Hydrophobe VI
6th International Conference on Water Repellent Treatment of Building Materials
Aedificatio Publishers, 155 – 164 (2011)

In Situ Polymerization of Acrylic Monomer with Low Molecular Weight Fluorinated Polymers for the Conservation of Stone

S. Vicini[1], E. Princi[1], G. Moggi[1] and L. Gaggero[2]
[1]Dipartimento di Chimica e Chimica Industriale, Università di Genova
Via Dodecaneso 31, 16146 Genova, Italy E-mail: silvia.vicini@unige.it
[2]Dipartimento per lo Studio del Territorio e le sue Risorse, Università di Genova, Corso Europa 26, 16132 Genova, Italy

Abstract

Acrylic resins are well known for their properties of surface aggregation and protection of natural and artificial degraded stones.

Promising results in term of water repellency and water vapour permeability have been obtained by in situ polymerizing a series of products based on acrylic monomers.

It is well known that the introduction of fluorine atoms into polymer structures has the effect of improving their chemical, thermal, photochemical stability and induces higher hydrophobicity. This characteristic had been exploited by the introduction in the polymerizing mixture of a low percentage (2-5 %) of a commercial high molecular weight fluoropolymer (Tecnoflon® TN of Solvay-Solexis).

This paper reports the evaluation of the effectiveness of in situ polymerization of 1,6-hexanediolediacrylate carried out in presence of higher amounts of fluorinated polymers with lower molecular weight (Tecnoflon® N 215 and N 535), chosen in order to increase the penetration depth. The efficiency of the products in situ synthesized at various fluorine content has been comparatively evaluated in terms of hydrophobicity and water vapor permeability on a selected stone substrate.

Keywords: fluorinated polymers, in situ polymerization, protection of stone

1 Introduction

Water, coming from rain or from the moisture condensation due to thermal excursion between day and night and/or summer and winter, is commonly considered the main cause of stone degradation since it carries the pollutants present in the atmosphere (CO_2, NO_x, SO_x) into the pores.

The penetration of water into the stones is due to their porosity. From this point of view it is important the pores size distribution (micropores, mesopores, macropores), since inside the micropores ($\varnothing$ < 20 Å) the capillary effect is enhanced; the polluting solutions can reach a higher depth and the stone is easily degraded. The reaction of the chemical components of the rocks with the pollutants leads both to an increase of the average stone porosity and to a shift of the size distribution towards mesopores ($20 < \varnothing < 500$ Å) and macropores ($\varnothing > 500$ Å). The increasing of porosity, in the deeper layers, is associated to the stone decohesion and to the reduction of adhesion of the degraded layers to the substrate, i.e. the original stone. Increasing of porosity is therefore also responsible of an higher water penetration inside the stone.

The use of polymeric materials for the conservation of stone is nowadays generally accepted [1]. Actually they show an important advantage in respect to the inorganic ones: they may also have a protective activity against water penetration joined to a remarkable surface consolidation. As a consequence, the application of only one product to the stone achieves two results, in terms of consolidation and protection, at the same time, with consistent reduction of restoration costs.

However some properties of the polymeric materials must still be fully studied: for example their stability on ageing [2]. On the other hand, other properties must be improved, mainly, the characteristics connected to the organic nature of the polymers; for instance some of them are not compatible with the inorganic nature of the stone.

Nevertheless the main problem with the polymeric compounds is related to their macromolecular nature. While inorganic substances have a very small molecule (a few Angstroms), polymers are made out of macromolecules with dimensions that increase with the square root of the molecular weight [3]. Therefore it is difficult for a macromolecule to penetrate inside the stone since its pores may have a very small diameter. It is obvious that the penetration depth will be very small: the polymer will be confined to the superficial layers. This is suitable for a polymer with only a protective action; but it is not acceptable for a material that must also be a consolidating product, because in this case a deep penetration is required.

These considerations are the basis for the in situ polymerization [4]. According to our technique not the preformed polymer but the monomer is introduced in the stone; it is in situ polymerized in a subsequent step. It is possible to foresee that, due the small dimension of the molecule of the monomer, the penetration will be easier.

In the past researches the feasibility and the potentialities of the in situ polymerization applying a series of products based on acrylic copolymers (ethyl methacrylate / methyl acrylate and butyl methacrylate / ethyl acrylate) were reported [5-7].

It is well known that the introduction of fluorine atoms into polymer structures has the effect of improving their chemical, thermal, and photochemical stability [8, 9], due to the stability of the C-F bond (bond energy 116 Kcal/mol). In addition, the formal substitution of hydrogen by fluorine atoms induces higher hydrophobicity as a consequence of the low surface energy brought by the fluorinated groups.

This characteristic has been exploited by the introduction in the polymerizing mixture of a low percentage (2 and 5 %) of preformed fluoropolymer. The choice of the commercial high molecular weight copolymer Tecnoflon TN® of Solvay-Solexis was due to it good miscibility with acrylic copolymers [7, 10].

Following all of these indications, this paper reports the assessment of the effectiveness of in situ polymerization of a pure monomer 1,6-hexanediole diacrylate (HDDA) carried out in presence of higher amounts of fluorinated polymers, with lower molecular weight (Tecnoflon® N 215 and N 535 of Solvay-Solexis), chosen in order to increase the penetration depth (solution used will be less viscous), in the framework of a systematic approach to the problem of the stone restoration. The efficiencies of the products synthesized in situ and variously fluorinated have been comparatively evaluated in terms of surface properties, i.e. water permeability on a selected stone substrate.

2 Experimental

2.1 Materials

Acrylic monomer (HDDA) and solvent (acetone) employed in this research were commercial products from Aldrich. The polymerization initiator (AIBN: 2,2'-azo bis isobutyronitrile) came from Fluka. Deionized water was used throughout the work.

The fluorinated polymer Tecnoflon TN® (Tg=-14 °C) was supplied by Solvay-Solexis; its molar composition is: vinylidene fluoride (64%), hexafluoropropylene (19%), tetrafluoroethylene (17%), for a total amount of fluorine equal to 67% wt. The molecular weights are: Mw=495000, Mn=90000.

Tecnoflon® N215 and N535 are supplied by Solvay-Solexis; with the composition: vinylidene fluoride (79%) and hexafluoropropylene (21%), for a total amount of fluorine equal to 65% wt (and lower Tg than TN), and molecular weights Mw=132000, Mn=51000 and Mw=336000, Mn=73000 respectively.

These polymers are soluble in acrylic monomers and exhibits thermodynamic compatibility with acrylic and methacrylic resins [7, 11]. Mixtures of HDDA containing 2, 5 and 10% wt of Tecnoflon were used.

The polymerization was performed with good results on a calcareous sedimentary stone of biological origin, easily available in Liguria, Italy, called Finale Stone. This is found in four different formations differing in the percentage of impurities and different colors, from white to rose, and presents two basic requirements: fairly high porosity, in order to reproduce a material degraded by the physical and chemical agents; and easily supplied in the standardized forms. Two varieties of Finale stone were employed: the Mascia variety (porosity: 31%) and the Castelgavone variety (porosity: 27%).

Polymerization of HDDA, in presence of fluoropolymers, was also processed outside the stone (in vitro). The reaction was performed in solution at 60°C, following the conventional mechanism of free-radical polymerization.

2.2 In situ polymerization

The in situ polymerization was carried out in acetone solution (20 % vol/vol of monomer). The experimental procedure consists of two steps:

- Absorption: the specimen absorbs by capillarity the mixture that must be polymerized putting the sample on a thick layer of cotton soaked in the reaction mixture; the operation was carried out at 4°C, in absence of light and the absorption time was standardized in four hours.

- Polymerization: the polymerization was carried out at 60°C for 24 hours (at this temperature AIBN –3% wt/wt of monomer- allows enough to reach a good conversion for our application) [12].

The amount of polymer present in the stone (Δ%), after the in situ copolymerization was calculated with the simple equation (1).

$$\Delta\% = [(W_f - W_i)/W_i] * 100 \qquad (1)$$

where W_f (g) and W_i (g) are the weights of the specimens after and before the treatments, respectively.

The application of in situ polymerizing mixture can be carried also out by brush on the stone as reported in [10] and at lower temperature [5, 7]. These aspects are important for practical applications.

2.3 Evaluation of treatments

To evaluate the protective properties of the in situ polymerized polymers, some tests were carried out. Each test was performed on three specimens (5x5x2 cm^3 and 5x5x1 cm^3) of the Finale stone samples, before and after each treatment.

The protective properties were evaluated by capillary water absorption and permeability to water vapor.

The capillary water absorption test was carried out using the gravimetric sorption technique [13]. The amount of absorbed water Q_i, at the time t_i per surface unit, is defined as follows:

$$Q_i = (M_i - M_0)/S \qquad (2)$$

where M_i is the specimen mass (g) at the time t_i (second), M_0 is the dry specimen mass (g) and S is the contact surface (cm^2).

The Q_i values (g/cm^2) are plotted against the square root of time ($t^{1/2}$), to give the capillarity absorption curve.

The angular coefficient of the first part of the curve enables to evaluate the capillary absorption coefficient CA and its value should be reduced with treatment. The results can also be expressed as protective efficiency PE%:

$$PE\% = [(Q_0 - Q_t)/Q_0]*100 \qquad (3)$$

where Q_0 and Q_t are the average value of water absorbed by untreated and treated stones after 1 hour respectively.

The permeability to water vapor test was carried out according to the corresponding Normal protocol [14] on the 5x5x1 cm^3 specimen put in a apposite cell. The test is carried out at constant temperature 20±0.5°C. The permeability is monitored by determining the weight decrease per surface unit (S, m^2) in the unit time (24 h):

$$\Delta M_i = (M_i - M_{i-1})/S \qquad (4)$$

where M_i is the weight system (cell and stone) at i-day (g).

ΔM_i (daily weight variation) is calculated when a stationary condition (constant vapor flow through the stone) is reached. The permeability to water vapor, after the treatment, must be as high as possible and not too different from the value of the untreated material.

Besides the water vapor permeability, we evaluated also the reduction in permeability RP% due to the treatment, according with the equation (5).

$$RP\% = [(P_0 - P_t) / P_0]*100 \qquad (5)$$

where P_0 is the permeability to water vapor of the untreated stones, used as reference and P_t the permeability to water vapor of the treated stones.

The measurements of contact angle, useful to evaluate the superficial hydrophobicity, was carried out on polymeric films instead of porous substrates, because the porosity, heterogeneity and roughness of stones strongly affect the results [15].

Contact angles have been measured with an optical Kruss goniometer, model G-1 N° 88127. A 1.5-2 mm diameter drop of water, dripped from a microsiringe, has been put on the sample surface, and immediately the value of the contact angle between the water drop and the material has been measured. The resulting contact angle measurements were averaged for each specimen and standard deviation was calculated.

3 Results and discussion

The quantities of polymer present inside the stone $\Delta\%$ after every experiment are collected in Table 1.

The amount of polymer in the Mascia stone is higher than in the Castelgavone: this is due to the different porosity and dimension of pores of the two kinds of stones used in the series of experiments; Mascia has slightly higher porosity, but much bigger diameter of pores.

After the in situ polymerization, the polymer amount in the stone is at least twice in comparison with that present after the absorption, in the same stone, of a preformed polymer solution (i.e. Paraloid B72®: the typical acrylic product used in conservation) [4-7]. This result confirms the main advantage of the in situ polymerization: the absorption of the monomer instead of the preformed polymer allows putting into the stone a larger amount of consolidating and protective material.

The presence of Tecnoflon TN, even if added at 2% reduces largely the $\Delta\%$. This result can be easily explained considering that Tecnoflon TN is a preformed polymer, with very high molecular weight; it increases the viscosity of the mixture applied to the rock, thus no deep penetration can be achieved.

The same explanation can justify the decreasing of $\Delta\%$, in both the stones, from the polymerization with HDDA to with HDDA + Tecnoflon N215 and N535 at 5% and at 10%. We can observe that the decreasing, as foreseen, strongly depends of the molecular weight, in fact even adding 10% of Tecnoflon N215 (lower MW) we don’t obtain the low level of $\Delta\%$ reached with 2% of Tecnoflon TN.

The protective properties correlated to the different treatments are generally linked to the amount of polymer present in the stone pores. Figure 1 shows the results of capillary absorption tests concerning the HDDA experiments with and without fluoropolymers in Mascia and Castelgavone stones.

The water capillary absorption test shows that the untreated stones rapidly absorb a great quantity of water: this effect is reduced by every treatment. The presence of all the Tecnoflon largely improves the water repellence of the in situ polymerized copolymer, even if the amount of polymer in the stone pores is lower. This fact this is due to the presence of the fluorinated repetition unit.

The remarkable effect on the water penetration reduction related to the presence of very little amount of fluorine, contained in the Tecnoflon has to be connected to a surface segregation of fluorinated groups.

Table 1: Weight variation ∆% of treated stones and performances of treated stones

POLYMER	∆%	CA ($g/cm^2\ t^{1/2}$)	PE %	P (g/m^2 24h)	RP %
Mascia stone					
Untreated	-	15.4±0.02 x 10^{-4}	-	30±3	-
HDDA	2.1	10.4±0.02 x 10^{-4}	32	7±1	77
HDDA + Tecnoflon TN 2%	0.2	7.5±0.02 x 10^{-4}	40	11±2	63
HDDA + Tecnoflon N215 5%	1.3	0.6±0.01 x 10^{-4}	90	9±1	70
HDDA + Tecnoflon N535 5%	1.2	1.1±0.01 x 10^{-4}	87	10±2	67
HDDA + Tecnoflon N215 10%	0.8	1.9±0.01 x 10^{-4}	90	10±1	67
HDDA + Tecnoflon N535 10%	0.4	1.3±0.01 x 10^{-4}	89	10±1	67
Castelgavone stone					
Untreated	-	3.1±0.02 x 10^{-4}	-	20±3	-
HDDA	0.5	2.8±0.02 x 10^{-4}	33	6±2	70
HDDA + Tecnoflon TN 2%	0.02	2.0±0.02 x 10^{-4}	33	9±2	55
HDDA + Tecnoflon N215 5%	0.4	0.5±0.01 x 10^{-4}	86	7±2	65
HDDA + Tecnoflon N535 5%	0.4	0.2±0.01 x 10^{-4}	93	7±2	65
HDDA + Tecnoflon N215 10%	0.07	0.4±0.01 x 10^{-4}	88	7±2	65
HDDA + Tecnoflon N535 10%	0.06	0.4±0.01 x 10^{-4}	87	8±1	60

As shown in Table 1, the capillary absorption coefficient of stone treated with HDDA and HDDA + Tecnoflon TN is higher than that obtained with the two Tecnoflon N(215 and 535), because the fluoropolymer forms a continuous film on the stone surface and it is more efficient, as hydrorepellent, when is present in higher concentration. In fact the best performance is realized by the N215 (lower Mw) at higher concentration. Obviously the CA for the untreated stones are the highest.

Data concerning the permeability test and the reduction of permeability after the treatments are reported in Table 1. The permeability of the untreated stones follows their porosity: actually the Mascia variety has porosity higher than that of Castelgavone variety and bigger diameter of pores and consequently the permeability decreases from 30 to 20 g/m^2 24h. The treatments with the polymers reduce the permeability (following the data of Δ%), but the experimental values are still acceptable. The reduction is larger for the Mascia stone, owing to the high porosity of the stone, whose pores are more easily filled up with the polymers. The behavior of the two Tecnoflon N (215 and 535) is similar and that of Tecnoflon TN it is not so different.

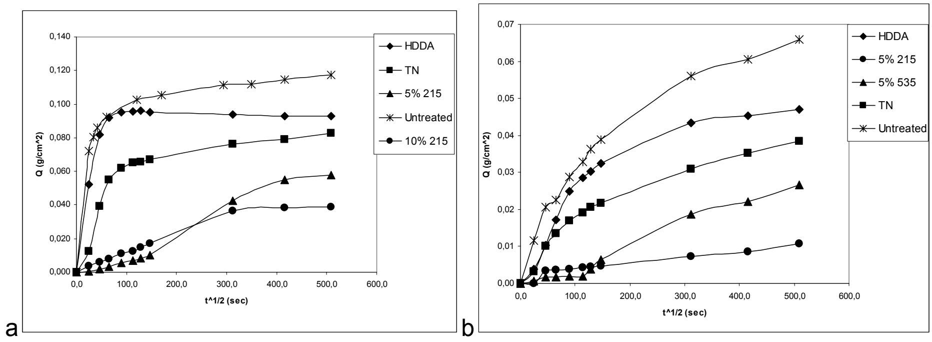

Figure 1: Results of capillary absorption test concerning the HDDA experiments with and without fluoropolymers in Mascia stone (a) and in Castelgavone stone (b)

The contact angle was measured on polymeric film on a glass support; the investigated surfaces were those exposed to air. As foreseen, the samples containing fluorine atoms (even in low percentage) show higher contact angles. Consequently the angle increases from 81°±2 to 96±2, by passing from film of HDDA to the film with the three Tecnoflon.

4 Conclusions

The experimental results presented on this paper support once again that the protective efficacy of a polymer can be improved if fluorinated compound are added. Our experiments show that a fluorinated elastomer can be dissolved in the acrylic monomer to be in situ polymerized and its Mw strongly affects its amount into the stone.

As seen in previous research, it is not opportune to use (with the acrylic monomer to be polymerized) Tecnoflon TN in % higher than 2% because otherwise the polymer is just confined on stone surface. Therefore in the present work we changed fluoropolymer choosing products with lower Mw. We verified that it is possible use it in higher percentage, obtaining better protective performance, even it is clear that, also in this case, increasing the percentage of polymer the Δ% decreases (solutions become more viscous). Our data lead to the conclusion that generally few percent of fluorinated compound is enough to largely improve the protective properties. This is remarkable since it reduces the cost of the restoration. Finally it is interesting notice that HDDA, having two acrylic groups, during the polymerization crosslinks and the fluoropolymer is included into the network as a Semi-IPN (Interpenetrate network), with the consequence that the system performs beside water repellency a good surface consolidation of the decayed stone.

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