Structure and behaviour of materials for the conservation of monumental buildings
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Abstract

Water repellence, aggregating properties and permeability to O_2, N_2 and CO_2 of perfluoropolyetheric amides, a fluorinated elastomer and an acrylic copolymer were determined. All polymeric materials had a good protective efficacy but very different permeabilities to the gases examined. A selective permeability of several polymers to various penetrants has been found. The fluorinated elastomer displays a favourable behaviour in terms of water repellence, aggregating properties and permeability to carbon dioxide much lower than the one to O_2 and N_2.

1 Introduction

Monumental buildings in stone exposed to the atmospheric agents do deteriorate now more rapidly than they used to in the past. The "usual" disaggregating influence of temperature fluctuations and of ligand dissolution by rain water have been greatly enhanced by the pollutants present in the atmosphere. Their concentration has in fact increased in the last decades and has caused a tremendous acceleration in the rate of decay of stone.

Pollutants like SO_2, SO_3, NO_x, CO_2, in the presence of water act as acids. Rain drops, while falling, collect pollutants from the atmosphere forming fairly concentrated solutions which then hit, when reaching the ground, the exposed surfaces. The first drops at the beginning of a rain event may have as low a pH as 2.5-3.0. The pH then slowly increases approaching neutrality.

Rain therefore bears most of the responsibility of the deterioration of stone acting both as solvent of the binding medium and as carrier of pollutants. The result of these processes is stone disaggregation which causes loss of material and deformation of the surface.

Conservation procedures involve therefore, in serious cases, both reaggregation of loose material and protection of the surface in order to prevent further damages.
Materials used in the conservation of monumental buildings must exert their role causing no harm, irreversible deposits or chemical reactions. In fact they must be "compatible" with the stone they are placed on, which means they must neither cause chemical nor physical changes to the system which might affect the stone behaviour.

The essential properties of a "benign" material for stone conservation are:

a) Chemical inertia towards the substrate  
b) Low volatility  
c) Transparency and absence of colour  
d) Insolubility in water and usual organic solvents  
e) Permeability to water vapour  
f) Chemical stability to atmospheric agents, light and heat  
g) Ability to ensure reversibility of the treatment

Most consolidants and protective agents in use to-day do not fulfil these requirements and therefore new and more appropriate materials must be devised, selected and developed. Their identification however is very difficult.

A reconsideration of the problems placed by stone conservation has therefore been undertaken in order to identify the minimum properties of benign materials for use in this field. Significantly new ideas came from this search.

Consolidation of stone surfaces in monumental buildings generally aims at preventing the loss of disaggregated material rather than at restoring the original properties of the stone. Chemically stable, elastic polymers capable of good adhesion may then be considered promising candidates to serve this purpose. These polymers would be very different indeed from those actually in use, both chemically and in their behaviour and, in principle, more benign.

The protection of stone exposed to the atmospheric agent is done by applying water repellent treatments, e.g. Delgado Rodrigues & Charola\(^1\), Biscontin\(^2\). These superficial treatments must not only have a good water repellence efficacy but also retain it as long as possible. Having to withstand severe chemical and physical attack they must be characterized by a great stability.

An other characteristic of polymeric materials, relevant in determining their validity when used as protective materials, is their permeability to gaseous penetrants. Such a characteristic has never been taken into consideration before in connection with the protection of stone or any other type of cultural heritage. We have thought that we might get interesting indications from the evaluation of the permeability to gaseous penetrants of a few selected polymeric materials used in conservation procedures.

Superficial protective treatments might in fact not only act as water repellents, as said before, but also as barrier to the access of "dry" pollutants to the surface of the objects exposed.
2 Materials

In consideration of the high stability of the C-F bond, fluorinated materials have been taken into consideration for use in the aggregation (e.g. Fratini et al.\(^3\) and Manganelli Del Fà et al.\(^4\)) and the protection of stone (e.g. Piacenti et al.\(^5\)). Among several fluorinated elastomers actually on the market we selected a hexafluoropropene-vinylidene fluoride copolymer having 67% fluorine and 360,000 a.m.w. (Akeogard CO). Tests were made on it for aggregating and protective properties as well as for the permeability to carbon dioxide. Perfluoropolyethers, which satisfy the properties listed before, were chosen several years ago as basic materials for the development of a new generation of protective agents by Piacenti et al.\(^6\), Matteoli et al.\(^7\). By now they have been used for years and applied on a considerable number of monuments of prestige with satisfactory results as Piacenti et al. reported\(^8\). Perfluoropolyethers as a result of being liquid with a low surface tension, however, show a tendency to diffuse in depth into the porous structure of the stone which leads to a slow decline of the protective efficiency. In order to prevent or reduce this migration tendency, the insertion of a polar group in their molecule was planned which was meant to fix the molecule to the stone by an interaction due to hydrogen bonding or Van der Waals forces. From the very first tests it was clear that the amides of the perfluoropolyetheric acid had an appropriate stability and a higher protective efficacy than the corresponding original perfluoropolyether. We have therefore synthesised mono-, di- and tetra-amides of perfluoropolyetheric acids and tested them (see below), e.g. Piacenti et al.\(^5\), Piacenti & Camaiti\(^9\). We are going to report these results together with those concerning the basic perfluoropolyether.

\[
\begin{align*}
\text{monoamide} & \quad R_f\text{-CO-NH-CH}_2\text{-CH(}CH_3\text{)}_2 \\
\text{diamide} & \quad R_f\text{-CO-NH-(CH}_2\text{)}_x\text{-NH-CO-R}_f \\
\text{tetramide} & \quad R_f\text{-CO-NH-(CH}_2\text{)}_x\text{-NH-CO-R}_z\text{-CO-NH-CO-R}_f \\
\end{align*}
\]

\[R_f = \text{-CF}_3\text{-O-(CF}_2\text{-CF}_2\text{-O)}_m\text{(CF}_2\text{-O)}_n\text{-CF}_3 ; \quad R_z = \text{-CF}_2\text{-O-(CF}_2\text{-CF}_2\text{-O)}_m\text{(CF}_2\text{-O)}_n\text{-CF}_2\cdot\]

In order to compare the permeability of the products described above with that of one of the most efficient and popular materials for aggregation and protection of stone, we have made the same determinations also on samples of isobutilmethacrylate sold under the trade name Paraloid B67.

The stone used as the support on which to apply the aggregating and protective treatments to be tested was Pietra di Lecce, a bioclastic biocalcarenite having 46% porosity. Although very porous this stone is rather homogeneous and provides, more easily than others, reproducible and reliable results.
3 Procedures

3.1 Protection efficacy

The efficacy of a protective treatment applied on the surface of a stone is determined through its influence on the rate of absorption of water which may be measured by a gravimetric determination as described in\(^\text{10}\). The amounts of water absorbed (ml/cm\(^2\)) in a given time by the surface before \((A_0)\) and after the treatment \((A_1)\), introduced in the equation reported below provide the value of the protective efficacy \(E\%\).

\[
E\% = \frac{(A_0 - A_1)}{A_0} \times 100
\]

The persistence of the protective efficacy is measured by additional determinations performed at subsequent times between the moment of the application of the treatment and that of the measurement. At least three different samples for each test must be used in order to have reliable results.

3.2 Aggregation efficacy

The aggregation efficacy \((A_g)\) is determined by comparing the loss of material from samples of disaggregated stone before and after the treatment, caused by an abrasion procedure performed under standard condition, e.g. Tiano et al.\(^\text{11}\).

3.3 Polymer permeability to penetrants

Sorption and transport of penetrant molecules in polymeric materials may be described in terms of a solution-diffusion mechanism: the penetrant is initially absorbed on the surface of the polymer, then dissolves into it and then diffuses in the polymer matrix from regions of high to low penetrant concentration. The absorption and diffusion of a penetrant in a polymer may be represented in terms of separate solubility and diffusivity coefficients.

The quantity of penetrant that solubilises into the polymer under equilibrium conditions is described by the solubility coefficient \(S\) which depends on the affinity of the penetrant to the polymer molecules and on the condensability of the penetrant. The solubility coefficient is defined as the ratio between penetrant equilibrium concentration \(C\) into the polymer to the penetrant partial pressure \(p\):

\[
S = \frac{C}{p}
\]

The equilibrium penetrant concentration can be derived from the weight of penetrant in a polymer sample at equilibrium conditions. It may be
determined by gravimetric determinations done using a Cahn balance with a sensitivity of $10^{-7}$ g as given by Piacenti et al.\textsuperscript{12}.

The transport of the penetrant may be represented by the polymer diffusion coefficient $D$ to the penetrant molecule. The polymer diffusion coefficient depends on the physical and chemical characteristics of both the polymer and the penetrant. Fick's First Law of Diffusion relates the flux of the penetrant $J$ in a polymer film of thickness $L$ to the polymer diffusion coefficient according to the relation reported below:

$$J = -D \cdot \frac{(c_1-c_0)}{L}$$

where $c_1$ and $c_0$ are the concentrations of the penetrant at the surface and inside the polymer. The diffusion coefficient may be derived from the shape of the absorption curve of the penetrant into the polymer.

The polymer permeability $P$ to the penetrant is given by the product:

$$P = S \cdot D$$

4 Results

The protective efficacy determinations performed on mono-, di- and tetra-amides gave the results reported in Table 1. In the same table we have included also those concerning the unfunctionalized perfluoropolyether YR.

In order to be able to compare the protective efficacy achieved in the various cases we have used approximately the same amount of all materials per unit of surface. The polyamides have all approximately the same efficacy. The unfunctionalized material YR has a much lower efficacy, and also the monoamide is not very effective from the very beginning.

In the case of the ethylenediamine derivatives the protective efficacy, initially high, seems to decline slowly after a few months. It remains practically unaltered even after one and a half year in the case of the hexamethylene diamine derivatives.

The tetraamides do not have better qualities than the diamides neither in terms of entity nor in terms of persistence of the efficacy.

The fluorinated elastomer applied in smaller amount than the perfluoropolyethers (100 g/cm$^2$) provides a good protective efficacy (98\%) and shows moreover a substantial aggregating property (75\%), e.g. Fratini et al.\textsuperscript{3}.

Diffusivity, solubility, permeability coefficients to carbon dioxide, oxygen and nitrogen are reported in Table 2 for all the products listed before.

The diffusivity coefficients to carbon dioxide of all polymers are much lower than those to nitrogen and oxygen: from one third in the case of the liquid polyethers to one order of magnitude in the case of the acrylic resin and of the fluorinated elastomer.
Table 1

Protective efficacy (E%) of some fluorinated products on Pietra di Lecce on aging.

<table>
<thead>
<tr>
<th>Product</th>
<th>Amount applied (g/m²)</th>
<th>E% - months after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>YR</td>
<td>159</td>
<td>33</td>
</tr>
<tr>
<td>IBAG2200</td>
<td>158</td>
<td>68</td>
</tr>
<tr>
<td>DC2G2200</td>
<td>142</td>
<td>92</td>
</tr>
<tr>
<td>DC6G2200</td>
<td>154</td>
<td>99</td>
</tr>
<tr>
<td>TC2G2200</td>
<td>145</td>
<td>79</td>
</tr>
<tr>
<td>TC6G2200</td>
<td>154</td>
<td>100</td>
</tr>
<tr>
<td>Akeogard CO</td>
<td>100</td>
<td>98</td>
</tr>
</tbody>
</table>

YR = F-Rf; G2200 = -Rf with av.m.w. of 2380.
The solubility coefficient to carbon dioxide of all polymers, on the contrary, is much higher than those to nitrogen and oxygen. There is hardly any difference between the solubility coefficients of the liquid products and those of the solid acrylate and of the fluorinated elastomer.

The permeability coefficient being the products of the other two reflects the differences outlined before. In the case of the liquid products there is not a great difference among the coefficients to the three gases: there is in fact a sort of compensative effect due to the inverse difference in the entity of the parameters concerning carbon dioxide in one case and oxygen and nitrogen in the other.

The acrylic resin shows a very low permeability to all gases, almost two orders of magnitude lower than that of the perfluoropolyethers.

The fluorinated elastomer has a permeability to carbon dioxide analogous to that of the acrylic resin. We have not yet been able to determine that to oxygen due to the very low value of the solubility.

5 Discussion

The functionalized perfluoropolyethers display a decidedly higher protective efficacy than the original material.

Higher and more persistence protection is provided by polyamides, and among those tested the best results were produced by the hexamethylene derivatives. There is no improvement in passing from the diamides to the tetraamides. In fact the best protection is provided among the polyether derivatives tested by the hexamethylene diamide both in entity and persistence.

The improvement detected in passing from the monoamide to the diamide, which may be attributed to a more firm attack of the molecule to the surface caused by the presence of two polar groups, is not increased by the presence of more amidic groups in the same molecule. The increase in size of the molecule which renders more difficult its setting on the surface probably balances or outweighs the beneficial effect of the increased number of polar groups present. An other possible explanation of this behaviour may be found in the intramolecular association of the polar groups which competes with their interaction with the surface of the stone.

As for the permeability of the polymeric films to the gases tested, from the data reported in Table 3 it appears that the permeability of all coatings considered is small, but not irrelevant. Liquid polymers are in fact rather permeable to gases and considerable volumes of them may easily go through them.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>Polymer Diffusivity to ( \text{CO}_2 ), ( \text{O}_2 ), and ( \text{N}_2 ) at 1 atm and 25°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \frac{\text{cm}^2}{\text{STP cm sec atm}} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{CO}_2 )</td>
</tr>
<tr>
<td>Paraloid B67</td>
<td>51</td>
<td>0.12</td>
</tr>
<tr>
<td>Akegard CO</td>
<td>Liquid</td>
<td>0.14</td>
</tr>
<tr>
<td>YR</td>
<td>Liquid</td>
<td>5.8</td>
</tr>
<tr>
<td>IBAG2200</td>
<td>Liquid</td>
<td>15</td>
</tr>
<tr>
<td>DC2G2200</td>
<td>Liquid</td>
<td>8.7</td>
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<td>Liquid</td>
<td>4.5</td>
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<td>TC2G2200</td>
<td>Liquid</td>
<td>6.0</td>
</tr>
<tr>
<td>TC6G2200</td>
<td>Liquid</td>
<td>5.7</td>
</tr>
</tbody>
</table>
CO₂ volumes* permeating through stone conservation polymers calculated from permeability coefficients.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)</th>
<th>CO₂ cm³ (cm³@p=76cmHg)</th>
<th>CO₂ cm³ (cm³@p=0.025cmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraloid B67</td>
<td>51</td>
<td>13,994</td>
<td>5</td>
</tr>
<tr>
<td>Akeogard CO</td>
<td>-</td>
<td>16.754</td>
<td>6</td>
</tr>
<tr>
<td>YR</td>
<td>liquid</td>
<td>788.400</td>
<td>259</td>
</tr>
<tr>
<td>IBAG2200</td>
<td>liquid</td>
<td>1,773,900</td>
<td>583</td>
</tr>
<tr>
<td>DC2G2200</td>
<td>liquid</td>
<td>1,156,320</td>
<td>380</td>
</tr>
<tr>
<td>DC6G2200</td>
<td>liquid</td>
<td>517,059</td>
<td>170</td>
</tr>
<tr>
<td>TC2G2200</td>
<td>liquid</td>
<td>722.700</td>
<td>238</td>
</tr>
<tr>
<td>TC6G2200</td>
<td>liquid</td>
<td>716,130</td>
<td>235</td>
</tr>
</tbody>
</table>

* cm³ gas @ STP permeating in 1 m² cross sectional area of each polymer measuring 0.1 mm thick at 20°C over in 24 hours.

Solids are much less permeable: we have found a difference of two orders of magnitude. But even in this case the volume of gas which goes through the film in a reasonable museum time scale, may not be irrelevant.

Very interesting is the fact that an elastomer, which has a much lower Tg than the acrylate tested, has a permeability which is nearly as low. This result suggests that real protection both from water and permeating gases or vapours does not need to be realised with solid stiff materials which may easily find counter indications in the application to other solid materials. Such a protection may be realised with elastic materials which have a higher probability of being compatible with the support they are going to be placed on.

From our results it seems possible to select water repellent polymers having selective permeabilities to gases as required by the protection of stone or other materials.

6 References


