FLUOROELASTOMER BASED COMPOSITIONS FOR THE SURFACE AGGREGATION AND PROTECTION OF STONE MATERIALS

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Abstract

Fluoroelastomers are well known for their properties of surface aggregation and protection of natural and artificial stones.
Promising results, in terms of aggregating properties, water repellency and water vapor permeability, have been obtained using fluoroelastomers in combination with other products such as waxes, polymethylmethacrylate, alkylalkoxysiloxanes.
The tested substrates have been a porous limestone, brick, hydraulic lime and mortar.

1. Introduction

Before addressing the problem of stone protection it is worthwhile to clarify the relation between the criteria of selecting the various treatment operations (without considering structural works) as a function of the conditions in which the stone exists, as shown in Table 1.
The use of fluoropolymers in protection and conservation of a natural stone was for the first time reported in 1981 (Piacenti [1], Frediani [2])
These compounds belong to the class of perfluoropolyethers (PFPE) and up to now, even with little structural modifications (Piacenti [3], Matteoli [4]), they continue to be investigated and applied to many historic and artistic monuments (Falcone [5]).
PFPE, although solving the problem of protecting the surface are not capable to exert a surface consolidating action due to their liquid nature.

A substantial improvment was obtained by the application of an organic solution of fluoroelastomers (Piacenti [6], Tiano [7]) which efficiently exerts both protecting and the consolidating function.

Table 1
Stone Degradation - Condition of degraded surfaces

The surface of stone material after long exposure to open air can present:	
Healthy	• recent material placed in position (some substitution involved) • stone material that has passed some of it's life in a protected atmosphere or has been subjected in continous maintenance • alterated stone material which presents a surface residue in good and stable conditions
Disaggregated	• can be brought back to a healthy state • can not be brought back to a healthy state in this case it is necessary: to reaggregate
Presence of incrostation peeling off scaliness cracking	• can be brought back to a healthy state • can not be brought back to a healthy state in this case it is necessary: to glue to seal the use of micronails
Always, in every case, it is necessary	to protect the stone

To protect and consolidate the stone surfaces, a product must have these essential requirement:

1. Ability to restore the cohesion between the particles of the surface layer of the decayed materials and the underlying integral part.
2. Exhibiting an adequate mechanical strength of the consolidated surface layer.
3. Retaining characteristic of elasticity within the consolidated surface layer in order to prevent the formation of a stiff surface layer having mechanical characteristics different from the substrate.
4. Chemical inertia toward the material to be protected and consolidated.
5. Low volatility.
6. Stability toward the action of atmospheric agents, of light and of heat.

7. Not altering the chromaticity of the material.
8. Preserving for a long time its solubility characteristics in order to assure the reversibility of the treatment.
9. Water repellency.
10. Maintaining a sufficient permeability of the treated surface to air and water vapor in order to prevent alteration phenomena underneath the impermeable film. due to condensed water within the interior of the same materials, allowing the stone to breath.

As can be seen, the requirements coincide with the characteristics of elastomeric compositions having high fluorine content and therefore strong chemical stability.

The highest chemical stability of fluoropolymers with respect to polymers widely used in stone protection can be explained from simple considerations of the principles of bonding in organic compounds.

Actually, the average increases of Bonding Dissociation Energy from C-H to C-F are of about 20 Kcal/mol; the ether linkage $-O-CF_3$ has a Bonding Dissociation Energy about 22 Kcal/mol higher than $-O-CH_3$ and C-H bonds (the latter present, for exemple, in fluoroelastomers) increase their stability when adjacent carbons are fluorinated (Smart [8]).

Concerning C-C bonds it is notable that they are usually strengthened by fluorination, e.g. in polytetrafluoroethylene this bond is almost 8 Kcal/mol stronger than polyethylene [8].

Moreover the polymer chain is sterically shielded by a shell of high electronegative fluorine atoms that renders the kinetics of chemical attack difficult (e.g. by aggressive chemicals in acid rain) and the O_2/O_3 photochemically prompted C-H abstraction followed by oxidation, impossible.

The aim of this work is to investigate the behavior of a series of systems containing fluoroelastomers (FKM) and other products used in stone conservation, in order to obtain the improvement of the performance of FKM and moreover, to determine if the application of FKM can be used over previous protective treatments.

These studies are in the preliminary stage.

2. Materials

The experiments were performed on 5x5x5 cm and 5x5x1 cm samples.

2.1. Pietra di Lecce

Biocalcarenite consisting of calcium carbonate, both as calcite cement and fossil remain.

The used sample had different porosity ranging from 35 ÷ 40%

2.2. Mortar

Composition: 11% water, 22% hydraulic lime, 67% sand (0,1-1,2 mm); the porosity is about 25%

2.3. Brick

The porosity of the used samples was about 39 %.
Some field tests were carried out on bricks from the abse of a Church in Verderio (Como, Italy), built 95 years ago.
The building is made almost entirely of brick, according to the traditional medieval Lombard style. In fact the use of brick is typical of the medieval architecture found in the cities of flat lands in North Italy.

3. Products

- The fluoroelastomer (FKM) was obtained by drying a solution of AKEOGARD CO from Syremont S.p.A.. The number average molecular weight was close to $1.5x10^5$. The solid elastomer was then dissolved in ethyl acetate (5 %) by weight and applied by brush.

- Beeswax and cristalline wax were commercial products. They were dissolved in terpentine solution at 5 % by weight and applied by brush.

- As an alkylalkoxysiloxane (AAS) Wacker 290L was used, dryed at room temperature, then dissolved in ethanol (6 % by weight) and applied by brush.

- Polymethylmethacrylate (PMMA): a DIAKON MG grade of I.C.I. has been used. It was dissolved at 5 % by weight in ethyl acetate or in chloroform. The solution was mixed togheter with a solution of FKM in a ratio to obtain the values in solid product reported in the table 3. The mix of the solution of PMMA and of FKM was applied to the stone after 10 to 60 minutes in order to prevent the gel formation. The solutions were applied by brush.

- FKM and PMMA gels.
  In the range explored, the reversible polymer gel is formed of 80-96 % by weight of FKM and 4-20 % of polymethylmetilacrylate (PMMA). The weight percentage of FKM and PMMA are calculated based on the total content of polymer components excluding the solvent.
  We have found that elastomeric FKM solution in ethyl acetate in the presence of PMMA solution in chloroform gives rise to reversible gels. The gels are prepared by a process in which , first, a solution of FKM and a solution of PMMA are separately prepared, then the two separated solutions are homogeneously mixed and kept in quiescent conditions until

the gelation is obtained. Gel formation increases the viscosity by 10-100 or more times with respect to the starting mix of the solutions.
In general, the gelation time ranges from about 5 to 30 days, depending on the concentration of the polymers and the kind of solvents used. The total concentration of FKM in the mixture, based on the dry ingredients, is comprised between 2 and 10 grams per 100 ml of solvent.

4. Methodologies

They have two principal aims:

1. To obtain reliable data on the degradation extent of untreated stones and also on new stones to understand the stone properties in order to prevent damnaging effects.
2. To evaluate the effectiveness of protecting agents before and after natural or artificial aging by applying the product and controlling its protectives properties.

Effectiveness (E.) is general expressed as:

$$E.\% = \frac{\text{(Data of untreated stone) - (Data of treated stone)}}{\text{(Data of untreated stone)}} \times 100$$

Selected tests, here cited, include: water penetration resistance, water vapour permeability and aggregating efficiency.

Water penetration can be measured using a device consisting of a graduate pipette filled with water connected to a cylindrical hollow chamber which is pressed against the surface of the stone and sealed by a O-ring. Readings can be made at various time intervals and the data are reported as microliters of water penetrated per cm^2 of surface. The relative protective efficiency (P.E. %) is calculated from the ratio of the difference between water absorption in 30 min by the same untreated and treated stone, and the water absorbed by the untreated stone. P.E. can also be measured according to the capillarity method (Normal [9]) which consists in measuring the amount of water absorbed for unit of surface. The obtained data of water absorbtion in the two methods are different, but the values of P.E. % are almost the same.

Water vapour permeability (W.V.P.) is very important, because when humidity remains in the treated stone it can cause cracking during freeze-thaw cycles. A simple test determines the amount of water evaporated (g/m^2) in 48 hours through a thickness of 1 cm of the untreated stone (Tiano [10]). This value is made = 100 % and compared to the value found in the treated sample, for which a value > 50 % is considered acceptable.

Aggregation efficiency (A.E.) is measured by abrasion of the stones surface, before and after aggregative treatment, with a technique using abrasive paper at a fixed working pressure, rate of advancement of the paper and time [10].

5. Results and discussion

Beeswax

As it is well known beeswax was among the first compounds to be used to treat and protect stones,

The chemical composition of such product is about 70 % of alkyl esthers of fatty acids and about 14 % of waxy acids, their structure is therefore polar.

Preliminary tests were carried out on applying by brush solution at 10 % in terpentine on degradated Carrara marble at 40 g/m^2 (active product). The obtained value of P.E. was about 75 % and of W.V.P. about 70 % but only slight aggregating behaviour was found.

With a further treatment by brush of 10 g/m^2 (active product) of FKM solution the value of P.E. increased to about 85 % and the W.V.P. remained almost unchanged, while the A.E. increased to 75 %.

It is also important to point out that the tendency of beewax to become sticky and to collect dirt was strongly reduced.

These preliminary results suggest that the FKM solution can be applied on stone surface previously treated with beeswax or similar waxes. This because there is compatibility beetwen the polar structure of FKM that can interact with the carboxylic groups present in the beeswax. These interactions are in agreement with an observed shift of carbonyl band found for beeswax in the presence of FKM.

Microcrystalline beeswax

This compound has a completely apolar structure and its application was found not be compatible with a further treatment of FKM.

AAS - FKM treatment on mortar

The application of AAS was made by brush from an ethanolic solution containing 6 % by weight of active product. After 30 min the application of FKM was made by brush from a 5 % by weight ethyl acetate solution.

Table 2 shows the amount of applied products, referred to as the active component and the Protecting Efficiency (P.E.), the Aggregating Efficiency (A.E.) as well the Water Vapour Permeability (W.V.P.) taken as being 100 % for the untreat sample (run 1).

The data point out that the result observed in runs 4 and 5 (those using a small amount of AAS) give a good balance of the examinated properties of P.E., A.E. and W.V. P.

A similar behaviour has been observed in runs carried out on artificially aged brick samples.

Table 2 - Application of AAS and FKM on mortar

Run	Total amount of products g/m^2	Amount of AAS g/m^2	Amount of FKM g/m^2	P.E. %	A.E. %	W.V.P. %
1	-	-	-	-	-	100
2	30	30	-	90	0	80
3	30	-	30	75	80	78
4	30	6	24	92	77	74
5	30	3	27	92	78	76

FKM - PMMA solution treatment on Pietra di Lecce

A 5 % by weight in ethyl acetate solution of FKM was mixed with a 6 % by weight solution of PMMA in the same solvent, and applied after 20 minutes in order to prevent the gel formation (see below), in a ratio such to have the amount of active products reported below. The application was made by brush. Table 3 shows the results of the tests.

Table 3 - Application of PMMA and FKM solution on Pietra di Lecce

Run	Total amount of products g/m^2	Amount of FKM g/m^2	Amount of PMMA g/m^2	P.E. %	A.E. %	W.V.P. %
1	-	-	-	-	-	100
2	50	-	50	90	82	10
3	50	50	-	72	78	80
4	50	40	10	69	70	75
5	50	45	5	71	73	78

Comparing these data it is important to point out that PMMA alone shows good values of P.E. and A.E. while the W.V.P. is very low and at this value the stone can not breath.

On the contrary the data of run 4 and 5 suggest that there is a synergic effect between the two components.

The observed satisfactory compatibility beetwen FKM and PMMA suggests that a similar behaviour might be found between FKM and other acrylic resins, similar in the structure to PMMA. This fact suggests a possible application of FKM solutions on a stone surfaces previously treated with acrilyc resins and in good conditions.

FKM - PMMA gel treatment on brick

The gels were prepared by mixing a solution (5 % by wight) of FKM in ethylacetate with a solution (6 % by weight) of PMMA in chloroform in a ratio to obtain the amount of active product below reported. The application has been done after 30 days in order to allow the gel formation. Solutions of FKM - PMMA were prepared, as described above, for the comparative runs.

The application of a gel containing FKM and PMMA macromolecules onto the surface of the materials gives superior performances with respect to the application of a solution containing the same amount of the polymers. Both the treatments were done by brush.

In table 4 are reported the results of the application from gel and from solution for comparaison.

Table 4 - Application of FKM - PMMA from solution and from gels on Brick

Run	Tipe of application	Amount of FKM g/m^2	Amount of PMMA g/m^2	P.E. %	A.E. %	W.V.P. %
1	-	-	-	-	-	100
2	sol	21	9	85	72	65
3	gel	21	9	92	81	67
4	sol	24	6	82	73	75
5	gel	24	6	88	82	75
6	sol	27	3	80	75	79
7	gel	27	3	88	88	80

The remarkable effect resulting from the application of FKM - PMMA from gels in comparaison with the application from solution can be explained examining the mobility in different situation of the macromolecules. In solution FKM and PMMA macromolecules are dissociated and freely undergoing Brownian motions.

In gels the macromolecules produce physical crosslinking and a localized association of the macromolecules like in micelle and the polymer chains are unable to form fully developed crystals but can only form areas of high order, i.e., the molecules come quite close each other developing high intermolecular forces which prevent them undergoing Brownian motion.

The threedimensional structure of the gel, after evaporation of the solvent, can be easily destroyed, and the reversibility of the treatment is therefore assured.

Natural Aging

Maintaining the efficiency for long periods of time is one of the fundamental requirements which is important to achieve with the use of protective and aggregative surface treatments on stones.

The performances after aging in terms of E.G. and A.G. (the latter only for the laboratory samples not being possible to carry out the abrasion test on site) are reported in Table 5 for laboratory samples as well as on site tests concerning the brick abse of the Verderio Church, over long term intervals (1-12-36-60-months.

Table5 - E.P. and A.G. after aging

Lithotype	Amount g/m^2	Ratio FKM / PMMA	E.P. (A.G.) 1 month	E.P. (A.G.) 12 months	E.P. (A.G.) 36 months	E.P. (A.G.) 60 months
Pietra di Lecce	50	45/5	92 (80)	88 (76)	89 (77)	88 (76)
Brick *	30	27/3	95 (-)	92 (-)	91 (-)	92 (-)
Brick *	30	only FKM	88 (-)	86 (-)	84 (-)	85 (-)

* Brick from the abse (Church of Verderio)

All the application have been made from solution.

These data show that protecting and aggregating efficiency of the treatments with FKM and FMMA have remained almost constant through 5 years.

6. Conclusion

These preliminary results suggest that:

1) The application of an FKM solution onto stones previously treated with beeswax can be carried out when the substrate is in need of a surface aggregation.
2) The treatment of an FKM solution onto stone surfaces gives aggregating properties to the previously treated surface with AAS.
3) The treatment of stones with FKM-PPMA gels allow to obtain superior performances to applications from solutions.

The final aim of this research is to substitute or reduce the use of solvents with water based formulations.

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