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# EVALUATION OF THE EFFICACY OF TRADITIONAL AND NANO PARALOID B72 FOR POTTERY CONSOLIDATION

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***Abstract***

*The pottery objects are suffering from many deterioration factors, essentially humidity. This factor leads to the weakening and fragility of archaeological pottery. This article shows the importance of the consolidation's effectiveness of pottery objects. The experimental study was conducted on lab-made pottery samples using Paraloid B72 in traditional and nano forms. Therefore, we can select the best formula for the consolidation of archaeological pottery. Pottery samples were fired at 800°C and then exposed to saline weathering. The aged samples have been brushed by the prepared consolidants. The treated samples were then exposed to artificial aging under altered environmental circumstances to assess the consolidants stability. In this study, some investigation techniques, physical and mechanical tests were used for the evaluation of the selected materials, where it includes transmission electron microscope, USB digital microscope, scanning electron microscope, stereo microscope, static water contact angle, color alteration, physical properties, and compressive strength test. Comparison between untreated and treated pottery before and after artificial aging showed that the application of nano Paraloid B72 at 5% concentration greatly enhanced the physical and mechanical properties of pottery treated. Additionally, nano Paraloid B72 has a high capability to protect pottery samples.*

***Keywords**: Pottery; Consolidation; Paraloid B72; Nano; Investigation*

## Introduction

Atmospheric water could permeate the porosity channels of things, creating direct deterioration effects in cultural heritage artifacts [1]. Water, in any physical form, is a significant degradation factor because of its potential to transfer chemical and biological material into and out of porous substances [2, 3]. Therefore, it is essential to decrease the rate of water [4]. Consequently, penetration of water into the pores leads to pottery deterioration due to salts in particular soluble salt [5]. Because water plays a role in causing damage to monuments, polymeric coatings must be able to prevent water from entering to prevent degradation [6]. As a result, the most critical criteria of preservation products are often consolidant properties and water repellence [2]. Consolidation is one of the fundamental aims for the conservation of archaeological pottery. The goal of this procedure is to achieve stability while improving physical and mechanical characteristics [7]. Traditional methods and materials are still used to conserve cultural heritage, and they often lack the requisite compatibility with ancient artifacts and great effectiveness in reacting to natural environmental changes [8]. To preserve the

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original appearance of the pottery, the ideal coating features should include good water repellent, chemical stability, and flawless optical properties [9].

Acrylic polymers were often employed in earlier decades and are currently used to preserve artwork [10]. Because of their optical clarity and mechanical properties, polymeric materials are well-known for their usage and applications in a variety of fields [11]. Polyacrylic exhibited good film characteristics and mechanical flexibility, suggesting that it might be used in a variety of environmental applications, including coating [12]. Polymeric coatings must be resistant to environmental alteration, and the coating layer must be proper with the surface [6]. The Paraloid B72 employed for the consolidation of the artifacts should be clear, colorless, and easy to apply in a thin layer [13].

The quantity of product absorbed and its dispersion throughout the item are heavily dependent on the products, the substrates, and the application technique's structures [14]. In general, the impregnation of polymers enhances mechanical resistance, decreases porosity, and changes water absorption behavior [15]. The fundamental disadvantage of acrylic polymers like Paraloid B72 is their low resistance to aging, particularly thermal and UV aging [16]. Furthermore, these polymers have several negative impacts due to their low physicochemical stability such as mechanical compressive on coating layers, the production of microfractures, and changes in chemical and physical characteristics [10].

Therefore, it is preferred to use another alternative material such as nanomaterials. These materials penetrate porous materials to a sufficient depth while keeping the original mass of the sample treated [7]. The application of nanomaterials as a protecting coating has been proposed as a practical possibility for artifact surface protection [1]. The nanomaterials treatment leads to obtaining super-hydrophobic surfaces of the objects. This is due to the presence of nanoparticles, which influence the morphology of the surface [17]. Nanomaterials are characterized by chemically inertness, thermal stabilization, good adaptation to a different environment, improvement the mechanical properties, and have water repellent properties [18]. The treated material's mineralogical and chemical structure, its surface structure, the extent of degradation of the material before treatment, and the temperature and moisture conditions at the time of application all influence the success of the nanomaterials-based consolidation process [7].

The primary aim of this study is to investigate the efficacy of paraloid B72 in conventional and nano forms as protective agents for deteriorated pottery, to choose the finest of them for archaeological pottery's conservation. The present research was carried out on eight pottery samples treated with two consolidating products applied by brushing. This study also aims to investigate the effective polymeric is in treating and preserving pottery, in addition to, investigating and comparing the effect of application of consolidation material. To prove the efficiency and possibility for practical use, their surface shape alteration because of product sedimentation, hydrophobic effect, color change, and physical and mechanical properties were studied. Furthermore, comparing the properties of various pottery samples before and after artificial aging. The overall aim is to develop the best conservation plan for these types of cultural objects in museums and archaeological sites.

## Experimental`

### *Materials*

#### *Preparation of consolidation materials*

Because of its widespread usage in conservation and restoration procedures, Paraloid B72 (made by Rohm & Haas) was chosen as a polymer matrix [15]. The Paraloid B72 was synthesized at 3-5% in acetone. Co-polymer emulsion lattices consisting of Ethyl Methacrylate (EMA) and Methyl Acrylate (MA) in a composition proportion of 70:30 was made using a semi-continuous process with solid contents varies from 10 to 50±1%. The polymerization of nano paraloid has been done as follows: in a 250mL three-nicked flask, the proper number of monomers were dissolved in the same volume of acetone in one hour using mechanical stirring (500 rpm) according to the specified composition ratio (70:30 EMA/MA). A redox initiation system, including Potassium Persulphate PPS (0.27g) and Sodium Bisulphite (SBS) (0.416g) was diluted in 40 ml distilled water and applied dropwise to the reaction mix for 30 minutes. The polymerization process has been done for three hours at 70°C with 500 rpm stirring. The reaction liquid was cooled to 50°C and then neutralized with aqueous Ammonium Hydroxide to achieve a pH of around 9 [19]. The used concentrations are shown in Table 1.

**Table 1.** The consolidation materials used in each treatment

| Sample code | The consolidation materials used |
|---|---|
| U | Untreated sample |
| A | Paraloid B72 at 3% |
| B | Paraloid B72 at 5% |
| C | Nano Paraloid B72 at 3% |
| D | Nano Paraloid B72 at 5% |
| E | Paraloid B72 at 3% after artificial aging |
| F | Paraloid B72 at 5% after artificial aging |
| G | Nano Paraloid B72 at 3% after artificial aging |
| H | Nano Paraloid B72 at 5% after artificial aging |

*Preparing the pottery samples*

The pottery samples were created in the laboratory using red clay that is the primary part of Egyptian pottery [20]. Raw red clay (60% wt.) was mixed with sand (25% wt.), grog (powder of new pottery) (10% wt.), and straw (5% wt.). To avoid structural defects during sample preparation, the proper amount of water was added to achieve the requisite plasticity. That process can take days before the clay is ready for shaping [21]. The clay was then shaped into cubes using a wooden mold. In the laboratory, the intermediate temperature and prorated moisture (RH) were 25°C and 50%, respectively. The size of samples was 3cm edge for cubes [22-25]. The shaped samples were first allowed to dry at room temperature for a day before being oven-dried for 24 hours at 105°C [26]. The dried samples were then burned at a rate of 5°C/min to achieve the required temperature of 800°C [27, 28].

After the pottery samples were created, they were subjected to a series of salt aging cycles. The purpose of this test is to decide the influence of salts on the surface of the pottery. For 10 hours, the samples were immersed in a saturated salt solution of Sodium Chloride at 20% concentration. The samples were then exposed to room temperature air for 14 hours [29]. Brushing was used to apply protective polymers to the surface of experimental pottery pieces in this research. The procedure was repeated three times with a half-hour interval between each application, and the treated samples were allowed to dry for 15 days [30]. Thermal aging was performed on the treated samples for 100 hours at a temperature of 100°C and relative dampness of 60%. Samples were placed in a temperature-controlled oven (FN500 - Germany) on a customized framing. The light aging test lasted 100 hours and was performed using a UV lamp (268 UVA Optimized/little shape sensor heads). The lamp is in the following condition: (power: 600W, wave extent of irradiation: 400 nanometers, space amongst specimen, and bulb: 15cm).

***Methods***

*Transmission Electron Microscope (TEM)*

The TEM pictures were captured using a JEM-1230 electron microscope set at 60kV (JEOL Ltd., Japan). The material was diluted in water at least ten times before the testing. After that, a drop of the fully dispersed diluted specimen was deposited onto a copper mesh (200-grid and covered with carbon film) and dried at room temperature. This process was carried out at the National Research Centre, Egypt.

*Scanning Electron Microscopy (SEM)*

EDX Unit (Energy Dispersive X-ray Analyzes) linked to SEM Model Quanta 250 FEG (Field Emission Gun), with accelerated voltage 30kV., enlargement 14× up to 1000000×, and minuteness for Gun.1n). The FEI Company, based in the Netherlands, was utilized. This method was conducted at the General Authority for Mineral Resources, Egypt.

*USB Digital Microscope*

Model: PZ01, produced by Shenzhen Supereyes Co., USB 2.0 interface, Linux, Mac OS & above 10.5.5, from (10X-500X), Ltd., China. This procedure was carried out at the Department of restoration, Faculty of Archaeology, Cairo University, Egypt.

*Stereo Microscope*

The Leica MZ6 stereo zoom microscope is a modular common main objective stereo microscope with a zoom range of 6.3× - 40× with 10× eyepieces, Germany. This method was conducted at the General Authority for Mineral Resources, Egypt.

*Static water contact angle*

Model T330, Generated with One Attension Version 2.7(r5433), Company name: Biolinscientific, Place: Finland. The test was conducted at the Egyptian Center for Nanotechnology at Cairo University, Sheikh Zayed**,** Egypt.

*Color alteration measurement*

The SDL Company's Optimatch 3100® was utilized to measure color alteration. This step was performed at the National Institute of Standards, Egypt.

*Physical properties measurement*

The dry weight and wet weight of each sample were used to determine the physical attributes of the samples. Before the tests, the specimens were dried at 105°C and weighing then immersing these samples in distilled water for 20 hours and weighing [4, 15]. The physical characteristics were computed as follows:

Bulk Density in g/cm$^3$ was defined in the following Equation:

$$D = W/V \tag{1}$$

where: W represents the initial weight in g and V represents the volume in cm$^3$ [31].

Water Absorption (WA) in % was determined in the following Equation:

$$WA(\%) = (W_2-W_1)/W_2 \tag{2}$$

where: W1 and W2 are the dry and wet weights in g respectively [32].

Apparent porosity (AP) in % was defined in the following Equation [33, 34]:

$$AP\ (\%) = (W_2-W_1)/V \times 100 \tag{3}$$

*Compressive Strength measurement*

A QMat5.37/Q3214 Tinius Olsen was utilized. The operating circumstances (Load Range: 10000N, Expansion domain: 10mm, Speed: 50mm/min, End: 5.0mm, Precharge: 1.0N). The testing was carried out at the National Institute of Standards, Egypt.

## Results and discussion

### *Transmission Electron Microscope (TEM)*

According to the TEM photos, the grain size of Paraloid B72 varied between 133.35 and 141.97nm. Furthermore, the nano Paraloid B72 particle size varied between 23 and 44nm. The picture of the nano paraloid indicates that the particles are generally spherical and agglomerated [35] (Fig. 1).

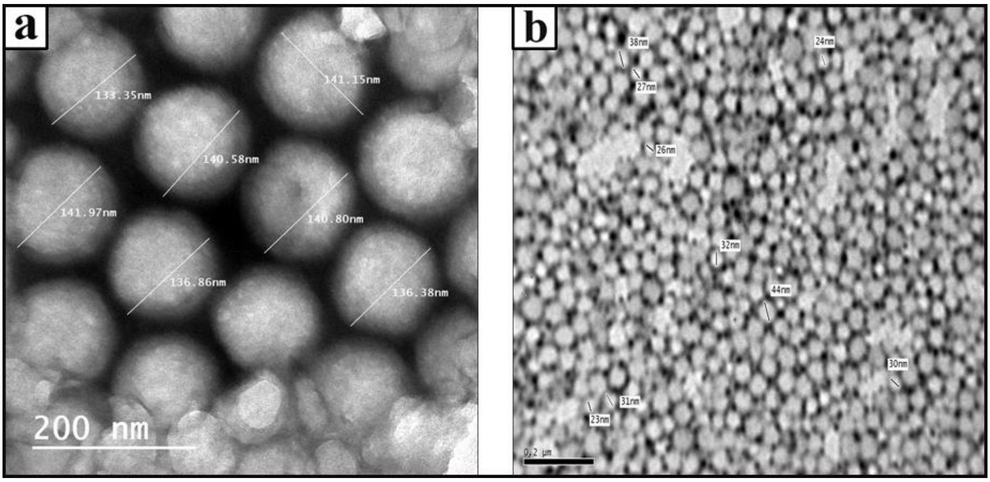


**Fig. 1.** TEM picture of tradition and nano Paraloid B72:
(a) Paraloid in the traditional shape, (b) paraloid in nano shape

***Scanning Electron Microscopy (SEM)***

The shape of the treated pottery surfaces is dependent on the polymer concentricity, As observed in the SEM photos [36]. SEM investigation was performed before and after the application of the consolidants then after artificial aging to evaluate the consolidation treatments' performance in terms of consolidant appearance and uniform distribution inside the structure of pottery [37]. (Fig. 2a) shows the untreated pottery sample with code (U), which has cracks, severe fragility, and less cohesion of granules. Sample A treated with Paraloid B72 at 3% concentration (Fig. 2b) shows the well spread of consolidation material on the surface, as well as inside the pores of the sample. Where the dispersal and the shape of the polymer layer within the sample do not appear to be considerable.

Sample B treated with Paraloid B72 at 5% shows the homogenous diffusion on the outer surface. Where the polymeric layer's distribution and shape within the sample do not appear to be relevant [4] (Fig. 2c). Sample C treated with nano Paraloid B72 at 3% shows a good distribution of the protective material between pores. The treated sample has a more homogeneous structure, indicating that the polymer coating lowers porosity (Fig. 2d). Sample D treated with nano Paraloid B72 at 5% concentration (Fig. 2e) shows this material helped to cover the outer surface well, which contributes to increasing the surface protection. Therefore, this polymer appeared as filler inside the structure of the sample causing the interior structure to combine [1].

On the other hand, the aged samples were investigated by SEM microscope to clarify the best materials that have not been affected by different environmental conditions. (Fig. 2f) shows sample E treated with Paraloid B72 at 3% after artificial aging, minor changes were seen on the sample appearance, in addition to the lack of the polymer distribution uniformity on the surface. (Fig. 2g) shows sample F treated with Paraloid B72 at 5%. It shows the lack of polymer distribution because of the effect of heat generated by artificial aging. (Fig. 2h) shows sample G treated with nano Paraloid B72 at 3%. It displays the effect of aging on the outer surface of the sample and the inability of the polymer to resist aging conditions. (Fig. 2i) shows sample H that coated with nano Paraloid B72 at 5%. The consolidant improves the stability of the treated samples under the influence of artificial aging.

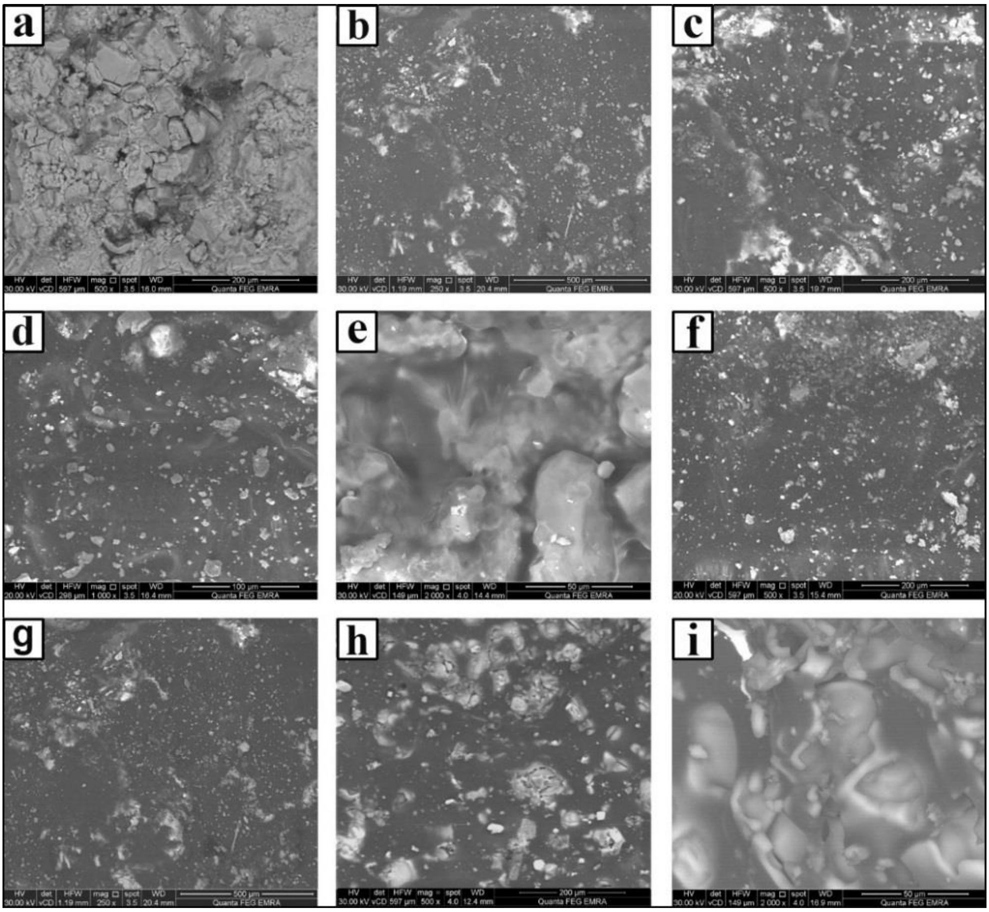

**Fig. 2.** The SEM micrographs of the untreated and treated specimens before and after artificial aging: (a) Untreated specimen, (b) Treated with Paraloid B72 at 3%; (c) Treated with Paraloid B72 at 5%; (d) Treated with nano Paraloid B72 at 3%; (e) Treated with nano Paraloid B72 at 5%; (f) Treated with Paraloid B72 at 3% after artificial aging; (g) Treated with Paraloid B72 at 5%; (h) Treated with nano Paraloid B72 at 3%; (i) Treated with nano Paraloid B72 at 5% after artificial aging

***USB Digital Microscope***

The purpose of using a USB digital microscope before and after treatment, then after aging is to show the brightness change of the pottery samples surfaces due to the application of consolidation materials. The untreated sample with code U (Fig. 3a) shows some pits, lack of cohesion, fragility, and some salt impurities. It was found that samples with code numbers A and B show a slight sheen with good coverage of the outer surface (Fig. 3b and c). Sample C shows the presence of some white spots on the surface (Fig. 3d). While sample D illustrates good surface coverage without any surface brightness (Fig. 3e). On the other hand, after artificial aging the samples with code E and F show a white layer on the surface of pottery, which alters the visual properties as shown (Fig. 3f and g). In addition to the lack of cohesion between the polymer and the surface. While samples G and H illustrate a good coverage of the consolidation material on the outer surface and the absence of shine (Fig. 3h and i).

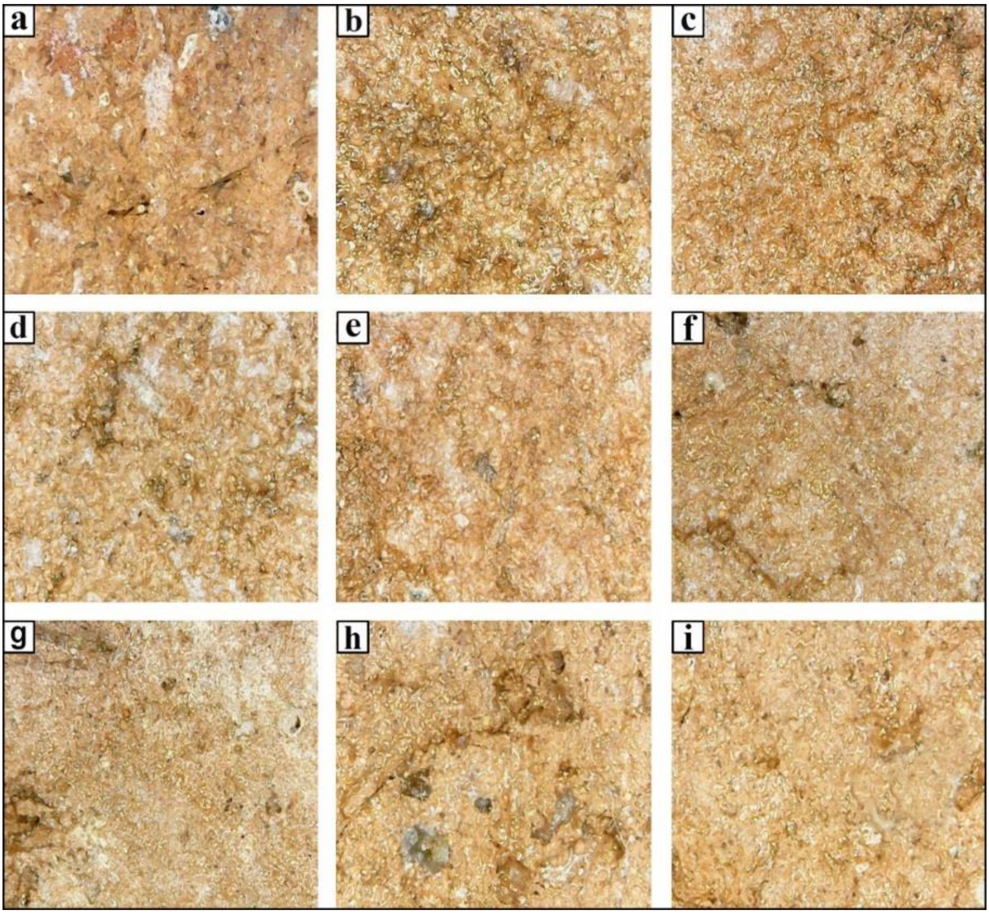


**Fig. 3.** Shows USB digital microscope photos of untreated and treated samples before and after artificial aging

***Stereo Microscope***

The visual examination of the surface by stereo microscope indicated that the untreated sample with code U suffered from fragility and weakness in the body in addition to the presence of some pits on the outer surface (Fig. 4a). The examination revealed that samples A and B have good coverage for the outer surface of pottery with the appearance of a slight shine (Fig. 4b and c). Additionally, samples C and D revealed the ability of the consolidation material to fully cover the outer surface without the brightness of the surface (Fig. 4d and e). After artificial aging, the effect of aging of the consolidation materials was studied using a stereo microscope. Samples E and F show that there is a white layer covering some parts from the surface of the pottery samples that led to deforming the external surface and changing the visual properties. So, it isn't preferred to use these treatments to protect pottery objects (Fig. 4f and g). While sample G shows the presence of a simple white film, in addition to a slight change in the external appearance (Fig. 4h). Sample H illustrates the ability of the consolidant to coat the sample's surface as well as the absence of the artificial aging effect. Therefore, it is preferable to use this material for the consolidation of pottery samples (Fig. 4i).

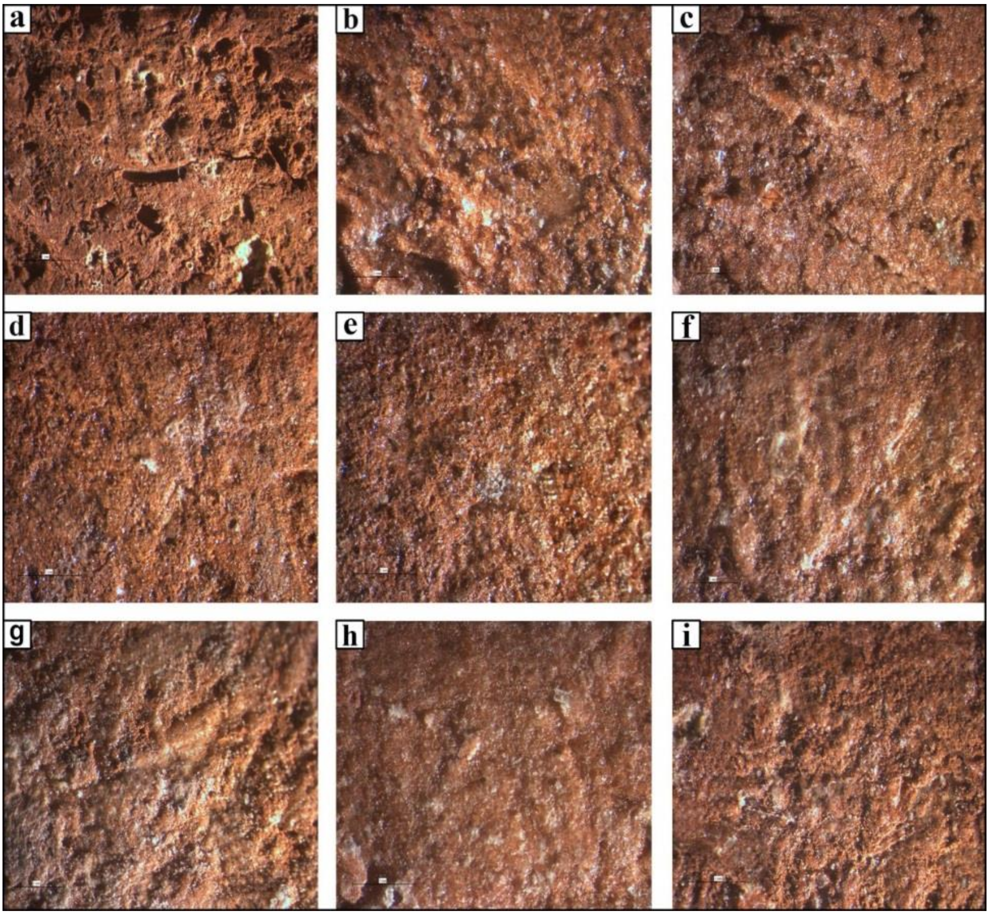


**Fig. 4.** Stereo-microscope images show the effect of applying the consolidation materials on pottery samples

***Static water contact angle***

Water is one of the most damaging factors for pottery objects because it causes dissolution and recrystallizes some salts. Additionally, it helps in increasing the activity of microorganisms [38]. So, the consolidation materials used to protect the pottery samples must have waterproof properties, to keep them safe from the impacts of water [39]. The data obtained from (Table 2) and (Fig. 5) of sample D show that the treatment with nano Paraloid B72 at 5% improved the hydrophobicity of the pottery sample. Where this sample had given the highest degrees in contact angles of 103° compared to the untreated sample, which registered an angle of 5°. Wherefore, this consolidation material is considered as one of the best materials that can be used to consolidate weak pottery. However, after artificial aging, the sample with code H was not affected much, where the water contact angle was 101°. This treatment causes a partial pore blockage, which helps to increase hydrophobic character [15]. On the other hand, sample A treated with paraloid B72 at 3% gave the lowest degree for contact angle about 79°. Where this percentage decreased after the artificial aging to 65°. Hence, it is not recommended to use this material for the consolidation of pottery objects due to the lack of suitable protection for the outer surface.

**Table 2.** Shows values of static contact angles for the studied samples

| Sample code | SCA (º) |
|---|---|
| U | 5° |
| A | 79° |
| B | 85° |
| C | 96° |
| D | 103° |
| E | 65° |
| F | 79° |
| G | 88° |
| H | 101° |

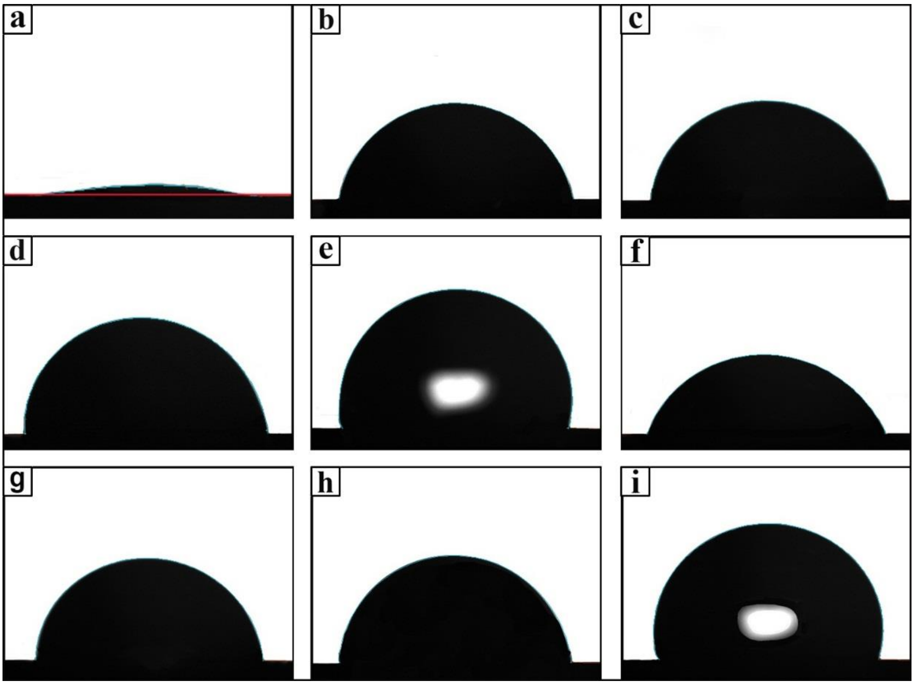


**Fig. 5.** Shows static contact angle measurement of the untreated and treated pottery specimens before and after artificial aging

***Color alteration***

The colorimetric study was conducted on the untreated and treated samples before and after aging to determine the influence of polymers on the general look of the pottery specimens. Color variations were measured by CIE $L^*$ $a^*$ $b^*$ system [40-42]. The following equation was used to determine the color change measurement for the samples:

$$\Delta E^* = \sqrt{(\Delta l*)^2 + (\Delta a*)^2 + (\Delta b*)^2}$$

which $\Delta L^*$ value describes a change in brightness [43], $\Delta a^*$ stands for the red-green parameter variation, $\Delta b^*$ stands for the blue-yellow parameter variation, and $\Delta E^*$ stands for the total color change [44-47]. The value of $\Delta E^*$ is considered exceedingly small and below the perception threshold if its value is ($\Delta E^* < 3$) [48]. However, if the value is ($\Delta E > 3$) it gives an appreciable difference [49, 50]. The obtained values in (Table 3) and (Fig. 6) show that the treatment of pottery samples with nano paraloid B72 did not result in a significant chromatic alteration ($\Delta E^*$ = 1.67, 1.89) for samples C, D respectively. Where the use of nano Paraloid B72 leads to a more decrease in $\Delta E^*$ values, improving the chromatic stability of the pottery and giving satisfactory results by the naked eye [51]. As well as these samples after artificial aging did not affect, which gave values less than 3. On the other hand, sample B before aging gave ($\Delta E^*$ = 2.42), but after aging increased this value. Where sample F after artificial gave value large than 6 ($\Delta E^*$ = 6.69). Treatments with paraloid B72 resulted in a darkening of the samples' surfaces in general.

**Table 3.** The color change values of the treated specimen before and after aging

| sample | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta E^*$ |
|---|---|---|---|---|
| A | 1.74 | 0.86 | -0.08 | 1.94 |
| B | -0.82 | -1.83 | -1.36 | 2.42 |
| C | 1.00 | 1.22 | 0.55 | 1.67 |
| D | -0.62 | -0.20 | 1.77 | 1.89 |
| E | 4.72 | -1.77 | -1.53 | 5.27 |
| F | 4.67 | -3.75 | -2.99 | 6.69 |
| G | 1.42 | -1.49 | 0.60 | 2.14 |
| H | 1.95 | -1.23 | -1.07 | 2.54 |

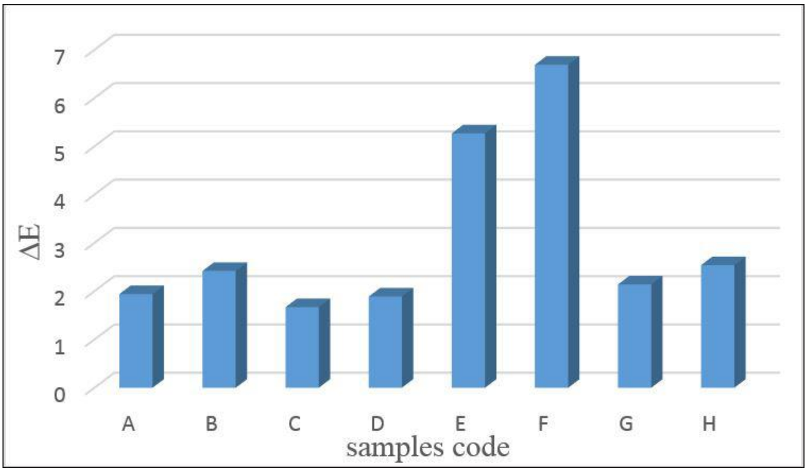


**Fig. 6.** Shows the values of total color change ($\Delta E^*$) of pottery samples before and after aging.

***Physical properties***

The results in (Table 4) and (Fig. 7) reveal that impregnation with nano Paraloid B72 causes significant changes in the behavior of the pottery samples, including porosity, water absorption, and density. Sample D shows a significant decrease in the water absorption coefficient (coated with nano paraloid B72 at 5%). Hence, the water absorption of the untreated sample was 18.19% and then converted to 8.13% after treatment. However, after aging, the water absorption percentage of sample H increased slightly to 9.37%. Compared to untreated specimens, coated samples with nano Paraloid B72 at 5% consolidant show a decrease in overall porosity. Consolidants have had an impact on pore distribution by decreasing macroporosity [52].

The porosity of sample D was reduced to 17.26% compared to the untreated sample of 27.41% because of the impregnation with nano paraloid B72. Moreover, after artificial aging, the ratio of porosity for sample H increased slightly to 18.96%. The efficiency of a consolidation treatment may also be evaluated by the increase of density of the samples. The initial density reflects the level of degradation reached to samples [36, 53]. Sample D gives the highest density of 2.12g/cm$^3$, which is higher than the untreated sample that was 1.51g/cm$^3$. However, the density of sample H decreased slightly after aging to 2.06g/cm$^3$.

***Compressive Strength***

The compressive strength test is performed to measure the maximum stress that may be reached before failure [54]. This test also reflects a sample's capability to withstand being shattered [55, 56]. The object's higher compressive strength shows its ability to sustain a greater crushing load [57]. To determine the effectiveness of the consolidation materials in increasing the hardness of the pottery samples, compressive tests were performed on both untreated and treated samples before and after artificial aging. The obtained data in (Table 4) and (Fig. 7) showed that sample D treated with nano Paraloid B72 at 5% gives the highest value for compressive strength, where its value is 421kg/cm$^2$ which is more than the untreated sample by about 61.30% which gives 261kg/cm$^2$. Nevertheless, the compressive strength of sample H decreased after aging by about 53.26%, with a value of 400kg/cm$^2$. Therefore, nano Paraloid B72 successfully consolidated the fragile pottery structure and enhanced its mechanical properties. When comparing the compressive strength of untreated samples to treated samples, it was discovered that adding the nano Paraloid B72 increases the compressive strength.

**Table 4** Physical and mechanical properties of untreated and treated pottery specimens before and after artificial aging

| Sample code | Water Absorption (%) | Porosity (%) | Density (g/cm$^3$) | Compressive strength (kg/cm$^2$) |
|---|---|---|---|---|
| U | 18.19 | 27.41 | 1.51 | 261 |
| A | 10.68 | 21.13 | 1.98 | 349 |
| B | 11.65 | 21.05 | 1.81 | 367 |
| C | 10.10 | 20.30 | 2.01 | 406 |
| D | 8.13 | 17.26 | 2.12 | 421 |
| E | 11.79 | 23.22 | 1.96 | 324 |
| F | 12.48 | 22.46 | 1.80 | 359 |
| G | 11.45 | 22.09 | 1.99 | 385 |
| H | 9.37 | 18.96 | 2.06 | 400 |

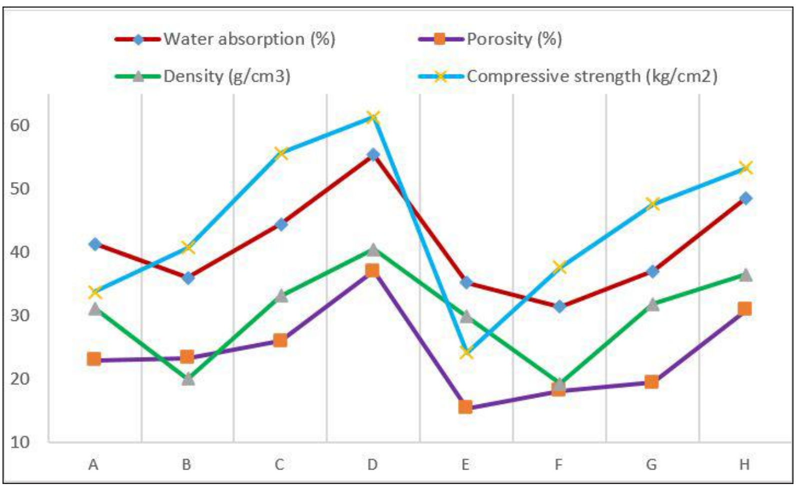


**Fig. 7.** Shows the improvement rate of the physical and mechanical tests of the treated pottery specimens before and after aging

## Conclusions

Archaeological pottery suffered from diverse types of damage such as water and salt crystallization. Where these damaging factors affect the durability and strength of pottery, which lead to the fragility and weakness of objects. Therefore, it was necessary to use consolidation materials to protect these pottery objects. This paper compared the basic properties of pottery samples before and after consolidation with Paraloid B72 in conventional and nano forms. For this purpose, some investigation, mechanical, and physical properties were achieved. The use of nanomaterial for pottery samples increased their capacity to consolidate and preserve the samples, according to the results. So, it has promising effects for conservation and protection purposes.

The results obtained by SEM, USB digital, and stereo microscopic investigation indicated that nano Paraloid B72 at 5% was the best material for the consolidation of pottery. Hence, it formed a homogeneous coating and increased the polymer's capacity to penetrate by filling the pores of pottery. The application of traditional polymers caused visible color differences as compared to untreated samples, but the nano Paraloid B72 had almost no optical influence on the color of the pottery objects. Furthermore, this coating provided excellent resistance against the penetration of water. The hydrophobic characteristics of the samples treated with nanomaterials were superior to those of the ones treated with pure polymers. Overall, it was demonstrated that the use of nano Paraloid B72 at 5% improved the mechanical and physical properties of the pottery samples. From this study, it can be recommended to use this material for the consolidation of archaeological pottery and ceramic materials.

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