Modified fluorinated polymers for the protection of stone surface from mural writings

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The use of fluoropolymers in the field of conservation of different litotypes is well known. In particular, perfluoropolyethers (PFPE) exhibit chemical and physical properties, that make them suitable to protect stone surface from both water penetration and the decay caused by mural writings (e.g. “graffiti” made by using spray paints, brush paints or inks). Early studies gave satisfactory results operating with high quantities of applied polymer (e.g. more than 100 g/m² of PFPE applied to a medium porosity sandstone) and in the presence of chlorofluorocarbon solvents (CFC) which are no longer usable for environmental reasons. These considerations prompted us to carry out new studies in this field, in order to develop a PFPE derivative displaying a good “antigraffiti” effect at low applied quantities and, if possible, in the absence of hazardous solvents.

In this work, a commercial copolymer based on perfluoropolyether (PFPE) blocks and containing carboxylate functional groups has been studied in aqueous microemulsion.

This polymer is able to interact with polyfunctional reactive molecules giving chain extension and crosslinking. The reaction takes place “in situ” and allow the PFPE derivative to be modified directly on the stone surface. The application of this material on different stone samples improves not only the substrate hydrophobicity (as expected for a perfluoropolyether derivative) but also the resistance to the dirtying which could be caused by mural writings (e.g. by inks).

1 Introduction

Monuments and buildings are commonly subject to decay caused by atmospheric components (e.g. water vapour and carbon dioxide) and pollutants (e.g. nitrogen and sulphur oxides). In the last decades mural writings or “graffiti” have represented a novel form of defacement because they always cause a modification of the substrate surface which is particularly undesirable for the monumental heritage. Application of specific protecting agents which allow an easy removal of graffiti from the stone surface represents a way to eliminate or reduce the damages resulting from vandalism.

In the last years several commercially available polymeric materials (e.g. polysiloxanes and polyacrylates) have been proposed as anti-graffiti agents. Such organic polymers, when used in the fields of protection and consolidation of stones, display some performance limits: (a) atmospheric agents (e.g. oxygen, sunlight) induce degradation processes with a consequent loss of their protection ability and an optical defacement [1, 2] ; (b) they may cause chromatic variations on a treated stone which are unacceptable if the aesthetic appearance of the monument is altered; (c) they may be sensitive to some components (e.g. solvents) of the paints used to draw graffiti.

Fluorinated polymers and, in particular perfluoropolyethers (PFPE, fluorine content close to 67 % w/w) attracted remarkable interest of scientists operating in the field of monumental heritage conservation, owing to their peculiar properties: they are chemically inert, thermally stable and strongly water repellent [3].

These considerations prompted us to carry out new studies in this field, in order to develop a PFPE derivative displaying a good “antigraffiti” effect at low applied quantities and, if possible, in the absence of hazardous solvents.

Here we report the results obtained from a study performed on the commercially available PFPE-based polymer named Fluorolink® P56 (see molecular structure sketched in Fig. 1).
In this study, Fluorolink® P56 (as water microdispersion) has been applied to the surface of Carrara Marble in the presence of an epoxysilane and of a polyaziridine (both as curing agent). The resulting anti-graffiti effectiveness has been evaluated and have been also compared to that obtained by applying the same fluorinated polymer without any curing agent.

## 2 Experimental

### 2.1 Materials

Slabs of white Carrara Marble, quarried from the Apuane Unit, have been used. This building material has a compact granoblastic polygonal structure and a very low porosity never exceeding 0.2%. Specimens of 20 x 10 x 2 cm were cut and divided into five equivalent areas of 4 x 10 cm, labelled from A to E.

Fluorolink® P56, a water microdispersion of an anionic fluorinated polyurethane based on PFPE, with a solid content of 26% w/w and $M_w$ of about $10^4$. It is manufactured by Solvay Solexis (Spinetta Marengo, Italy) and commercialized by the same company (http://www.solvaysolexis.com).

Remover® AC, a mixture of γ-butyrolactone (49%), dipropylene glycol monomethylether (49%) and Triton® X100 (2%), was supplied by Syremont S.p.A. (Italy) as cleaning agent.

Xama 7 (pentaerythrytol tris [3-(1-aziridinyl)propionate]) is produced by Flevo Chemie (The Netherlands).

### 2.2 Application of protecting material on the stone surface and study of surface properties

In a typical experiment, the fluorinated polymer Fluorolink® P56 (16.8 g, 2.75 meq of carboxylate function considering an equivalent weight of 1592) and the curing agent (0.65 g of 3-glycidyloxypropyltrimetoxysilane or 0.39 g of Xama 7), were mixed for 30 min under magnetic stirring and the resulting mixture applied by a small brush on the surface of the stone samples. Increasing amounts of the polymeric mixture were applied to the areas labeled from B to E on the stone surface (area A was not treated and used as the reference surface). The final applied quantities of protecting material for each area were: A: 0; B: 10; C: 15; D: 25; E: 35 (g/m$^2$).

A similar experimental procedure was followed to apply the fluorinated polymer without curing agent.

The tests performed on the stone samples in order to evaluate the surface properties and the anti-graffiti effectiveness were carried out one week after the application.

Stone colour changes were measured on each sample area (after the polymer application as well as after the staining/cleaning process) by a Konica Minolta CM-S100W Spectra Magic NX spectrophotometer, determining the L*a*b* coordinates of the CIELAB space [4] and expressed as global chromatic variations ΔE*.

Static contact angle measurements on the treated surfaces were performed by a Lorentzen & Wettre instrument according to the method adopted by UNI-NorMaL Commission.

**Fig. 1:** Molecular structure of fluorinated polymer Fluorolink® P56.
Stone surface was stained by a BIC Permanent Marker (black ink) in all A-E areas. Cleaning was performed after 2 h after the staining by using Remover AC, a brush and a cotton wad. The surface properties were studied again after the complete evaporation of the cleaning solvent.

3 Results and discussion

The protecting material considered in the present study, commercially known as Fluorolink® P56, is a copolymer containing perfluoropolyether PFPE sequences interrupted by urethane blocks and carboxylate side groups (see structure in Fig.1; tetraalkylammonium counterions have been omitted). The anionic functions allow the preparation of water microdispersion and can be exploited to promote crosslinking reactions in the presence of proper curing agents.

The curing agents used in the present study are the commercially available 3-glycidyloxypropyltrimethoxysilane and the tris-aziridine Xama 7.

The reaction involving carboxylate group and epoxide or is well known [5] and is currently exploited as curing process of different polymers (e.g.polyurethanes)[6].

Also the reaction involving carboxylate and aziridine groups is well known [7] and already exploited as curing process of polymers [8].

Fluorolink® P56 and the curing agents were homogeneously mixed just before application in order to let the curing reaction take place on the stone surface. The study of the surface properties have been carried out after one week, when the water was completely evaporated and the curing reaction completed.

The results obtained from the investigations carried out on the stone samples after the application of the protecting material are discussed in the following paragraph.

3.1 Surface properties of treated stone and evaluation of anti-writing effectiveness

The variations in the stone surface properties induced by the application of the protecting material were preliminarily studied in terms of chromatic changes and waterproofness. The variations of stone colours (expressed as ∆E*) and contact angle values determined for the treated samples are summarized in Table 1. The same experiments were also performed on stone specimens treated with the fluorinated polymer only, in order to compare the properties of the cured and uncured protecting material (tab. 1).

Table 1 Colour changes evaluated as global chromatic variation (ΔE*) and contact angle values (standard deviation in parenthesis) measured after the application of the protecting material on the surface of Carrara Marble specimens (A= 3-glycidyloxypropyltrimethoxysilane; B= Xama 7).

<table>
<thead>
<tr>
<th>Applied quantity (g/m²)</th>
<th>Cured with A</th>
<th>Cured with B</th>
<th>Uncured</th>
<th>Cured with A</th>
<th>Cured with B</th>
<th>Uncured</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.8</td>
<td>0.3</td>
<td>2.0</td>
<td>101 (5)</td>
<td>102 (3)</td>
<td>101 (4)</td>
</tr>
<tr>
<td>15</td>
<td>2.3</td>
<td>0.6</td>
<td>1.6</td>
<td>106 (2)</td>
<td>103 (2)</td>
<td>104 (8)</td>
</tr>
<tr>
<td>25</td>
<td>2.4</td>
<td>0.6</td>
<td>1.7</td>
<td>103 (2)</td>
<td>103 (5)</td>
<td>99 (4)</td>
</tr>
<tr>
<td>35</td>
<td>1.6</td>
<td>0.5</td>
<td>1.5</td>
<td>105 (4)</td>
<td>96 (3)</td>
<td>99 (4)</td>
</tr>
</tbody>
</table>

In all experiments the application of the fluorinated polymer both uncured and cured with 3-glycidyl-oxypropyltrimethoxysilane or Xama 7 induced unimportant chromatic variations: in fact ΔE* values lower than 5 correspond to colour changes which cannot be detected by naked eye [9].

Moreover Fluorolink® P56 afforded to the surface of stone samples a considerable water-repellency which was quite the same for both cured and uncured material. In fact contact angle values higher than
90° were observed in all cases, even with the lower applied quantities. In particular, contact angles close to 100° were determined for all the treated samples, showing a remarkable decrease of wettability.

These results suggest that the behaviour of the fluorinated polymer on the stone surface, in terms of chromatic effect as well as of water repellency, is not significantly influenced by the curing process.

In order to evaluate the effectiveness of both cured and uncured Fluorolink® P56 as protecting material from mural writings, the surface of treated stone samples were stained by using a common permanent marker pen, then the ink removed with a specific solvent mixture (Remover® AC).

Afterwards, each sample was examined by naked eye and by a microscope to verify if the removal of ink was satisfactory from a qualitative point of view. Moreover, the surface properties were studied again and the results compared with those obtained before the staining/cleaning cycle, in order to evaluate the efficiency of the protecting action.

The variations of stone colour (expressed as ΔE*) and contact angle values determined after the staining/cleaning procedure are summarized in Table 2.

ΔE* values reported for the “cleaned” stones indicated the eventual colour modification of the treated surfaces due to traces of residual ink. Therefore such values were directly correlated to the efficiency of dirty removal as well as to the effectiveness of the protecting action. ΔE* was very low for the samples treated with cured Fluorolink® P56 according to a satisfactory if not complete removal of the ink stains at any of the considered applied quantities. Higher values of ΔE* were observed for samples treated with uncured Fluorolink® P56 indicating again its less efficient protecting action.

Table 2 Colour changes evaluated as global chromatic variation (ΔE*) and contact angle values (standard deviation in parenthesis) measured after the staining/cleaning procedure (A= 3-glycidyloxypropyltrimethoxysilane; B= Xama 7).

<table>
<thead>
<tr>
<th>Applied quantity (g/m²)</th>
<th>Cured with A</th>
<th>Cured with B</th>
<th>Uncured</th>
<th>Cured with A</th>
<th>Cured with B</th>
<th>Uncured</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.7</td>
<td>0.9</td>
<td>6.5</td>
<td>96 (2)</td>
<td>100 (1)</td>
<td>90 (8)</td>
</tr>
<tr>
<td>15</td>
<td>4.3</td>
<td>1.1</td>
<td>11.9</td>
<td>95 (8)</td>
<td>98 (7)</td>
<td>79 (8)</td>
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<tr>
<td>25</td>
<td>4.1</td>
<td>1.5</td>
<td>14.2</td>
<td>101 (2)</td>
<td>92 (2)</td>
<td>79 (4)</td>
</tr>
<tr>
<td>35</td>
<td>4.4</td>
<td>2.0</td>
<td>12.4</td>
<td>99 (3)</td>
<td>91 (5)</td>
<td>93 (4)</td>
</tr>
</tbody>
</table>

After the cleaning step the contact angle values were almost unchanged for “cured” samples indicating that the crosslinked polymeric material is quite unaltered on the stone surface after the dirty removal (tab. 2). On the other hand, the decrease of contact angle values observed in the case of “uncured” samples suggests that some amount of the protecting material was removed together with the ink owing to the mechanical action rather than the solvent action in the cleaning step.

References