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Evaluation of Archaeological Bone Physical and Mechanical Properties after Treatment with Nano Paraloid

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ABSTRACT

Archaeological bones are exposed to many different factors of damage as a result of some natural weathering in the burial environment. The aim of this research is to identify the most important physical, mechanical and chemical problems of such bone and to present one of the new solutions to improve its properties by using Nano applications represented in the use of Nano – paraloid dissolved in acetone at a concentration of 3 % as one of the proposed strengthening methods, Visual assessment and several analytical techniques were used for the evaluation of the selected Strengthening. The analytical techniques are transmission electron microscope (TEM), Fourier-Transform infrared Spectroscopy (FTIR), Measurement of Mechanical Properties (pressure strength) , and Measurement of physical Properties(Color Change CIE Lab, Density, Porosity and Water Absorption) , The bone samples were subjected to accelerated aging (thermal - chemical) after applying the stiffener, The results obtained from transmission electron microscopy showed that the size of nanoparticles of paraloid was between 58 and 78 nanometers. The results of measuring the pressure strength of the reinforced samples and comparing them with the standard sample (ST) (70.86 kg/cm2), where the reinforcement sample of nano-paraloid recorded (NP), the highest measurement (258.93 kg / cm2). Color change revealed gave the higher level of total color differences (ΔE), the (NP) sample was (16.45) .

Key words

Bone, Thermal Aging , Chemical Aging, CIE Lab, Porosity.

1. INTRODUCTION

The bone material is one of the most important ethnographic organic materials, which man relied on for various and different uses, whether for functional goals or for technical and aesthetic purposes in his daily life. Bone consists of two parts, the inorganic part, which is calcium hydroxyapatite $Ca_{10} (PO_4)_6 (OH)_2$ [1], which represents about 90% of its chemical composition [2] , and the organic part, which is collagen, which represents about 10% of its chemical composition, which is the main component of bone protein where it is formed Collagen is made of a group of amino acids in the form of interlocking chains [3] .

Most of the archaeological excavation sites are not free of archaeological bone remains, whether they are human remains or animal remains, and many studies depend on preserving them well, as the environment in which the bone remains are located varies, and in different environments, the factors causing damage to the manifestations of damage resulting to bone damage vary from humidity, heat and conditions The burial, as well as the burial environment itself, the conditions of its oxidation and reduction, and the materials and components it contains that cause the various processes of bone damage [4], Also, the effect of the soil may appear in the form of small pits on the surface of the bones, which is a local damage to the surface of the bones confined to a small area, and it takes the form of cavities and sharp depressions may occur in the surface of the bones as a result of chemical erosion.

In Harvest canals, erosion occurs on the edges of the canals, and a change in bone color is an indication of loss of organic and inorganic properties [5], Bones can interact in the burial environment with the components of the soil such as minerals and chemical compounds, and in the presence of high relative humidity in some humid environments, which causes a change in the color of the bones and erosion of the bones as a result of the interaction of the chemicals in the soil with the components of the bones [6], Damage rates increase in the presence of high heat as it has A clear effect on the chemical, physical and biological processes that take place in the soil, as it was found that the deterioration of the organic components of the bone is faster at high temperatures[7] .

Paraloid B-72 has been used for conservation purposes since 1986 until nowadays due to its properties as chemical inertness and environmental stability [8]. Paraloid B-72 is an acrylic co-polymer of ethyl methacrylate and methyl acrylate (70/30), The Paraloid B-72 is characterized by good adhesion strength as well as oxidation and light resistance, transparency and mechanical resistance. Acetone is the best and most suitable solvent. Paraloid B-72 has tg 40 °C [9]. Various research studies have shown that Paraloid B-72 is a adhesion strength over time [10]. The various experiments have shown that Paraloid B-72 has achieved excellent results in all tests, including thermal, yellowing, adequate working time for this and high resistance to the effect of different chemical materials [11]. Paraloid is also a somewhat reversible material that can be decomposed in the future using acetone solvent. Nano materials are homogeneous liquid that relies on the chemical composition of the use of very small Nano droplets to reach a new technique for archaeological conservation [12]. Nanoparticles are used to improve mechanical properties [13]. The improvements in strength, thickness، mechanical performance and overlap length obtained by using the Nano materials in the process on joining [14]. The uses of Nano materials give a good quality to the mechanical properties [15]. Nano paraloid consentration of 3% was chosen in this study, according to some previous stedies [16-17-18].

And through the various examinations and analyzes that you can find, you will find it in watching the size of the bone, knowing the educational methods and means in the total in the world, and preserving, as these examinations include microscopic examination, mechanical and physical tests, color change test .

Measuring the mechanical properties and knowing the bearing capacity of the pressure forces of the samples before the strengthening operations.

Color change CIE Lab It is an international system for measuring color change and depends on the symbols (L* - a* - b* - ΔE) [19] [20] [21], and the extent of color change between two samples is measured by comparing the values of Lo*- ao*- bo*) in the standard sample And the values of L1* - a1*- b1*) in the sample whose color change is to be identified, where the Colorimeter gives these values for each sample [22] , and through the following equation it is possible to measure the color change Total, which expresses the actual degree of chromatic difference of the samples before the aging process and after the aging process $\Delta E^* = [\ (\Delta L^*)^2 + (\Delta b^*)^2 + (\Delta a^*)^2\ ]^{1/2}$ [23] [24]. This study aims to evaluate the efficiency of using nano Paraloid B- 72 in strengthening archaealgical bones and to compare treated samples before and after aging processes. Knowing the efficiency of the nano-material used in strengthening the bone. And To identify the effectiveness of the strengthening material through examinations and analyzes.

2. Materials

2.1. Preparation of Bone samples

Archaeological bones samples of sheepwere collected from El-Hawawish excavations in akhmim, sohag, situated at a distance of 12 km from east and north east the city of sohag. This site dates back to the late period, that is about 2000 B.C. After the process of applying Nano -paraloid, thermal aging was carried out at a temperature of 120 ° C for 10 hours, according to several previous studies carried out by: (**Wang, et al, 2010[25],. Hiller, 2003[26],. Kalsbeek and Richter, 2006[27],. Figueiredo, 2010 [28),** and Chemical aging was performed by immersing the samples in a solution of hydrochloric acid (Sigma-Aldrich, Schnelldorf, Germany) At a concentration of 3% in distilled water for a period of One month, according to several previous studies for: **(Kalsbeek and Richter, 2006,. Figueiredo, et al, 2012 [29],.Walker, 2011 [30]),** In order to evaluate the Nano- paraloid material and compare the samples before and after the aging processes treated for the samples treated with the Nano -paraloid concentration 3% , The samples were divided into 4 samples: a standard sample (ST), a sample treated with 3% nano-paralloid (NP), a treated and thermally aging sample (NPH), and a chemically aging treated sample (NPK).

2.2. Preparation of Nano Parloid B 72

Nano-Paraloid concentration of 3% dissolved in acetone Paraloid B72 was prepared as a co-polymer of methyl methacrylate/ethyl acrylate (MMA/EA) monomers (Aldrich, Darmstadt, Germany) with a composition ratio of 70/30. It was prepared by solution polymerization technique with solid content 3% as a pure copolymer . The polymerization was carried out according to the following procedure: in a 250-mL three-nicked flask, the desired amount of the monomers with the selected composition ratio (70/30 MMA/EA), was stirred with Acetone for 30 min at room temperature using a mechanical stirrer (500 rpm).

Then, the mixture was heated to 80 ºC. Then، the initiator potassium persulphate (PPS) (0.27 g) (Sigma-Aldrich, Schnelldorf, Germany) dissolved in 50mL of Acetone and Sodium dodecyl sulphate (SDS) as emulsifier dissolved in 45 mL of Acetone was added to the reaction mixture under continuous stirring for 3 h to obtain the solutions of Paraloid B72. The concentration was selected based on Bone nature and porosity.

3. Methods

3.1.1. Transmission electron microscope (TEM) .

The TEM images were obtained by a JEM-1230 electron microscope operated at 60 KV (JEOL Ltd., Tokyo, Japan). Prior to examination, the sample was diluted at least 10 times by water. A drop of well-dispersed diluted sample was then placed onto a copper grid (200-mesh and covered with a carbon membrane) and dried at ambient temperature. This procedure was conducted at the National Research Centre in Dokki –Egypt.

3.1.2. Fourier-Transform infrared Spectroscopy (FTIR)

Fourier-Transform infrared Spectroscopy (FTIR) was done with an infrared spectrophotometer, the device model is (FTIR.B RUKER, Alpha, made in German), in the range of 4000 - 400 cm-1, in transmission mode. The analysis was performed at the Chemistry Laboratory, Faculty of Science, Sohag University , and the analysis was done after grinding about less than a gram of the sample and adding 0.1 grams (KBR).) and mix them and then compress them together into a hard disk.

3.1.3. Digital Microscope (DM).

Samples were examined with a microscope (Digital Microscope Rohs1600X 2 MP Zoom Microscope 8Led), A digital microscope with a magnification of 100 X was used for samples before and after the hardening operations

3.1.4. *Measurement of Mechanical Properties .*

Samples were prepared with dimensions of (3 x 2 x 2 *cm*), The mechanical properties (compression) test was carried out with a Galdabini-Quasar 600-made in Italy and measured in N/mm2 The working conditions (Load Range: 10000N, Extension Range: 10mm, Speed: 50 mm / min, Endpoint: 5.0 mm, preload: 1.0N). The test was conducted at the Antiquities Restoration Center at the Grand Egyptian Museum, Al-haram, Giza، Egypt.

3.1.5. *Measurement of physical properties (Color Change CIE Lab, Density, Porosity and Water Absorption).*

- *Measurement of Color Change (CIE Lab) :*

An Optimatch 3100 ® from the SDL Company was used to measure color change. This procedure was carried out at the National Institute of Standards, Al-haram, Giza، Egypt.

- *Density*

It is defined as the mass of a unit volume of a substance and is measured by the following law:

Density = ((g) mass)/((cm3) volume)

Since the shape of the samples is cylindrical, the volume was determined by the following law [31] [32] [33]:

m2 x h x i

Where radius (n) = 0.50 cm

And the height (p) = 3 cm, and the value (i) = 3.14

The volume = 3.14 x 3 x $(0.50)2$ = 2.3561 cm3.

- *Porosity*

Porosity is a measurement of the spaces between the grains of the material, and it is also known as the ratio of the pores to the total volume of the material. To calculate the porosity value through the following equation:

Porosity (PT) = (Pore Volume (VP) ÷ Total Volume (VT)) x 100

Measuring the size of the pores depends on calculating the volume of extracted air in the sample, or calculating the volume of the liquid saturated with the sample as follows:

Pore volume = total volume of the sample (weight of the sample when it is saturated) - volume of the solid component of the sample (weight of the sample when it is dry) [34-35] .

- *Water Absorption*

To calculate the Water Absorption value through the following equation [36] : Water absorption =

$$\frac{mass\ of\ sample\ after\ immersion - mass\ of\ sample\ before\ immersion}{mass\ of\ sample\ before\ immersion} \times 100$$

4. Results and Discusstion

4.1. Transmission electron microscope (TEM)

From the images, it is clear thatthe particle size of nano Paraloid B-72 ranged between 58 and 79 nm. The image also shows that the prepared nano paraloid has spherical shape nano particles with uniform morphology (Fig. 1). Where nanostructures represent a stage of matter between agglomerated molecules and structures and are typically characterized by a large surface area that affects their physicochemical properties [37]. The nanomaterials have the following attributes: thermal stability, biologically and chemically inertness, stable toward visible or near UV light, good adaptability to various environment, good adsorption in solar spectrum and improvement the mechanical properties. In addition, these treatments can also have water repellent properties [38].

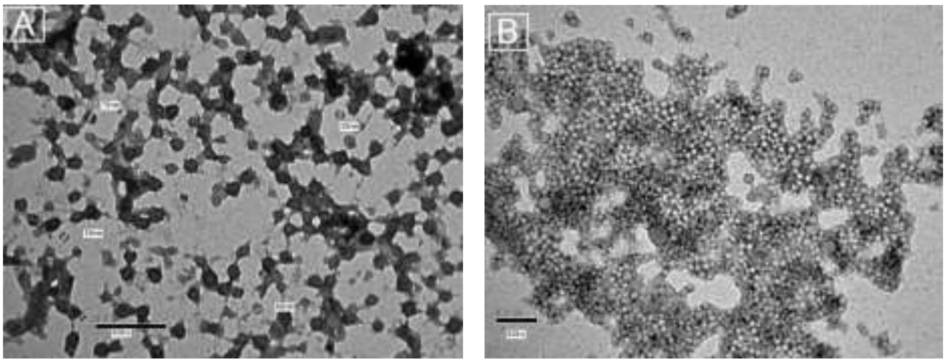

Fig (1) Shows the TEM images of nano Paraloid B-72. (A) paraloid in nano form at 0.5 nm, (B) paraloid in nano form at 0.2 nm.

4.2. Fourier-Transform infrared Spectroscopy (FTIR).

FTIR is a common tool in characterizing the surface chemical composition. In this study, it is clear that, the characteristic peaks of Nano Paraloid B-72 as C H stretching (2,900–3,000 cm–1), ester carbonyl stretching (C O) at 1,720 cm–1, C H bending at 1,445 and 1,383 cm–1, while (O H) stretching peak appears in the range of 3,400–3,520 cm–1 and stretching of C O C ester bonds from 1,200 to 1,132 cm–1 have been appeared [39, 40] (Fig. 2).

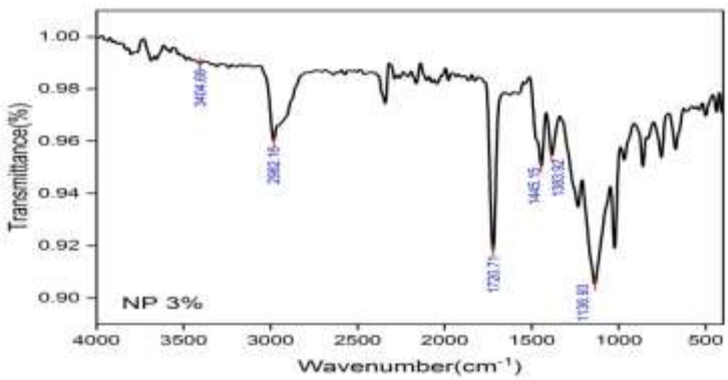

Fig (2) Fourier-Transform infrared Spectroscopy (FTIR) the characteristic peaks of Nano Paraloid B-72

4.3. Digital Microscope (DM).

Fig (3) DM shows samples of nano paraloid 3% where (A) represents the standard sample ST and (B) the Strengthening sample NP and (C) a thermally aging Strengthening sample NPH (D) a chemically aging Strengthening sample NPK

4.4. Measurement of Mechanical Properties .

Table (1) shows the results of pressure tests for nano-paraloid 3% samples.

M	Sample	Stress endurance (kg/cm2)	Stress endurance (N/mm2)
1	ST	70 .86	694.98
2	NP	258.93	2539.30
3	NPH	70.59	692.27
4	NPK	57.42	563.13

From the previous table (1) The results of measuring the mechanical properties showed varying changes in the values of the mechanical properties of the samples treated with hardening compared to the standard sample, whether thermally aging samples after hardening or chemically aging samples after hardening. The results came as follows:

The results of measuring the pressure strength of the reinforced samples and comparing them with the standard sample (ST) (70.86 kg/cm2) resulted in some samples having an increase in the ability to resist pressure forces , where the reinforcement sample of nano-paraloid recorded a concentration of 3% (NP), the highest measurement (258.93 kg / cm2), The results of the compressive strength of the reinforcing and thermally aging samples compared to the standard sample (70.86 kg/cm2) (ST), where it was found that some samples had a slight effect on the mechanical properties, after the samples reinforced with nanomaterial's were exposed to heat aging. And a 3% nano- paraloid sample (NPH) (70.59 kg/cm2), The results of the compressive strengths of the reinforced and chemically aging samples compared to the standard sample (70.86 kg/cm2) (ST), where it was found that some samples had an increase in mechanical properties and their ability to resist pressure forces compared to the standard sample, after the samples reinforced with nanomaterial's were exposed to chemical aging. Where recorded Nano-paraloid 3% (NPK) sample (57.23 kg/cm2).

4.5. Measurement of Physical Properties (Color Change CIE Lab, Density, Porosity).

- *Color Change (CIE Lab).*

Table (2) shows the chromatic change values of nano-paraloid 3% samples.

M	S	L	A	b	ΔL	Δa	Δb	ΔE
1	ST	62.71	4.87	12.96	-	-	-	-
2	NP	65.04	6.38	18.80	12.74	2.27	10.16	16.45
3	NPH	49.81	3.15	6.47	-2.49	-0.96	-2.17	3.43
4	NPK	49.61	2,75	7.06	-2.69	-1.36	-1.58	3.40

From the previous table (2)

It is clear that the values of (L) in the (NP) sample were (65.04), as it was fading as a result of its increase in the values of (L) for the standard sample ST, which was (62.71), while the samples (NPH) and the sample (NPK) gave values of (49.81) and (49,61), respectively, it was significantly darker compared to the standard sample.

As for the values (Δa), the (NP) sample was (2.27) gave a slight and unnoticeable color change to the red color, while the samples (NPH) and (NPK), which gave values of (-0.96) and (-1.36), respectively, and gave a slight and unnoticeable color change to green, and for the values (Δb), the (NP) sample was (10.16), which gave a moderately yellow color change. It is noteworthy that the samples (NPH) and (NPK) gave values of (-2.17) and (-1.58), respectively, and gave a significant and noticeable color change to blue.

As for the values of (ΔE), the (NP) sample was (16.45) and it gave a significant and noticeable total color change for the sample, while the samples (NPH) and (NPK) gave values of (3.43) and (3.40), respectively, and gave medium total color change for the samples. And noticeable.

- *Density*

Table (3) shows the density of nano-paraloid samples with a concentration of 3%

M	Sample	Density (g/cm3)
1	ST	3.1133
2	NP	3.2496
3	NPH	3.0377
4	NPK	3.2190

Through the previous table (3), which clarified the density of the samples and compared it with the standard sample ST (3.1133 g/cm3), it was found that the samples are (NP) and (NPK), whose results came (3.2496 g/cm3) and (3.2190 g/cm3) , respectively, is the highest density compared to the standard sample, while the sample (NPH) and its result (3.0377 g/cm3) is less dense compared to the standard sample.

- *Porosity*

Table (4) shows the proportions of the samples to calculate the porosity of the samples

M	Sample	Sample volume *before immersion (g)*	Sample volume *after immersion (g)*	Void volume *(g)*	Porosity (%)
1	ST	1.36	1.64	0.28	20.58
2	NP	1.74	1.96	0.22	12.64
3	NPH	1.88	2.16	0.28	14.89
4	NPK	1.32	1.71	0.39	29.54

Through the previous table (4), which showed the porosity of the samples and their comparison with the standard sample ST (20.58 %), it was found that the samples are (NP) and (NPH), whose results came (12.64 %) and (14.89 %), respectively. It is less porous compared to the standard sample, while the sample (NPK) and its result (29.54 %) has higher porosity compared to the standard sample.

- *Water Absorption*

Table (5) shows the proportions of the samples to calculate Water Absorption of the samples

M	Sample	Sample volume before immersion (g)	Sample volume after immersion (g)	Void volume (g)	Water Absorption (%)
1	ST	1.36	1.64	0.28	17.07
2	NP	1.74	1.96	0.22	11.22
3	NPH	1.88	2.16	0.28	12.96
4	NPK	1.32	1.71	0.39	22.80

Through the previous table (5), which showed the Water Absorption of the samples and their comparison with the standard sample ST (17.07%), it was found that the samples are (NP) and (NPH), whose results came (11.22%) and (12.96%), respectively. It is less Water Absorped compared to the standard sample, while the sample (NPK) and its result (22.80%) has higher Water Absorption compared to the standard sample.

Conclusion

The transmission electron microscopy (TEM) revealed that the particle size of nano paraloid (58:79nm). It is known that archaeological bones are exposed to many types of damage, whether in the burial environment or when extracting them, due to their impact on various physical and mechanical damage factors, and through the aging processes (thermal and chemical) that were carried out in the study to predict these effects and evaluate the efficiency of the reinforcing material used in the future and the extent of its impact With the damage factors, the mechanical effect was confirmed, which is a strong pressure drop of the NPK bone sample after being subjected to chemical aging processes, which recorded 57.42 kg / cm2 compared to the standard sample 70.86 kg / cm2, There was a clear impact and damage to the samples, as there was a significant increase in the porosity and water absorption of the chemically aging samples NPK compared to the standard sample, and a decrease in the density of the thermally aging samples NPH compared to the standard sample, and there was a severe impact on the values of the total color change of the thermally and chemically aged samples NPH, NPK which scored 3.43, 3.40.

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