Ca $(OH)_2$ Nanoparticles Based on Acrylic Copolymers for the consolidation and protection of Ancient Egypt Calcareous Stone Monuments

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Abstract. The deterioration of calcareous stones materials used in artistic/architectural field is one of the most serious problems facing conservation today. The aim of this study was to evaluate the effectiveness of nanosized particles of calcium hydroxide (slaked lime) as a consolidation and protection material dispersed in acrylic copolymer, poly ethylmethacrylate/methylacrylate (70:30) (Poly (EMA/MA), for calcareous stone monuments and painted surfaces affected by different kinds of decay. The synthesis process of Ca $(OH)_2$ nanoparticles/polymer nanocomposites have been prepared by in situ emulsion polymerization system. The prepared nanocomposite containing 5% of Ca $(OH)_2$ nanoparticles showed obvious transparency features and represent nanocomposites coating technology with hydrophobic, consolidating and well protection properties.

Keywords: Calcium hydroxide nanoparticles, consolidation, nanocomposites, Compatibility, Ancient Egypt Calcareous Stone Monuments, Conservation.

1. Introduction

Limestones from local quarries have been used for the construction of monuments in Egypt from Pharaonic times until today [1]; limestone monuments are suffering from various environmental conditions. The weathering as a natural process is actually one of the most important factor controlling the durability of stone. The deterioration takes the form of loss and granular disintegration of the surface layers of limestone, differential erosion and development of black crusts and orange patinas [2-5].

The water repellence effect for the surface protection of lime stone monument is commonly obtained by the application of polymeric films. Use of water-repellent polymers increases the building materials durability and improves the substrate cleanliness [6, 7]. Acrylic-based compounds have been widely applied for stone consolidation, but with the time, it is worth to mention that the polymer coating appeared, after almost twenty years, quite satisfactory [8, 9]. Therefore, application of nanotechnology to the conservation of artistic and architectural heritage has aroused great interest amongst scientists, conservators and archaeologists and various synthetic routes have been designed to obtain new nanocomposites for conservation purposes [10].

The aim of this study was to evaluate the effectiveness of inorganic compatible treatments, based on nanosized particles of calcium hydroxide (slaked lime) dispersed in acrylic polymer {(poly ethylmethacrylate/methylacrylate (70:30)} in order to improve its properties and compose suitable nanocomposites to be used in the consolidation and protection of limestones and painted surfaces affected by different kinds of decay.

2. Experimental

2.1. Materials

An acrylic copolymer one of the most largely applied copolymers is poly ethylmethacrylate/methylacrylate (70:30) (Poly EMA/MA), commercial name (Paraloid- B72), usually have been widely used, in the treatment of stone artworks and construction materials of historical monuments for consolidation and conservation of such structures [13]. Nanosized particles of calcium hydroxide $Ca(OH)_2$ (with particle mean diameter <50 nm) were purchased from sigma Aldrich.

Nanocomposite preparation by in situ emulsion polymerization system

The $Ca(OH)_2$/polymer nanocomposite has been prepared by different methods as in situ polymerization which was the first method used to synthesis polymer/nanocomposites based on polyamide 66 [14, 15]. The procedure consisted of, synthesis the acrylic polymer with fixed concentration 3% w/v (solid content 3gm/100ml), then the $Ca(OH)_2$ nanoparticles were added during the synthesis of the polymer with concentration 5%, the $Ca(OH)_2$ nanoparticles concentration depends on polymer solid content (See Table 1).

The nanocomposite preparation processes were carried out as in the order 250-mL round flask, monomer, 50 mL deionized water, 0.2 g KOH, 0.5 g emulsifier sodium dodecyl sulfate (SDS), $Ca(OH)_2$ nanoparticles were added with concentration (5%) and stirred for 30 min at room temperature, then the mixture was heated to 80ºC. After that the initiator (SPS/SBS) added to the mixture under continuous stirring for 3 h. After cooling, the product precipitated in methanol 1:3(1% methanol and 3% nanocomposite). The precipitated nanocomposites hybrid filtered and washed with methanol. Then dried under vacuum for 24 h at 60ºC.

Table 1: Concentrations of used consolidation materials

Consolidation material	$Ca(OH)_2$ nanoparticles concentration	$Ca(OH)_2$ solid content	Polymer solid content	The obtained nanocomposite
Paraliod B-72	-	-	100 ml/3gm	Zero composite
$Ca(OH)_2$ nanoparticles	5%	0.15gm	100 ml/3gm	$Ca(OH)_2$nanoparticles / polymer nanocomposites (5%)

2.2. Preparation of stone samples and application of protective materials

The limestone blocks (samples) as one of the most type of the calcareous stones commonly used for monuments were collected from the quarry of Mokattam limestone plateau east of Cairo city, one of the most important quarries of limestone in Egypt. The specimens were squared blocks, and cut following the UNI10859:2000 [16], then dried in an oven at 105 ◦C for 24 h, and before the application of the treatments, the stones were kept at 23±2 ºC, 50 ± 5% R.H. for 24 h [17].
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% to allow the polymerization process to take place. Some of 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.

2.3. Thermal-aging cycles

Thermal-aging was selected to simulate the natural conditions; the treated samples were put in a temperature-controlled oven "Herous-Germany" on special frames. The samples were thermally aged separately at temperature of 105oC for 24 hours, then the samples output from the oven and immersion in water for 24 hours; this process was repeated 30 cycles [18].

2.4. SEM

SEM Philips (XL30), was used to evaluate the distribution and behaviour of the protective materials on the treated samples and treated aged samples. Images were acquired in backscattered mode (BSE).

2.5. Colorimetric measurements

Colorimetric tests were carried out using a CM-2600d Kon-ica Minolta spectrophotometer to assess chromatic variations before and after treatment and after thermal aging. 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) [19].

2.6. Mechanical properties measurement

The measurement of compression strength was carried out before and after treatment and after thermal aging, using an Amsler compression-testing machine, three weeks after treating samples with acrylic polymer and nanocomposite. The average values of compression strength were recorded [20].

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2.7. Water absorption

The water absorption measurements were carried out using the gravimetric method [21].The limestone samples were completely immersed in deionized water at room temperature. After 24hours, the samples were taken out, wiped with tissue paper carefully and weighed immediately.

The amount of the absorbed water was calculated using the following equation:

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

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

3. Results and discussion

3.1. Scanning electron microscope (SEM) investigations

The examination by SEM was used to study the ability of consolidation materials to consolidate and protect the limestone samples. The SEM micrographs of the untreated sample, (figure 1a), appeared to be very fragile, suffered from granular disintegration, and presence of some voids was noticed because of dissolving and disappearance of binding materials. The SEM examination of the samples treated with pure Paraloid B-72(figure1b), showed that, the consolidant filled most of the pores and obscured many of particles, however material has failed to fill the fine cracks in some depth areas. On the contrary, the samples treated with Ca $(OH)_2$ /polymer nanocomposites (figure 1C), showed a homogeneous coating of the particles more than the coating with Paraloid B-72 without nanoparticles, no visible cracks are seen in the film of coating, this may be due to the fact that the higher physical-chemical and physicalmechanical compatibility with the original materials as well as the possibility to penetrate deep into damaged zones without limitations due to the particle size and better stability. After artificial thermal aging, small changes were observed in samples treated with both products, the film uniform and homogeneity was affected as a result of aging, which was illustrated further in samples treated with Paraliod B-72(figure 1d), On the other hand, it was found that the addition of nanoparticles to the polymers (figure 1e), improve the stability of microstructure of the product under the effect of the artificial thermal aging compared to those coated with Paraliod – B72 without the nanoparticles.

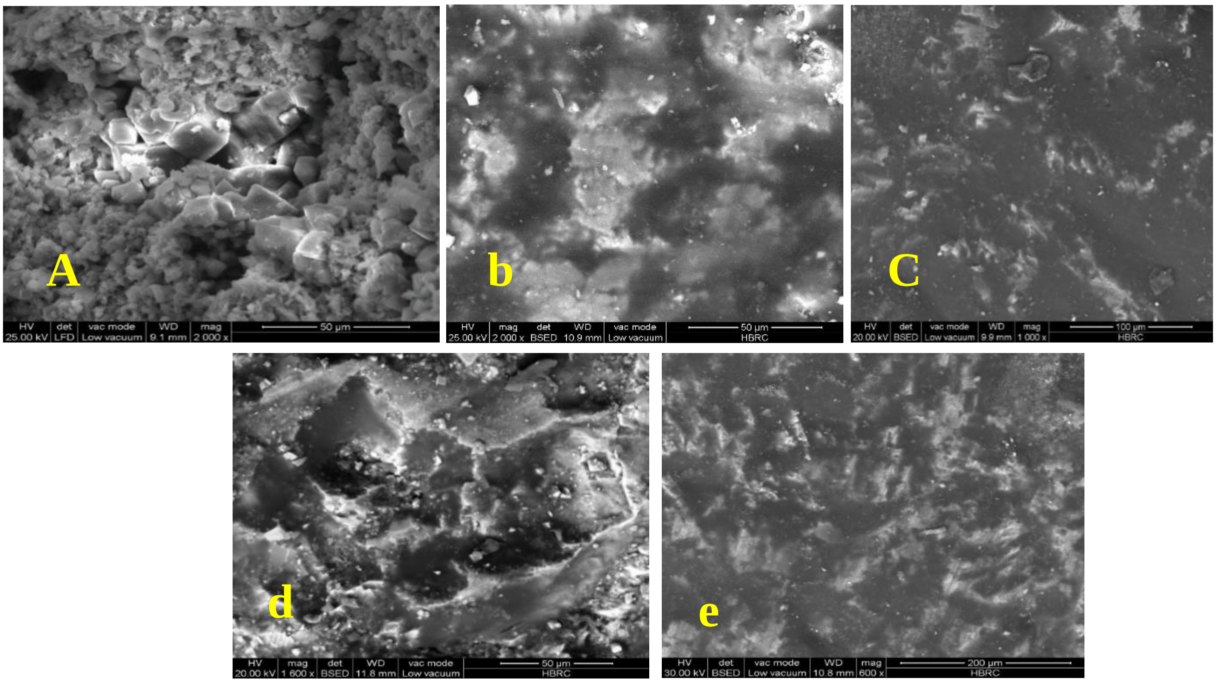

Figure.1. Shows the SEM micrographs of (A) untreated sample, (b). Sample treated with Pure Paraliod – B72, (c). Sample treated with Ca (OH) 2 /polymer nanocomposites, (d). Sample treated with Paraliod – B72 after thermal aging and (e). Sample treated with Ca (OH) $_2$ /polymer nanocomposites after thermal aging.

3.2. Mechanical Properties

The mechanical properties of the untreated, treated and treated samples after artifial aging were determined by testing the compressive strength. Table 2 shows the average values of compressive strength for limestone samples. By comparison, it was found that the addition of nanoparticles to the polymer increase its compressive strength values. This may be attributed to the role of nanoparticles in reinforcing the polymer, and also improving its interaction with the stone grains.

Table 2. Average values of compressive strength for untreated, treated and treated aged limestone samples

Consolidation material	Compressive strength Cm^2/ Kg	
	After treatment	After treatment and thermal aging
Untreated samples	210	---
Paraloid B72	230	215
Ca $(OH)_2$/Polymer nanocomposites	245	235

3.3. Color measurement

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

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

Where ΔL*, Δa* and Δb* are the differences in the, L*, a* and b* coordinates (according to CIEL AB color space) of the treated and untreated limestone samples. According to Italian guidelines for the restoration of stone monuments, the ΔE value must be < 5, After treatment and aging, negligible color variations were observed, and all values are in acceptable limit (ΔE value < 5), thus confirming the suitability of the product for restoring purposes. The obtained data are fully listed in Table.3

Table 3. Color measurement in treated and aged samples

Applied consolidation materials	Δ (treated and untreated samples)				Δ (thermal aged and untreated samples)			
	Δ*L**	Δ*a**	Δ*b**	Δ*E*	Δ*L**	Δ*a**	Δ*b**	Δ*E*
Paraloid B72	- 1.08	- 0.38	0.79	1.39	2.03	0.41	0.66	2.17
Ca $(OH)_2$/Polymer nanocomposites	3.39	0.48	1.85	3.89	3.61	0.54	1.74	4.04

3.4. Water absorption

Since the water is considered to be the major deterioration factor, it is very important the materials of consolidation and protection are able to reduce water penetration into the stone bulk. It is evident, from the physical measurements, that the treated samples are higher in their bulk density. 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.
The efficiency of the nanocomposite in formation of a protective layer appears from the reduction in water absorption and porosity, which can be referred to the penetration of the nanoparticles into voids and pores, also this is attributed to the improving of physiochemical properties of the polymers by nanoparticles, which also led to decreasing the cracking rates during the drying process [22,23]. Table 4 shows the average values of water absorption for the treated and untreated sandstone samples.

Table 4. Average values of water absorption for treated and aged lime stone samples

Consolidation material	Water absorption%	
	After treatment	After treatment and thermal aging
Untreated Samples	4.8 %	---
Paraloid B72	3.9 %	4 .3 %
Ca $(OH)_2$/Polymernanocomposites	1.769	2.02 %

4. Conclusion

In this study, $Ca(OH)_2$/polymer nanocomposites were successfully prepared by in situ emulsion polymerization system, to produce coating with high transparency. Adding of Ca $(OH)_2$ nanoparticles to poly ethylmethacrylate/methylacrylate (70:30) (Poly (EMA/MA) in order to improve its physiochemical and mechanical properties, in order to use it in the consolidation and protection of limestones. Samples treated with (Poly (EMA/MA), and Ca $(OH)_2$/polymer nanocomposites; were tested before and after treatment and under artificial thermal aging; the results showed that the addition of nanoparticles to acrylic polymer improved its ability to consolidate and protect the limestone samples. The polymer containing Ca $(OH)_2$ nanoparticles have the great advantage of high compatibility with the constituting materials of limestone samples, which achieve a deeper penetration of the dispersion, better stability and avoid the formation of white glazing on the treated surface. Moreover, the addition of Ca $(OH)_2$ nanoparticles enhances the physical and mechanical properties of the polymer and treated samples, compared to those treated with polymer without the nanoparticles.

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