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A Survey of Polymeric Treatments applied on the Liberty Glazed Tiles of the Hungaria Façade

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Abstract

Several studies have been published about deterioration processes of polymer treatments applied on bricks, stone, mural paintings, but data are still lacking for the same treatments on ceramic in outdoor environment. The present work reports the evaluation of physico-chemical behaviour of organic and inorganic polymers applied as coating on lead glazed ceramic tiles, decorating the façade of the Liberty Hungaria Hotel in the Venice Lido, Italy, which in 2007 was restored due to its bad state of conservation. In conjunction with the conservative project, an assessment in marine environment of the durability of traditional products, i.e. acrylic Paraloid B72, poly methylphenyl siloxane Rhodorsil RC90 and innovative SiO2 coating applied by sol-gel technique, was performed. The study has been conducted on the products applied on original tiles exposed for three years on the façade. Optical and electron microscopy (FEG-ESEM) have been used to appreciate the morphological modification of the treatments, FT-IR micro-spectroscopy has been performed in order to detect possible chemical changes of the polymers, while surface wettability has been evaluated by contact angle measurements. The results obtained have shown that polymers underwent chemical changes due to the interaction with environment, which reduce their water-repellent efficiency.

Keywords: polymeric treatments, Paraloid B72, polymethylphenylsiloxane, sol-gel silica, modern architecture

1 Introduction

The protection of the ceramic artworks is a recent subject, and only few works have been published on the polymeric treatments suitable for these materials [1, 2, 3]. In Italy, one standing example of ceramic façade in outdoor environment is the Liberty palace in Venice Lido, named Hungaria Hotel, whose façade (700 m^2) was totally decorated in 1914 with polychrome glazed ceramic tiles (Figure 1-a) by the famous Italian master of pottery Luigi Fabbris (Bassano del Grappa, 1883-1952) [4]. The conservation of the façade was undermined by the typical environment of the Venice lagoon. A scientific survey on conservation products was planned with the aim to identify suitable materials for the protection of the ceramics exposed to the environment. Acrylic Paraloid B72, polymethylphenylsiloxane Rhodorsil RC90 and a sol-gel silica coating, prepared ad hoc in the laboratory of Padua University, were tested on samples of original ceramic tiles. The physico-chemical monitoring of polymers behaviour in sea environment lasts for three years, performing measurement campaigns every year. Contact angle measurements were executed before and after protection to value the surface hydrophility; the structural changes of the polymers induced by the natural ageing were studied by micro FT-IR spectroscopy, and scanning electron microscopy analyses investigate the different coatings over tiles surfaces their thickness and possible decay morphology. The conservation treatment of the whole façade was executed accordingly to the most suitable products identified in the experimental survey, i.e with the acrylic-silicone mixture.

2 Experimental

2.1 Sampling and materials

Samples of original glazed tiles were courtesy provided by Soprintendenza per i Beni Architettonici e Paesaggistici di Venezia e Laguna. For the contact angle measurements, semi-plane samples with a 2x2 cm^2 surfaces and a 0,5 cm thickness were tested. Furthermore, two ceramic tiles were destined to the monitoring of the treatments exposed to the outdoor environment and each one was cut in nine samples with 5x5 cm^2 surface (Figure 1-b).

The acrylic copolymer Paraloid B72 (ethylmethacrylate-methylacrylate, 30/70 w/w%) produced by Rhom & Haas, the solvents nitro diluents and white spirit are commercial products purchased from CTS, Altavilla Vicentina, Italy. The silicon-based product Rhodorsil RC90 an ethyl silicate associated with a neutral catalyst and a phenylmethyl resin was produced by BLUESTAR SILICONI ITALIA S.p.a. and courtesy purchased from Siliconi Padova, Italy. The sol-gel silica coating has been prepared using ethanol as solvent, tetraethyl orthosilicate (TEOS) as sol-gel precursor, deionized water for the hydrolysis and hydrochloridric acid as catalyst [5].

The glazed ceramic samples were treated by brushing, respectively with a Paraloid B72 solution (3%) in nitro diluent (A), an acrylic-silicone mixture prepared with a nitro diluents solution of Paraloid B72 (3%) and a white spirit solution of Rhodorsil RC90 (10%) (B) in acetone and chloroform solvent's mixture, and with sol-gel silica (C).

Every treatment was applied totally on six samples (Table 1); all the samples were exposed on the façade in 2007. They underwent natural weathering by direct exposition to sun, wind and rain action and marine aerosols deposition; the physico-chemical monitoring was executed annually for three years (2008-2010).

Fragments were collected from the model tiles and prepared as cross sections by embedding in an epoxy resin, dissected and polished by SiC paper with a decreasing granulometry (600, 1200, 1400 mesh).


a

b

Figure 1: a) the façade of the Hungaria palace; b) a monitored ceramic tile, composed by nine samples, treated with the polymeric coatings

Table 1: Sampling time of the sample with 5x5 cm^2 surface and corresponding polymeric treatments

Products	Sample								
	AIO	AIIO	AIIIO	BIO	BIIO	BIIIO	CIO	CIIO	CIIIO
Paraloid B72	2008	2009	2010						
Acrylic-silicone mixture				2008	2009	2010			
Sol-gel silica							2008	2009	2010

2.2 Physical-chemical measurements

2.2.1 Contact angle measurements

The apparatus consists of a contact-angle meter including a light source, optical system, specimen stage and liquid delivery system. The light source is a LED-type lamp. A CCD camera Dinolite is used to collect the images with magnification range 10-50x, 200x. The liquid delivery system is a pump-driven microsyringe controlled via software of 100 μl capacity. For all these contact angle analysis it has been used only distilled water.

Five measurements for each sample, executed before and after the polymeric treatments, were performed after a period of 24 h of conditioning respectively in a heater at 60 °C and in dryer. A droplet of water of volume between 3-5 μl was suspended on the sample and then the sample was approached slowly in order to achieve a steady transfer. The measurements were performed according to the International Standard ISO 15989:2004 (corr. 2007) [6, 7].

2.2.2 Micro FT-IR measurements

μ-FT-IR measurements were carried out on powders collected from the sample's surface to evaluate polymer structural changes as a function of ageing time. The spectra were collected with a Nicolet microscope connected to a Nicolet 560 FT-IR system, equipped with a MCT (Mercury Cadmium Telluride) detector, involving OMNIC32 software. IR spectra were collected from 4000 to 650 cm^{-1} range, with a resolution of 4 cm^{-1}. Recorded spectra have been expressed by absorbance units and baseline corrected.

2.2.3 Optical and scanning electron microscopy

A preliminary observation of cross section was carried out by an Olympus BX-51 instrument equipped with UV light source Olympus U-RFL-T and UV filters.

Morphological observations were performed by scanning electron microscopy (SEM) to study the treated surfaces and the natural weathering effects, such as its porosity, thickness, crackings and detachments. They were carried out on the cross sections after C-coating by electron-deposition using a MED 10 instrument working at 10^{-5} mbar pressure. The analyses were executed in a instrument equipped with a field emission gun as electron source (FEG-ESEM FEI Quanta 200F) and EDS (Energy Dispersion System) microprobe for chemical analyses. Measurements were collected in high vacuum mode, at a working distance of 10.7 mm, with 25 kV of voltage and with a spot size of 4.0.

3 Results and discussion

3.1 State of conservation

FT-IR spectroscopy, scanning electron microscopy and energy dispersion spectroscopy (ESEM-EDS) have been performed on samples collected from the Hungaria´s façade to define the causes and the effects of the its decay.

The first causes of deterioration is related to the productive technology of the tiles. They are soft earthenware that were produced with a double firing method. The raw materials employed for the making of the ceramic bodies were the illitic clay of the Tretto´s quarry (Vicenza), quartz and calcite, while for the glaze a clay, quartz sand and a lead compound were used [8]. The ceramic bodies have high porosity, while the glazes bubbles and vertical fractures in part connected to the productive technology. Thus, these aspects can be considered the *ab origine* causes of decay.

Furthermore, salt crystallization inside the ceramic bodies, the surface and the fractures of the glazes have been detached. In the ceramic body sulphate and chloride salts, while near the body-glaze interfaces lead salts connected to the leaching of the lead ions have been revealed (Figure 2-a).

Growth of microorganisms such as bacteria, fungi and algae have been observed inside the body and near the body-glaze interface (Figure 2-b) [9].

The effects of the deteriorating causes have been observed especially in the glazes. Several craqueleres and vertical fractures are present (Figure 2-c), which are presumably connected both with the salt crystallization, the hot/warm cycles and the growth of microorganisms.

3.2 Contact angle measurements

The set treated with Paraloid B72 (A) are the most uniform and best preserved specimens in comparison to the ones treated with acrylic-silicone blend (B) and silica coating (C): no macrocrackings were detectable and the analysed surfaces were mostly flat without any vertical bends or hills. The results obtained for the untreated and treated sets are reported in Table 2, while measurements after ageing are still running.

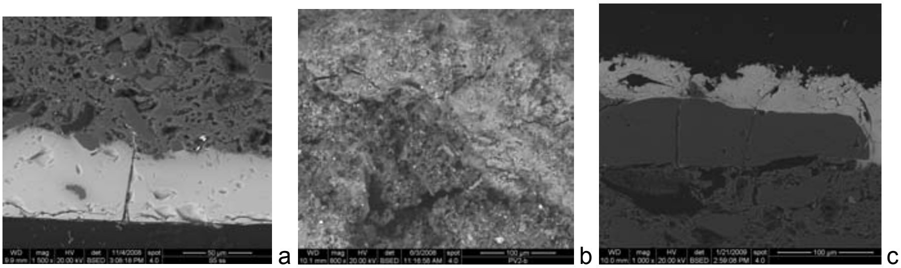

Figure 2: a) a vertical fracture in the glaze; b) microorganisms in the ceramic body; c) craquelers in the glaze

Table 2: Results obtained for contact angle measurements; the label “nt” indicates untreated sample, while label “t” treated sample

Sample set	Sample	Mean nt	DIV nt	Mean t	DIV t	Δ%
A	A1	55,84	3,86	83,86	8,90	50
	A2	57,86	7,09	74,92	3,07	29
B	B1	54,72	11,88	82,62	6,68	51
	B2	43,82	9,08	80,51	3,95	84
C	C1	55,74	10,40	59,51	5,94	7
	C2	54,12	14,74	51,38	6,59	-5

Because of the bad conservation state of the artwork appearing in some samples as cracks and/or scratched parts, the results obtained for sets B and C, before the treatments, are quite different (Table 2), similarly, the standard deviation is quite wide and increases from set A to set C. After the treatments, there is a strong increase of the waterproofing of the substrate showing an improvement between about 30-50% (set A: Paraloid B72) and 50-80% (set B: acrylic-silicone mixture) (table 2); in fact the side chains of the polymers, as $–CH_3$, $-OCH_3$ $–OCH_2CH_3$ and phenyl, create a chemical barrier towards the liquid water adsorption. Instead, the sol-gel silica coating didn’t affect the wettability of the tiles surface neither their water proofing, in accordance with the silica composition which hasn’t any non polar side group. It is also very important to underline the fact that the spread of the standard deviations for the treated samples is much narrower than untreated samples: this means that the coatings have been effective on all the different parts of substrate, sealing the micro-cracks of the weathered untreated surfaces.

3.3 Micro FT-IR spectroscopy

3.3.1 Acrylic polymer Paraloid B72

Applied products were collected from the surface of treated samples at different times (AIO, AIIO, AIIIO) to verify if any decay process of the polymer was in act. Micro FT-IR spectra has shown the characteristic absorbances of Paraloid B72 (spectra not reported), a methylacrylate-ethylmethacrylate copolymer. ν C-H aliphatic stretches and the corresponding δ C-H bending have been identified at 2983, 2951 cm^{-1} and 1465-1383 cm^{-1}respectively. A strong absorption peak due to ν C=O occurs at 1740-1720 cm^{-1}, while ν C-O stretches are present in the range 1270-900 cm^{-1} where, in particular, between 1180 and 1154 cm^{-1} ν C-C(=O)-O and ν C(=O)O-C stretches occur [10 - 12]. From the comparison of the spectra it has been noted that the ν O-H stretches at 3434 cm^{-1} is increased for the sample AIIIO, and that there is a broadening of the ν C=O stretching band with the presence of a shoulder at 1793 cm^{-1} in AIIO and AIIIO; in sample AIIIO a weak broad band at 1662 cm^{-1} and an increased absorption of δ CH bending have been noted. These small absorption changes indicate that the acrylic polymer is interested by a degradation process promoted by photo-oxidative ageing; in fact, the appearance of the shoulder at 1780 cm^{-1} is due to the formation of γ-lactones, while the broadening of this peak towards 1640 cm^{-1} suggests the formation of double bonds in the chain; as described also by other authors [12-14], the photo-oxidative degradation of Paraloid B72 takes place in two pathways: a chain scission followed by macroradicalic disproportion and terminal double bond formation for the ethylmethacrylate unit and subsequent the formation of γ-lactones for the methylacrylate units due to addition of O_2 to the radical units or to oxidation reaction.

3.3.2 Actylic- silicone mixture

Polymers from the samples (BIO, BIIO, BIIIO) treated with an acrylic-silicone mixture was collected at different times to verify chemical changes of the polymers. The commercial product Rhodorsil R90 is constituted by ethyl silicate and phenylmethylsiloxane; the FT-IR spectra (Figure 3) show a weak broad band at 1630 cm^{-1} due to the ν C=C stretches of phenyl groups, a medium peak at 1430 cm^{-1} due to Si-phenyl stretching band and a strong broad band in range 1100-1000 cm^{-1} due to ν Si-O-C and Si-O-Si stretching frequencies [10, 15]. In the spectra the characteristic peaks of Paraloid B72 occur at 2983-2953 cm^{-1} (ν C-H stretches), 1738-1728 cm^{-1}

(ν C=O stretches), and 1443-1383 cm^{-1} (ν C-H bending). Comparing the spectra of the acryl-silicone mixture at the three times, from BIO to BIIIO, in the silicone part an increase of the absorption of ν O-H stretches and a broadening of the ν Si-O-C and Si-O-Si with the presence of a shoulder at 970 cm^{-1} have been noted; this aspect can be related to the formation of silanolic groups promoted by the interaction with the atmospheric moisture which can enhance the polymerization process. For the acrylic component, the broadening of the carbonyl stretching band with the appearance of a weak peak at 1791 cm^{-1}, associated to the formation of γ-lactones, has been noted [10,16].

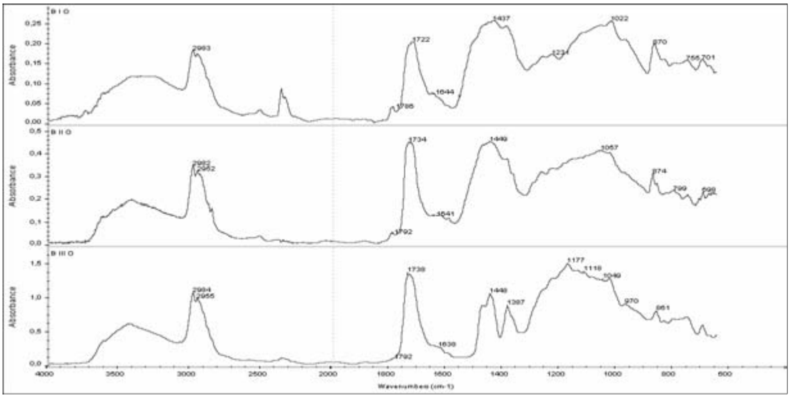

Figure 3: Micro FT-IR spectra of sample treated with acrylic-siloxane mixture naturally aged in marine environment

3.3.3 Sol-gel silica

The spectra of the samples collected at the three different times, show peaks of the ν Si-O-Si stretches in the range 1100-1030 cm^{-1} characteristic of silica (spectra not reported) [10]. By comparing the spectra it has been noted an increase of ν O-H stretches from CIO to CIIIO, due to the interaction of Si-O-Si chains with environmental moisture.

3.4 Optical and scanning electron microscopy

Observations by optical and scanning electron microscopy have been executed to verify the decay morphology of the polymer exposed to marine environment. The glazes are fragmented especially next to the surface, and the applied acrylic polymer occurs as a surface sealing coating, thick about 10-20 μm, that does not penetrate into the glaze's fractures (Figure 4-a). The analyses have shown also that in the time Paraloid B72 is interested by decay's process; after one year of ageing it is continuous on the surface, but sometimes it assumes a globular aspect with neo-formation pores (Figure 4-b). After two year of ageing, there is an increase of the coating pores in width and numbers and several coating detachment for the glaze surface (Figure 4-c). Finally, in the three years aged sample the film is almost absent on the tile surfaces, with the exception of few areas where it is still adherent (Figure 4-d). Morphological observation on tiles treated with acrylic-silicone mixture and sol-gel silica coating are in progress.

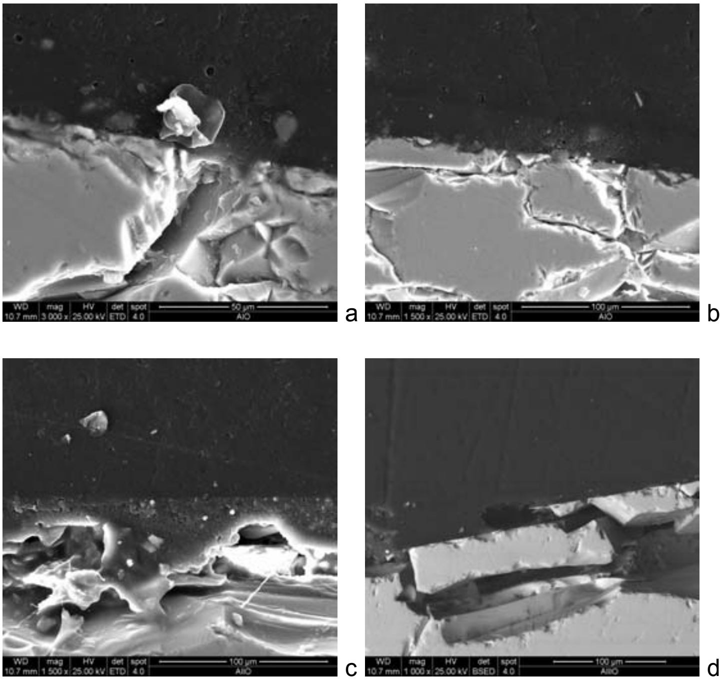

Figure 4: a) A detail of the fragmented glaze where acrylic Paraloid B72 remains only on the surface, SEM-LFD image with 3000x magnification; b) SEM-LFD images with 1500x magnification of AIO sample one year aged; c) SEM-LFD images with 1500x magnification of AIIO sample two years aged; d) SEM-LFD images with 1000x magnification of AIIIO sample three years aged

4 Conclusions

In the present paper the surface hydrophobicity of glazed ceramic tiles before and after treatments with three polymers and the films ageing were studied. In particular, the acrylic polymer Paraloid B72, an acrylic-siloxane mixture prepared with Paraloid B72 and Rhodorsil RC90 and sol-gel silica were applied on the original ceramic tile of the façade of Hungaria palace, a Liberty building in Venice Lido. The treated samples, subjected to a natural ageing, were collected at specific time to monitor their behaviour as a function of time. The contact angle measurements have shown that samples treated with Paraloid B72 and the acrylic-silicone mixture improved significantly the surface's hydrophobicity, thanks to their non polar side chain groups. On the other hand, the sol-gel silica coating coherently didn't influence the surface's physical behaviour towards water. Preliminary results obtained from tiles treated with the acrylic polymer show that after three years of outdoor exposition in marine environment the coating underwent severe modification; actually it is almost absent on the treated tile surface and the small amount still present is interested by structural changes due to photo-oxidation process. These data, together with those from the research still in progress on acrylic-silicone mixture and silica applied via sol-gel, represent a valuable scientific contribution in the selection of suitable water-proofing products, finalized to the development of correct conservation actions.

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