Short communication

Influence of acrylic coatings on the interfacial, physical, and mechanical properties of stone-based monuments

M.K. Khallaf a, A.A. El-Midany b,∗, S.E. El-Mofty b

a Faculty of Archaeology, Fayoum University, Fayoum, Egypt
b Mining, Petroleum, and Metallurgy Department, Faculty of Engineering, Cairo University, Cairo, Egypt

ARTICLE INFO

Article history:
Received 5 November 2009
Received in revised form 28 June 2011
Accepted 29 June 2011

Keywords:
Acrylic
Limestone
Sandstone
Conservation
Interfacial interaction
Adhesion

ABSTRACT

Conservation of historical buildings is an important issue. The environmental conditions seriously affect the monumental stones. Although different coating materials were tested, the polymeric materials have been showing the most promising results for protection of archeological stones. Therefore, in the current study, the acrylic polymer was used for conservation of monuments made of sandstone and limestone. The adsorption of the acrylic polymer onto both stones was analyzed and the durability of the coatings under different environmental conditions was tested and simulated by artificial aging. Moreover, the mechanism of polymer–stone interactions was elucidated by interfacial characterization techniques.

The results showed that the adsorption of polymer onto either stones is physical as shown by Fourier transform infra-red (FTIR) and electrokinetic measurements. In addition, the presence of polymer coating shows a significant improvement in physical and mechanical properties of the treated stones, e.g., increase in bulk density from 1.9 to 2.3 g/cm3 and decrease in porosity from 15.8% to 2.7% as well as the noticeable increase in compressive strength. All these measures indicated the suitability of acrylic polymer for conservation of either stones.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Egypt is one of the invaluable historical places. It represents different targets of humanity along thousand of years from different civilizations. Nevertheless, the historical buildings are suffering from various environmental conditions. Several approaches have been addressed, by local and international experts, to protect them. The protection of the cultural heritage buildings and monuments by surface treatment with polymers is a common practice due to their ability to form a protective layer on the monumental surface as well as to control the transport of different fluids from the surface to monument interior [1–6]. For example, polymeric membranes can selectively regulate the transport of the corrosive species (i.e., CO2 and SO2) from the surroundings to the surface of the stones [7–11]. The failure of some of these treatments was referred to the monument surface deterioration and/or coating-layer/stone interaction. The improper interaction leads to damage of the surface layer and in some cases to remove the coloring and textural details on the monument surface [12–16].

Since at least the early 1960s, acrylic resins were used for conservation purposes. Poly methyl methacrylate (PMMA) and polybromide methacrylate (PBMA) were actually used for consolidation and protection not only on museum objects but also on monuments [17]. Acrylic polymer has several advantages such as its good solubility in several solvents, transparency, good adhesive power, and low rigidity of the polymer at room temperature.

In some cases, the acrylic was used as a “first aid” reversible interventions over badly deteriorated carved surfaces until more in-depth consolidation can be undertaken. In addition, acrylic polymer was used for the conservation of mural paintings such as early extensive treatment the early 14th century marble architrave of the Siena Cathedral by Tino da Camaino [18]. It is worth to mention that the polymer coating appeared, after almost twenty years, quite satisfactory [19]. On the other hand, conservative treatments with acrylic resins have been reported for wood, paper, mosaics, pigments, lacquer wares, amber, fossils, ceramics, glass and stones [20–25].

Recently, water-repellent polymers are widely used in conservation processes. Their use increases the building materials durability and improves the substrate cleanliness. The examples of water problems, that affect the monumental stones, are water expansion and transport of salt, contaminants to the substrate, and solubilization of atmospheric chemicals such as; sulfates, nitrates, chloride, and carbon dioxide. The salts, solubilized chemicals, and contaminants have serious negative effects on the surface textures by causing sanding, pitting, or a weathered appearance [26–28].

∗ Corresponding author.
E-mail address: aelmidany@gmail.com (A.A. El-Midany).

0300-9440/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2011.06.021
2.1. Therefore, the present study aims at investigating the interaction of methylacrylate–ethylmethacrylate binary copolymer with the monument stones (sandstone and limestone). The characterization of the stones before and after the interaction was conducted using zeta potential, Fourier transform infra-red (FTIR), polarizing microscopic and scanning electron microscope (SEM) to elucidate the nature and mechanism of adsorption. In addition, the behaviour of the coating layer under different artificial environmental conditions was investigated. Physical and mechanical properties, before and after treatment, with and without the artificial aging were determined.

2. Experimental

2.1. Materials

2.1.1. Studied samples and sites

The sandstone and limestone samples were carefully picked up from the fallen fragments of Ramesseum temple and Horemheb tomb, Figs. 1 and 2, respectively.

The Ramesseum temple belongs to Pharaoh Ramesses-II. It is located in the Theban necropolis in Upper Egypt, across the River Nile from the modern city of Luxor. The design of Ramesses’s mortuary temple abides by the standard canons of New Kingdom temple architecture. Oriented northwest and southeast, the temple itself comprised two stone pylons (gateways, some 60 m wide), one after the other, each mechanism into a courtyard. Beyond the second courtyard, at the centre of the complex, was a covered 48-column hypostyle hall, surrounding the inner sanctuary, Fig. 1.

On the other hand, Horemheb tomb at Saqqara was excavated in the 1970s. The tomb dates to the time of Tutankhamen when Horemheb was an army leader. The tomb was later used for the burial of Horemheb’s wife, Queen Mutnedjemet. The tomb is about 48 m long and 15 m wide. The superstructure consists of a fore-court, a pylon, an outer courtyard, a statue room flanked by two storerooms, an inner courtyard, and three offering-chapels, Fig. 2 [29].

2.1.2. Chemicals

The acrylic polymer, Primal AC33, is binary copolymers of methylacrylate–ethylmethacrylate (MA/EMA), which was diluted with distilled water to get a concentration of 3%.

2.2. Methods

2.2.1. Microscopic examination

Minerals characteristics as well as grain size were investigated by mineralogical examination of hand-picked samples. Thin sections were used for identification of minerals under polarizing microscope.

2.2.2. X-ray diffraction (XRD)

Identification of the mineral composition of the samples was conducted by X-ray diffraction patterns, using A “Philips” X-ray diffractometer (PW 1010). The patterns were run with Ni-filtered copper radiation (\(\lambda = 1.5404 \text{Å}\)) at 30 kV and 10 mA. The scanning was limited from 2\(\theta\) = 1 to 2\(\theta\) = 80° range.

2.2.3. Scanning electron microscope (SEM)

Scanning electron microscope, Philips XL-20, was used to determine the morphology of the particles, voids and weathering status of the particles, and cracks of coating after particle treatment with polymer.

2.2.4. Artificial aging and physical properties

These tests aim at simulating the actual environmental deteriorating conditions and at quantifying the durability of the treatments. Three types of weathering, mentioned below, were
2.2.4.4. against strength cycles conducted sequentially and termed as “artificial aging”. In addition, bulk density, porosity, water absorption as well as compressive and tensile strength were determined before and after treatment with polymers. In each test, three treated-samples were compared against three untreated-samples. All tests were applied on stone samples measuring 5 cm × 5 cm × 5 cm [30].

2.2.4.1. Wet-dry cycles. The test was used to find the effect of water on the rock by trying to simulate the climatic change from sunny to wet rainy weather. Thus, this test consists of 40 cycles of immersion and drying as follows: 16 h of total immersion in distilled water then 8 h in an oven at 60 °C.

2.2.4.2. Salt crystallization weathering. The samples were subjected to cycles of immersion in a saturated Na₂SO₄ solution for 4 h followed by 28 h of exposure to air in normal room conditions (25 °C and 40% R.H.) then 16 h in an oven at 60 °C.

2.2.4.3. Acid water weathering. This test was used to evaluate the effect of acidity by performing 30 cycles using H₂SO₄ (3%) then 20 cycles using H₂SO₄ (5%).

2.2.4.4. Mechanical properties. The measurement of compression strength was carried out, using an Amsler compression-testing machine, three weeks after treating samples with polymer. The average values of compression strength were recorded. The tensile strength was evaluated using the indirect tension test (Brazilian test) on cylindrical specimens [31]. Experiments were performed based on the International Society of Rock Mechanics (ISRM) guidelines, where each specimen was mounted in curved jaws and loaded under a constant load rate of 200 N/s until failure.

2.2.5. Electrophoretic measurements

0.1 g of ground mineral sample was added to 100 ml distilled water. The suspension was agitated using magnetic stirrer for 15 min during which the pH was adjusted, followed by 15 min of conditioning after adding polymer at the desired dosage. Then, the supernatant was transferred into a standard cuvette for zeta potential measurement using a Brookhaven ZetaPlus Zeta Potential Analyzer. Solution temperature was maintained at 25 °C. Ten measurements were taken and the average was reported as the measured zeta potential.

2.2.6. Fourier transform infrared (FTIR)

FTIR spectra were collected on FTIR spectrophotometer, PerkinElmer, on the range of 400–4000 cm⁻¹ using resolution 4 and 32 scans. The acrylic mix with sandstone and limestone (which are completely opaque samples) were done using HATR (horizontal attenuated total reflectance) accessory using a Zn–Se plate, 45° angle in the range of 650–4000 cm⁻¹ using resolution 4 and 32 scans.

3. Results and discussion

3.1. Polarizing microscope observations

The limestone sample, Fig. 3(a), consists mainly of fine-grained calcite crystals in addition to iron oxides, quartz, clay minerals and fossils. On the other hand, the sandstone sample, Fig. 3(b), includes white grains of crystalline silica in addition to clay minerals such as kaolinite and feldspars.

3.2. X-ray diffraction (XRD)

Fig. 4 shows the XRD patterns of the sandstone and limestone samples. It is clear that the sandstone is mainly quartz with traces of kaolinite and feldspar. On the other hand, the limestone consists mainly of calcite associated with dolomite and quartz as impurities, Fig. 4. These patterns indicated that the impurities in both samples are minor, which is not expected to play a significant role during the weathering and even during the protection process.

3.3. SEM investigations

The SEM images of the samples are shown in Fig. 5(a)–(f). The voids can be identified in the untreated-samples, Fig. 5(a) and (b). Limestone sample shows erosion and disintegration between its grains, Fig. 6(a), while the presence of voids, in sandstone sample, because of dissolving and disappearance of binding materials was noticed, Fig. 6(b). After treatment with polymer, Fig. 5(c)

![Fig. 3. Thin sections of (a) limestone-Horemheb tomb and (b) sandstone-Ramesseum temple, 100×.](image)

![Fig. 4. XRD pattern of original sandstone and limestone.](image)
and (d), the images showed a random penetration as well as a film formation of polymer on the stone surface. Artificial aging of polymer-treated stone showed some cracks in the coating layer, Fig. 5(e) and (f).

3.4. FTIR investigations

The rock samples and polymer were identified by FTIR spectra before and after interaction, Fig. 6(a)–(e). The IR spectra of limestone show that the calcite is the main mineral phase as observed at 1438, at 875, and at 712 cm⁻¹, Fig. 6(a). On the other hand, the IR spectra of sandstone, Fig. 6(b), show that the quartz is the main component of this stone by its doublet at 796 and 778 cm⁻¹. In addition, there is no absorption observed at 3504 or 1647 cm⁻¹ which means that there is no molecular water.

In the case of the acrylic polymer, Fig. 6(c), the IR spectra are dominated by the stretching aliphatic bonds (ν-(CH₃ + CH₂)) at 2952 and 2870 cm⁻¹, the deformation of methyl group (1397 cm⁻¹) and both methyl and methylene groups (δ-(CH₃ + CH₂), 1463 cm⁻¹). They also display distinct bands assigned to carbonyl groups (ν-(C=O), 1730 cm⁻¹) and strong band near 1123 cm⁻¹ is due to the CH₂-OH stretch of the polyethylene oxide side chain. In addition, three distinct bands at 2068, 1633, 693 cm⁻¹ are attributable to the stretching mode of amides (the band at 1650 in the amide region assigned to the stretching vibration of the C=O group that forms a hydrogen bonding with the NH). Also, Fig. 6(c) shows a strong and broad band at 3444 cm⁻¹ which could be assigned to the hydroxyl and amide groups.

Fig. 6(d) shows the IR spectra of acrylic-coated sandstone. The bands appearing at 1060, 790, 772 cm⁻¹ could be assigned to the stretching vibration of Si-O and Si-C bonds and/or due to the adsorption of polymers onto quartz and kaolinite (acrylic-sandstone). An additional band at 1536 cm⁻¹ could be assigned to the bending mode of amide due to the presence of the same group in the original polymer (before interaction with rock surface).

The IR spectra of acrylic-coated limestone, Fig. 6(e), are dominated by the stretching aliphatic bonds (ν-(CH₃ + CH₂)) at 2953 and 2840 cm⁻¹ and the deformation of methyl (1395 cm⁻¹) and both methyl and methylene groups (δ-(CH₃ + CH₂), 1460 cm⁻¹). They also display distinct bands assigned to carbonyl groups (ν-(C=O), 1730 cm⁻¹) and strong broader band near 1120 cm⁻¹ is due to the CH₂-OH stretch of the polyethylene oxide side chain. In addition, Fig. 6(e) shows four strong absorption bands at 1410, 1115, 871, and 711 cm⁻¹. These could be attributed to the acrylic/limestone interaction.
3.5. Electrokinetic measurements

For detailed description of the adsorption and electrical properties of the solid–solution interface, the zeta potential of suspended rock solid particles was measured.

The zeta potential results of sandstone and limestone particles, with and/or without polymer, are shown in Fig. 7(a) and (b). The electrical double layer compression of the limestone particles was noticed in the presence of polymer, which indicates the adsorption of polymer in double layer region next to surface of examined particles. On the other hand, it was observed that the zeta increases significantly the surface charge of the sandstone particles which can be attributed to either physical or chemical adsorption.

Moreover, the results indicated that the surface sites remain accessible to potential determining ions (H\(^+\) and OH\(^-\)) and the IEP remains unchanged during polymeric adsorption, thus implying that the polymer does not alter the surface potential. It can be considered, as other investigators asserted [32–34] that the decrease in zeta potential relating to adsorption of polymers is not due to a decrease in charge and surface potential, but rather to a shift of the shear plane. This finding confirms the FTIR observations where no chemical reaction was appeared and the adsorption of polymers on the surface of stones is physical.

3.6. Artificial aging and its effect on physical and mechanical properties

The physical and mechanical properties of studied stones were determined for bare stones, after treatment with polymer, and for treated stones after artificial aging. The physical and mechanical properties of limestone and sandstone before and after their treatment with polymer are shown in Figs. 8 and 9, respectively.

It is evident, from the physical measurements, that the treated-samples are higher in their bulk density. The efficiency of the polymer in formation of a protective layer appears from the reduction in water absorption and porosity, which can be referred to the penetration of the polymer into voids and pores.

On the other hand, the mechanical measurements indicated that the polymer increases the compressive strength to more than 20 MPa. The effect of treatment is higher in case of limestone. The improvement of physical properties reflects the importance of using these polymers in consolidation processes.
main component of limestone associated with traces of dolomite and quartz.

The results of FTIR and electrokinetic measurements indicated that the adsorption of the acrylic is mainly physical. Moreover, physical and mechanical properties, for bare stones and after treatment with polymer, indicated the effect of polymer in protection and consolidation process. In other words, the treated samples showed increase in the bulk density (from 1.9 and 1.6 to 23 and 2.2), compressive, and tensile strengths and decrease in water absorption (from 8.4 to 1.7–1.8) and porosity (15.6–2.4%).

The physical nature of the polymer interaction (reversible interaction) with sandstone and limestone in addition to its positive effects on the physical and mechanical properties and under the simulated weathering and artificial aging indicates the suitability of this polymer in conservation process under the studied conditions.

References


4. Conclusions

The damage and deterioration of the historical buildings is one of serious problems that attracts the researcher efforts all over the world. The protection of stones, from harmful surrounding conditions, by polymer treatment is one of the possible techniques that have been tested. Ramesses temple and Horemheb tomb, suffered from weathering, represent two types of stones; i.e., sandstone and limestone, were selected for the current study. Characterization of both stones indicated that the sandstone consists mainly of quartz and traces of clay minerals; while, the calcite is the