American Journal of Mechanical Engineering, 2019, Vol. 7, No. 3, 138-145
Available online at http://pubs.sciepub.com/ajme/7/3/4
Published by Science and Education Publishing
DOI:10.12691/ajme-7-3-4

Mechanical Properties of Thebes Limestone Treated by Nano Filler Particles

Ahmed F. Mohamed[1,4], A.F. Gelany[2,*], M.S. Abd El-sadek[3], Abbas M. Mansour[2]

[1]Mechanical Engineering Department, Faculty of Engineering, Sohage University, Egypt
[2]Geology Department, Faculty of Science, South Valley University, Qena
[3]Nanomaterials Lab, Physical Department, Faculty of Science, South Valley University
[4]Mechanical Engineering Department, College of Engineering and Islamic Architecture, Umm Al-Qura University, Makkah, KSA
*Corresponding author: drahmedgelany953@gmail.com

Received July 18, 2019; Revised August 24, 2019; Accepted August 30, 2019

Abstract Composite material nowadays has a competitive role in controlling other material. Therefore, coating other material using such composite material help to enhance the mechanical compressive and failure strength of deteriorates ancient materials Thebes limestone is attractive source for a lot of researcher. Natural weathering like rains, rockslides, moisture, salty groundwater absorption and changing temperature can damage or even may weaken the strength of such deteriorates ancient buildings. Compression Samples of ancient Thebes limestone are coated with Nano calcium carbonate and Nano Calcium Hydroxide. While single edge notch bending samples are treated cracked face using Nano calcium carbonate. The results showed an enhancement in both compression and fracture strength.

Keywords: *Nano calcium carbonate, Nano calcium hydroxide, Thebes limestone, compression*

Cite This Article: Ahmed F. Mohamed, A.F. Gelany, M.S. Abd El-sadek, and Abbas M. Mansour, "Mechanical Properties of Thebes Limestone Treated by Nano Filler Particles." *American Journal of Mechanical Engineering*, vol. 7, no. 3 (2019): 138-145. doi: 10.12691/ajme-7-3-4.

1. Introduction

Since pharaonic times local Thebes limestone has been used in Luxor monuments constructions. Weathering forms are the visible result of weathering processes that are increasing by environmental weathering factors. Many forms of weathering have been investigating as rifts, cracks, coloration (alteration of the original stone color), soiling (dirt deposits on the stone surface) and carbonation processes in limestone which is working to disintegrate surface to weak surface and the rise depth of the rift, Especially in the presence of rain and atmospheric carbon dioxide. Rate of carbonation processes and experimental analysis and investigation were serious in this year (2017) for construction, buildings, cement and mortar researchers as [1-11]. Calcium Carbonate and Calcium Hydroxide give a good result in treating the cracks and other deteriorated limestone [12] but most cracks Show previously again because the treatment processes were general and did not stop the cracks. Here we think to stop the ultrafine point in cracks which we are first called it (Rift Zero Point). So Nanoparticles (Nano calcium carbonate and Nano calcium hydroxide) are more coefficients to hold the ultrafine cracks which called rift zero points. The ancient mortar had been studied before by [13,14]. Zoi Metaxa et al. [15] refer to that improve the mechanical performance of cement materials by adding carbon nanotubes for the restoration of cultural heritage monuments. In addition to using three-point bending tests which use in these topics. Restoration process must require characteristic mortars used to complete the missing parts and fill cracks. Such as appearance, touching, hardness and forming. This mortar must be coefficient to original rock in component, texture, and color. This is not yet the mortar must be sculpted.

2. Experimental Works

2.1. Synthesis of Nano Materials

Where three materials had synthesis from Thebes Limestone from nature, $CaCO_3$ after treatment and purification Chemically. And Calcium Hydroxide after ignition and hydration chemically. Ball milling machine that uses in synthesis these three materials Nano Thebes Calcium Carbonate, Nano Calcium Carbonate, and Nano Calcium Hydroxide. Synthesis processes were carried out according to one of ball milling programs as (Total time work 6.30 minutes, stopped two times 15 seconds after 2 minutes and 4.15 minutes) that for synthesis 25 gram.

2.2. Structural Analysis

2.2.1. X-Ray Fluorescence for Powder

Figure 1 Scheme for (a) X-Ray Fluorescence for Nano Calcium Carbonate (b) X-Ray Fluorescence for Nano Calcium Hydroxide. It is illustrating that the percent of calcium at Nano calcium carbonate is 98.66 with traces of silicon 0.87 and strontium 0.47 whereas the percent of calcium at Nano calcium hydroxide is 99.03 with a trace of cadmium 0.97.

2.2.2. FT – IR Analysis

Figure 2 FT- IR analysis for (a) Sample of treated Nano Calcium Carbonate (b) Sample of processing Nano Calcium Hydroxide (c) Sample of naturally Nano Thebes Calcium Carbonate.

In Table 1 A according to chemistry report by Miguel Galvan-Ruiz et al.2009; the description FT-IR analysis sample (a) for hydrated calcium carbonate, Sample (b) anhydrous calcium hydroxide and sample (c) for hydrated calcium carbonate with some organic materials such as (acids and Sulphur compounds. The sample number (c1cac) refer to Nano Calcium Carbonate, sample number (c2cah) refer to Nano Calcium Hydroxide and sample number (c3cac) refer to Nano Calcium Carbonate Thebes, Wavenumbers, cm^{-1} 3642 cm^{-1} corresponded to O─H bond matching with a low concentration of Ca(OH)2 that clear in processing materials in samples of Nano calcium carbonate and sample of Nano calcium hydroxide but in contrast in sample Thebes calcium carbonate. Wavenumbers cm^{-1} 1798 cm^{-1}Corresponding to C=O from Carbonate Ion and wavenumbers cm^{-1} 470 cm^{-1} and wavenumbers 712 cm-1corresponds to the Ca─O bonds there are only in samples of Nano Thebes calcium carbonate due to environmental process as carbonation process. Wavenumbers cm^{-1}799 cm^{-1} SiO2 impurity that only divides from air pollution in the sample of Thebes limestone.

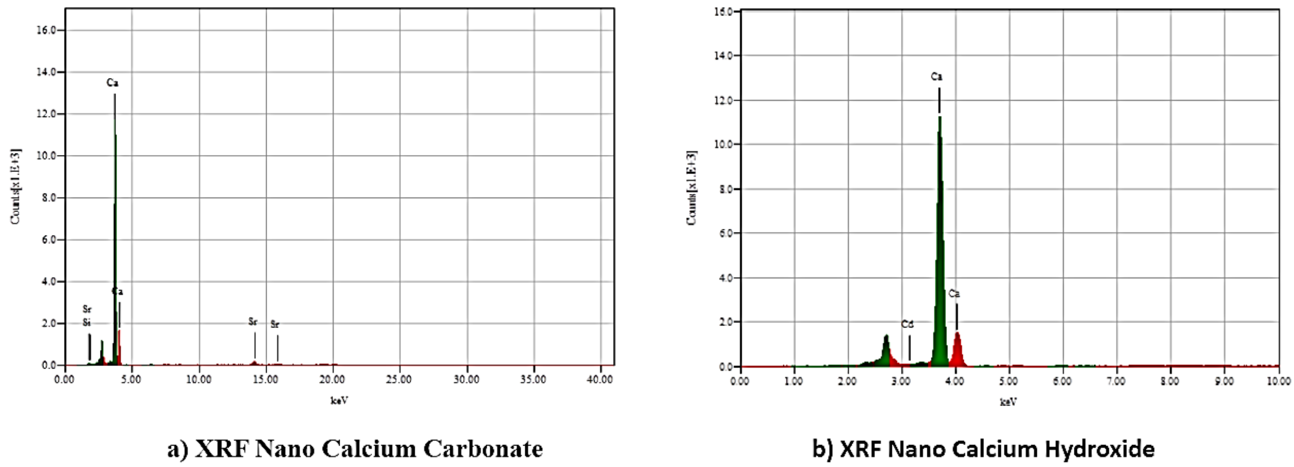

Figure 1. Scheme for (a) EDAX Nano Calcium Carbonate (b) EDAX Nano Calcium Hydroxide

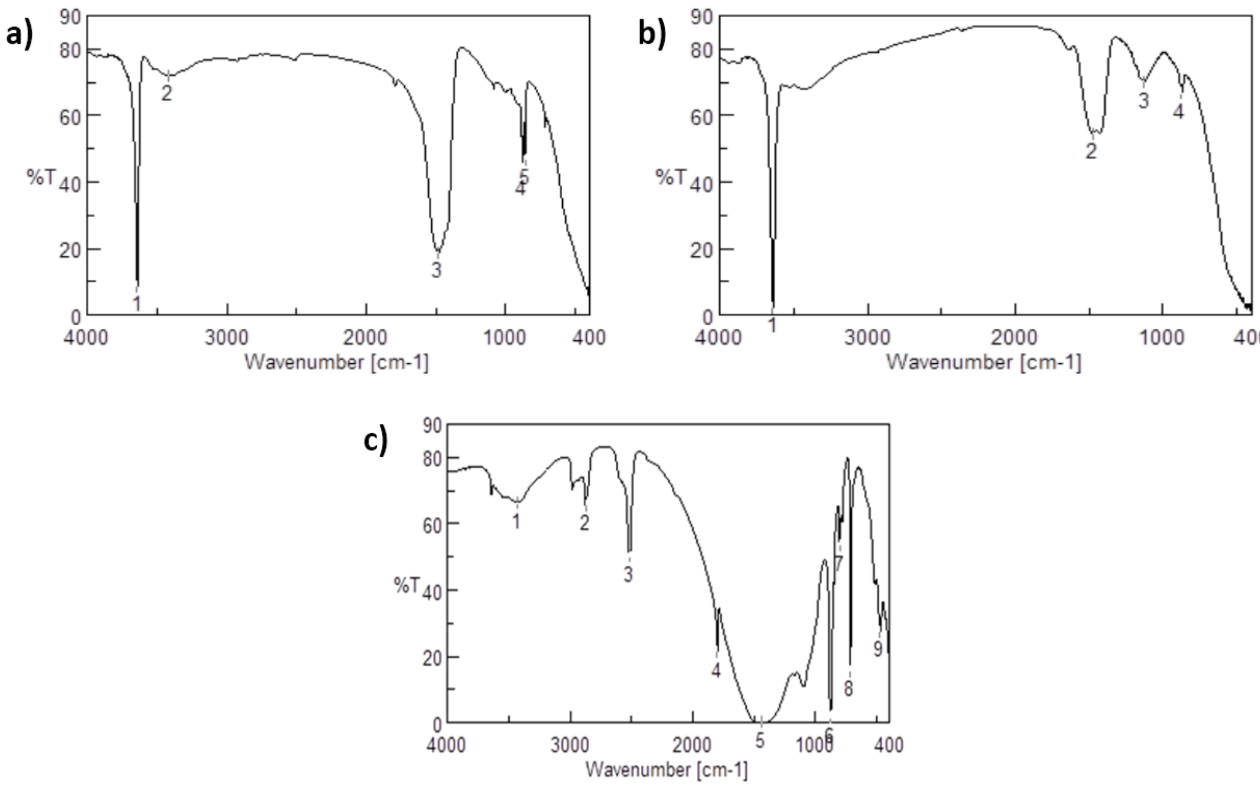

Figure 2. FT – IR analysis for (a) Nano Calcium Carbonate (b) Nano Calcium Hydroxide (c) Nano Thebes Calcium Carbonate

Table 1. Functional groups detected by FTIR Spectroscopy for samples of Nano lime

Wavenumbers, cm^{-1} sample No. c1cac	Wavenumbers, cm^{-1} sample No. c2cah	Wavenumbers, cm^{-1} sample No. c3cac	Type of Vibration
3642 cm^{-1}	3642 cm^{-1}		corresponded to O─H bond matching with a low concentration of $Ca(OH)_2$
3422 cm^{-1}		3428 cm^{-1}	OH water
		2875 cm^{-1}	CH-hydrocarbon
		2512 cm^{-1}	harmonic vibration of these elongation modes.
		1798 cm^{-1}	Corresponding to C=O from Carbonate Ion
1480 cm^{-1}	1475 cm^{-1}	1435 cm^{-1}	Asymmetric Carbonate CO_3^{-2}
	1122 cm^{-1}		related to SiO2 (Quartz)
875 cm^{-1}	874 cm^{-1}	874 cm^{-1}	symmetric Carbonate CO_3^{-2}
857 cm^{-1}			corresponds to C─O bond
		799 cm^{-1}	SiO_2 impurity
		712 cm^{-1}	related to Ca-O bonds

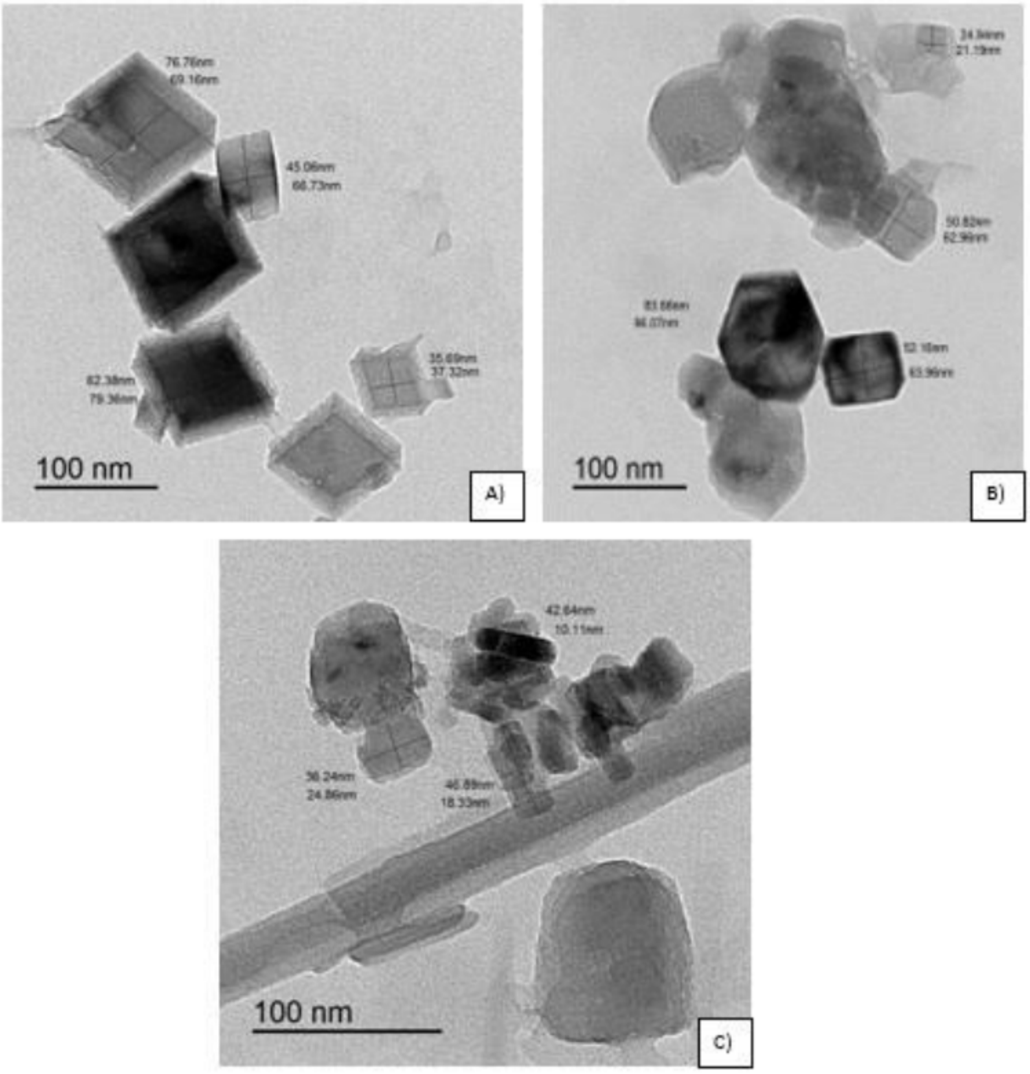

Figure 3. Transmission Electron Microscope TEM for three synthesis Nanomaterials (a) Nano Calcium Hydroxide (b) Nano Calcium Carbonate (c) Nano Thebes Calcium Carbonate

2.2.4. Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) is used to describe morphology; size, shape, arrangement of particles on a scale of atomic diameter, Crystallographic information, and Compositional information according to Pavel Zinin 2006. Figure 3 TEM detect Nano size for several materials which synthesis in this topic. TEM that used at central S.V.U lab.

2.3. Treatments Processes

Nano Materials for Consolidate Stones:

Rodica-Mariana Ion et al. 2015 use nanomaterials to improve the mechanical properties of ancient stones. Whereas in this study there are four steps to use nanomaterials (Nano calcium carbonate, Nano calcium hydroxide and Nano Thebes calcium carbonate) for consolidate and improvement of mechanical properties of

Thebes Limestone (1) Putting a shore for stones pore space from free particles by using water bath (shower) in ultrasonic device with chemical magnets for 3 hours. (2) Drying in the oven for temperature 70°C for 72 hours. (3) Flipping every one of different nanomaterials in a water suspension at different processes (4) Drying in the oven for temperature 70 co for 72 hours. Samples tested in the mechanical engineering lab after these procedures and exam with SEM Scanning Electron Microscope to illustrate different between before and after treatment processes.

2.4. Microstructure Analysis

Figure 4 SEM Coated Samples with Nano Thebes Calcium Carbonate in two scales which show irregular shape for all particles (origin stone particles and Nano Thebes Calcium Carbonate particles). It's clear that pore space and pre-rift were not filled by Nano Thebes Calcium Carbonate particles because Nano Thebes Calcium Carbonate particles were irregular shape and Impurities. The comparison between porous and gaps for samples uncoated, samples coated with 15% Nano Thebes Calcium Carbonate, and samples coated with 30% Nano Thebes Calcium Carbonate it is clear that porous filled more where using more percent of Nano Thebes Calcium Carbonate that means where increasing nanoparticles, pore space more filled.

Figure 5 SEM Coated Samples with Nano Calcium Carbonate in two scales which show development filling process from no treatment case to treated with 15% and 30% Nano Calcium Carbonate. It's clear that pore space and pre-rift (connected pore space) were partially filled by Nano Calcium Carbonate particles. The comparison between porous and gaps for samples uncoated, samples coated with 15% Nano Calcium Carbonate, and samples coated with 30% Nano Calcium Carbonate it is clear that porous filled more where using more percent of Nano Calcium Carbonate that means where increasing nanoparticles, pore space more filled.

Figure 6 SEM Coated Samples with nano Calcium Hydroxide in two scales which show development filling process from no treatment case to treated with 15% and 30% Nano Calcium Hydroxide. It's clear that pore space and pre-rift (connected pore space) were partially filled by nano Calcium Hydroxide particles but more than using Nano Calcium Carbonate. The comparison between porous and gaps for samples uncoated, samples coated with 15% Nano Calcium Hydroxide, and samples coated with 30% Nano Calcium Hydroxide it is clear that porous filled more where using more percent of Nano Calcium Hydroxide that means where increasing nanoparticles, pore space more filled.

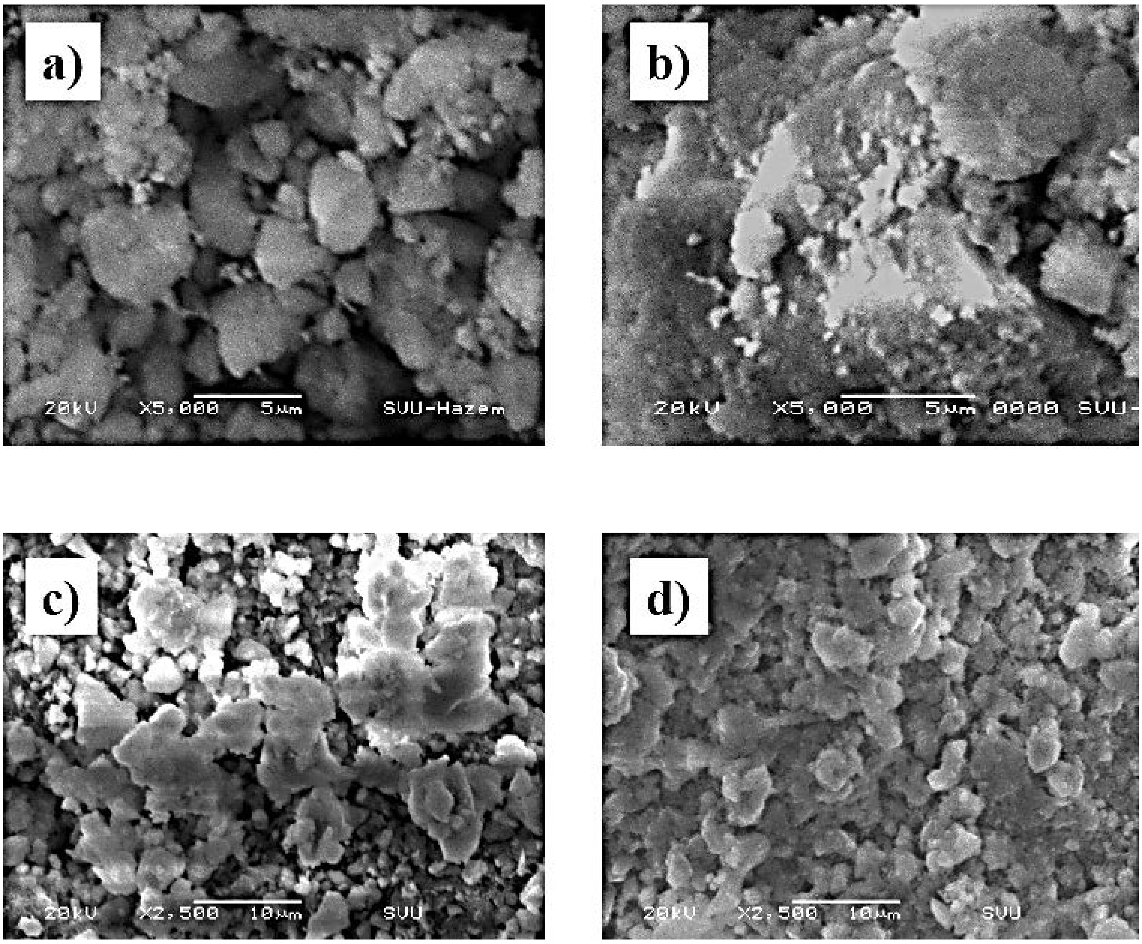

Figure 4. SEM Coated Samples with Nano Calcium Carbonate a) Nano Calcium Carbonate Powder, b) Fresh Samples of Old Thebes Limestone Quarry, c) Coated Samples with 15% Calcium Carbonate, d) Coated Samples with 30% Nano Calcium Carbonate

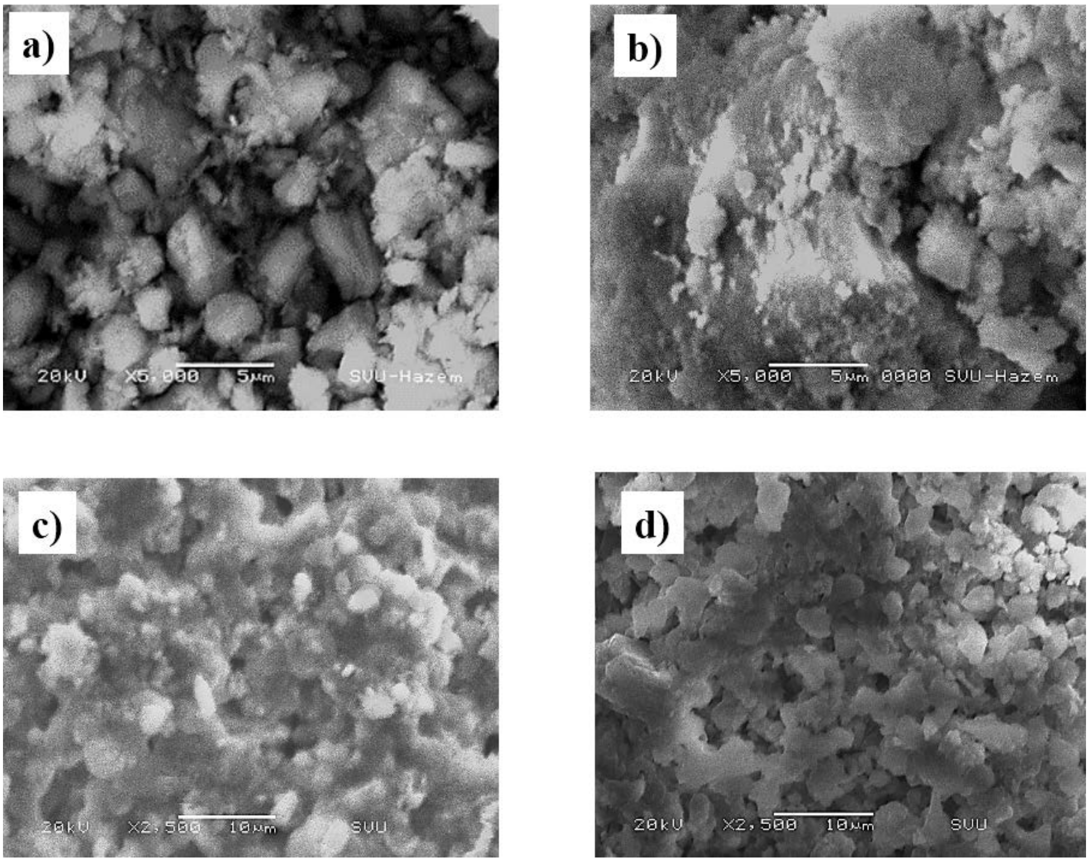

Figure 5. SEM Coated Samples with Nano calcium hydroxides) Nano calcium hydroxide Powder, b) Fresh Samples of Old Thebes Limestone Quarry, c) Coated Samples with 15% calcium hydroxide, d) Coated Samples with 30% Nano calcium hydroxide

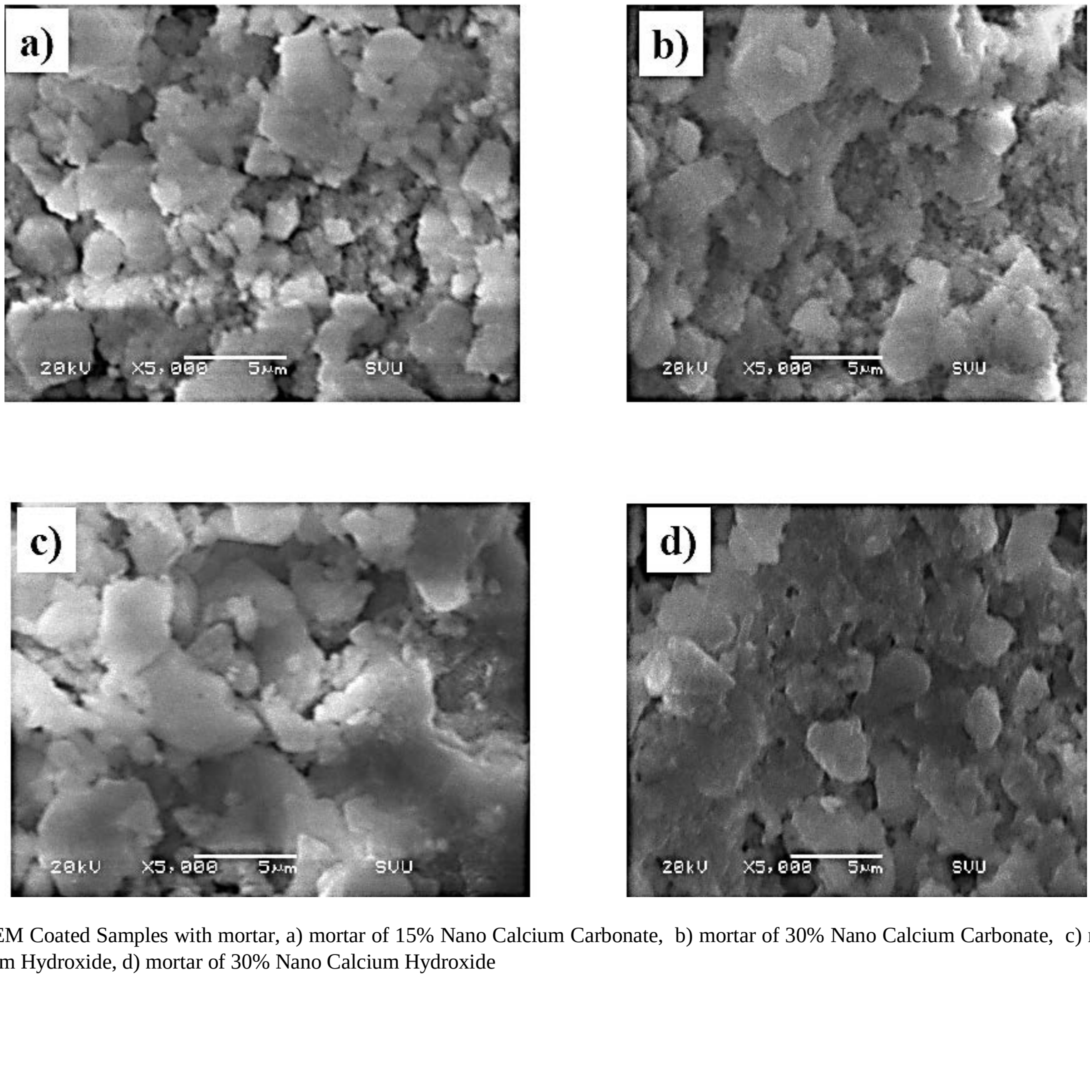

Figure 6. SEM Coated Samples with mortar, a) mortar of 15% Nano Calcium Carbonate, b) mortar of 30% Nano Calcium Carbonate, c) mortar of 15% Nano Calcium Hydroxide, d) mortar of 30% Nano Calcium Hydroxide

Figure 7. Samples of Thebes limestone (a) Cubic samples (b) Elongated fractured samples

2.5. Mechanical Testing

Compression test

The as-received limestone of (30 mm ×30 mm ×30 mm) is tested in compassion using the computerized universal testing machine (model WDW-100) at 1mm/min crosshead speed. The compression test is carried out according to ASTM D2938-95 [16] and [17]. The 5 samples of each coated limestone are tested until cracks appeared then the machine is stopped. Dry conditions platens are used. Samples from old Thebes limestone quarry at Gabel Al Quran near the valley of the kingdom were cut as cubic shape and Parallel rectangles shape for suitable deferent purpose. These samples are previously treated with the previous Nano-fillers material as shown in Figure 7 (a) Cubic shape for the coated treatment process and compressive strength test, (b) Fracture parallel rectangles shape for (Three-Point Bending Single-Edge Notched Fracture Test).

Single edge notch bending

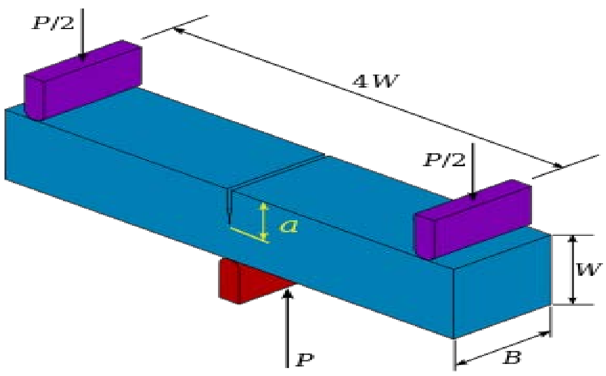

Figure 8. The single edge notch bending specimen (SENB)

The single edge notch bending test is performed to evaluate the bonding strength between crack faces (see Figure 8). Different nanomaterials mix with distal water to make fluid past. Sample Cracks make by small saw and fillers by nanomaterials paste using a very thin needle. Logically inside every mortar of real particle size, there is a real portion of pore space which disadvantage mortar by weak and easier to restart cracks and rifts again as described hold zero-point theory.

3. Results and Discussion

Figure 9 shows diagram stress/strain for the result of the compressive test for samples of mortar from Calcium Carbonate mixed with a deferent portion from Nano Thebes Calcium Carbonate, or Nano Calcium Carbonate. whereas samples of mortar from calcium hydroxide with 15% Nano Calcium Hydroxide and 30% Nano Calcium Hydroxide were tested in the second diagram. The first samples of mortar are from quarried Thebes Calcium Carbonate mortar without and with a portion of Nano Thebes Calcium Carbonate. This sample was not solid due to the presence of impurities from clay minerals and others as an interpretation of the chemical analysis. Whereas, the stress/strain diagram for compressed cubic mortar of Calcium Carbonate without and with 15% Nano Calcium Carbonate and with 30% Nano Calcium Carbonate tests. Diagram illustrates the result of the compressive test for mortar of calcium carbonate less than 0.05 Mega Pascale. The carve of the compressed test result of mortar from calcium carbonate with 15% move in the same path of the carve for of compressed test result of mortar from calcium carbonate only but with the bigger result which reaches to 0.2 mega Pascale. But the carve motion for the result of compressed mortar of Calcium Carbonate with 30% of Nano Calcium Carbonate is less result than before case. Instead of that third stress/strain diagram for compressed cubic mortar of Calcium hydroxide without and with 15% and 30% Nano Calcium Hydroxide show triple result compared with Calcium Carbonate mortar case. Carve of Calcium Hydroxide mortar is more strain due to the presence of pore space and voids between Calcium Hydroxide particles. Whereas stress carves for Calcium Hydroxide mortar with 15% and

30% Nano Calcium Hydroxide is more than without Nano Calcium Hydroxide and increase with increasing Nano Calcium Hydroxide concentration. This three diagrams for mortar of Thebes Calcium Carbonate, Calcium Carbonate with and without Nano Calcium Carbonate and Calcium Hydroxide with and without Nano Calcium Hydroxide illustrate that mortar from Calcium Hydroxide with Nano 30% Nano Calcium Hydroxide is more efficient and appropriate mortar for complete and restoration application in Thebes limestone heritage buildings.

It is clear that all results for samples notched fracture and treated by filling by Nano Calcium Hydroxide or Nano Calcium Carbonate was good, but results for samples notched fracture and treated by filling by Nano Calcium Hydroxide are better than results for samples notched fracture and treated by filling by nano Calcium Carbonate. It is shown in Figure 10 that CiCp and CiHp give a similar result and best result for samples notched fracture and treated by filling by Nano Calcium Hydroxide. Whereas carve of CiCa and carve of CiHa give a similar result and less in consolidate than the result for samples notched fracture and treated by filling by Nano Calcium.

The fracture toughness calculated using the following equation [18,19,20] is listed in Table 2.

$$K_I = Y\frac{4P\sqrt{\pi}}{B\sqrt{w}}$$

Where

$$Y = 1.63\left(\frac{a}{w}\right)^{1/2} - 2.6\left(\frac{a}{w}\right)^{\frac{3}{2}} + 12.3\left(\frac{a}{w}\right)^{\frac{5}{2}} - 21.3\left(\frac{a}{w}\right)^{\frac{7}{2}} + 21.9\left(\frac{a}{w}\right)^{9/2}$$

and a, b and w specimen geometry are shown in Figure 7.

Table 2. Fracture Toughness of tested material

material	Fracture toughness K_I $MP\sqrt{m}$
Ca (OH)2	3.7
CaCo3	3.61
Thebes CaCo3	2.71
Free fracture	2.44

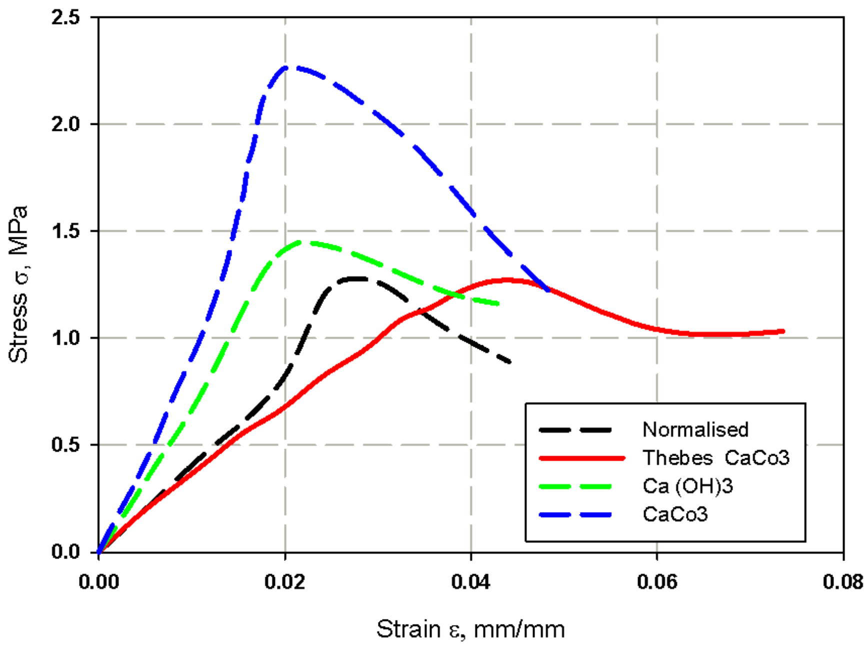

Figure 9. Stress-Strain diagram for treatable limestone

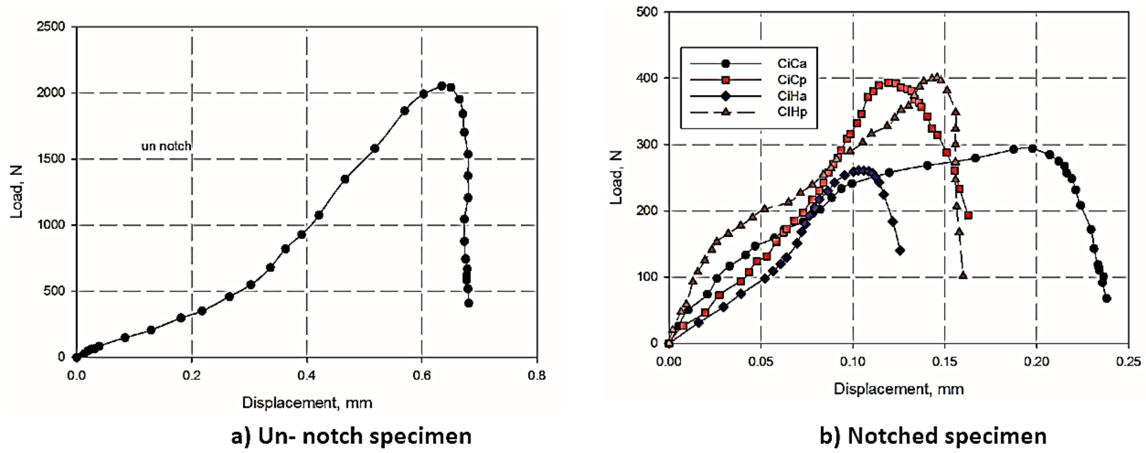

Figure 10. Stress-Strain diagram for treatable limestone

4. Conclusion

Three materials had synthesis from Thebes Limestone from nature, $CaCO_3$ after treatment and purification Chemically. And Calcium Hydroxide after ignition and hydration chemically. The clay minerals present in Gebel Al Qurna clay fraction were montmorillonite as a major constituent, as well as kaolinite and hillite as minor constituents. The compressive strength of treatable limestone is enhancement well and the debonding strength between the nanomaterial and the limestone is well and the $CaCO_3$ Nano powder gives an increasing and better results, nanomaterials are more suitable for holding the (Rift Zero Point) therefore, it is recommended in the heritage and limestones maintenances applications.

Acknowledgments

A lot of thanks to Associate Professor Dr., Mohammed Y. Abdellah (MechanicalEngineering Departments, Faculty of Engineering, South Valley University) for his support in engineering tests.

References

[1] C. W. Hargis, B. Lothenbach, C. J. Müller, and F. Winnefeld, "Carbonation of calcium sulfoaluminate mortars," *Cement and Concrete Composites,* vol. 80, pp. 123-134, 2017.

[2] C. Jiang, Q. Huang, X. Gu, and W. Zhang, "Experimental investigation on carbonation in fatigue-damaged concrete," *Cement and Concrete Research,* vol. 99, pp. 38-52, 2017.

[3] I. Karatasios, P. Theoulakis, A. Kalagri, A. Sapalidis, and V. Kilikoglou, "Evaluation of consolidation treatments of marly limestones used in archaeological monuments," *Construction and Building Materials,* vol. 23, pp. 2803-2812, 2009.

[4] S. Liu, Z. Dou, S. Zhang, H. Zhang, X. Guan, C. Feng, *et al.*, "Effect of sodium hydroxide on the carbonation behavior of β-dicalcium silicate," *Construction and Building Materials,* vol. 150, pp. 591-594, 2017.

[5] M. A. Oliveira, M. Azenha, P. B. Lourenço, A. Meneghini, E. T. Guimarães, F. Castro, *et al.*, "Experimental analysis of the carbonation and humidity diffusion processes in aerial lime mortar," *Construction and Building Materials,* vol. 148, pp. 38-48, 2017.

[6] K. Polikreti, Y. Maniatis, Y. Bassiakos, N. Kourou, and V. Karageorghis, "Provenance of archaeological limestone with EPR spectroscopy: the case of the Cypriote-type statuettes," *Journal of Archaeological Science,* vol. 31, pp. 1015-1028, 2004.

[7] A. Rezagholilou, V. G. Papadakis, and H. Nikraz, "Rate of carbonation in cement modified base course material," *Construction and Building Materials,* vol. 150, pp. 646-652, 2017.

[8] W. Tang, C. I. Davidson, S. Finger, and K. Vance, "Erosion of limestone building surfaces caused by wind-driven rain: 1. Field measurements," *Atmospheric Environment,* vol. 38, pp. 5589-5599, 2004.

[9] M. Yu, H. Bao, J. Ye, and Y. Chi, "The effect of random porosity field on supercritical carbonation of cement-based materials," *Construction and Building Materials,* vol. 146, pp. 144-155, 2017.

[10] D. Zhang, Z. Ghouleh, and Y. Shao, "Review on carbonation curing of cement-based materials," *Journal of CO2 Utilization,* vol. 21, pp. 119-131, 2017.

[11] M. Y. Abdellah, A. Gelany, and M. M. A. Zeid, "Compressive and Failure Strength of Sand Stone with Different Strengthen Materials," *American Journal of Materials Engineering and Technology,* vol. 2, pp. 43-47, 2014.

[12] M. Y. Abdellah, A. Gelany, A. F. Mohamed, and A. B. Khoshaim, "Protection of Limestone Coated with Different Polymeric Materials," *American Journal of Mechanical Engineering,* vol. 5, pp. 51-57, 2017.

[13] M. Gambino, M. A.-a. A. Ahmed, F. Villa, and F. Cappitelli, "Zinc oxide nanoparticles hinder fungal biofilm development in an ancient Egyptian tomb," *International Biodeterioration & Biodegradation,* vol. 122, pp. 92-99, 2017.

[14] J. Mao, D. C. Olk, X. Fang, Z. He, and K. Schmidt-Rohr, "Influence of animal manure application on the chemical structures of soil organic matter as investigated by advanced solid-state NMR and FT-IR spectroscopy," *Geoderma,* vol. 146, pp. 353-362, 2008.

[15] Z. Metaxa, S. Boutsioukou, S. Nitodas, and S. K. Kourkoulis, "Nano-additions of multiwall carbon nanotubes in white cement for restoration of monuments of Cultural Heritage."

[16] A. D2938-95, *Standard Test Method for Unconfined Compressive Strength of Intact Rock Core Specimens* West Conshohocken, PA: ASTM Internationa, 1995.

[17] M. M. M. Mohammed Y. Abdellah, Ashraf T. Mohamed, "Hot Extrusion of Reinforced Aluminum Powder Compacts," *International Journal of Materials Lifetime,* vol. 1, pp. 1-6, 2014.

[18] M. Y. Abdellah, M. K. Hassan, and M. S. Alsoufi, "Fracture and Mechanical Characteristics Degradation of Glass Fiber Reinforced Petroleum epoxy Pipes," *Journal for Manufacturing Science and Production,* vol. 16, pp. 33-40, 2016.

[19] M. K. Hassan, Y. Mohammed, T. Salem, and A. Hashem, "Prediction of nominal strength of composite structure open hole specimen through cohesive laws," *Int. J. Mech. Mech. Eng. IJMME-IJENS,* vol. 12, pp. 1-9, 2012.

[20] C. H. Wang, *Introduction to fracture mechanics*: DSTO Aeronautical and Maritime Research Laboratory Melbourne, Australia, 1996.