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A COMPARISON BETWEEN NANO CALCIUM CARBONATE, NATURAL CALCIUM CARBONATE AND CONVERTED CALCIUM HYDROXIDE FOR CONSOLIDATION

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ABSTRACT

Nano technology produce new materials with new properties in compared with the known material (Bulk) as the nano calcium hydroxide became to be the successful consolidation material as it converted into calcium carbonate which connected the insidious structure together. There is no doubt that nano materials have many advantages as they are pure and less weight, bright, without salts and impurities. Currently in this paper a comparison is made between natural Calcium carbonate, nano Calcium carbonate and the converted calcium hydroxide in to calcium carbonate (new born) regarding appearance, color, weight, porosity, absorption, the hardness of samples, the bursting strength to detect the advantages of the nano materials, and the major reason behind the great success of nano lime which converted in to calcium carbonate after application.

KEYWORDS: calcium carbonate, converted calcium hydroxide, consolidation, hardness.

1. INTRODUCTION

The choices of an effective consolidate for carbonate stones is a general key goal in cultural heritage conservation. In the stone surfaces where high rates of mass loss are identified, consolidation is intended to slowdown or stop erosion, also attempting to restore the mechanical characteristics of the stone when it was originally placed in the monument (Costa, 2012; Ruba Ahmad Al-Omary et al., 2018). The penetration of nano materials inside the objects is totally different in compared with the natural material (López-Arce, 2010) and the mechanical characteristics of the treated objects with nano materials are improved. Thus, the comparison of natural calcium carbonate, nano calcium carbonate and converted nano calcium hydroxide into calcium carbonate (new born) is to assure the advantages of nano-materials were definitely used in consolidation field. Especially, as the nano-materials are weightless and the natural calcium carbonate is connected together very well and with the presence of interior spaces and impurities, currently the comparison is achieved by preparation of non-standard samples of nano calcium carbonate. The natural calcium carbonate and the converted nano calcium hydroxide (which left in open air for a month to assure the converting from $Ca(OH)_2$ to $CaCO_3$) is compared for defining the difference in color, weight, porosity, the hardness of samples, while the bursting strength data will be used in clearing the advantages of using nano-materials in conservation field especially in consolidation.

Relevant past works are reported (Salama et al 2017a, b; 2018).

2. MATERIAL AND METHODS

2.1. *Materials*

All the chemicals were of analytical grade and were used without further purification. The materials required for the comparison the natural calcium carbonate powder and Calcium oxide was purchased from Aldrich and used for preparation of calcium carbonate. Water was purified by a Millipore Elix 3 apparatus: the resistance of the ultra-pure water was 18 MΩ.cm.

2.2. *Synthesis of nano-calcium carbonate and nano calcium hydroxide*

$CaCO_3$ nano-particles were prepared by using the reaction system $Ca(OH)_2$–H_2O–CO_2 as described in our previous work Bulk CaO was firstly calcined at 1000 °C for 2 h then slaked into lime milk in mono-distilled water at 80 °C. The lime milk was cooled to room temperature (20 °C). At this temperature, the CO_2 gas was injected into the lime milk (1000 mL min 1 flow rate and 1 M CaO concentration) with vigorous stirring. The pH recorded on-line with a pH-meter (Jenway 3305) and a conduct meter (Jenway 4510). When the pH value decreased from 14 to 9 and the electric conductivity showed a sharp decrease, this was an indication that the reaction was completed, the CO_2 flow was stopped. $CaCO_3$ particles were obtained and dried at 120 °C in a drying oven for at least 24 h (Morsy, 2014) The nano calcium hydroxide was synthesized by preparing two initial aqueous solutions of 100 mL containing 3.33 g of $CaCl_2$ (corresponding to 0.3 mol/L of $CaCl_2$) and 2.40 g of NaOH (corresponding to 0.6 mol/L of NaOH), respectively. Then Triton X-100 was added to calcium chloride initial aqueous solution, which is later mixed simultaneously to the aqueous sodium hydroxide one, at the fixed temperature of 90 ^{o}C (Daniele, 2012).

2.3. *Samples preparation*

A comparison between non–standard samples the first one is nature calcium carbonate, The second one is nano calcium carbonate and the third one is the converted nano calcium hydroxide (which was left in open air for a month to assure the converting from $Ca(OH)_2$ to $CaCO_3$). The samples prepared under pressure 80-120 bar using piston in the (CRMDI) labs (Fig. 1).

Figure 1 the used piston in CRMDI lab

2.4 *Characterization*

The morphology was examined by scanning electron microscope model Quanta 250 FEG Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n.FEI company, Netherlands). Sample preparation consisted of application of a superficial gold film by sputtering to prevent electro-static charge.

2.5 *Hardness and bursting*

Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 mm - 1.4

mm diameter, with a 30° conical point, 0.1 mm radius tip. This exerts 44.64 N of force (Sophie, 2012) The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54 mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to newton to be 44.45 N (Kopeliovich, 2016).

Tinuis Olsen H5KT machine (www.tinusolsens.com) was designed for using in Research and Quality Control to measure material's strength and performance. All tests are designed and implemented by Tinius Olsen in accordance with key international testing standards including ISO, ASTM, EN and other industrial standards. The load measurement accuracy: ± 0.5% of applied load from 2% to 100%, and position measurement accuracy: ±0.01% of reading or 0.001 mm (Sližkova and Drdacky, 2015).

3. DISCUSSION

The comparison of the samples natural calcium carbonate, nano calcium carbonate and the converted calcium hydroxide shows that: the natural calcium carbonate is connected together very well, as the presence of interior spaces and impurities, on the other hand its color is darker than the color of nano materials as its porosity too, so the dirties stuck on surface unlike the nano-material which prevent and resist dirties and the weight of nano-material is light than the natural material (Fig. 2). In case of the converted nano calcium hydroxide this sample is as hard as the natural calcium carbonate as the particles connected together with combination with carbon dioxide in air and that sample exhibits what has taken place inside the objects treated with nano lime.

Figure 2. The samples of natural calcium carbonate, nano calcium carbonate and converted calcium hydroxide and the difference in color.

3.1 The description of the tests and comparison

The Weight

The weight of sample was measured using sensitive weight and the nano-materials were lighters than nature calcium carbonate.

The Color

The color of samples were compared visually (Fig.2).

The Treatment

The samples were measured before soaking then the sample soaked in deionized water for one hour then left for one hour in the lap air, then soaked for one hour and left for 24 hours in the lap then the weight of the two samples were measured.

The Absorption

A drop of water was added to samples surface and the time of absorption is measured.

Table 1. The comparison of weight of the calcium carbonate and nano calcium carbonate before and after immersing in water.

Comparison	Nano-$CaCO_3$	$CaCO_3$	Nano-$Ca(OH)_2$ converted in to ($CaCO_3$) new born
Weight	**16.22**	**16.46**	16
Color	**Totally white**	**Yellow**	Totally white
Porosity and weight	**Less**	**More**	Less
Absorption	**less**	**More**	**less**
weight after immersed in water after one hour	**16.24**	**16.74**	**16.24**
weight after immersed in water after 24 hour	**16.27**	**17.20**	**16.27**

4. THE RESULTS

The following observations are made:

-The nano calcium carbonate samples were lighter than the nature calcium carbonate sample.

-The color of nano calcium carbonate samples were whiter than the nature calcium carbonate sample.

-The porosity of the nano calcium carbonate samples were less than the natural calcium carbonate sample. Table 1 shows the increase of absorbed water by natural $CaCO_3$ in compared with nano-$CaCO_3$ as the weight of the sample of nano calcium carbonate (16.24 gm) and the weight of nature calcium carbonate (16.74 gm).

-the absorption of the nano calcium carbonate samples were less than the nature calcium carbonate sample as the nano calcium carbonate sample (120 min) takes longer time for absorption than the nature calcium carbonate (30 min).

4.1 Canning Electron Microscope

Two samples from Fig. 2 indicate the presence of impurities and the agglomeration is observed in Fig. 3 (A-D). Fig. 3 A,D gives a comparison between nano cacium carbonate and natural calcium carbonate on magnification 5000X is made, and Fig.3 C,D a comparison between nano calcium carbonate and natural calcium carbonate on magnification 40000X shows impurities and the agglomeration in nature calcium carbonate in comparing with the pure nano calcium carbonate.

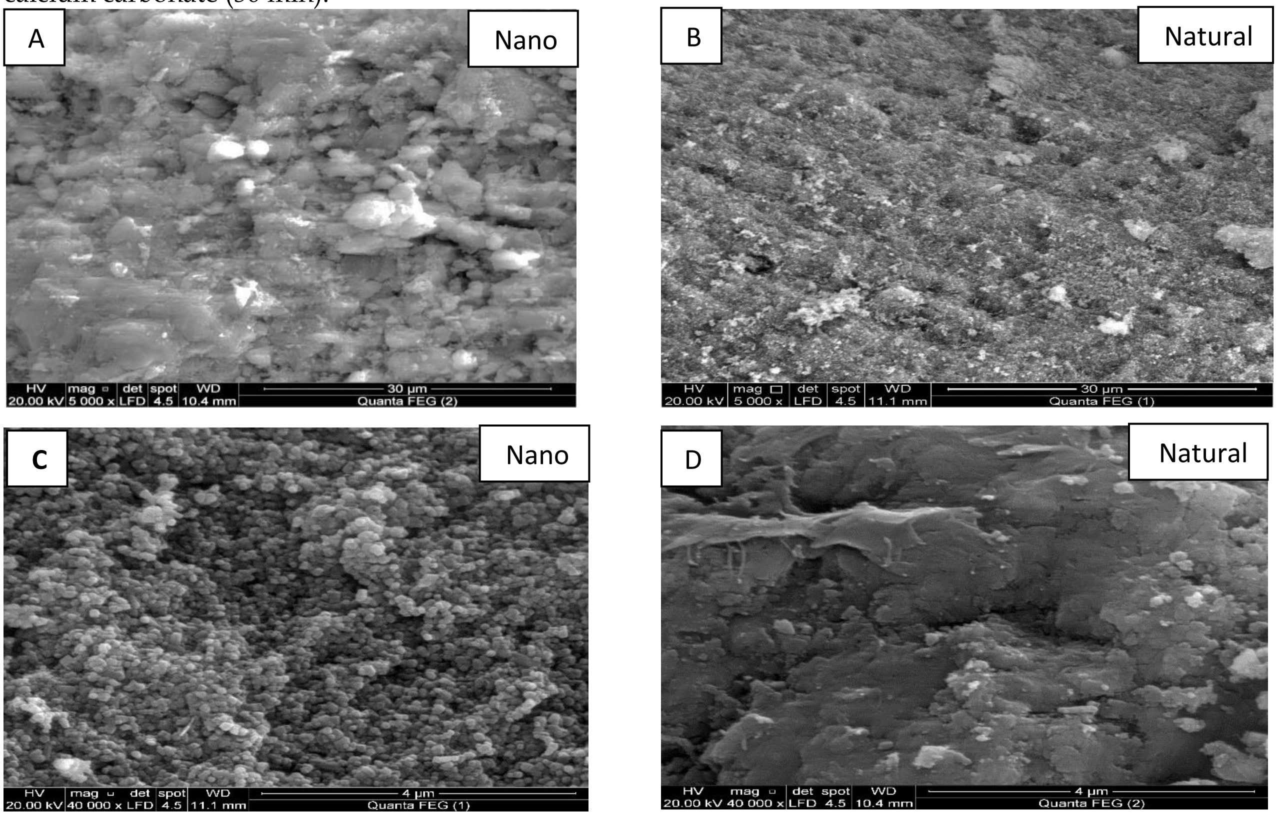

Figure3 (A) and (C): SEM of nature calcium carbonate. (B) and (D) SEM of nano calcium carbonate, The interior spaces and the impurities which played important roles in determining the performances of natural $CaCO_3$.

4.2 Hardness and bursting

A. The hardness tests using Shore D

The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 mm - 1.4 mm diameter, with a 30° conical point, 0.1 mm radius tip. This exerts 44.64 N of force (Fig. 4) (Sophie, 2012) The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54 mm, (Kopeliovich, 2016) the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to Newton to be 44.45 N. Hardness tests for calcium carbonate is 71 shore, for nano calcium carbonate is 28 shore the wide difference back to the purity of the nano calcium carbonate that makes the connection of the natural material is harder results presented in Table 2 and the nano calcium hydroxide which converted in to the calcium carbonate (new born) is 55 shore D because of the connection between $CaCO_3$ particles which connected with CO_2.

Figure 4. Testing samples for Hardness using Shore D and bursting strength test using Tinuis Olsen

Table 2. Shore D hardness results

Sample	Average hardness shore D	Shore D (Newtons)
calcium carbonate	71 ± 0.5	31 N
Nano-calcium carbonate	28± 0.5	13 N
Converted Calcium hydroxide	55± 0.5	25 N

B. The bursting strength tests or compressive strength using tinuis olsen

Bursting strength or compressive strength express the ability of samples to bear compressive strength to be broken (Fig. 5) (Sližkova and Drdacky, 2014) The results presented in Table 3. The bursting strength for calcium carbonate is 433 N/mm^2 and for nano calcium carbonate is 100 N/mm^2 the wide difference back to the purity of the nano calcium carbonate and the nano calcium carbonate doesn't contain the interior spaces which exist in the natural calcium carbonate that spaces and impurities make the natural calcium carbonate connecting together very well and the converted calcium hydroxide 250 N/mm^2 as the $Ca(OH)_2$ connected with CO_2.

Table 3. Bursting strength of samples

Sample	Bursting strength (Newton /mm^2)
calcium carbonate	433 N/mm^2
Nano-calcium carbonate	100 N/mm^2
Converted Calcium hydroxide	250 N/mm^2

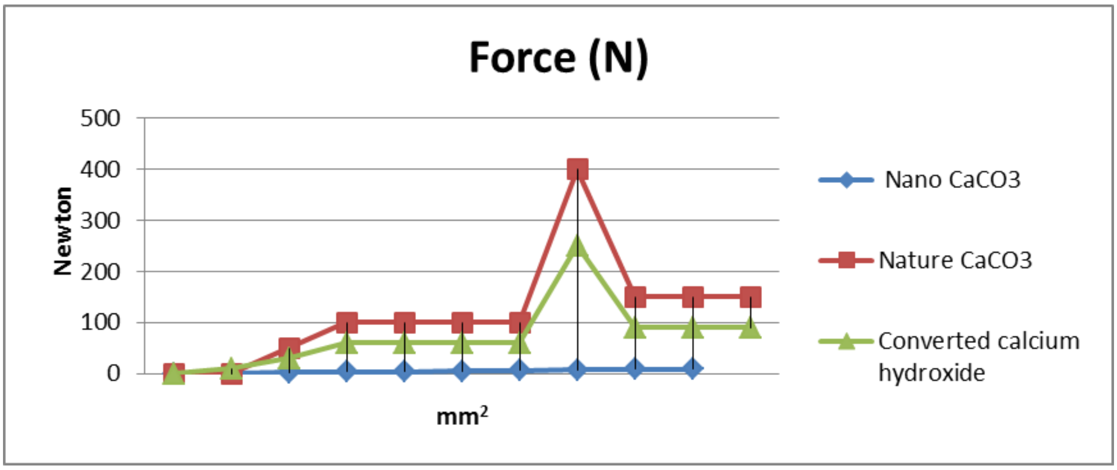

Figure 5: Bursting strength for calcium carbonate, nano calcium carbonate and converted calcium hydroxide (new born calcium carbonate).

5. CONCLUSION

In this study the nano-$CaCO_3$ and natural $CaCO_3$ were experimentally investigated to assured the purity of nano materials and the success of nano -$Ca(OH)_2$ in conservation field as the mold of it is as hard as the natural $CaCO_3$ so the deteriorated calcareous stones renewed its interior structure so the mechanical characteristics are improved. The color of nano materials is whiter, the weight is lighter and porosity is less than the natural $CaCO_3$, on the other hand the results of bursting and hardness tests revealed that the natural calcium carbonate is more harder than the nano-$CaCO_3$ because of the presence of interior spaces and the impurities which played important roles in determining the performances of natural $CaCO_3$.. But in case of converted nano calcium hydroxide (calcium carbonate new born) the physical characteristics is like the nano calcium carbonate, while concerning the mechanical characteristics the nano $Ca(OH)_2$ connected with CO_2 generated $CaCO_3$ (new born) connected together so the treated objects are mechanically improved because of the calcium carbonate.

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