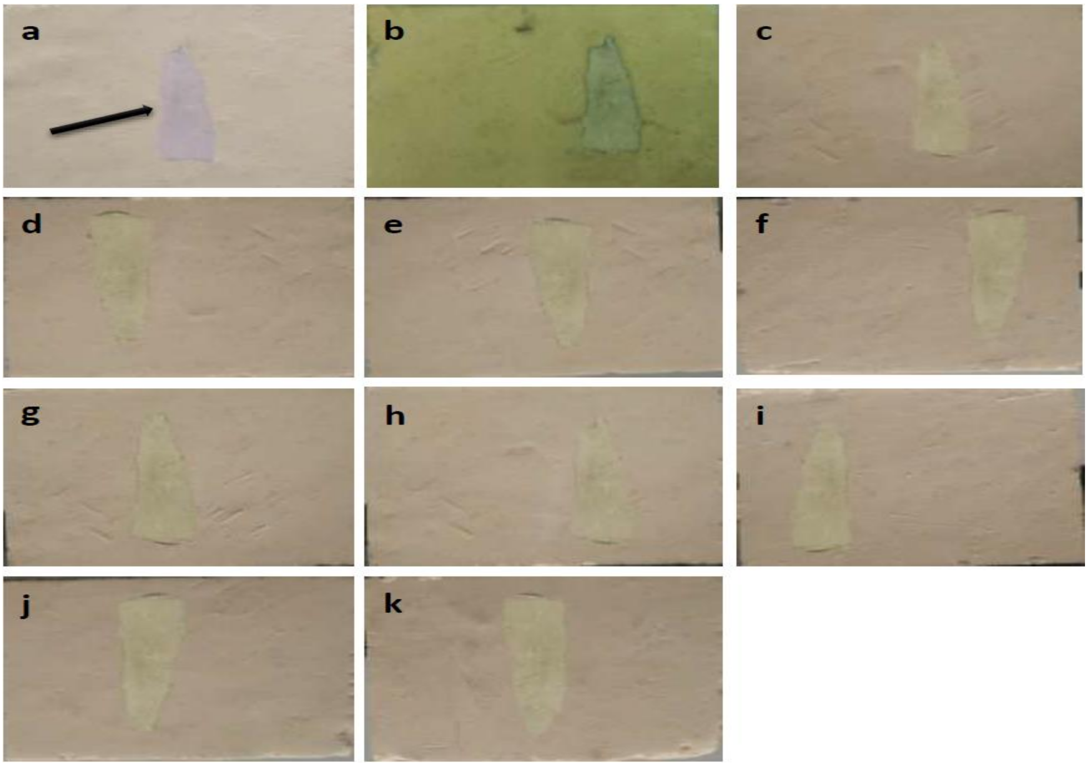


Figure 6. Measurement of abrasion surface in the Wide Wheel Abrasion test (**a**) Untreated samples, and (**b**) sample treated with pure Paraloid B72, and (**c**) sample treated with $Ca(OH)_2$ nanoparticles/polymer nanocomposites, and (**d**) sample treated with clay nanoparticles/polymer nanocomposites, and **(e)** sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites, and **(f)** sample treated with SiO_2 nanoparticles/polymer nanocomposites. **(g)** sample treated with pure Paraloid b72 after artificial aging, and (**h**) sample treated with $Ca(OH)_2$ nanoparticles/polymer nanocomposites after artificial aging, and **(i)** sample treated with clay nanoparticles/polymer nanocomposites after artificial aging, and **(j)** sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites after artificial aging, and **(k)** sample treated with SiO_2 nanoparticles/polymer nanocomposites after artificial aging.

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 6 reported the contact angle θ for the different treatments on the investigated stones. θ is an average value obtained by measurements on three drops [69]. 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 different types of nanoparticles were added. The Ca(OH)$_2$/polymer nanocomposite achieved the best values for contact angle after treatment and artificial aging, due to the effect of the carbonation process on Ca(OH)$_2$ particles, faster carbonation rate, and higher physical-chemical and physical-mechanical compatibility with the original materials. Following it is the treatment with clay and SiO$_2$–polymer nanocomposites, which may be attributed to their chemical properties and hydrophobic character. 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 favourable, and the fluid will spread over a large area of the surface. Contact angles greater than 90° (high contact angle) generally mean that the wetting of the surface is unfavourable, so the fluid will minimize contact with the surface and form a compact liquid droplet [70]. The water droplets form almost perfect spheres with contact angles of less than 150°. There is a small increase in the surface hydrophobicity after treatment by pure Paraloid B72 and after the addition of nanoparticles the values of surface hydrophobicity were increased. However, the results are satisfactory and within the acceptable limits in the stone conservation field because the main purpose is to obtain a reduction in water absorption ratios. This was confirmed in the 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 [71, 72]. Figure 7 shows the average values of static water contact angle for the treated and untreated limestone samples.

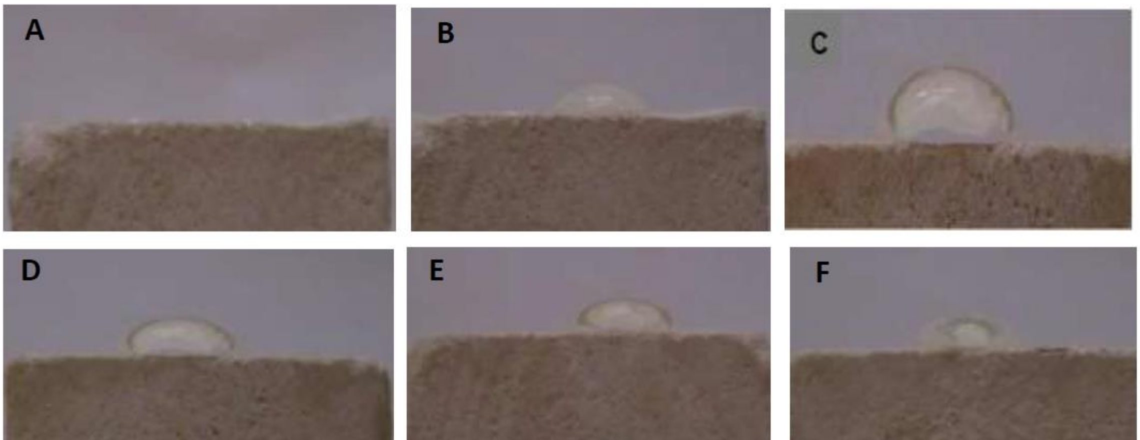


Figure 7. Drops of distilled water on the surface of the limestone for static contact angle measurement (**A**) Untreated samples, and (**B**) sample treated with pure Paraloid B72, and (**C**) sample treated with $Ca(OH)_2$ nanoparticles/polymer nanocomposites, and (**D**) sample treated with clay nanoparticles/polymer nanocomposites, and **(E)** sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites, and **(F)** sample treated with SiO_2 nanoparticles/polymer nanocomposites. **(G)** sample treated with pure Paraloid B72 after artificial aging, and (**H**) sample treated with $Ca(OH)_2$ nanoparticles/polymer nanocomposites after artificial aging, and **(I)** sample treated with clay nanoparticles/polymer nanocomposites after artificial aging, and **(J)** sample treated with $CaCO_3$ nanoparticles/polymer nanocomposites after artificial aging, and **(K)** sample treated with SiO_2 nanoparticles/polymer nanocomposites after artificial aging.

Table 6. 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°	102°
Samples treated with $CaCO_3$/Polymer nanocomposites	108°	106°
The samples treated with $Ca(OH)_2$/Polymer nanocomposites	112°	111°
The samples treated with Clay/Polymer nanocomposites	109°	107°
The samples treated with SiO_2/Polymer nanocomposites	109°	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.

3.7. Water Absorption

To evaluate the protective efficacy of the water repellence treatments, the UNI 10921:2001 norm was used [73]. Evaluation of the efficacy of water repellence treatments applied on stone materials of cultural and artistic interest requires the measurement of capillary water absorption. Since 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 a reduction of their water absorption rates. This is attributed to the improvement of physiochemical properties of the polymers by nanoparticles, which also led to a decrease in the cracking rates during the drying process. And the results confirmed the values obtained in water contact angle and mechanical properties tests, which revealed that addition of $Ca(OH)_2$ nanoparticles to polymer gave the best result for water absorption values. In addition, the result revealed that, it is preferable to use calcium hydroxide nanoparticles rather than calcium carbonate nanoparticles and the superficial consolidating and protective effect of the treatment based on the carbonation process and the complete conversion of calcium hydroxide into calcium carbonate by reaction with atmospheric carbon dioxide. Moreover, calcium hydroxide nanoparticles are considered more compatible with $CaCO_3$-based substrates than other materials such as clay and silica. 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, the reduction ratio in water absorption value before and after treatment is significant as the important point in reducing the water penetration inside stone does not prevent all water penetration. Table 7 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 7. Average values of water absorption for treated and treated aged limestone samples.

Samples	Water Absorption for Treated Samples			
	Before Artificial Aging		After Artificial Aging	
	Average Value %	Change %	Average Value %	Change %
Untreated samples	20.12	0.0	nd*	nd
The samples treated with Paraloid B72	17.08	- 15.10	18.35	- 8.79
The samples treated with $CaCO_3$/Polymer nanocomposites	14.83	- 26.29	16,86	- 16.20
The samples treated with $Ca(OH)_2$/Polymer nanocomposites	12.53	- 37.72	15.98	- 20.57
The samples treated with Clay/Polymer nanocomposites	13.41	- 33.34	16.50	- 17.99
The samples treated with SiO_2/Polymer nanocomposites	16.29	- 19.03	17.04	- 15.30

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

3.8. Salt migration to stone surface

The migration of a salt to the surface of a porous stone material is one of the most serious deterioration factors. The only way to completely and permanently prevent efflorescence in historical porous materials is by using special admixtures [74]. In fact, the nanomaterials in these additives can be up to 100,000 times smaller than even the smallest sand particles and binding materials in stone structure. This allows their molecules to literally pass through calcite and sand particles and ultimately to become part of the stone structure with which they react and to protect porous building materials against salt efflorescence [75, 76]. The results showed that, the treated samples had a greater resistance to damage than the untreated samples. Following the salt weathering tests, the surfaces of the samples were visually observed by stereo-microscopy investigation. While the untreated samples had a powdery rough texture, the results showed that the samples treated with $Ca(OH)_2$/polymer nanocomposite had a smoother surface with less deterioration visible, and gave the best results in resistance to salt efflorescence on stone surfaces compared to those coated with pure polymer without the nanoparticles and the samples coated with other nanocomposites, see Figure. 8a-8f.

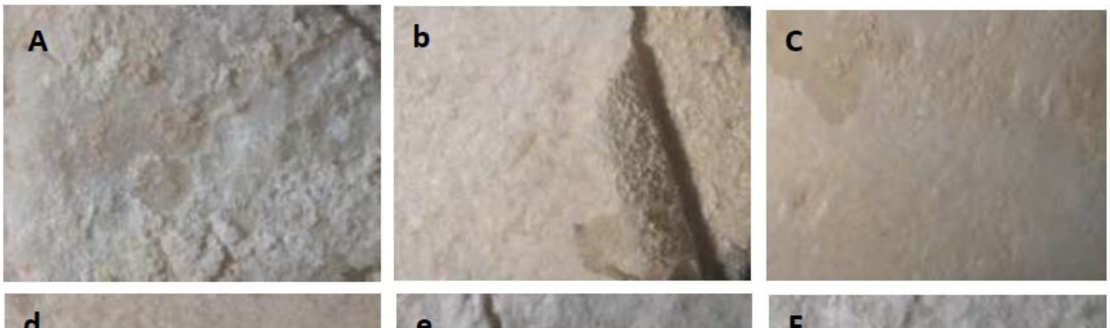


Figure 8. Stereo-microscopy images, showing the effect of the salt weathering on (A) untreated samples, and (b) the sample treated with pure Paraloid B72, and (C) sample treated with Ca $(OH)_2$ nanoparticles/polymer nanocomposites, and (d) sample treated with Ca CO_3 nanoparticles/polymer nanocomposites, and (e) sample treated with clay nanoparticles/polymer nanocomposites, and (f) sample treated with SiO_2 nanoparticles/polymer nanocomposites.

4. Conclusions

Limestone is a material prone to being affected by weathering and environmental deterioration factors. The damage to and deterioration of historical limestone are one of the serious problems that attract research efforts all over the world. In this study, clay, SiO_2, $Ca(OH)_2$ and $CaCO_3$ nanoparticles were added to an acrylic-based polymer (EMA/MA) in order to improve its physiochemical and mechanical properties, determine comparatively what are the best materials for use in the consolidation and protection of the limestone artworks, and to use them in the consolidation and protection of limestone artworks. The results obtained on the investigation of historic limestone showed that the sample consists mainly of fine calcite crystals, aluminium, iron, potassium, magnesium, and trace amounts of halite. The results of the experimental study showed that the addition of nanoparticles to the acrylic polymer improved its ability to consolidate and protect the limestone samples. The obtained nanoparticles/polymer nanocomposite has been prepared by in situ emulsion polymerization system. Samples treated with pure polymer and nanoparticles/polymer nanocomposites were tested under artificial aging. The results showed that the addition of nanoparticles to the acrylic-based polymers improved the ability of the polymers to consolidate and protect the limestone samples. The results obtained by colorimetric test, values of polymer uptake and hydrophobic measurements showed that the treatment by $Ca(OH)_2$ and clay /polymer nanocomposites achieved the highest values. However, the experimental evidence shows an effective consolidating action of $Ca(OH)_2$ nanoparticles, and the results obtained by SEM microscopic investigation indicated that, $Ca(OH)_2$ nanoparticles are the best nanomaterial, which filled the polymer matrix, increased the polymer ability to penetrate into stone pores and form a homogeneous coating. Moreover, it is observed that the results of $Ca(OH)_2$ and clay /polymer nanocomposites achieved the best results in improving the mechanical properties of the polymer and improved its interaction with the stone grains. This can be attributed to the effect of the carbonatation process on Ca $(OH)_2$ particles in limestone samples, high reactivity and fast reactions in the treated zones, higher physical-chemical and physical-mechanical compatibility with $CaCo_3$-based substrates, and the chemical composition of clay as a layered silicates. Nanosized-layer-filled polymers can exhibit dramatic improvements in mechanical and thermal properties at low clay contents because of the strong synergistic effects between the polymer and the silicate platelets on both the molecular and nanometric scales. In terms of multifunctional features, hydrophobic and photoactive, the consolidation by $Ca(OH)_2$ and clay /polymer nanocomposites seems to give the best performance for limestone monuments. The polymer containing $Ca(OH)_2$ and clay nanoparticles could significantly reduce the water absorption rates inside stone bulk in addition to enhancing the stone durability as compared to other materials. Thus, this work presented a novel study about the improvement of the consolidation and protection material used in the consolidation of limestone monuments. The study confirmed that $Ca(OH)_2$ and clay nanoparticles can be considered a good candidate for improving the polymeric materials that are used in the consolidation of stone artworks, and the suitability of the obtained nanocomposites in the conservation process under the studied conditions.

Acknowledgments: The authors are much grateful to King Abdulalziz City for Science and Technology (KACST), Riyadh, Saudi Arabia for the valuable and continues scientific and moral support. The authors acknowledge the valuable assistance given by Sagita Mirjam Sunara, Vice-Dean for Arts, Science, International Collaboration and ECTS · Split, Croatia, and Dr. Graham, McMaster, for their valuable technical support.

Author Contributions: Sawsan S. Darwish, Sayed M. Ahmed, and Mohammad A. Aldosari conceived and designed the experiments; Sayed M. Ahmed and Mahmoud A. Adam performed the experiments; Sawsan S. Darwish, Nagib A. Elmarzugi, and Mahmoud A. Adam analyzed the data; Mohammad A. Aldosari and Nagib A. Elmarzugi contributed reagents/materials/analysis tools; Sawsan S. Darwish and Sayed M. Ahmed wrote the paper.

Conflicts of Interest: The authors have no conflicts of interest to declare.

References

1. Tucci, P.; Armiento, G.; Menichini, P.; Esposito, R.; I materiali lapidei della facciata de "Le Monacelle" di Ostuni e le loro antiche cave di appartenenza, in III International Symposium on the Conservation of Monuments in the Mediterranean Basin, V.Fassina, Ott H., Zezza F. (Eds), Venezia, 22-25 Giugno **1994**.

2. Cassar, J. Deterioration of the Globigerina Limestone of the Maltese Islands. In: Siegesmund, S., Weiss, T., and Vollbrecht, A. (eds). Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies. 205: 33-49. Geological Society London, London **2002**.
3. P.S. Griffin.; N. Indictor.; R.J. Koestler. The biodeterioration of stone: a review of deterioration mechanism, conservation case histories and treatment, Int. Biodeterior. 28 (**1991**) 187–207.
4. M. Del Monte. The cultural heritage: causes of damage, in: N.S. Baer, C. Sabbioni, A.I. Sors (Eds.), Proceedings of the European Symposium Science, Technology, and European Cultural Heritage, Bologna, Italy, **1991**, pp. 78–89 (13–16 June **1989**, ICCROM).
5. K. Zehnder.; A. Arnold. Crystal growth in salt efflorescenses, J. Cryst. Growth 97 (**1989**) 513–521.
6. Fitzner, B.; Heinrichs, K.; Bouchardiers, D. *Limestone Weathering of Historical Monuments in Cairo, Egypt*; Special Publication, Geological Society of London: London, UK, **2002**; Volume 205, pp. 217–239.
7. J.M.C. Garrido, The Portal of the Monastery of Santa Maria de Ripoll , Monumentum 1 (**1967**) 79–98.
8. J. Ciabach, Investigation of the cross-linking of thermoplastic resins affected by ultraviolet radiation, in: J.O. Tate, N.H. Tennent, J.H. Townsend(Eds.), Proceedings of the Symposium Resins in Conservation, Scottish Society for Conservation and Restoration, Edinburgh, **1983**, pp. 51–58 (Edinburgh, 21–22 May **1982**).
9. J. Brus, P. Kotlik, Consolidation of stone by mixtures of alkoxysilane and acrylic polymer, Stud. Cons. 41 (2) (**1996**) 109–119.
10. G. Fazio, Sull'efficacia di alcuni trattamenti di restauro realizzati dopo il **1960**, Bollettino d'Arte, "Materiali lapidei" Supplemento a1 N.41 (**1987**) 197–214.
11. Sasse, H.R.; Senthlage, R. Evaluation of stone consolidation treatments, science and technology for cultural heritage. *J. Com. Natl. Sci. Tecnol. Beni Cult. CNR* **1996**, *5*, 85–92.
12. Littmann, K.; Sasse, H.R.; Wagener, S.; Hocker, H. Development of polymers for the consolidation of natural stone. In Proceedings of the International RILEM UNESCO Congress on Conservation of Stone and Other Materials, Paris, France, 29 June–1 July **1993**; pp. 681–688.
13. C. Danehey, G. Wheeler, S.C. Su, The influence of quartz and calcite on the polymerization of MTMOS, in: J. Rodrigues Delgado, F. Henriques, F. Jeremias Telmo (Eds.), Proceedings of the Seventh International Congress on Deterioration and Conservation of Stone, Laboratório Nacional de Engenharia Civil, Lisbon, **1992**, pp. 1043–1052 (Lisbon, Portugal, 15–18 June **1992**).
14. Horie, C. *Materials for Conservation*, 2nd ed.; Butterworth-Heinemann: London, UK, **2010**; Volume 27.
15. Cessari.L, L; Cenzia.B; Elena.G; Maria, G. Sustainable technologies for diagnostic analysis and restoration techniques: the challenges of the green conservation, In Proceedings of the 4th International Congress Science and Technology for the Safeguard of Cultural Heritage of the Mediterranean Basin, Cairo, Egypt, 6–8 December **2009**.
16. P.K. Sekhar, N.S. Ramgir, R.K. Joshi and S. Bhansali, "Selective Growth of Silica Nanowires using Au Catalyst for Optical Recognition of Interleukin-10", Nanotechnology, 19, 245502 (**2008**)
17. Dimitrijevic, M.; Karabasil, N.; Boskovic, M.; Teodorovic, V.; Vasilev, D.; Djordjevic, V.; Kilibarda, N.; Cobanovic. N. Safety Aspects of Nanotechnology Applications in Food Packaging. *Procedia Food Sci.* **2015**, *5*, 57–60.
18. Ibrahim, R.K.; Hayyan, M.; AlSaadi, M.A.; Hayyan, A.; Ibrahim, S. Environmental application of nanotechnology: Air, soil, and water. Environ. *Sci. Pollut. Res. Int.* **2016**, *14*, 13754–13788.
19. Mamalis, A.G. Recent advances in nanotechnology. *J. Mater. Process. Technol.* **2007**, *181*, 52–58.
20. Cessari.L, L; Cenzia.B; Elena.G; Maria, G. Sustainable technologies for diagnostic analysis and restoration techniques: the challenges of the green conservation, In Proceedings of the 4th International Congress Science and Technology for the Safeguard of Cultural Heritage of the Mediterranean Basin, Cairo, Egypt, 6–8 December **2009**.

21. P. Baglioni, R. Giorgi, D. Chelazzi, *Nano-materials for the conservation and preservation of movable and immovable Artworks*, International Journal of Heritage in the Digital Era (Progress in Cultural Heritage Preservation - EUROMED **2012**), 1(IS1), **2012**, pp. 313-318.
22. L. Pinho, M. J. Mosquera, *Photocatalytic activity of TiO_2–SiO_2 nanocomposites applied to buildings: Influence of particle size and loading*, Applied Catalysis B: Environmental, 134, **2013**, pp. 205–221.
23. Manoudis, P.; Karapanagiotis, I.; Tsakalof, A.; Zuburtikudis, I.; Panayiotou, C. Super-hydrophobic polymer/nanoparticle composites for the protection of marble monuments. In Proceedings of the 9th International Conference on NDT of Art, Jerusalem, Israel, 25–30 May **2008**; pp. 1–8.
24. Manoudis, P.; Tsakalof, A.; Karapanagiotis, I.; Zuburtikudis, I.; Panayiotou, C. Fabrication of superhydrophobic surfaces for enhanced stone protection. *J. Surf. Coat. Technol.* **2009**, *203*, 1322–1328.
25. Gao, N.; Yan, Y.Y.; Chen, X.Y.; Zheng, X.F. Superhydrophobic composite films based on THSand Nanoparticles. *J. Bionic Eng.* **2010**, *7*, 559–566.
26. Mohammad A. Aldoasri.; Sawsan S. Darwish.; Mahmoud A. Adam.; Nagib A. Elmarzugi.; Sayed M. Ahmed. Enhancing the Durability of Calcareous Stone Monuments of Ancient Egypt Using $CaCO_3$ Nanoparticles. Sustainability **2017**, 9, 1392, 1-17.
27. P. Baglioni, R. Giorgi, Soft and hard nanomaterials for restoration and conservation of cultural heritage, Soft Matter 2 (**2006**) 293-303.
28. R. Giorgi, L. Dei, P. Baglioni, A new method for consolidating wall Paintings based on dispersion of lime in alcohol, Studies in conservation 45 **(2000)** 154-161.
29. Z. Zhang, C. Wang, Y. Meng, K. Mai, "Synergistic effects of toughening of nano-$CaCO_3$ and toughness of β-polypropylene," Compos. Part A: Appl. Sci. Manuf., 43 (1), 189–197, **2012**.
30. S. Sinha Ray and M. Okamoto, "Polymer/layered silicate nanocomposites: a review from preparation to processing," *Progress in Polymer Science*, vol. 28, no. 11, pp. 1539–1641, **2003**.
31. A. Gu and G. Liang, "Thermal degradation behaviour and kinetic analysis of epoxy/montmorillonite nanocomposites," *Polymer Degradation and Stability*, vol. 80, no. 2, pp. 383–391, **2003**.
32. Bartholmai M, Schartel B. Layered silicate polymer nanocomposites: New approach or illusion for fire retardancy? Investigation of the potentials and the tasks using a model system. Polym Adv Technol **2004**;15:355–64.
33. Wilkie C. Recent advanced in fire retardancy of polymer–clay nanocomposite. In: Lewin M, editor. Recent advances in flame retardancy of polymers. Norwalk, CT: Business Communications Co Inc; **2002**. vol. 13. p. 155–160.
34. De Ferri, L.; Lottici, P.; Lorenzi, A.; Montenero, A.; Salvioli-Mariani, E. Study of Silica Nanoparticles-Polysiloxane Hydrophobic Treatments for Stone–based Monument Protection. *J. Cult. Herit.* **2011**, *12*, 356–363.
35. E.K. Kim, J. Won, J. Do, S.D. Kim, Y.S. Kang, Effects of silica nanoparticle and GPTMS addition on TEOS-based stone consolidants, J Cult Heritage 10 (**2009**) 214–221.
36. P.N. Manoudis, S. Papadopoulou, I. Karapanagiotis, A. Tsakalof, I. Zuburtikudis, C. Panayiotou, Polymer-Silica nanoparticles composite films as protective coatings for stone-based monuments, J Physics: Conference Series 61 (**2007**) 1361–1365.
37. Mansour, S. Comparative Study to Evaluate Efficiency of the Conventional Composites and Nano-Composites in Cleaning and Self-Protection for Some Archaeological Stone Surfaces. Applied on Selected Objects. Master's Thesis, Conservation Department, Faculty of Archaeology, Cairo University, Giza, Egypt, June **2014**.
38. Buasri, A.; Chaiyut, N.; Borvornchettanuwat, K.; Chantanachai, N.; Thonglor, K. Thermal and Mechanical Properties of Modified $CaCO_3$/PP Nanocomposites. *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.* **2012**, *6*, 1–4.
39. Eirasa, D.; Pessanb, L.A. Mechanical Properties of Polypropylene/Calcium Carbonate Nanocomposites. *Mater. Res.* **2009**, *12*, 517–522.

40. Licciulli, A.; Calia, A.; Lettieri, M.; Diso, D.; Masieri, M.; Franza, S.; Amadelli, R.; Casarano, G. Photocatalytic TiO_2 coatings on limestone. *J. Sol-Gel Sci. Technol*. **2011**, *60*, 437–444.
41. Vaz, M.F, Pires, J.; Carvalho, A.P. Effect of the Impregnation Treatment with Paraloid B-72 on the Properties of Old Portuguese Ceramic Tiles. *J. Cult. Herit.* **2008**, *9*, 269–276.
42. La Russa, M.F.; Ruffolo, S.A.; Rovella, N.; Belfiore, C.M.; Palermo, A.M.; Guzzi, M.T.; Crisci, G.M. Multifunctional TiO_2 coatings for Cultural Heritage. *Prog. Organ. Coat.* **2012**, *74*, 186–191.
43. Man-Wai Ho .;Chun-Ki Lam .; Kin-tak Lau .; Dickon H.L. Ng .;David Hui. Mechanical properties of epoxy-based composites using nanoclays. Composite Structures 75 (**2006**) 415–421
44. Mohamed, W.S.; Effenberger, F.; Schweizer, M. Synthesis and characterization of some polyacrylate/montomorillite Nanocomposites by In situ Emulsion polymerization Using Redox Initiation system. *J. Appl. Polym. Sci.* **2009**, *112*, 1–7.
45. Feng, L.L.; Eonardo, M. Preparation and Characterization of Polymer TiO_2 Hybrid Nanocomposites via In situ Polymerization. Master'S Thesis, Applied Science in Chemical Engineering, University of Waterloo, Waterloo, ON, Canada, **2006**; pp. 77–80.
46. Bakr. A.M. Evaluation of the reliability and durability of some chemical treatments proposed for consolidation of so called-marble decoration used in 19th century cemetery (Hosh Al Basha), Cairo, Egypt. *J. Arab Archaeol. Union* **2011**, *12*, 75–96.
47. Helmi, F.M.; Hefni. Y.K. Using nanocomposites in the consolidation and protection of sandstone. *Int. J. Conserv. Sci.* **2016**, *7*, 29–40.
48. Lazzari. M.; Chiantore, O. Thermal-Ageing of Paraloid Acrylic Protective Polymers. *J. Polym.* **2000**, *41*, 6447–6455.
49. Shashaua, S. Mechanical Testing of Resins for USE in Conservation. ICOM Committee for Conservation, Washington, **1993**, 58.
50. Khallaf, M. K., El-Midany, A. A. and El-Mofty, S. E. Influence of Acrylic Coatings on the Interfacial, Physical, and Mechanical Properties of Stone-Based Monuments." *Progress in Organic Coatings* 72, **2011**, 592-598.
51. EN 12370. **2000**. Natural Stone Test Methods – Determination of Resistance to Salt Crystallisation.
52. Schanda, J. *Colorimetry*; Wiley-Interscience John Wiley & Sons Inc: Hoboken, New Jersey, USA **2007**; Budapest, Hungary p. 56.
53. Darwish, S.S. Evaluation of the effectiveness of some consolidants used for the treatment of the XIXth century Egyptian cemetery wall painting. *Int. J. Conserv. Sci.* **2013**, *4*, 413–422.
54. American Society for Testing ... and Protection of Stone Monuments.*Standard Test Methods for Compressive Strength of Natural Building Stone; ASTM C 170*; Unesco: Paris, France, 1976.
55. EN 14157-**2004** Natural Stones—Determination of Abrasion Resistance, European Standard–Wide Wheel Abrasion Resistance BS; European Standard (EN): Czech Republic, pp. 19.
56. Çobanolu, I.; Çelik, S.B.; Alkaya, D. Correlation between wide wheel abrasion (capon) and Bohme abrasion test results for some carbonate rocks. *Sci. Res. Essays* **2010**, *5*, 3398–3404.
57. Persia, F.; Caneve, L.; Colao, F.; D'Amato, R.; Giancristofaro, C. Performance of nanocomposites for conservation of artistic stones. In Proceedings of the 12th International Congress on the Deterioration and Conservation of Stone, Columbia University, New York, NY, USA, 21–25 October **2012;** pp. 66–78.
58. Helmi, F.M.; Hefni, Y.A. A simple method for measuring the static water contact angle for evaluation the hydrophobicity of the consolidating and protective materials. In Proceedings of the First International Conference of Egypt and Mediterranean Countries through Ages, Faculty of Archaeology, Cairo University, 15–18 October **2014**; Volume 3, pp. 327–341.
59. UNI 10859 (**2000**) Cultural Heritage—Natural and artificial stones—Determination of water absorption by capillarity.

60. A. Calia, M. Masieri, G. Baldi, C. Mazzotta, the evaluation of nanosilica performance for consolidation treatment of an highly porous calcarenite, 12th International Congress on the Deterioration and Conservation of Stone, Columbia University, New York, **2012**, pp. 2-11.
61. M. Ambrosi, L. Dei, R. Giorgi, C. Neto, P. Baglioni, Colloidal particles of Ca(OH)2: properties and applications to restoration of frescoes, Langmuir 17 (**2001**) 4251–4255.
62. Ziegenbalg, G., Brümmer, K., Pianski, J. **2010**. Nano-lime - a new material for the consolidation and conservation of historic mortars. In: Historic Mortars - HMC 2010 and RILEM TC 203-RHM final workshop; edited by J. Válek, C. Groot and J.J. Hughes; e- ISBN: 978-2-35158-112-4; pp. 1301 – 1309.
63. Luigi Dei .; Barbara Salvadori. Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay, Journal of Cultural Heritage 7 (**2006**) 110–115
64. NorMal, R. Misure Colorimetric he Strumentali di Superfici opache. Available online: http://www.architettiroma.it/fpdb/consultabc/File/ConsultaBC/Lessico_NorMal-Santopuoli.pdf (accessed on 02 August **2017**)
65. Limbo, S.; Piergiovanni, L. Shelf life of minimally processed potatoes Part 1. Effects of high oxygen partial pressures in combination with ascorbic and citric acids on enzymatic browning. *Postharvest Biol. Technol.* **2006**, *39*, 254–264.
66. J. Choi, S. Park, J. Won, Y. S. Choi, Y. S. Kang, M. S. Lee, effect of pretreatment for TEOS based stone consolidants, 12th International Congress on the Deterioration and Conservation of Stone, Columbia University, New York, **2012**, pp. 119-128.
67. Valeria Daniele.; Giuliana Taglieri.; Raimondo.; Quaresima. The nanolimes in Cultural Heritage conservation: Characterisation and analysis of the carbonatation process, Journal of Cultural Heritage 9 (**2008**) 294-301
68. McNally Tony, Raymond Murphy W, Lew Chun Y, Turner Robert J, Brennan Gerard P. Polyamide-12 layered silicate nanocomposites by melt blending. Polymer **2003**; 44:2761–72.
69. UNI 11207 (**2007**) Cultural heritage—Natural and artificial stones Determination of static contact angle on laboratory specimens.
70. Cappelletti, G.; Fermo, P. Hydrophobic and superhydrophobic coatings for limestone and marble conservation. In *Smart Composite Coatings and Membranes*; Elsevier: Amsterdam, the Netherlands **2016**; pp. 421–452.
71. Cassie, A.B.D.; Baxter, S. Wettability of porous Surfaces. Trans. Faraday Soc. **1944**, 40, 546–551.
72. Bico, J.; Thiele, U.; Quéré, D. Wetting of textured surfaces. Colloids Surf. A **2002**, 206, 41–46.
73. .UNI 10921 (**2001**) Evaluation of the efficacy of water repellent treatments applied on stone materials of cultural and artistic interest.
74. A.E. CHAROLA, *Salts in the Deterioration of Porous Materials: An Overview*, J. American Institute for Conservation (JAIC), **39**(3), pp. 327–343, **2000.**
75. R.M. Espinosa-Marzal & G. W. Scherer, "Advances in Understanding Damage by Salt Crystallization", Accounts of Chemical Research 43 [6] (**2010**) 897-905.
76. R.M. ION, R.C. FIERASCU, M. LEAHU, M.L. ION, D. TURCANU-CARUTIU, *Nanomaterials for conservation and preservation of historical monuments*, Proc. EWCHP, pp. 97–104, **2013**.