www.maajournal.com

Mediterranean Archaeology and Archaeometry
Vol. 22, No 1, (2022), pp. 67-78
Open Access. Online & Print.

DOI: 10.5281/zenodo.5906797

EVALUATION OF THE IMPACT OF SILICA AND ALUMINA NANOCOMPOSITES IN CONSOLIDATION AND PROTECTION OF CORRODED GLASS FROM EARLY ISLAMIC PERIOD IN EGYPT: AN MULTISCIENTIFIC EXPERIMENTAL AND ANALYTICAL STUDY

Rania A. Eloriby*[1], Wael S. Mohamed[2], Ahmed S. Alkaradawi[3]

[1] *Conservation Department, Faculty of Archaeology, Cairo University, Giza, Egypt*
[2]*Polymer Department, National Research Centre, Dokki, Giza, Egypt*
[3]*Medieval History and Archaeology, Faculty of philosophy and letras, University of Granada, Spain*

Received: 10/12/2021
Accepted: 10/01/2022
**Corresponding author: (rania88@cu.edu.eg)*

ABSTRACT

This paper aims to evaluate of silica and alumina nanocomposites in consolidation and protection of archaeological glass from early Islamic period in Egypt. Archaeological glass is exposed to deterioration by moisture, as water is considered one of the most dangerous damage factors that attack glass artifacts. This results in many aspects of deterioration including weeping glass, cracks, dulling, formation of weathering crusts, salt growing, and corroded surfaces. From this standpoint, materials which are used in the consolidation and protection of those glass artifacts must have the property of hydrophobicity in order to protect them from the harmful effects of water. In the last decade, polymer-nanoparticle composites have attracted great interest in the field of culture heritage conservation due to their unique multifunctional properties resulting from the high surface area and chemical activity of the nanoparticles dispersed in the polymers. In this study, Silicon dioxide (SiO_2) and alumina oxide (Al_2O_3) nanoparticles are added to silicon-based polymer (poly alkyl siloxane) (Silres BS-290) in order to improve their physiochemical and mechanical properties. This produced a significant improvement in the ability of the polymers to consolidate and protect archaeological glass. The treated samples are exposed to artificial ageing to test the efficiency of the consolidation materials. The properties of untreated, treated and aged glass samples were evaluated by TEM, stereo microscope, scanning electron microscope (SEM), colormetric measurements, static water contact angle, density and hardness tests (physical and mechanical properities). Results showed that the treated sample with SiO_2/Al_2O_3/Poly siloxane nanocomposites are good candidates for consolidation and protection of glass objects.

KEYWORDS: archaeological glass, Nanoparticles, silicon dioxide, Alumina oxide, nanocomposites, water contact angle, consolidation, protection.

1. INTRODUCTION

Unlike most materials, Archaeological Glass is considered a relatively stable material in the normal preservation when compared to other materials. However, moisture is one of the most important damage factors that affect archaeological glass (Papadopoulos and Drosou, 2012; Tournie et al., 2008; Domenech-Carbo´, et al., 2006; kunicki-goldfinger, 2008; Davison and Newton 2003; Abd-Allah, 2007; Majerus et al., 2020) because many pieces of glass are sensitive to moisture. Sodium and potassium are slightly soluble in some glass compositions. In the presence of high relative humidity, these components can be leached to the surface of the glass where they are converted to carbonates (Netwon, 1974; Brill, 1975; Schreiner, 2004; Bellendorf et al., 2010). These carbonates attract moisture and hence small droplets of water begin to appear on the surface of glass forming weeping glass. The leaching process causes tiny cracks to appear in the glass and eventually the glass can become opaque with small flaking surface (El-Shamy, 1972; Fitz, 1991; Abd-Allah, 2013; Zacharias et al., 2020).

So Water is the main factor in deterioration of glass when subjected to intensive corrosion and other deterioration aspects such as pitting, cracking, encrustation, dulling and salt crystallization (Sterpenich and Libourel, 2006; Abd-Allah, 2012; Panagopoulou et al., 2018). From this point of view, the used materials in the glass objects treatment must have the property of hydrophobicity in order to protect them from the harmful effects of water.

In the last few years, nanoparticles have widely been used in the fields of restoration and conservation of cultural heritage. The minimizing of particles size into nanoscale, results in better properties from the large grain size of the materials of the same chemical composition. A dispersion of nanoparticles in the polymers used in the consolidation and protection is carried out in order to significantly enhance their physiochemical and mechanical properties (Manoudis et al., 2009; Waked, 2011; Baglioni et al., 2012; Darwish, 2013; Chelazzi et al., 2013; Barberio et al., 2015; Helmi et al., 2019).

Therefore, nanoparticles (silica and Alumina) are added to the silicon based material (Hydrophobic poly alkyl siloxane) (Silres BS-290) considered as silicon polymers which is characterized by its homogeneity with archaeological glass (Horie, 1987; Ershad-Langroudi et al., 1997; Schottner, 2001; Holubová et al., 2015). The product is obtained using the sol–gel process to create a silica-based inorganic matrix compatible with the glassy substrate functionalized with organic chains to obtain a good surface water-repellency and a certain degree of elasticity of the film to avoid the formation of cracks during the drying process. (Dal Bianco et al., 2008; De Bardi, 2014; Manoudis et al.,2017; Ibrahim et al., 2021). It is provided by poly alkyl siloxane, which is dissolved in white spirit to prepare solution of 7% wt as a pure polymer and in the presence of 2% of SiO_2 and Al_2O_3 nanoparticles to prepare nanocomposite in order to improve their properties and compose suitable nanocomposites to be used in the consolidation and protection of glass samples.

The silica nanoparticles are chosen due to the great homogeneity between them and the components of the glass (Wang and Luo, 2012), and the alumina nanoparticles are characterized by their water-repellent properties (Karapanagiotis et al., 2012). The percentage of NPs concentration is stated at 2% to prevent aggregation on the surface of glass (Manoudis, 2007; Al Bawab et al., 2018). Silica (SiO_2) and alumina (Al_2O_3) nanoparticles are used as additives to roughen the surface of siloxane polymer coatings as well as to achieve extreme wetting properties and to achieve an enhancement of the hydrophobicity contact angles up to 160° (Chatzigrigoriou et al., 2020; Afifi et al., 2021).

This study aims at investigating the efficiency of selected polymeric nanocomposites in the consolidation and protection of archeological glass. The obtained nanocomposites are applied directly to glass samples and tested in order to evaluate the potential uses of silica and alumina nanoparticles in the consolidation and protection of archaeological glass before and after artificial ageing. The behavior of the nanocomposites exposed to artificial ageing is thoroughly investigated. The properties of the treated, untreated and aged glass samples are evaluated comparatively by using different methods such as stereo microscope, scanning electron microscope, colorimetric measurements, measuring of static contact angle, density, and hardness. The results demonstrate that the addition of nanoparticles into the silicon-based polymers produce a significant improvement in their efficiency to consolidate and protect glass samples.

2.MATERIALS AND METHODS:

2.1. Materials

2.1.1. Glass samples

The experimental study is done on archaeological fragments of glass (big fragment break down to small fragments) excavated from the ruins of Al-Fustat Islamic Site in Egypt (dated back to2nd AH/8th AD) have been collected, cleaned, and prepared for treatments (Fig.1 a,b).

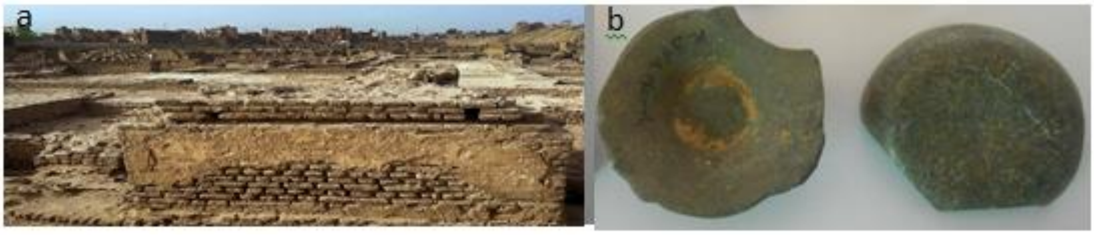

Figure 1. (a) Al-Fustat excavation site, (b) sample of glass used in Experimental study

2.1.2. Preparation of Poly Siloxane and Its Nanocomposites with Nano SiO_2 and Nano Al_2O_3

Silres BS-290, a poly alkylsiloxane produced by Wacker. Poly alkylsiloxane (7%) is prepared by dissolving 7 gm of polyalkylsiloxane in 100 ml white spirit and the mixture is sonicated for 15 min using 400 watts of ultrasonic irradiation system. Siloxane nanocomposite solutions are prepared by the addition of 0.14 g of each of the NPs SiO_2 or Al_2O_3 nano powder < 100 nm particle size obtained from (Sigma-Aldrich, Munich, Germany) separately into 100 ml white spirit containing 7 gm poly alkylsiloxane or adding 0.7 g of SiO_2 and 0.7 g of Al_2O_3 into 100 ml white spirit containing 7 gm poly alkylsiloxane. Each solution is mixed for about 10 min. then the mixture is sonicated for 15 min using 400 watts of ultrasonic irradiation system. The concentration was determined based on the composition of the glass samples. Table 2 summarizes the concentrations that were applied.

Table 2. Concentrations of used consolidation materials

Sample code	The materials used for consolidation
A	Untreated sample
B	Silres BS-290 at 7%
C	Nano Silica at 2% with Silres BS-290 at 7%
D	Nano Alumina at 2% with Silres BS-290 at 7%
E	Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7%
F	Silres BS-290 at 7% after artificial ageing
G	Nano Silica at 2% with Silres BS-290 at 7% after ageing
H	Nano Alumina at 2% with Silres BS-290 at 7% after ageing
I	Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% after ageing

2.1.3. Procedures of protection

Different consolidation and protections materials are 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 and controlled RH 50% to allow the polymerization process to take place (Al-dosari et al., 2019).

2.1.4. Artificial ageing

Thermal ageing is applied to the treated glass samples for 100 hours at a temperature of 100 °C and relative humidity of 60% (Ibrahim et al., 2020). The light ageing test is also performed for 100 hours by (268 UVA Optimized / low profile sensor heads) using a UV lamp. The lamp is in the following condition: (power: 600 w, wave-length of radiation: 400 nanometers, distance between samples and lamp: 17 cm) (De Ferri et al., 2013).

2.2. *Methods*

Various methods and techniques are used for the present investigation.

2.2.1. Energy Dispersive X-ray Analyses (EDX)

An Energy Dispersive X-ray instrument, with accelerating voltage 30 K.V. was used to determine the chemical composition of archaeological of glass which excavated from Al-Fustat ruins. This method was the most precise for determining the elemental composition and concentration of elements in a sample. It was preferred because it required only a small amount of sample, which suited small glass samples and falling glass crusts Analysis with energy dispersive is used for the samples.

2.2.2. Transmission Electron Microscope (TEM)

The examination of nanocomposites materials is carried out using transmission electron microscopy (TEM) to ascertain the size of the nanoparticles The

TEM images are obtained by a JEM-1230 electron microscope operated at 60 KV (JEOL Ltd., Tokyo, Japan). Prior to examination, the sample is diluted at least 10 times by water. After that, a drop of well-dispersed diluted sample was placed onto a copper grid (200-mesh and covered with a carbon membrane) and dried at room temperature. This procedure is carried out at the National Research Centre in Dokki District, Cairo, Egypt

2.2.3. Stereo Microscope

It is used to study some aspects that are difficult to see with the unaided eye, using a binocular microscope which gives a stereoscopic image of three dimensions (Davison, 2006). The sample is placed on a holder of translucent glass with a light source behind it. The examination is carried out using a Leica MZ6 stereo zoom microscope that is a modular common main objective stereo microscope with a zoom range of 6.3x - 40x with 10x eyepieces. This method is carried out at the General Authority for Mineral Resources in Dokki District, Cairo, Egypt.

2.2.4. Morphological Characterization by SEM

SEM observation of uncoated, coated, and coated aged glass samples is performed through scanning electron, Philips (XL30). SEM operated in Backscattered mode (BS) to investigate the compositional structure and accurately determine the crystalline phases present. Furthermore, the characterization is performed to evaluate the distribution behavior of coating materials on glass surfaces and surface morphology. The examination is carried out in SEM lab, Housing and Building National Research Center, Cairo, Egypt).

2.2.5. Static Water Contact angle

Contact angle measurements are carried out in order to determine the wettability by means of custom apparatus made in compliance with standard UNI EN15802 – 2010 (Helmi and Hefni, 2016). This test is performed on the glass samples before and after coating. A high-resolution Canon camera with 18–55 lens is used to take the images, then a dedicated software program is used to calculate the contact angles values of water droplets on the glass surface. The test is conducted at the National Research Centre in Dokki District, Cairo.

2.2.6. Colorimetric tests

Colorimetric measurements of uncoated and coated glass samples are carried out using An Optimatch 3100® from the SDL Company to measure the change of color. This process is carried out at the National Institute of Standards, Al-Haram District, Giza, Egypt. Measurements are performed on the same points before and after coating.

2.2.7. Measurement of Physical Properties

Density measurement is one of the most important physical properties of glass samples. The density is calculated as follows:

Bulk Density (d) in g/cm3 is defined in the following equation:

D = W/V

Where: W is the original weight in g and V is the volume in cm3 (El-Badry and El-Betal, 1973). The density is determined for treated and untreated glass. The test is measured at the Housing and Building National Research Centre in Cairo (HBRC)

2.2.8. Measurement of Mechanical Properties

Micro hardness test determines the material's ability to withstand scratching (Malzbender, 2002). It has been measured for samples treated with selected nanomaterials and untreated ones in order to identify the efficiency and ability of these materials to improve the mechanical properties and to know the extent of the success of the treated nanomaterials in resisting scratching of the surface. The test is conducted at the National Research Centre (NRC).

3. RESULTS AND DISCUSSION

3.1. Energy Dispersive X-ray Analyses (EDX)

Analytical results given in table (1) indicate that the major components of the glass samples are silica (SiO_2=63.22%), soda (Na_2O=3.91%), lime (CaO=2.64%), and alumina (Al_2O_3=7.15%) and magnesia (MgO =4.75%).

Table 1. Chemical Composition of Archaeological Glass Sample Used in Experimental Study

Oxides	SiO_2	Al_2O_3	Na_2O	CaO	MgO	MnO	CO_2	Total
Weight%	63.22	7.15	3.91	2.64	4.75	1.98	16.35	**100**

3.2. Transmission Electron Microscope (TEM)

Fig. 2 shows how TEM micrographs of the obtained nanocomposites are used to evaluate the combination process between SiO_2 and Al_2O_3 nanoparticles. The characterization by TEM show that the nanoparticles are homogenously dispersed and interacted in the nanocomposites without aggregates of nanoparticles in polymer matrix. Investigation size of nanoparticles SiO_2/Poly siloxane after the mixing process indicate that the nanoparticles diameter lies in the range 56 to

77 nm with a spherical morphology (Fig.2b). In addition, the particle size of Al_2O_3 / Poly siloxane nanocomposite ranges between 61 to 64nm (Fig.2c). The particle size of a mixture of Nano Al_2O_3 and Nano SiO_2/Poly siloxane, on the other hand, extends from 32 to 73 nm (Fig.2d).

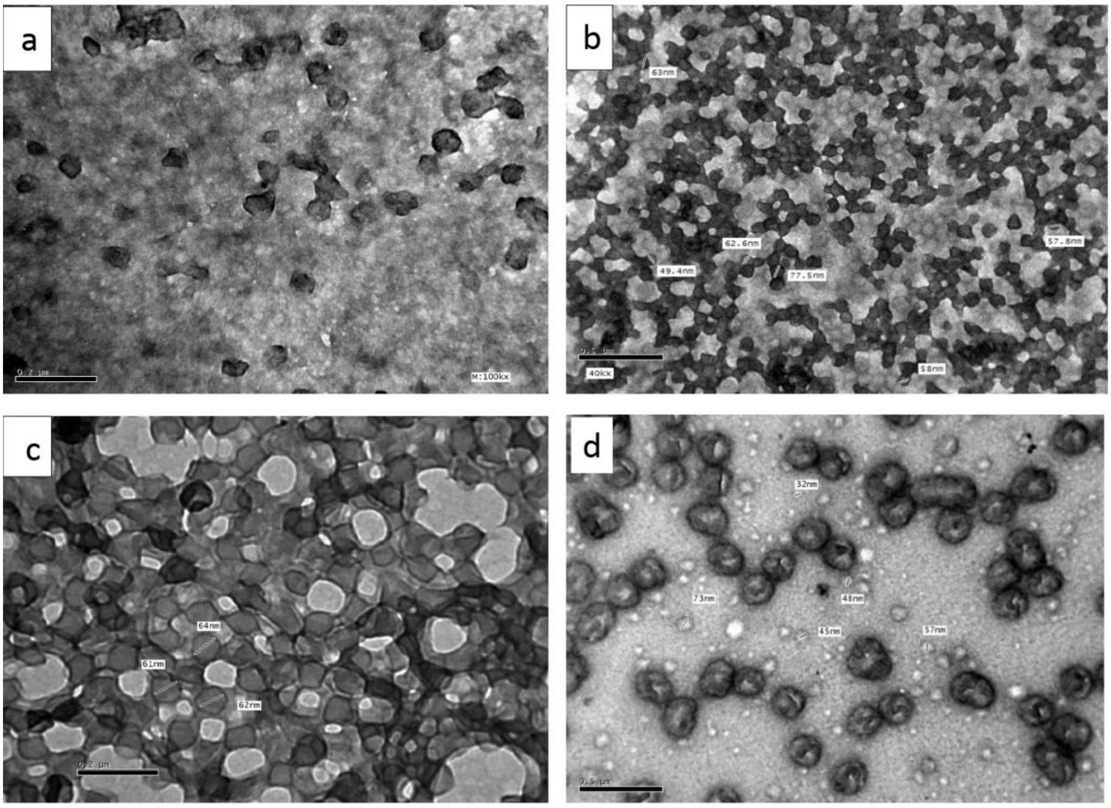

Figure 2. TEM micrographs nanocomposites polymer after the synthesis process. (a) Silres BS-290 at 7%, (b) Nano Silica at 2% with Silres BS-290 at 7%, (c) Nano Alumina at 2% with Silres BS-290 at 7%, (d) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7%

3.3. Stereo Microscope

Stereo microscope was considered one of the developed techniques that was used for studying and documenting different features of archaeological surfaces. Therefore, it was used to study the surface of untreated, treated, and aged glass samples.

(Fig.3a) indicates the untreated glass sample which shows the presence of pitting, cracking, and the phenomenon of iridescence. Sample was treated with polysiloxane (Fig.3b) shows the effectiveness of the treatment material in filling the voids (gap filling) on the surface and superficial homogeneity. Furthermore, this material was caused in darkening the iridescence zones. Sample C was treated with nano silica/polymer nanocomposites (Fig.3c) shows the homogenous diffusion and well covering the surface but this consolidated material led to the occurrence of complete opacity of the phenomenon of iridescence. Sample D was treated with Alumina/polymer nanocomposites (Fig.3d) shows homogeneous coating and a uniform distribution of the spread of the treatment material with the granules of glass. Additionally, the glass surface retaining part of the iridescence. Sample (E) was treated with silica/Alumina/ polymer nanocomposite shows that the surface of the glass retains the iridescence phenomenon unchanged with the regular penetration of the treatment material into the depths of the corrosion layers and filling the wide pores between the granules besides good distribution and superficial homogeneity. A stereo microscope was used after artificial ageing to determine the occurred changes in the protected materials. Sample (F) shows a slight opacity on the surface of the treated glass after artificial ageing (Fig.3f). In sample (G), it is observed that the phenomenon of iridescence is relatively retained with a heterogeneous diffusion of the treated material. Sample (H) shows the transformation of the surface to opacity. It leads to distort the external surface and change the visual appearance. Sample (I) shows that the treatment is effective, no changes were observed on the sample appearance in addition to the homogeneity and stability of the treated material on the surface. Furthermore, retaining the phenomenon of iridescence clear. Consequently, it is preferable to use this material in the consolidation of the archaeological glass.

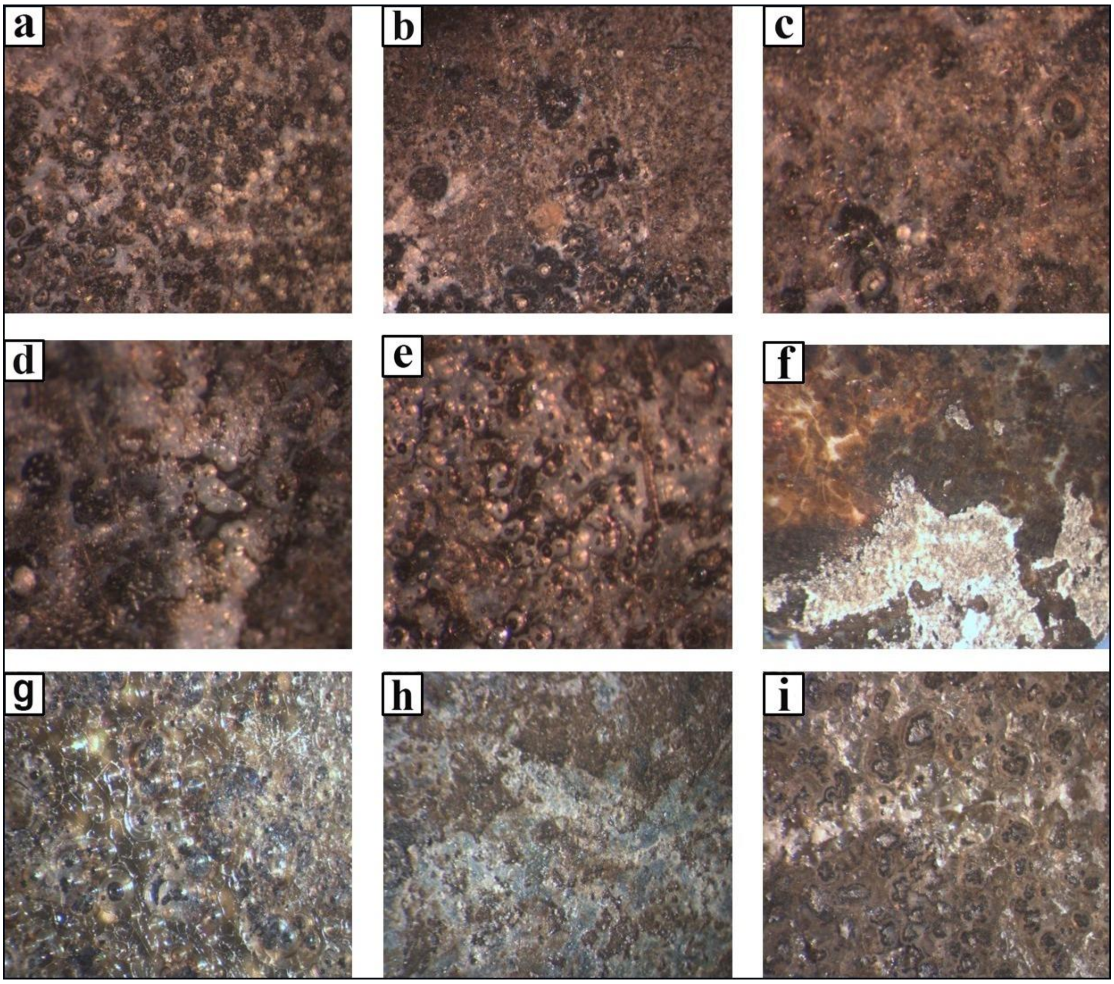

Figure 3. Stereomicroscope images showing the effect of applying the consolidation materials on glass samples before and after artificial ageing at 0,02mm. (a) Untreated sample, (b) Silres BS-290 at 7% , (c) Nano Silica at 2% with Silres BS-290 at 7%, (d) Nano Alumina at 2% with Silres BS-290 at 7% , (e) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% , (f) Silres BS-290 at 7% after artificial ageing, (g) Nano Silica at 2% with Silres BS-290 at 7% after ageing, (h) Nano Alumina at 2% with Silres BS-290 at 7% after ageing, (I) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% after ageing.

3.4. Scanning Electron Microscope (SEM)

Scanning electron microscope was used on the glass samples before and after treatment and after thermal ageing to examine the surface of samples as well as the distribution of the consolidation materials. The SEM micrographs of an untreated glass sample (Fig.4a) appeared to be very fragile has many cracks, weakness, lack of cohesion of granules, and suffered from granular disintegration. (Fig.4b) shows sample was treated with pure poly siloxane. It appeared that the consolidation material was not well distributed over the sample surface. The polymer does not able to cover the whole surface and leads to the formation of small aggregates. The samples were treated with nanocomposites materials (Fig. 4c, d, e) showed a more homogenous appearance. It was found that the addition of nanoparticles to the polymers improve their interaction with the glass grains in addition to increasing their ability to fill the big pores between the grains. After applying artificial ageing, some changes were observed in samples treated with both products SEM micrograph of the sample microscope was used to identify the capability of the consolidation materials to resist various environmental conditions (Fig.4f) showed sample treated with poly siloxane, exposing cracks of the resins. There was an appearance of many cracks on the surface of the polymer after the artificial ageing in addition to the lack of the polymer distribution uniformity on the surface. (Fig. 4g) the samples were treated with nano silica/polymer nanocomposites showed small aggregation of polymer with some pores on the surface of glass. (Fig.4h) showed sample was treated with Alumina /polymer nanocomposites small fine cracks were observed on the coating film but without any side effects on the film uniform and homogeneity. (Fig. 4i) showed sample was treated with silica/Alumina/ polymer nanocomposite that improve the stability of the consolidation compound microstructure under the influence of artificial ageing. According to the SEM results, SiO_2 / Al_2O_3 nanoparticles appeared to be the best nanomaterial on glass surface. They fill the polymer matrix, increase the ability of the polymer to penetrate the glass pores and form a homogeneous coating.

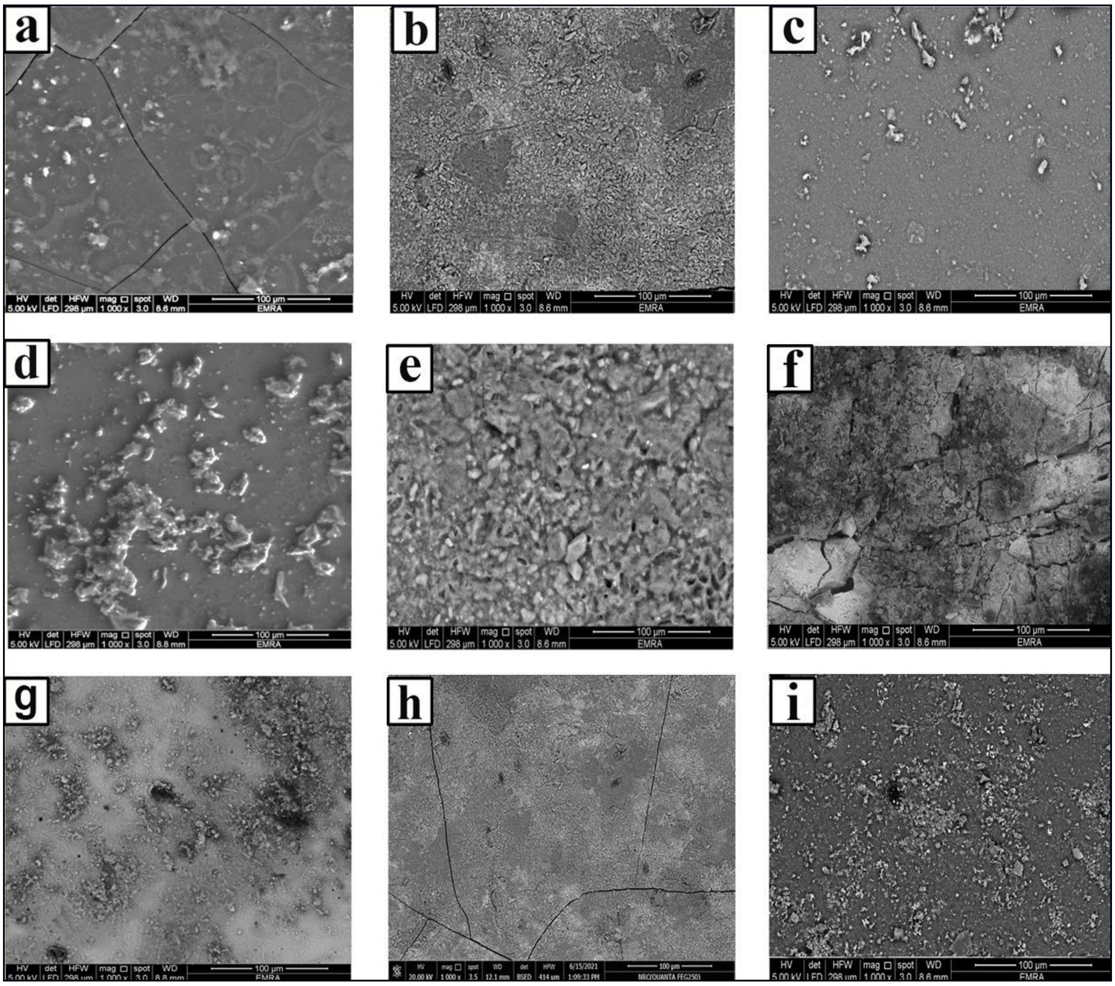

Figure 4. SEM micrographs of the untreated and treated glass samples and after artificial ageing at 1000x. (a) Untreated sample, (b) Silres BS-290 at 7% , (c) Nano Silica at 2% with Silres BS-290 at 7%, (d) Nano Alumina at 2% with Silres BS-290 at 7% , (e) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% , (f) Silres BS-290 at 7% after artificial ageing, (g) Nano Silica at 2% with Silres BS-290 at 7% after ageing, (h) Nano Alumina at 2% with Silres BS-290 at 7% after ageing, (I) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% after ageing.

3.5. Static Water Contact Angle

The results of the contact angle test (table 3) (figure. 5) were revealed that nanoparticles improved the hydrophobicity of polysiloxane. The Pure poly alkylsiloxane treatment had the ability to repel water, but it was found to be less hydrophobic than polyalkylsiloxane added to nanoparticles. Moreover, after treatment and artificial ageing SiO_2 / Al_2O_3 polymer nanocomposite attained the best contact angle values which give (130 °, 105º) before and after ageing. The maximum hydrophobic activity was determined by the chemical and physical characteristics of the polymer as well as the nanoscale roughness of the surface, which causes air to be trapped between the water droplet and the rough surface (Bico et al., 2002; De Ferri et al., 2011; Goswami et al,. 2011). Furthermore, the extremely low porosity of glass surface contributed to the surface being inherently more hydrophobic. Although nanoparticles help increase the hydrophobic character of the coating and also play an effective role in enhancing the polymer with self-protection properties, the hydrophobic action was primarily attributed to the polymer, not nanoparticles (Kumar, 2014).

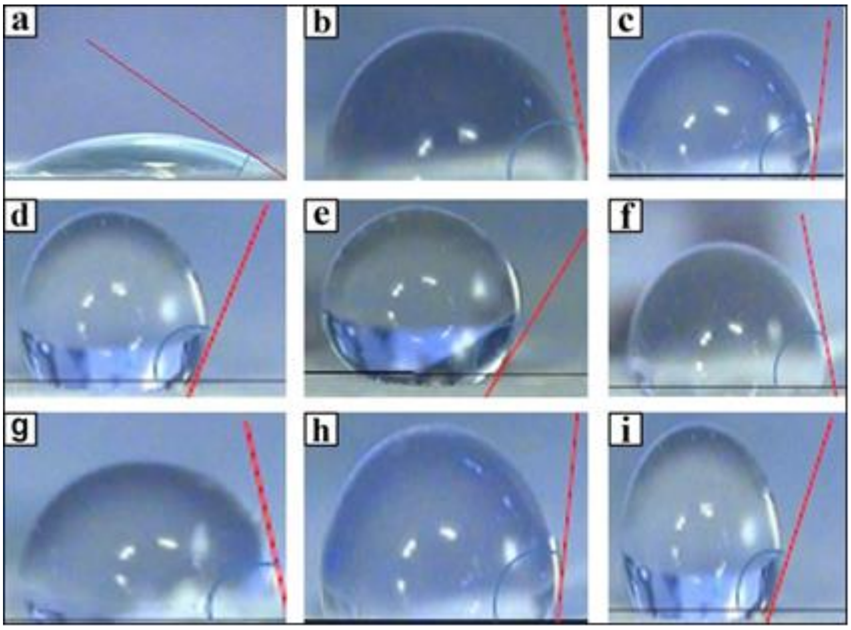

Table 3. Values of the Static Contact Angle (SCA) of the Studied Samples

Sample code	SCA (°)
A	12°
B	82°
C	100°
D	110°
E	130°
F	70°
G	86°
H	95°
I	105°

Figure 5. Static contact angle measurement of untreated glass samples, treated samples and after artificial ageing. (a) Untreated sample, (b) Silres BS-290 at 7% , (c) Nano Silica at 2% with Silres BS-290 at 7%, (d) Nano Alumina at 2% with Silres BS-290 at 7% , (e) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% , (f) Silres BS-290 at 7% after artificial ageing, (g) Nano Silica at 2% with Silres BS-290 at 7% after ageing, (h) Nano Alumina at 2% with Silres BS-290 at 7% after ageing, (I) Mixture of Nano Alumina and Nano silica 2% with Silres BS-290 at 7% after ageing.

3.6. Colorimetric Measurements

As esthetics and historic values are very important issues in conservation science, the color variations were measured before and after the application of the coatings to evaluate their aesthetic impact. Color alterations were expressed by the ΔE parameter which indicated the difference between each chromatic coordinate (ΔL*, Δa*, and Δb*). The color Differences ΔE, calculated by comparing the coated and the uncoated samples, were reported in Table 4. No significant changes are produced by the coatings for all the selected treatment materials, being ΔE < 4 a value normally accepted as a limit for the visual impact of surface treatments (European Environmental Agency, 2011; De Ferri et al., 2013).

Before and after exposure to artificial ageing, the covered glass samples are characterized by colorimetric measurements to assess any color changes produced by the ageing process. The sample treated with polysiloxane after ageing increase color change to (ΔE = 4.96) which indicates change in the naked eye. On the other hand, samples treated with nanocomposite treatment do not vary significantly after ageing and the ΔE values always remain < 4. The results show that the sample treated with silica / alumina /polymer nanocomposite give the best results after ageing (ΔE = 2.01). It is considered a very slight color change and the change is unclear to the unaided eye.

Table 4. Color change values of a treated sample before and after ageing

Applied Treatment Materials	ΔE^*_{ab} *Before ageing*
Silres BS-290	0.98
Silres BS-290 +SiO_2 Nano particles	1.98
Silres BS-290 +Al_2O_3 Nano particles	2.17
Silres BS-290 +Al_2O_3 SiO_2 +Nano particles	0.85
	After ageing
Silres BS-290	4.96
Silres BS-290 +SiO_2 Nano particles	3.29
Silres BS-290 +Al_2O_3 Nano particles	3.59
Silres BS-290 +Al_2O_3 SiO_2 +Nano particles	2.01

3.6. Measurement of Physical Properties

Density

It is clear from (table 5) that the nano-strengthening and protection compounds have improved the density values of the glass samples where the polysiloxane compound with nano-silica and nano-alumina give the highest density value of (3.52-3.49 g/cm^3) before and after ageing. This can be attributed to the fact that the nanoparticles filled the voids and pores in the surface of the glass. so the improvement in density values appeared.

3.7. Measurement of Mechanical Properties

Micro Hardness Test

The hardness test determines the extent of the material's ability to withstand scratching. The hardness is measured for untreated, treated and exposed glass samples with the aim of identifying the efficiency and ability of nanomaterials to improve mechanical properties and to determine the success of treated nanomaterials in resisting scratching of the surface. As shown in (table 5) The treated sample with silica / alumina /polymer nanocomposite is given the highest value (375-360 kg/mm^2) before and after ageing respectively, while the sample treated with polysiloxane with nano-silica gives a value of (364-352 kg/mm^2) on the other hand, the sample treated with polysiloxane with nano-Alumina gives a value of (354-334 kg/mm^2).

Table 5. Physical and Mechanical Properties of the Glass Samples before ageing (A) un treated sample, (B) silres BS-290 at 7%, (C) Nano silica at 2% with silres BS-290 at 7%, (D) Nano Alumina at 2% with silres BS-290 at 7%, (E) Mixture of Nano Alumina and Nano Silica 2% with silres BS-290 at 7% and after Ageing (F) Silres BS-290 at 7%, (G) Nano Silica at 2% with silres BS-290 at 7%, (H) Nano Alumina at 2% with Silres BS-290 at 7%, (I) Mixture of Nano Alumina and Nano Silica 2% with Silres BS-290 at 7%.

Sample code	**Density** (g/cm^3)	**Hardness (HV)** (kg/mm^2)
A	2.39	256
B	2.44	337
C	2.89	364
D	2.74	354
E	3.52	375
F	2.42	300
G	2.76	352
H	2.61	334
I	3.49	360

4. CONCLUSIONS

Silicon dioxide (SiO_2) and alumina oxide (Al_2O_3) nano particles are added to poly(alkyl siloxane) (Silres BS-290) to improve its physiochemical and mechanical properties and determine comparatively what the best materials are to use in the consolidation and protection of the archaeological glass. Samples treated with pure polymer and nanoparticles/polymer nanocomposites are tested under artificial ageing. The results show that the addition of nanoparticles to the silicon –based polymers improve the ability of polymers to consolidate and protect glass samples.

The results obtained by stereo and SEM microscopic investigation indicated that the mixture (SiO_2) and (Al_2O_3) nanoparticles is the best nanomaterial which fills the polymer matrix, increases the polymer ability to penetrate into glass surface and form a homogeneous coating. The samples treated with SiO_2 / Al_2O_3 / polymer nanocomposites show hydrophobic properties better than the samples treated with nano particles of silica and alumina individually with polymer. 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 show that the treatment by SiO_2 / Al_2O_3/polymer achieves the highest values. Physical properties for sample treated with SiO_2/Al_2O_3/polymer nanocomposite gives the best results in improving the property of density. Furthermore, the hardness test of sample (E) is given the highest results before and after ageing. Thus, this composition is considered the best consolidator material for glass objects. The study demonstrates that Silica and Alumina nanoparticles are suitable choices for enhancing polymers employed in the consolidation and protection of glass artefacts.

AUTHOR CONTRIBUTION

Rania A. Eloriby and Wael S. Mohamed conceived, designed and performed the experiments. Rania A. Eloriby analyzed data and prepared the original draft. Ahmed S. AlKaradawi revised the paper and contributed to the final editing.

ACKNOWLEDGMENTS

The authors would hereby like to acknowledge the Archaeologists in the Department of Antiquities of Fustat for their cooperation in brought the glass samples. Gratitude is also to National Research centre (NRC) team for their support. Thanks also are to the anonymous refereed for their critical reviews and constructed suggestions.

REFERENCES

Abd-Allah, R. (2012) Damage assessment and chemical characterization of glass objects excavated from Gadara, Northern Jordan. *Progress in Cultural Heritage Preservation*, Euromed, pp.278.

Abd-Allah, R. (2007) Stabilization and treatment of corroded glass objects displayed in the museum of Jordanian heritage. *Mediterranean Archaeology and Archaeometry*, Vol. 7, pp.19-28.

Abd-Allah, R. (2013) Chemical cleaning of soiled deposits and encrustations on archaeological glass: A diagnostic and practical study. *Journal of Cultural Heritage*, Vol. 14, No.2, pp.97-108.

Al Bawab, A., Al-Omari, R., Abd-Allah, R., Bozeya, A., Abu-Zurayk, R., and Odeh, F. (2018) The Application of a Modified Sol-Gel Silica Coating for the Protection of Corroded Roman Soda-Lime- Silica Glass: An Experimental and Analytical Study. 10th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Natural and Anthropogenic Hazards and Sustainable Preservation (Maria Koui, Fulvio Zezza, Dimitrios Kouis Editors) https://doi.org/10.1007/978-3-319-78093-1_19. *Springer International Publishing AG*, part of Springer Nature.

Aldosari, M., Darwish, S., Adam, M., Elmarzugi, N., and Ahmed, S. (2019) Using ZnO nanoparticles in fungal inhibition and self-protection of exposed marble columns in historic sites. *Archaeological and Anthropological Sciences*, Vol. 11, pp. 3407-3422.

Afifi, H., Hassan, R., and Menofy, S. (2021) An experimental study for consolidation of archaeological cartonnage Using Klucel G and chitosan, with nanocalcium hydroxide. *Scientific Culture*, Vol. 7, No. 2, pp. 49-68

Baglioni, P., Giorgi, R., and Chelazzi, D. (2012) Nano-materials for the conservation and preservation of movable and immovable Artworks. *International Journal of Heritage in the Digital Era* (Progress in Cultural Heritage Preservation - EUROMED 1(IS1), pp. 313-318.

Barberio, M., Veltri, S., Imbrogno, A., Stranges, F., Bonanno, A., and Antici, P. (2015) TiO2 and SiO2 nanoparticles film for cultural heritage: conservation and consolidation of ceramic artifacts. *Surface & Coatings Technology*, Vol.271, pp.174-180.

Bellendorf, P., Roemich, H., Gerlach, S., Mottner, P., López, E., and Wittstadt, K. (2010) Archaeological glass: The surface and beyond. Glass and Ceramics Conservation 2010: *Interim Meeting of the ICOM-CC Working Group*, pp.137-144.

Bico, J., Thiele, U., and Quéré, D. (2002) Wetting of textured surfaces. *Colloids Surf. A*, 206, pp.41–46.

Brill, R. H., (1975) Crizzling - A Problem in Glass Conservation." Conservation in Archaeology and the Applied Arts, *Stockholm Congress*, pp. 121-134.

Chatzigrigoriou, A., Karapanagiotis, I., and Poulios, I. (2020) Superhydrophobic Coatings Based on Siloxane Resin and Calcium Hydroxide Nanoparticles for Marble Protection. *Coatings*, Vol.10, pp.334-339

Chelazzi, D., Poggi, G., Jaidar, Y., Toccafondi, N., Giorgi, R., and Baglioni, P. (2013) Hydroxide nanoparticles for cultural heritage: Consolidation and protection of wall paintings and carbonate materials. *Journal of Colloids and Interface Science*, 392, pp. 42-49.

Dal Bianco, B., Bertoncello, R., Bouquillon, A., Dran, J.C., Milanese, L., Roehrs, S., Sada, C., Salomon, J., and Voltolina, S., (2008) Investigation on sol–gel silica coatings for the protection of ancient glass: interaction with glass surface and protection efficiency. *J Non-Cryst Solids,* 354, pp. 2983–2992

Darwish, S. (2013) Evaluation of the effectiveness of some consolidants used for the treatment of theXIXth century Egyptian cemetery wall painting. *International Journal of Conservation Science*, Vol. 4, pp.413-422.

Davison, S. (2006) Conservation and restoration of glass. *Butter worth- Heinemann*, Elsevier, p.228.

Davison, S., Newton, R.G. (2003) Conservation and Restoration of Glass, 1st ed. *Butterworth-Heinemann,* Oxford, pp.159.

De Ferri, L., Lottici, P., Lorenzi, A., Montenero, A., and Salvioli-Mariani, E. (2011) Study of silica nanoparticles – polysiloxane hydrophobic treatments for stone-based monument protection. *Journal of Cultural Heritage*, Vol. 12, pp 356-363.

De Ferri, L., Lottici,P., Lorenzi, A., Montenero, A., and Vezzalini, G. (2013) Hybrid sol–gel based coatings for the protection of historical window glass. *Journal of Sol-Gel Science and Technology*, Vol.66, pp. 253-263.

De Bardi M et al (2014) Sol–gel silica coating for potash–lime– silica stained glass: applicability and protective effect. *J Non-Cryst Solids,* 390, pp.45–50.

Domenech-Carbo´, M.T., Domenech-Carbo, A., Osete-Cortina, L., and Saurı´-Peris, M.C. (2006) Astudy on Corrosion Processes of Archaeological Glass from the Valencian Region (Spain) and its Consolidation Treatment. *Microchimica Acta154,* pp.123-142.

El-Badry, KH., and El-Betal, H. (1973) The refractive index and density of some borosilicate glasses and the mixed alkali effect. *J.Chem.*, Vol.5. pp.45-56.

El-Shamy, T., and Douglas, R. (1972) Kinetics of the reaction of water with glass. *GlassTechnology*,Vol. 13, pp.77-80

Ershad-Langroudi, A., Mai, C., Vigier, G., Vassoille, R. (1997) Hydrophobic hybrid inorganic–organic thin film prepared by sol–gel process for glass protection and strengthening applications. *J. Appl. Polym. Sci,* Vol.65, pp. 2387–2393

European Environmental Agency-Technical report | No 12/2011., (2011) Air quality in Europe-report, Ed Publication Office of the European Union, Luxemburg.

Fitz, S. (1991) Glass objects:causes,mechanisms and measurement of damage. *Science Technology and European Cultural Heritage*, Butterworth-Heinemann, pp. 180-189

Goswami, D., Medda, S., and De, G. (2011) Super hydrophobic Films on Glass Surface Derived from Trimethylsilanized Silica Gel Nanoparticles. *Journal Applied Materials Interfaces*, Vol.9, pp 3440-3447.

Helmi, F., and Hefni, Y. (2016) Using nano composites in the consolidation and protection of sandstone. *International Journal of conservation science*, Vol.7, pp.29-40.

Helmi, F., Abu Ayana, Y., and Omar, S. (2019) Nano- copper composite conservation of an Egyptian bronze sacred Ibis birid statue: case study. *Mediterranean Archaeology and Archaeometry*, Vol. 19, No 1, pp. 61-69.

Horie, C., V. (1987) Materials for conservation. *Butterworth*, London.

Holubová, B., Zlámalová Cilova, Z., Kucerova, I., and Zlamal, M. (2015) Weatherability of hybrid organic–inorganic silica protective coatings on glass. *Progress in Organic Coatings*, Vol.88, pp.172-180.

Ibrahim, M., Mohamed, W., and Mohamed, H. (2020) Comparative and Experimental Studies for Evaluation of Paraloid B-72 in Traditional and Nano Forms for Joining of Pottery Samples. *Journal of Nano Research*, Vol. 61, pp. 61-71.

Ibrahim, M., Mohamed, W., and Mohamed, H. (2021) experimental study for evaluation of paraloid® b72 and its nanocomposite with nano TIO2 and nano ZNO for consolidation of pottery samples, *Scientific culture*, Vol. 7, No. 2, pp. 101-111

Karapanagiotis, I., Manoudis, P., Savva, A., and Panayiotou, C. (2012) Superhydrophobic polymer-particle composite films produced using various particle sizes. *Surface and Interface Analysis*, Vol.44, pp.870–875.

Kumar, A., Kashyap, K., Liao, K., Hou, M., and Yeh, J. (2014) Super hydrophobic/Super hydrophilic Transparent Nanostructured Glass Fabricated by Wet Etching. *Proceedings of the 9th IEEE International Conference on Nano/Micro Engineered and Molecular Systems,* April 2014, pp.113-116

Kunicki-goldfinger, J. (2008) Unstable historic glass symptoms, causes, mechanisms and conservation. *Reviews in Conservation*, vol.9, pp.47-60.

Majérus, O., Patrice, L., Biron, I., Alloteau, F., Narayanasamy, S., and Caurant, D. (2020) Glass alteration in atmospheric conditions: crossing perspectives from cultural heritage, glass industry, and nuclear waste management. *npj Materials Degradation*, vol.27, pp.1-16.

Malzbender, J., Toonder, J., Balkenende, A., and With, G. (2002) Measuring mechanical of coatings: a methodology applied to nano – particle-filled sol-gel coatings on glass. *Materials Science Engineering,* Published by Elsevier Science, pp.47-103.

Manoudis, P., Papadopoulou, S., Karapanagiotis, I., Tsakalof, A., Zuburtikudis, I., and Panayiotou, C. (2007) Polymer-Silica nanoparticles composite films as protective coatings for stone-based monuments. *Journal of Physics:* Conference Series. 61. 1361. 10.1088/1742-6596/61/1/269.

Manoudis, P.N., Karapanagiotis, I., Tsakalof, A., Zuburtikudis, I., Kolinkeová, B., and Panayiotou,C. (2009) Superhydrophobic films for the protection of outdoor cultural heritage assets. *Appl. Phys. A*, Vol. 97, pp.351–360

Manoudis, P.N, Gemenetzis, D., and Karapanagiotis, I. (2017) **A** comparative study of the wetting properties of a superhydrophobic siloxane material and rose petal. *Scientific Culture*, Vol. 3, No.2, pp. 7-12 DOI: 10.5281/zenodo.438182

Newton, R. (1974) The deterioration and conservation of painted glass, Acritical bibliography and Three Research Papers, *Oxaford university press*, London, pp.9-68.

Papadopoulos, N., and Drosou, C. (2012) Influence of weather conditions on glass properties. *Journal of the University of Chemical Technology,* Vol.47, pp.429-439.

Panagopoulou, A., Lampakis, D., Christophilos, D., Beltsios, K., and Ganetsos, Th. (2018) technological examination of Iznik ceramics by SEM-EDX, RAMAN, XRD, PLM: a case study. *Scientific culture*, Vol. 4, No. 3, pp. 27-33.

Schottner, G., (2001) Hybrid sol–gel-derived polymers: applications of multifunctional materials. *Chem. Mater*, Vol.13, pp.3422–3435.

Schreiner, M. (2004) Corrosion of historic glass and enamels, *comprehensive analytical chemistry*, chapter 16, pp.713-754.

Sterpenich, J., Libourel, G., (2006) Water diffusion in silicate glasses under natural weathering conditions: evidence from buried medieval stained glasses. *Journal of Non- Crystalline Solids,* 352, pp.5446-5451.

Tournie, A., Ricciardi, P., and Colomban, P. (2008) Glass corrosion mechanisms: A multiscale analysis. *Solid State Ionics*, Vol. 179, pp.2142–2154.

Waked, A. (2011) Nano materials applications for conservation of cultural heritage. *Structural Repairs and Maintenance of Heritage Architecture XII,* Vol .118, pp.577-588

Wang, S-D., and Luo, S.-S. (2012) Fabrication of transparent super hydrophobic silica-based film on a glass substrate, *Appl. Surf. Sci*, 258, pp.5443–5450.

Zacharias, N., Palamara, E., Kordali, R., and Muros, V. (2020) Archaeological glass corrosion studies: composition, environment and content, Scientific *Culture*, Vol. 6, No. 3, pp. 53-67.