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EXPERIMENTAL STUDY TO EVALUATE THE EFFICIENCY OF SOME GAP FILLING MATERIALS OF ARCHAEOLOGICAL POTTERY

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Abstract

Gap filling is considered one of essential stages in the restoration of archaeological pottery. Gap filling helps in supporting the pottery object, where the missing fragment represents the weakest part. Therefore, the materials used in the gap filling must be identified, studied, and tested before application to reach the best pastes that can be used in this process. Three pastes were prepared to fill the gaps of some pottery fragments. These pastes consist mainly of powder of new pottery (grog) to complete the archaeological pottery. In addition, other mixtures, such as dental plaster, glass micro-balloons and Metylan Dufix are used. After the final drying, these pastes were exposed to artificial ageing for 100 hours. The workability of the gap filling materials and the degree of shrinkage were determined. Besides, some tests have been done such as measuring the colour change and physical and mechanical properties to evaluate the efficiency of these pastes after artificial ageing. Through the results of the various tests, it was found that the mixture of grog, dental plaster, and Primal AC33 is the best paste. The workability of this paste was very appropriate; hence, it remained enough period for shaping and polishing. Additionally, this paste gave the lowest shrinkage rate (3.3%), the lowest total colour change (0.81), and the highest degree of compressive strength (2921 N/mm^2). Accordingly, it is recommended to use this paste, which gave the best results in the restoration of the archaeological pottery in excavations and museums.

Keywords: pottery, gap filling, colour change, physical properties, compressive strength

1. Introduction

The importance of the gap filling process appears in the preservation of the archaeological pottery from any erosion of the edges of the missing part [1]. The pressure of the soil above the pottery objects has a very dangerous effect, which eventually leads to the breakage and destruction of these objects within the burial environment, which ultimately requires intervention to complete the missing parts [2, 3]. The use of gap filling materials is well established in pottery

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conservation and restoration [4]. The gap filling method is still a manual procedure that needs experience from the restorers. The materials used in filling the gaps and cracks can be considered as filler materials mixed with an adhesive [5]. Gap filling has been done primarily for aesthetic reasons, in addition to providing support for the missing parts from the body of the archaeological pottery [6]. The gap filling must respect two requisites: homogeneity and recognisability of the intervention. This last may be obtained by colouring the added part with a lighter colour than that of the original pottery [7, 8]. Additionally, any type of material used for gap filling work should have characteristics that are similar, both mechanically and chemically, to the original body [9]. The materials used to complete the archaeological pottery must be characterized by reversibility and chromatic stability [10]. Choosing the material that was used to fill the missing parts depends on the shape of the pottery object and the technique used to apply the filling material [11]. The materials and methods used for gap filling vary based on the type of gap (size and location) and the environmental conditions (interior, exterior) [8].

The gap filling can be applied using a suitable filling material, according to the state of the pottery object [12]. This process is essential to reinforce the pottery objects for the museum display [2, 13]. The materials used in the gap filling vary between dental plaster and acrylic resins [12]. Dental plaster is an ideal integrant for pottery because it is not hydroscopic, and as an inert material does not attract or release soluble salts into the pottery objects. Dental plaster can be mixed with grog to form a suitable mixture to complete the archaeological pottery [14]. Dental plaster consists of calcium sulphate hemihydrate ($CaSO_4 \cdot 2H_2O$). The dental plaster manufacturing process depends on rapid and direct heating of the calcium sulphate dihydrate in open air, thus resulting in a powder with irregular porous particles [15, 16]. The differences in the particle's shape, size and distribution affect the water/powder ratio and consequently the physical properties of the dental plaster [17]. Additionally, plaster filler is suitable for museum conditions, i.e. when not interacting with the object, because plaster is stable enough and resistant in these situations [8]. Primal AC33 is considered as a product made and commercialized by Rohm and Haas, widely used as an adhesive agent for art works due to its excellent properties of flexibility, transparency and ease of application [18]. Primal AC33 can be used as binder with dental plaster, where it increases the hardness of plaster [19].

Metylan Dufix can be used to reconstruct the archaeology pottery. It is considered as one of the filling gaps materials, its composition is based on calcium sulphate with methylcellulose and synthetic resin. Additionally, this material is mixed with water; it is considered one of the stable materials with low shrinkage and its degree of expansion is similar to that of pottery [20]. Metylan Dufix is characterized as easy to use, cures without cracks, thick layers that can be applied in one-step and can be coloured. According to the technical datasheet, Metylan Dufix is considered ideal for filling cracks, holes, levelling uneven surfaces [https://businessdocbox.com/Construction/70848499-Metylan-dufix-technical-data-sheet-crack-filler.html, access on 1.07.2021]. Glass micro-balloons can also be used to complete the missing parts of the archaeological pottery [21]. In addition, this material is characterized by its low weight and decrease in density [22]. As the glass micro-balloons will not react with pottery objects, they may have a wide range of applications in conjunction with materials commonly used by conservators [23]. Paraloid B-72 can also be used with glass micro-balloon because it gave good results in terms of hardness and durability for different weather conditions [24]. Powder of new pottery is one of the best fillers that used to complete pottery, due to the similarity between its properties and the original body. Grog can be used with an adhesive such as Primal AC33 to form a suitable paste for the gap filling process [2]. Grog can be added to Paraloid B72 to achieve a similar texture for the filling of missing areas [25, 26]. The current investigation aimed to evaluate the effectiveness of gap filling materials that were used to complete the missing parts for the archaeological pottery.

2. Materials and methods

2.1. Preparation of pastes

The laboratory experiments were carried out on three different pastes. Experimental pastes were prepared at the laboratory of the Conservation Department, Faculty of Archaeology, Cairo University, Egypt. Paste (1) consists of grog, dental plaster and Primal AC33 (15%) in water. It was prepared by mixing grog with dental plaster with a ratio of 1:1 in Primal AC33. Paste (2) consists of grog, glass micro-balloons and Paraloid B72 (10%) in acetone. It was prepared by mixing grog with glass micro-balloons with a ratio of 1:1 in Paraloid B72. Paste (3) consists of grog, Metylan Dufix and distilled water. It was prepared by mixing grog with Metylan Dufix with a ratio of 1:1 in distilled water. The pastes were moulded into cubic shapes with a 3 cm edge for cubes. The samples were left to dry completely at room temperature for one month. The pastes 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 a UV lamp by (268 UVA Optimized/low profile sensor heads). The condition of the lamp as follows (power: 600W, wavelength of radiation: 400 nanometres, distance between samples and lamp: 15cm) [27].

2.2. Methods of testing and analysis

2.2.1. Determination of pastes workability

The different properties of the selected gap-filling materials in the form of cubes are studied. These properties included dry time and the extent of its ability of shaping and polishing after the completion of the drying and hardening process.

2.2.2. Measurement of the degree of shrinkage

The pastes are prepared then poured into moulds with known dimensions then left to dry completely until stability of dimensions. The dry length was measured after a month of preparing the samples. Additionally, the degree of shrinkage for each paste was measured by comparing the length after complete drying with the original length of the moulds used.

2.2.3. Measurement of colour change

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

2.2.4. 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 equation (1):

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

where: W is the original weight in g and V is the volume in cm^3 [28].

Water Absorption (W.A) in % was determined in equation (2):

$$W.A = \frac{W_2 - W_1}{W_1} X\ 100 = \% \tag{2}$$

where: W_1 and W_2 are dry and wet weight in g [29].

Apparent porosity (A.P) in % was defined in equation (3):

$$A.P = \frac{W_2 - W_1}{V} X\ 100 = \% \tag{3}$$

where: W_1 and W_2 is dry and wet weight in g and V is the volume in cm^3 [30].

2.2.5. 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: 5.0mm, preload: 1.0N). The test was conducted at the National Institute of Standards, Al-haram, Giza, Egypt.

3. Results and discussion

3.1. Determination of pastes workability

The paste (1), made of grog and dental plaster with Primal AC33, is characterized by a working time sufficient for shaping and polishing, as it hardens in a period ranging from 20 to 25 minutes. Thus, there is enough time for the restorer to perform the filling process. The period of drying also depends on the percentage of plaster and Primal added to the powder of new pottery [14]. The use of grog reduced the high strength of the dental plaster and thus made it more suitable, especially when there was no need for structural support. The addition of the grog also created a surface appearance sympathetic to the original [25] (Figure 1). In addition, the paste after drying is characterized by medium weight (33.13 g). The paste (2) that consists of grog and glass micro-balloon with Paraloid B72 as an adhesive, is characterized by a drying period ranging between 15 to 20 minutes. Therefore, it is considered a sufficient period for the possibility of completing the missing parts. Besides, the paste after drying is characterized by low weight (15.14 g). The paste (3) that included in its composition grog and Metylan Dufix has a drying period of 60 minutes. It can be coloured with some acrylic colours. The paste can be easily removed using warm water. Additionally, the paste after drying is characterized by high weight (34.88 g).

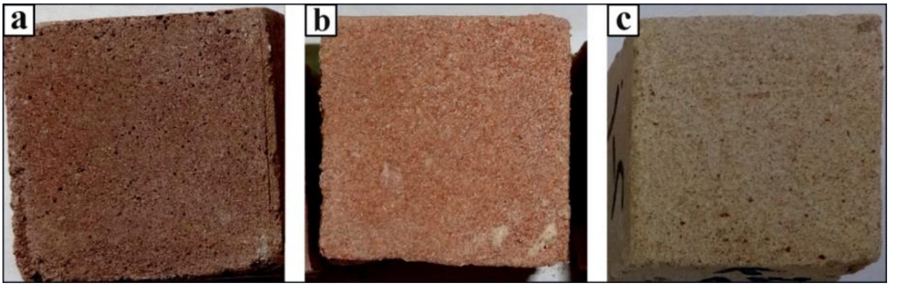

Figure 1. The surface appearance of pastes: (a) paste 1, (b) paste 2, (c) paste 3.

Table 1. Shrinkage measurement of the gap filling materials after complete drying.

Samples	Wet length (cm)	Dry length (cm)	Shrinkage degree (%)
Paste (1)	3	2.9	3.3
Paste (2)	3	2.8	6.6
Paste (3)	3	2.7	10

3.2. Measurement of the degree of shrinkage

The degree of shrinkage of the pastes was measured by calculating the length changes before and after complete drying. It is clear from Table 1 that the different gap filling materials have a different degree of shrinkage after drying, as a result of the variation in their proportions and components. The paste (1) shows a small degree of shrinkage due to the use of dental plaster and Primal AC33, which is characterized by a low shrinking level after drying. Paste (2) exhibits a medium shrinkage degree compared to other ones. It can be supposed that the spherical shape of the glass micro-balloons causes a medium shrinkage.

The bubbles are easily mixed into resins [23]. Lastly, the paste (3) has a high shrinkage degree due to the use of Metylan Dufix, which shrinks by a large percentage after complete drying. The high shrinkage is caused by the evaporation of water from this paste [19].

3.3. Measurement of colour change

The measurement of colour change was carried out to evaluate the variation of colour before and after the artificial ageing. Therefore, three-dimensional colorimetric system L*a*b* (also known under the name of CIELAB) was used [31]. The total colour differences (ΔE*), which express the value of the full chromatic alteration, were calculated according to equation (4) [32]:

$$\Delta E^* = ([\Delta l^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2)^{1/2} \tag{4}$$

where [Δl*], [Δa*] and [Δb*] are the differences in the respective values before and after artificial ageing.

Table 2. Colour change values of the pastes after artificial ageing.

Samples	Paste (1)				Paste (2)				Paste (3)			
	Colour changes				Colour changes				Colour changes			
	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
Before ageing	60.79	7.10	8.17	-	66.68	11.84	23.22	-	57.88	8.89	11.02	-
After artificial ageing	62.04	6.12	7.41	1.67	66.20	10.43	18.92	4.55	67.00	6.79	9.05	9.56

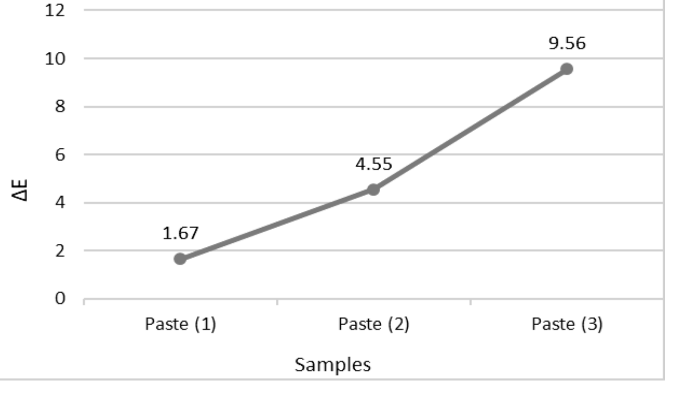

Figure 2. Values of total colour change (ΔE*) of the pastes.

The value of ΔE* gives indications about the perception by human eye of a surface colour change. A value of 3 for ΔE* is considered as threshold to establish if colour change is perceptible by human eye [33]. It is clear from Table 2 and Figure 2 that the selected materials showed a change in the total colour as a result of exposure to thermal and light ageing processes, with an increasing values ranging from paste (1) to paste (3). In fact, the paste (1) shows a colour change value of less than 3 (ΔE^* = 1.67), hence not noticeable by naked eye. The paste (2) exhibits a colour change value greater than 3 (ΔE^* = 4.55), so this is a noticeable colour change that may be appreciated by naked eye. Lastly, the paste (3) shows a high colour change value (ΔE^* = 9.65), that is certainly appreciated by naked eye and could distort the optical properties of the surface.

3.4. Measurement of physical properties

Moisture is considered the most dangerous deterioration factor for artefacts, so gap filling materials must be able to resist the damage caused by water and reduce water penetration [34]. Physical tests were performed to measure the ratio of physical change of the samples in comparison with their original state before artificial ageing [35]. The results from Table 3 and Figure 3 show that paste (1) achieves the lowest water absorption, in respect to the other ones before ageing, but after the ageing, it increased to 5.07%. The use of dental plaster and primal AC33 helped to increase the cohesion. While the porosity of this paste shows the lowest value 5.88%. However, after artificial ageing, this value increased to 7.12%. In addition, this paste has a density of 1.43 g/cm^3 that decreased to 1.35 g /cm^3 after ageing.

Table 3. Physical properties of the pastes before and after artificial ageing.

Samples	Paste (1)			Paste (2)			Paste (3)		
	Water absorption (%)	Porosity (%)	Density (g/cm^3)	Water absorption (%)	Porosity (%)	Density (g/cm^3)	Water absorption (%)	Porosity (%)	Density (g/cm^3)
Before ageing	4.11	5.88	1.43	13.69	9.44	0.69	19.29	32.47	1.68
After artificial ageing	5.07	7.12	1.35	18.97	12.89	0.58	32.31	49.12	1.25

In the case of paste (2) the water absorption undergoes a significant increase as a consequence of ageing ranging from 13.69% to 18.97%. A similar increase can be observed for the porosity values of this paste after artificial ageing. The density of this paste is low (0.69 g/cm^3) due to its low weight. After ageing, density decreases to 0.58 g/cm^3. Therefore, the use of glass micro-balloon filler is not recommended to support structural weight in the case of the very large and heavy objects [21]. Paste (3) exhibits the highest water absorption rate before ageing, moreover after ageing this percentage increased significantly to 32.31%. This is due to the use of Metylan Dufix, which is characterized by high water absorption. Further, the porosity of this paste has high value (32.47%) and it increases to 49.12% after artificial ageing. Lastly, the density of this paste decreases from 1.68 g/cm^3 to 1.25 g/cm^3 as a consequence of ageing.

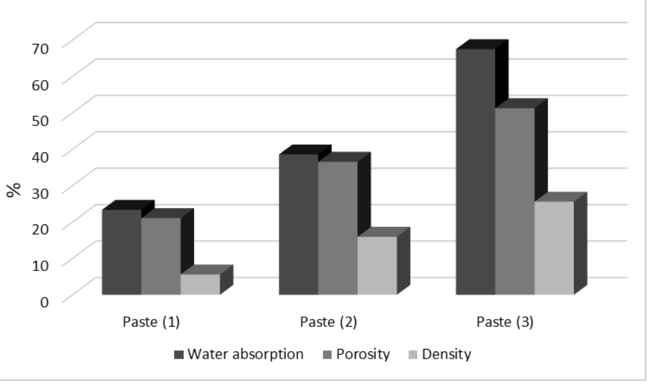

Figure 3. Percentage decrease in the physical tests due to ageing.

3.5. Measurement of compressive strength

The obtained data show that paste (1) achieved the highest resistance to compressive strength before ageing (2921 N/mm^2), but after the ageing it decreased to 2800 N/mm^2 (Table 4). Paste (2) also has a high resistance before ageing (2473 N/mm^2), but this value decreases after ageing (2058 N/mm^2). At last, paste (3) exhibits the lowest resistance before ageing (1752 N/mm^2), and after ageing it decreases significantly reaching the value of 204 N/mm^2.

Table 4. Results of the compressive strength test (N/mm^2).

Samples	Paste (1)	Paste (2)	Paste (3)
Before ageing	2921	2473	1752
After artificial ageing	2800	2058	204

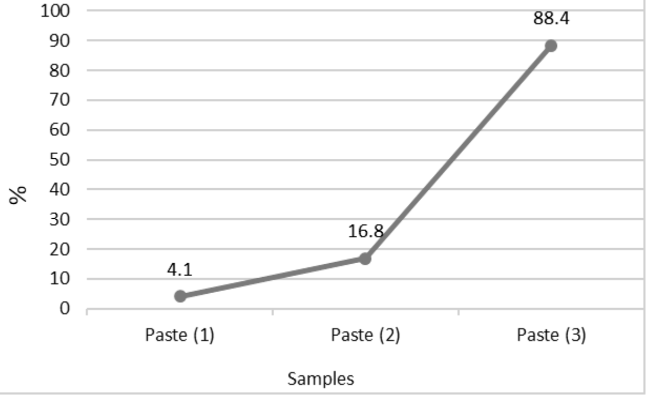

Figure 4. Percentage decrease in compressive strength as a consequence of ageing.

The results show that the paste (1) is more resistant having the highest compressive strength and that this parameter undergoes a little decrease (4.1%) due to ageing. Hence, this paste is considered one of the best materials that achieved excellent results after artificial ageing [16]. Paste (2) has a little lower compressive strength in respect to paste (1) and its value decreases of 16.8% as a consequence of ageing Paste (2) can be considered a good gap filling material that isn't much affected by ageing. On the contrary, paste (3) compressive strength is greatly affected by the artificial ageing; in fact, this parameter undergoes a decrease of 88.4%. Therefore paste (3) seems not suitable as material for gap filling (Figure 4).

4. Conclusions

Pottery artefacts suffer from various forms of damage, the most important of which is the loss of some parts from the body. It is clear from the obtained results that paste (1) is one of the best mixtures that can be used in the restoration of the archaeological pottery. The paste (1) is characterized by appropriate workability to a certain extent and remains sufficient for shaping because it hardens in a period ranging from 20 to 25 minutes. Besides, this paste showed the lowest value of shrinkage. The total colour difference ΔE^* of paste (1) has the lowest value after ageing if compared to those of the paste (2 and 3). The results of physical property measurements for paste (1) before and after artificial ageing also showed the best results in terms of water absorption, porosity, and density. Additionally, the mechanical properties revealed that paste (1) exhibited a low decrease in compressive strength after ageing (4.1%). On the other hand, paste (3) showed a high decrease in compressive strength value (88.4%). In general, the results of all tests showed that paste (1) gave the best results in gap filling. So, it is recommended in the future to use this paste in the restoration process of the archaeological pottery and ceramic materials. These results may improve the conservation procedures commonly used in museums and excavation sites.

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