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EXPERIMENTAL STUDY FOR EVALUATION OF PARALOID® B72 AND ITS NANOCOMPOSITE WITH NANO TiO_2 AND NANO ZnO FOR CONSOLIDATION OF POTTERY SAMPLES

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ABSTRACT

The archaeological pottery artifacts are the major finding in excavations and inhere a particular deterioration aspect, especially fragility. The consolidation process is necessary to keep these objects for a long time. Several consolidants are using in the field of pottery conservation, such as Paraloid B72. This paper presents an experimental study to compare and evaluate the effect of the addition of TiO2 and ZnO nanoparticles on the physical and mechanical properties of Paraloid B72. It is applied to improve the polymer properties and increase its ability to consolidate and protect the pottery objects. In this study, pottery samples were prepared at 800°C and have exposed to salt weathering. The aged pottery samples have consolidated with the prepared consolidants by brushing. Then, the treated samples were exposed to artificial aging to test the efficiency of the consolidation materials. Some investigation with analytical methods were used for the evaluation process. TEM was used to measure the size of prepared nanocomposites. Microscopic investigation with SEM, USB digital, and stereo were used for the surface morphology. The measurement of the contact angle was performed for the evaluation of the hydrophobic properties of the consolidants used in this study. The color change, physical and mechanical tests were also evaluated. It has been proven that the treated sample with Paraloid B72/ZnO nanocomposites gave the best results, suitable to use of this nanocomposite for the consolidation of pottery objects.

KEYWORDS: Pottery, deterioration, Paraloid B72, polymeric, nanocomposites, conservation, archaeological

1. INTRODUCTION

Pottery objects are exposing too many factors and aspects of deterioration that affect the internal structure. These aspects include the presence of cracks at different depths, the fragility of the surface layer, and the separation of the outer coating layer from the pottery surface (Moutinho et al., 2019). Water spread into the objects is considered the main responsible for its deterioration, particularly for porous materials (Sabatini et al., 2018). Additionally, it is a catalyst and activator for most other damage factors. For this reason, the protection and consolidation materials must have the property of hydrophobic for the protection of the surface of cultural heritage (Manoudis et al., 2009). It must take multiple variables, such as conservation status, forms, and mechanisms of degradation, and environmental factors, which make necessary the choice of the suitable materials and procedures to achieve proper preservation (Pinto and Rodrigues, 2008).

The development of modern materials and methods for consolidating the artifacts is considered the subject of global interest in research conservation. Moreover, these consolidation materials should be characterization by improved efficiency and potential reversibility (Traistaru et al., 2012). Therefore, the improvement of novel materials or methodologies to consolidate and protect the decayed pottery from physical and chemical deterioration is considered very important (Adam et al., 2015). Consolidated materials are using to improve the cohesion of archaeological objects. These materials are using when dangerous deterioration patterns and cohesion loss are present. Consolidation treatments are the most hazardous preservation actions because of the inability to retrieve consolidated materials (Pinto and Rodrigues, 2008). The use of synthetic resins in preservation for artifacts is associated with good handling properties, flexibility, and transparency (Cataldi et al., 2014). Consolidants should not alter the object's chemical or optical appearance. (Del Grosso et al., 2019).

Consolidation is intending to increase the resistivity and coherence of the damaged object. Therefore, we obtain a compact and stable material, which can withstand environmental effects (Brus and Kotlik, 1996). Good consolidants should meet performance requirements concerning durability, depth of penetration, the effect on porosity, and compatibility with the object material (Prudêncio et al., 2012). Additionally, Coatings for porous materials should provide impermeability to liquid water, permeability to water vapor, chemical inertness, and environmental stability (Pagliolico et al., 2016; Constancio et al., 2010). As well as protective coating must be capable to an avoid the entry of chemicals. Additionally, it is essential susceptible too easy to application and reversible, or at least, the protective coating must be easy to remove (Sabatini et al., 2018). The coating materials should remain colorless and soluble in the solvents (Braccia and Melob, 2003).

Paraloid is considered one of the acrylic resins most frequently used in the consolidation of artifacts due to its characteristic mechanical properties and ease of use. Therefore, using a polymer requires dissolving it in a solvent, such as acetone or toluene (Vinçotte et al., 2019). Paraloid B72 is the most used acrylic polymer, although there are numerous kinds of Paraloid formulations available, such as Paraloid B-66 and Paraloid B-67 (Constancio et al., 2010). When using Paraloid B72 in consolidation, it doesn't cause discoloration for the surface, and thus it is considered acceptable material for cultural heritage preservation. Moreover, Paraloid B72 also increases the water-resistance of artifact surfaces (Kaplan et al., 2019).

To avoid the disadvantages of using resins, a modern method for the consolidation by nanomaterials has appeared. This new method was mainly used to support mechanical properties (Salama et al., 2018). In the recent period, the use of nanomaterials in the field of cultural heritage preservation has become increasingly widespread due to the improvement of the performance of the materials used in treatment. Nanosized titanium dioxide has demonstrated its efficiency in many application fields, such as its water-repellent effect (La Russa et al., 2016). Improving the inherent hydrophobic character of a polymer is highly desired as it can promote their protection efficiency against the deterioration effects, which are inducing by humidity. Therefore, the addition of nanoparticles achieves this purpose (Manoudis et al. 2017). Water repellent polymer-nanoparticle composite can be used for the protection and preservation of surfaces of the cultural heritage (Chatzigrigoriou et al., 2013). Titanium dioxide nanoparticles were used with a Paraloid B72 to improve its mechanical properties, obtain a transparent, chemically stable, and non-yellowing coating (Scalarone et al., 2012).

ZnO nanoparticles are the materials used to form a protective coating on the surface of artifacts (Aldosari et al., 2019). Modified ZnO nanoparticles can be hydrophobic, so this material is essential to protect the archaeological objects (Ruffolo et al., 2010). The use of zinc nanoparticles in the consolidation has a great influence on the physical and mechanical properties. The advantages of this material are related to good chemical stability and resistance to thermal stress (Ditaranto et al., 2015). Both titanium dioxide (TiO2) and zinc oxide (ZnO) nanoparticles have shown excellent biocidal properties. Where ZnO nanoparticles cause the degradation of the cell wall and the plasmatic membrane of the bacteria. While TiO2 nanoparticles enhance the oxidation of the cell wall and can interfere in the respiratory processes of the organism (Becerra et al., 2020). The research reported in this paper was aimed at the preparation and characterization of new formulations of an acrylic consolidant based on Paraloid B72 and containing TiO_2 or ZnO nanoparticles. The present research was carried on six pottery samples treated with three consolidating products applied by brushing. This study aims to examine the efficiency of polymeric nanocomposites in the treatment and preservation of pottery objects. Besides, investigate and compare the effect of the application of the consolidation material. Moreover, evaluating the changes in a certain pottery sample property before and after artificial aging. The overall aim is to the establishment of the best strategy for the conservation of this type of cultural objects in museums and archaeological sites.

2. MATERIALS

2.1. *Preperation of Paraloid B72 and its nanocomposites with nano TiO_2 and nano ZnO*

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 5% as a pure copolymer and in the presence of 3% of ZnO and TiO_2 nanoparticles to prepare nanocomposite. 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 water for 30 min at room temperature using a mechanical stirrer (500 rpm). In addition, the presence of 0.03 g of ZnO or TiO_2 nanoparticles (nanopowder, < 100 nm particle size (BET), 99.5% trace metals basis obtained from Sigma-Aldrich, Schnelldorf, Germany). Then, the mixture was heated to 80 ºC. Then, the initiator potassium persulphate (PPS) (0.27 g) (Sigma-Aldrich, Schnelldorf, Germany) dissolved in 50 mL of distilled water and Sodium dodecyl sulphate (SDS) as emulsifier dissolved in 45 mL of distilled water was added to the reaction mixture under continuous stirring for 3 h to obtain the solutions of Paraloid B72, Paraloid B72/TiO_2 and Paraloid B72/ZnO nanocomposites. The concentration was selected based on pottery nature and porosity. 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 5%
B	Nano titanium at 3% with Paraloid B72 at 5%
C	Nano zinc at 3% with Paraloid B72 at 5% at
D	Paraloid B72 at 5% after artificial ageing
E	Nano titanium at 3% with Paraloid B72 at 5% after ageing
F	Nano zinc at 3% with Paraloid B72 at 5% after ageing

2.2. *Preparation of pottery samples*

The laboratory experiments were carried out on six new pottery samples. Experimental pottery samples were prepared at the laboratory of the Conservation Department, Faculty of Archaeology, Cairo University, Egypt. Red clay (60 % wt.) was mixed with quartz sand (25 % wt.), grog (powder of new pottery) (10 % wt.), and straw (5 % wt.). Clay was mixed with water until the proper plasticity and then kneaded to make a paste. That process can take days before the clay is ready for shaping (Wodzińska, 2009; Ibrahim and Mohamed, 2019). The clay material was molded into cubic shapes. The sizes of samples were 3 cm edge for cubes (Cultrone and Madkour, 2013). The samples were then left to dry completely in the open air for two weeks. Then they were gradually fired in an electrical kiln reaching a temperature of 800oC. Red clay is the main component of pottery mainly in Egypt (Ibrahim et al., 2020).

The ancient Egyptians fired this clay at temperatures around 700 to 800 °C. The surface after firing is usually dark red or brown (Wodzińska, 2009). After the pottery samples were prepared, they were exposed to successive cycles of salt ageing. Each cycle consists of immersion in a 20% salt solution of sodium chloride for 10 hours, then drying at room temperature for 14 hours (Helmi and Abdel-Rehim, 2016). Different consolidation materials were applied by brushing, and this process was repeated three times within two hours between each application. Then the samples were left to dry for one month at room temperature (Aldossari et al., 2019; Licchelli et al., 2014). The consolidated pottery samples were exposed to thermal ageing at the temperature of 100 °C and 60 % relative humidity for 100 hours. The light ageing test was also applied for 100 hours using UV lamp by (268 UVA Optimized / low profile sensor heads). The condition of the lamp as follows (power: 600 w, wavelength of radiation: 400 nanometers, distance between samples and lamp: 15 cm) (Ibrahim et al., 2020).

3. METHODS OF TESTING AND ANALYSIS

Various methods and techniques are used for the present investigation.

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.

Scanning electron microscope (SEM): SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyzes), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolutions for Gun.1n). FEI Company, Netherlands was used. This procedure was carried out at the General Authority for Mineral Resources in Dokki – Egypt.

Stereo microscope: The Leica MZ6 stereo zoom microscope is a modular common main objective stereo microscope with a zoom range of 6.3x - 40x with 10x eyepieces, Germany. This procedure was carried out at the General Authority for Mineral Resources in Dokki – Egypt.

Static water contact angle: Model T330, Generated with OneAttension Version 2.7(r5433), the volume of the drops was 7.29 µl. Company name: biolinscientific, Place: Finland. The test was conducted at the Egyptian Center for Nanotechnology at Cairo University, Sheikh Zayed, Egypt.

Measurement of Color Change: 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.

3.1 Measurement of physical properties

The physical properties of these samples were defined by measuring the dry weight and the wet weight of each sample. The physical properties were calculated as follows:

Bulk Density (d) in g/cm^3 was defined in the following Equation:

$$D = W/V$$

Where: W is the original weight in g and V is the volume in cm^3. (Modestou et al., 2015)

Water Absorption (W.A) in % was determined in the following Equation:

$$W.A = \frac{W_2 - W_1}{W_1} X\ 100 = \%$$

Where: W1 and W2 is dry and wet weight in g. (Ibrahim et al., 2018)

Apparent porosity (A.P) in % was defined in the following Equation: (Hemeda et al., 2018)

$$A.P = \frac{W_2 - W_1}{V} X\ 100 = \%$$

Where: W1 and W2 is dry and wet weight in g and V is the volume in cm^3

3.2 Measurement of compressive strength

A Tinius Olsen QMat5.37 / Q3214) was used. 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 National Institute of Standards, Al-haram, Giza, Egypt.

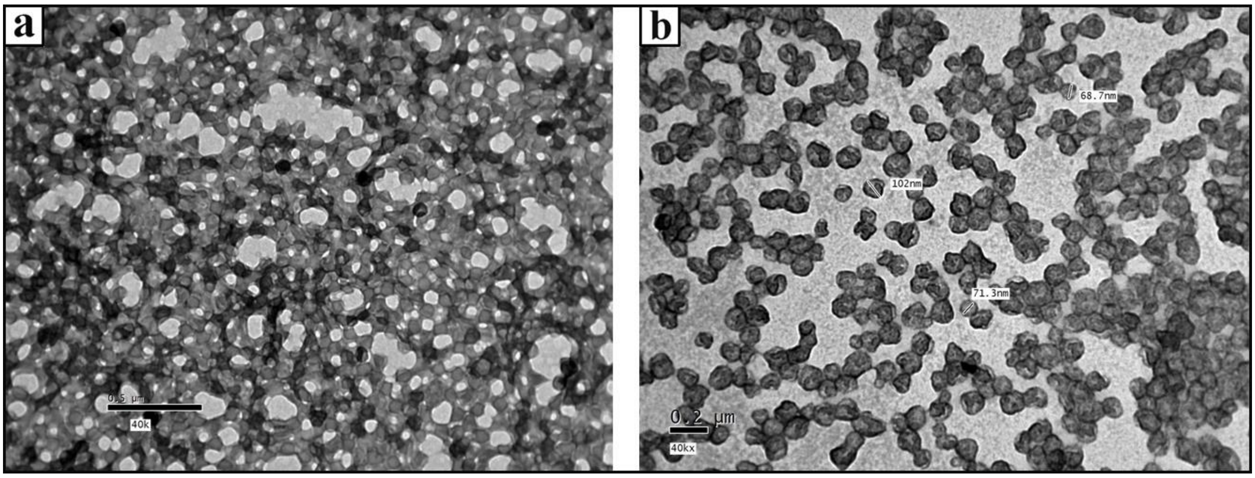

Figure 1. TEM micrographs nanocomposites polymer after the synthesis process. (a) Shows the homogeneous dispersion between TiO$_2$ nanoparticles with Paraloid B72, and (b) showing the homogeneous dispersal between nano zinc with Paraloid B-72.

4. RESULTS AND DISCUSSIONS

4.1. Transmission electron microscope (TEM)

TEM micrographs of the obtained nanocomposites are applied to estimate the combination process between TiO_2, ZnO nanoparticles. The description by TEM showed that nanoparticles were dispersed homogeneously. Additionally, nanoparticles reacted in the nanocomposites without aggregates of nanoparticles in the polymer matrix (Aldosari et al., 2019). The size of Paraloid B72/TiO_2 nanocomposite after the mixture process showed that the nanoparticles diameter lies in the range of 66 to 74 nm (Fig. 1a). On the other hand, the particle size of Paraloid B72/ZnO nanocomposite ranges between 68 to 71 nm (Fig. 1b).

4.2. Scanning electron microscope (SEM)

It has been demonstrating that scanning electron microscopy can use as an analytical tool to obtain information regarding the investigation of pottery samples before and after the application of the consolidants then after artificial ageing (Grammatikakis et al., 2019). It is applied to examine the surface of samples as well as the distribution of the consolidation materials. (Fig. 2a) indicates the untreated pottery sample with a code U, which shows the presence of cracks, fragility, weakness, and lack of cohesion of granules with the presence of some salt. Sample A treated with Paraloid B72 (Fig. 2b) shows the homogenous diffusion and well covering of the outer surface. Furthermore, this material has failed to penetrate deeply into the pottery structure. Sample B treated with Paraloid B72/TiO_2 nanocomposite (Fig. 2c) shows that the consolidation material is not well distributed over the sample surface and between the internal grain. Additionally, this polymer is not able to cover the whole surface. Besides, it is a whitening effect on the treated material surface, which is particularly noticeable on darker pottery (Al-Omary et al., 2018).

Sample C treated with Paraloid B72/ZnO nanocomposite (fig. 2d) showed a good penetration of polymer in-depth and filling the wide pores between the granules. Besides, good distribution and penetration of polymer and covering the grains. In addition to nano zinc distributed with a good arrangement on the pottery surface. After applied artificial aging, SEM microscope was used to identifying the capability of the consolidation materials to resist various environmental conditions. It is applied to choose the best materials that have not a clear change due to ageing. (Fig. 2e) shows sample D treated with Paraloid B72 after artificial ageing, minor changes were observed on the sample appearance, in addition to the lack of the polymer distribution uniformity on the surface. (Fig. 2f) shows sample E coated with Paraloid B72/TiO_2 nanocomposite, it showed the effect of artificial ageing on the consolidation material. Besides, large areas have not been covered by the protection material with some cracks (Fig. 2g) shows sample F treated with Paraloid B72/ZnO nanocomposite that improved the stability of the consolidation compound microstructure under the influence of artificial aging.

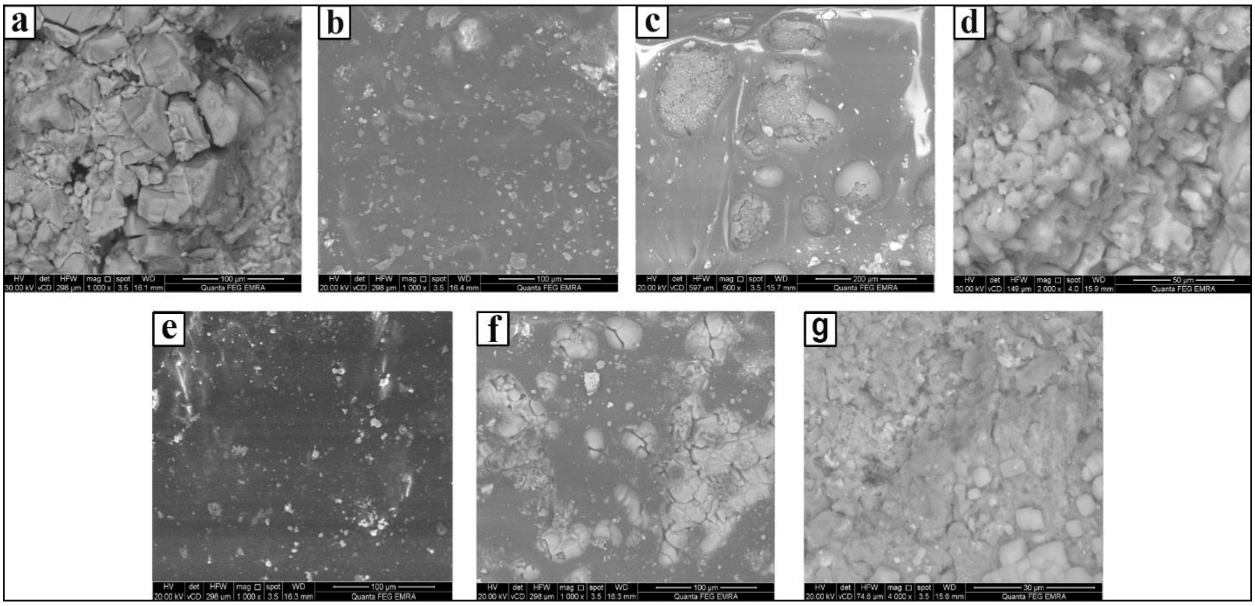

Figure 2. The SEM micrographs of the untreated, treated samples and after artificial ageing. (a) Shows untreated samples, (b) sample treated with Paraloid B72, (c) sample treated with Paraloid B72/TiO_2 nanocomposite, (d) sample treated with Paraloid B72/ZnO nanocomposite, (e) sample treated with Paraloid B72 after artificial ageing, (f) sample treated with Paraloid B72/TiO_2 nanocomposite after artificial ageing, and (g) sample treated with Paraloid B72/ZnO nanocomposite after artificial ageing.

4.3. Stereo microscope

The colored images through using a stereo microscope are considered one of the useful methods used for studying and documenting changed surface features of archaeological objects. So, it is a helpful tool for the evaluation of future deterioration (Elgohary, 2008). Untreated sample with code U shows the presence of some salt, granular disintegration, and weakness (Fig. 3a). It is clear through examination that sample A shows good coverage of the consolidation with the appearance of a slight shine that does not affect the outer surface (Fig. 3b). Sample B shows there is a white layer covering the pottery surface with the presence of some bubbles in this layer. It is led to distort the external surface and change the visual appearance (Fig. 3c). Besides, sample C shows a good spread of the consolidated material overall parts of the sample without brightness on the surface (Fig. 3d).

A stereo microscope was used after artificial ageing to determine the occurred changes in the protected materials. On the other hand, sample D shows the presence of some white spots, which causes deformation of the optical properties of the outer surface (Fig. 3e). Sample E shows the transformation of the surface to a very dark white color causes deformation of the optical properties. As well, ageing leads to the appearance of polymer degradation on the surface. Therefore, it is not preferred to use this type of material in pottery consolidation (Fig. 3f). Sample F shows that the ageing process does not affect the consolidation material. Additionally, the ability of material to cover all parts of the sample. Consequently, it is preferable to use this material in the consolidation of the archaeological pottery (Fig. 3g).

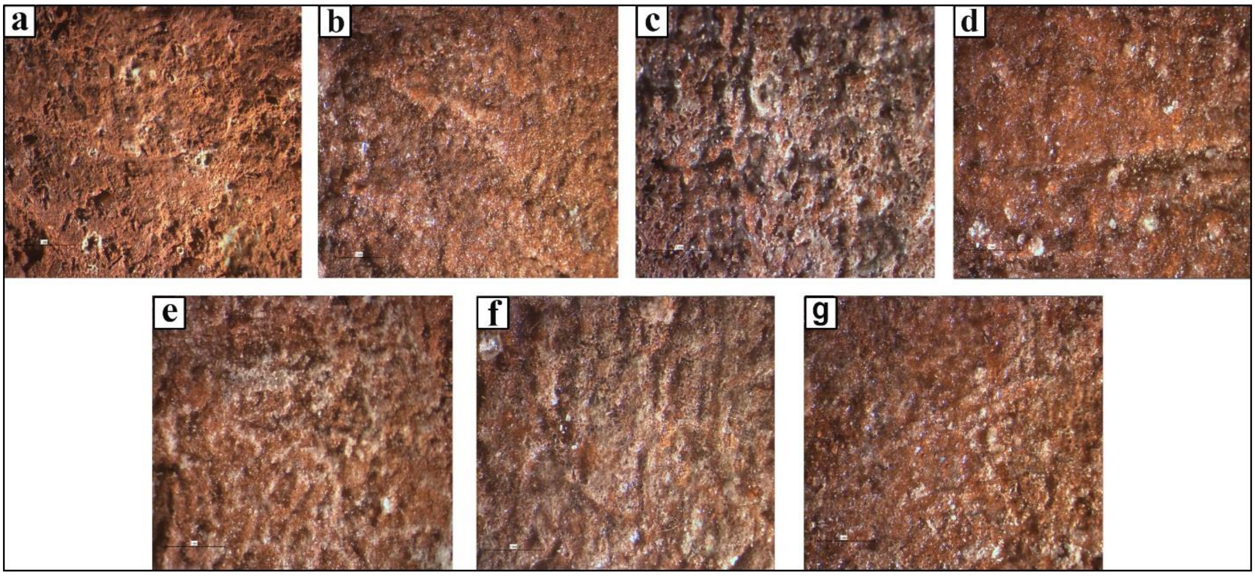

Figure 3. Stereomicroscope images showing the effect of applying the consolidation materials on pottery samples before and after artificial ageing.

4.4. Static water contact angle

The obtained data from the contact angle test (table 2) (fig. 4) revealed that samples C and F gave the highest degree (106.8°, 99.7°) before and after ageing respectively. The highest values obtained from these samples may be caused by adding ZnO nanoparticles to Paraloid B72. The use of nanoparticles leads to some advantages for the treated samples, such as increasing the contact angles > 90° (Chatzigrigoriou et al. 2013), improving the hydrophobic properties for the protection of the cultural heritage (Manoudis et al. 2007; Nteliaa and Karapanagiotisa, 2020) and enhancing the surface morphology (Manoudis et al. 2009). Manoudis and Karapanagiotis (2014) confirmed that result, where they mentioned that adding ZnO nanoparticles for polymer Paraloid B-72 matrix leads to the water repellency improvement (Manoudis and Karapanagiotis, 2014). Moreover, Liu and Liu (2016) stated that the treatment with Paraloid B72 / ZnO nanocomposite gave a clear hydrophobic behavior (Liu and Liu, 2016). This treatment leads to a partial pore blockage, which helps to increase hydrophobic character (Vaz et al. 2008). So, it is considered one of the best materials that can be used to consolidate weak pottery.

On the other hand, the treated samples with pure Paraloid B72 without any additives for samples A and D gave the lowest values (50.2°, 27.8°) before and after ageing respectively. The low value in the contact angle test <90° is considered a hydrophilic characteristic (Manoudis et al. 2017; Ruffolo and La Russa, 2019; Nteliaa and Karapanagiotisa, 2020). The results showed that the addition of nano zinc to the Paraloid B72 enhanced the hydrophobic nature. In comparison, the consolidation with Paraloid B72 could be water repellent, but it was found to be less hydrophobic than Paraloid added to nanoparticles (Aldosari et al., 2018). Therefore, it isn't recommended to use pure Paraloid B72 in archaeological pottery protection because it doesn't give appropriate protection.

Table 2. Shows the values of the static water contact angle of the studied samples.

Sample code	SCA (°)
U	6.3°
A	50.2°
B	85.5°
C	106.8°
D	27.8°
E	73.9°
F	99.7°

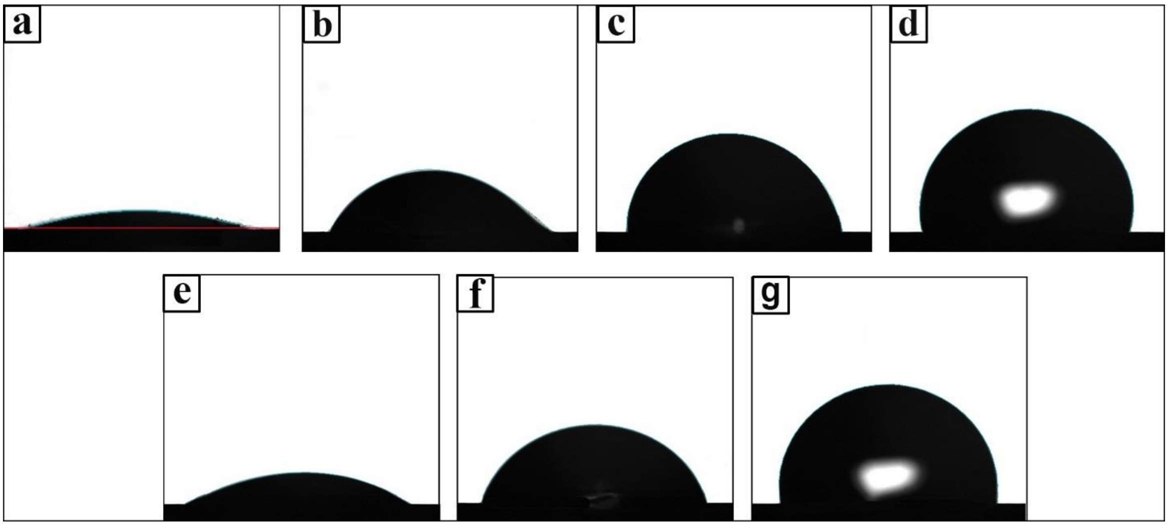

Figure 4. Shows static contact angle measurement of untreated pottery samples, treated samples and after artificial ageing.

4.5. Measurement of color change

The colorimetric measurements were carried out at different stages to evaluate color variations of pottery samples before and after treatment (Ibrahim et al., 2020). The color change is expressed by the ΔE parameter of pottery samples treated with Paraloid B72 and nanoparticles. This indicates the variability between both chromatic coordinate (ΔL*, Δa*, and Δb*) in untreated, treated, the total color change (ΔE) was calculated using the following equations (Aldosari et al., 2019):

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

Where [ΔL*], [Δa*], and [Δb*] are the differences in the respective values before and after applying the treated material.

The color change value of less than 3 indicates a slight change in the naked eye, while color change is considered visually if ΔE is above than 3 (Al-harbi et al., 2014). In addition to the values over 6 gives a strong difference for the naked eye (Salama et al., 2020; Dubey et al. 2012). It is clear from the obtained results in (table 3), that after applying the different consolidation materials, a change occurred in the ΔE value in different proportions according to the nature of the protection material. Where the results showed that the sample with code C gave the best results (ΔE = 1.61). It is considered a very slight color change and the change was unclear to the naked eye. Where the sample F was not affected after ageing greatly (ΔE = 2.24) (Al-harbi et al., 2014). On the other hand, sample B gave a large color change (ΔE = 8.39) after the application of the consolidation material. After the artificial ageing sample with code E increased color change to (ΔE = 14.08). The high total color change obtained from Paraloid B72/TiO_2 nanocomposite consolidant was a highly noticeable color change and deform the visual properties of the samples (Terziev and Boutelje, 1998).

Table 3. shows the color change values of a treated sample before and after ageing.

Sample code	Δl*	Δa*	Δb*	ΔE
A	1.74	0.86	-0.08	1.94
B	6.65	-3.16	-.4.03	8.39
C	0.17	-1.32	-0.90	1.61
D	4.67	-3.75	-2.99	6.69
E	10.78	-5.42	-7.25	14.08
F	1.59	-1.23	-0.99	2.24

4.6. Measurment of physical properties

Moisture is one of the most effective factors of deterioration for archaeological pottery; due to the high porosity of pottery material that absorbs water (Santos et al., 2012). Preservation materials must be able to resist the deterioration caused by water and decrease water permeation. Hence, it is important to estimate the effectiveness of the conservation process that aims to make the object water repellent, by determining its water absorption, its porosity, and its density (Aldosari et al., 2019). Differences in the final consequences are always to expected because of subtle variations in the testing conditions (Pinto and Rodriguesb, 2012).

The results in (table 4) showed that the water absorption in a sample with code C treated with nano zinc at 3% in Paraloid B72 at 5% gives the lowest water absorption of 3.87%, which low than the control one by about 78.72%, which was 18.19%. However, after ageing, the water absorption percentage of sample F increased by 5.63% slightly, with a value of 69.05%. While the porosity of sample C shows a low porosity of 8.35%, which lower than the standard sample by about 69.54% that was 27.41%. Moreover, after ageing, the ratio of porosity for sample F increased by 12.10% a little, with a value of 55.86%. In addition, the density of sample C gives the highest density of 2.16g/cm^3, which higher than the control sample by about 43.05% that was 1.51g/cm^3. However, the density of sample F decrease after ageing by about 2.14 g/cm^3 slightly, with a value of 41.72%.

4.7. Measurement of compressive strength

A particular compressive strength test is very important to evaluate the efficiency of the consolidation materials in increasing the hardness of the pottery samples (Šál, 2019). The compressive strength test is used to find out whether the pottery samples can resist the pressures and loads or not. Additionally, this test is considered a general indicator showing the extent to which these materials have good physical and mechanical properties (Russo et al., 2011). The obtained results in (table 4) showed that a sample with code C treated with Paraloid B72/ZnO nanocomposite gives the highest value for compressive strength. Where its value is 475 kg/cm^2, which is more than the untreated sample by about 81.99% that give 261 kg/cm^2. However, the compressive strength of sample F decrease after artificial ageing by about 446 kg/cm^2, with a value of 70.88%.

Table 4. physical and mechanical properties of the pottery samples before and after ageing

Sample code	Water absorption (%)	Porosity (%)	Density (g/cm^3)	Compressive strength (kg/cm^2)
U	18.19	27.41	1.51	261
A	11.65	21.05	1.81	367
B	10.14	21.20	2.09	399
C	3.87	8.35	2.16	475
D	12.48	22.46	1.80	359
E	12.82	23.02	1.79	353
F	5.63	12.10	2.14	446

5. CONCLUSION

Pottery objects are exposed to different factors and aspects of deterioration that affect the internal structure. In this study, titanium dioxide (TiO_2), and zinc oxide (ZnO) nanoparticles, were added to Paraloid B72 to improve its physiochemical and mechanical properties. The results showed that the addition of nanoparticles to the acrylic-based polymers improved their ability to consolidate and protect the pottery samples. The results obtained by SEM, digital, and stereo microscopic investigation indicated that Paraloid B72/ZnO nanocomposite was the best nanomaterial for the consolidation of pottery. Hence, it filled the polymer matrix, form a homogeneous coating, and increasing the ability of the polymer to penetrate the pores of pottery. The samples treated with Paraloid B72/ZnO nanocomposites showed hydrophobic properties better than the samples treated with pure polymers. However, the hydrophobicity of samples mainly depends on the nature and chemical composition of polymers, it can be enhanced by the addition of nanoparticles. The results obtained by hydrophobic measurements, and color change test, showed that the treatment by Paraloid B72/ZnO nanocomposite achieved the highest values. Physical properties for sample (C) after treatment with Paraloid B72/ZnO nanocomposite gave the best results in improving the properties of water absorption, porosity, and density. Additionally, the Compressive strength of sample (C) is given the highest results before and after ageing. Therefore, this composition is considered the best consolidant material for pottery objects. These results help us in the decision-making of the preservation procedures regarding the choice of the right materials and the suitable surrounding conditions, especially archaeological pottery. The obtained information will use in further research studies about the conservation of pottery and ceramic materials.

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