Chapter 9.4

IN SITU POLYMERIZATION WITH ACRYLIC MONOMERS FOR STONE CONSOLIDATION AND PROTECTION

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Abstract: In this paper the in situ copolymerization of acrylic monomers, i.e. mixtures of ethyl methacrylate and methyl acrylate, is once again proposed as a remarkable technique in order to increase the amount of polymer present inside the stone and consequently to improve the consolidating properties of the substrate. To make better the protective properties of the copolymers two different possibilities are indicated: either to copolymerize a third fluorinated acrylic monomer, i.e. 2,2,2 trifluoroethyl methacrylate, or to dissolve in the copolymerizing mixture a fluorinated elastomer, i.e. Tecnoflon TN®. In both cases our results show that small amounts of fluorinated compounds are sufficient to improve remarkably the protective properties of the polymers.

Key words: In situ polymerization; acrylic copolymers; stone consolidation and protection.

1.   INTRODUCTION

Water is commonly considered the main cause of stone degradation since it carries the pollutants which are present in the atmosphere, owing to the combustion processes i.e. carbon dioxide, sulphuric and nitric oxides. Water comes from rain or from condensation of moisture, due to thermal excursion between day and night and/or summer and winter.

The degradation level depends on the chemical nature of the rocks; actually, the limestones are damaged more than silicatic ones since calcium carbonate is easily transformed by acid rain in calcium hydrogen carbonate, sulphate and calcium nitrate. The penetration of water into the rocks is due

to the porosity of the stone[1,2]. From this point of view the pores size distribution is particularly important (micropores, mesopores, macropores), since inside the micropores ($\varnothing < 20$ Å) the capillary effect is more enhanced and the polluting solutions can reach higher depths.

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 is associated to a decohesion of the material, that loses its intrinsic mechanical properties, and to a reduction of adhesion of the degraded layers to the substrate, i.e. the undegraded stone. The main purpose of the so called "consolidation" treatment consists in leading back the average porosity and the pore size distribution to the original values characteristic of the undegraded stone, improving both the adhesion of the altered layers to the substrate and the cohesion of the degraded material, in order to recover the original mechanical properties.

The consolidation can be performed with both inorganic and organic substances, introduced into the stone by capillary absorption of solutions or suspensions. Organic consolidants are polymeric compounds[3]; owing to the large dimensions of their molecules[4,5] in comparison with the pores sizes, they can not penetrate deeply into the degraded stone, but they often remain in the external layers. For this reason their consolidation properties are rather insufficient. On the other side, polymers can have water-repellent properties and therefore they can perform a protective action, forming a superficial barrier between stone and environment which hinders the penetration of liquid water. This means a peculiar characteristic, which puts polymeric compounds in a leading position if compared with inorganic consolidants, which do not exhibit hydrophobic properties.

Obviously one faces with two problems. First of all, the polymer must penetrate in the smallest pores and besides this the water repellence must be improved. The first topic can be settled with the in situ polymerization, carried out in the laboratory as described by Vicini et al.[5-8]. With this technique, the degraded stone is treated not directly with the polymer, but with the corresponding monomers: these molecules have small dimensions and therefore they can easily penetrate inside the micropores, where they are polymerized in a subsequent step following a usual radical mechanism.

As far as the water repellence is concerned, fluorinated polymers or monomers can be used[9-13]. It is well known that the introduction of fluorine atoms into polymer structures has the effect of improving their chemical, thermal, and photochemical stability, 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. The high cost of these products leads to minimize their amounts in the compounds used for the consolidation and protection. In this paper the results of in situ polymeri-

zation of acrylic monomers carried out in presence of small amounts of both fluorinated polymer and monomer, with the purpose of improving the performances of the restoration treatments, are reported.

2.   EXPERIMENTAL

2.1   Materials

The monomers used in the experiments, i.e. ethylmethacrylate (EMA), methylacrylate (MA) and 2,2,2 trifluoroethylmethacrylate (TFEMA), were commercial products supplied by Aldrich. They contain an inhibitor (hydroquinone monomethylether) that has been removed before the polymerization, passing through an Aldrich *Inhibitor Removers* column. The pure monomers were subsequently stored at low temperature (4 °C) in the dark, in order to avoid polymerization.

The fluorinated monomer TFEMA has been chosen since it is comercially available at a reasonable low price. On the other hand, its conversion in homopolymer is rather high (86% in dioxane)[12] and it copolymerizes easily with other unfluorinated acrylic monomers. The homopolymer exhibits a quite high chemical, thermal and photochemical stability[14]. Acrylic monomeric mixtures containing 2.5% and 10% (mol/mol) of TFEMA were used, indicated in the following as Terpolymer 2.5 and Terpolymer 10. The polymerization initiator (2,2′ azobisisobutyronitrile, AIBN)[15] was supplied by Fluka.

The fluorinated polymer was Tecnoflon TN® supplied by Solvay Solexis; its composition is the following: vinylidene fluoride (64%), hexafluoropropylene (19%), tetrafluoroethylene (17%). The total amount of fluorine is 67% wt. The molecular weights are: Mw=495000, Mn=90000; the polydispersity index is 5.5; the glass transition temperature is -14 °C. This polymer is soluble in acrylic monomers and exhibits thermodynamic compatibility with acrylic and methacrylic resins[16-18]. Use was made of solutions in acrylic monomers of Tecnoflon TN® containing 2, 5 and 10 % w/w, indicated in the following as EMA/MA + Tecnoflon 2, Tecnoflon 5 and Tecnoflon 10, respectively.

Paraloid B72®, used for a comparative study since it is widely employed in stone restoration, was a commercial acrylic resin produced by Rohm and Haas, with a composition of 67 % EMA and 33 % MA[19]. The ratio between the repetition unit of EMA and MA in the copolymers used in the present series of tests has been purposely kept similar to the analogue Paraloid B72®. Solvents were laboratory grade products from Aldrich and they were used without any further purification.

Deionized water was employed throughout the work.

Obviously, specimens of deeply degraded stones coming from monuments of historical interest were not available in so large number to perform the

whole investigation. For this reason one is obliged to choose a quarry rock, which has to satisfy two basic requirements: high porosity, to reproduce a stone weathered by physical and chemical agents and easy availability in standardized shapes, suitable for the experiments.

Two varieties of Finale stone, a calcareous sedimentary rock of biological origin, easily available in Liguria (Italy)[20] and with a fairly high porosity were used:

- the Mascia variety (porosity: 27%) for the experiments with the terpolymer EMA/MA/TFEMA (in the following experiments A).
- the Pale variety (porosity: 40%) for the experiments with Tecnoflon TN® (in the following experiments B).

2.2   In situ polymerization

The in situ polymerization is performed in three subsequent steps: absorption, polymerization and purification. In the first step, stones absorb by capillarity the different mixtures that must be polymerized, placing the sample on a thick layer of cotton soaked in the reaction mixture; the absorption time was standardized in 4 hours at 4 °C, in absence of light. Polymerization was carried out at 50 °C; this temperature is very close to that corresponding at the best performance of AIBN (the half period of AIBN is 25 hours at 60 °C and 50 hours at 50 °C); the reaction time was 24 hours. In these conditions the conversion is high. The purification involves the removing of the solvent and the unreacted monomers still present after the polymerization. The amount of AIBN was 2% wt of the monomer mixture.

The reactions have been performed in acetone (20% vol/vol of the monomer mixture), in order to avoid the large volume contraction which leads to fractures in the stone, when the polymerization is carried out in bulk.

The percentage of fluorinated compounds in the reaction mixture was intentionally limited to small values since the cost of these products is quite high; on the other side the solutions of Tecnoflon TN® in the acrylic monomer have a rather high viscosity, which hinders a good penetration into the stone.

To compare the results of the in situ polymerization with those obtainable from the traditional technique of application of consolidants, some stone specimens have been treated by capillarity for 4 hours with a 3% wt solution in acetone of Paraloid B72® or of a mixture Paraloid B72® / Tecnoflon TN® containing the 2% wt of the fluorinated elastomer (in the following indicated as commercial mixture).

The amount of polymer present in the stones ($\Delta M\%$), after the in situ copolymerization and the absorption of the preformed polymers, has been calculated using the simple equation:

$$\Delta M \% = [(P_f - P_i)/P_i] * 100$$

where P_f and P_i are the weights of the specimens after and before the treatments, respectively.

2.3   Consolidation and protection tests

To evaluate the consolidating and protective properties of the in situ polymerized copolymers, some tests have been carried out[21,22]. Each test has been performed on three specimens (5x5x2 cm) of the Finale stone samples, before and after each treatment.

The consolidating properties were evaluated with an original instrument[8], made up by a wood rail (100 cm of length x 5 cm of width) having a strip of sandpaper (granulometry: 60 mesh) on the top. The sample with the largest area surface (5x5 cm) is set on the rail and loaded with a weight of 2.0 kg; it runs for 30 times (equivalent to 30 meters of sandpaper) along the sandpaper with a constant driving force of 2.5 kg; every 5 meters it is weighed and the weight loss percent (WL%) is calculated. The test allows the calculation of the efficacy of superficial aggregation (EA) with the formula:

$$EA = [(WL_0 - WL_t) / WL_0] * 100$$

where WL_0 is the average value of the weight loss percent of three untreated stones after 30 meters and WL_t is the average value of the weight loss percent of three treated stones after 30 meters. The quantity of removed material is a function of the aggregation of the sample, and so it is different for treated and not treated samples.

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, according to the Normal protocol[23]. The stone specimen is laid on a filter paper pad, around 1 cm thick, partially immersed in deionized water, with the treated surface in contact with the pad. The amount of water absorbed by capillary force is determined by weighing the specimen after 10′, 20′, 30′ and 1, 2, 4, 6, 24, 48, 72 and 96 hours, to obtain the wet specimen mass M_i (M ± 0.0001 g).

The amount of absorbed water Q_i, at the time t_i per surface unit, is defined as follows:

$$Q_i = (M_i - M_0) / S$$

where M_i is the specimen mass (g) at 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 one to evaluate the capillary absorption coefficient CA: this value should be reduced with treatments. The results can also be expressed as protective efficiency EP %:

$$EP \% = [(Q_0 - Q_t)/Q_0] * 100$$

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

The permeability to water vapor test was carried out according to the corresponding Normal protocol[24] on 5x5x1 cm specimens, using a measurement cell consisting in a cylindrical PVC chamber with open top fitted with an o-ring rubber seal, where the stone specimen is employed as the lid of the chamber; the chamber is sealed with the lid by means of an aluminium flange with an o-ring. The cell is partially filled with deionized water, therefore allowing measurement by gravimetry of the amount of water vapor that diffuses through the stone specimen with fixed thickness (1 cm) between two parallel surfaces. The test is carried out at constant temperature 20 ± 0.5 °C, with the cells placed into a desiccator. The driving force for the diffusion of water vapor is, therefore, the constant difference between the water vapor pressure inside and outside the cell (in the presence of activated silica gel desiccant).

The permeability is monitored by determining the weight decrease per surface unit (S, m^2) in the unit time (24 h):

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

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

The cell is weighed ($M \pm 0.0001$ g) and ΔM_i (daily weight variation) is calculated when a stationary condition (constant vapor flow through the stone) is reached; stationary flow was considered to be reached when:

$$(\Delta M_i - \Delta M_{i-1}) \times 100/\Delta M_i \leq 5 \%$$

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, the reduction in permeability RP % due to the treatment was evaluated, also, according to the following equation:

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

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 ones.

3.   RESULTS AND DISCUSSION

The amount of polymer present inside the stones ($\Delta M\%$) is reported in Tables 1 and 2 for the experiments A and B respectively.

Table 1. ΔM % in the experiments A.

POLYMER	(ΔM %)
Paraloid B72®	0.10
EMA/MA copolymer	0.20
Terpolymer 2.5	0.30
Terpolymer 10	0.30

Table 2. ΔM % in the experiments B.

POLYMER	(ΔM %)
Paraloid B72®	1.6
EMA/MA copolymer	3.1
EMA/MA + Tecnoflon 2	2.4
EMA/MA + Tecnoflon 5	0.9
EMA/MA + Tecnoflon 10	0.3
Commercial mixture	1.1

The amount of polymer present in the stone in the experiments B is higher than in the experiments A, either if one applies the commercial copolymer Paraloid B72® or if one copolymerizes in situ the mixture EMA/MA. This is due to the different porosity of the stones used in the two series of experiments, 27% for the Mascia (A) and 40% for the Pale (B), respectively.

In both experiments, the in situ copolymerization of the mixture EMA/MA leads to ΔM% values double than those measured after the absorption of the Paraloid B72® solution. This result confirms what could be easily foreseen, namely that the absorption of the monomers by the stone instead of the preformed polymer sets up a real advantage since it allows introducing into the pores of the stone a larger amount of the consolidating and protective material.

In the experiments A, when the fluorinated monomer is present in the mixture copolymerized in situ, ΔM% reaches values of 0.3%. It is supposed that this result could be explained if one takes into account that the mixture with the fluorinated monomer reacts faster; since the polymerization time is standardized in 24 hours, the conversion yield is higher.

In the experiments B, the presence of Tecnoflon TN® mixed with the acrylic monomers reduces ΔM%, increasing in large amount the percentage of the fluorinated elastomer (from 2 to 10%). This result can be easily explained if one considers that Tecnoflon TN® is a preformed polymer; therefore, it increases the viscosity of the mixture applied to the rock that cannot penetrate deeply in the pores of the stone.

This explanation justifies the decreasing of ΔM% from 2.4% with the in situ copolymerized mixture EMA/MA + Tecnoflon 2 to 1.1% with the solution of the two polymers Paraloid B72®/ Tecnoflon TN® (commercial mixture with 2% of Tecnoflon TN®). Also in this case the in situ polymerization is favorable in comparison with the absorption of the preformed polymers.

The consolidating and protective properties related to the different treatments reflect the amount of polymer present in the pores of the stone.

Figures 1 and 2 show the results of abrasion and capillary absorption tests obtained from the experiments A.
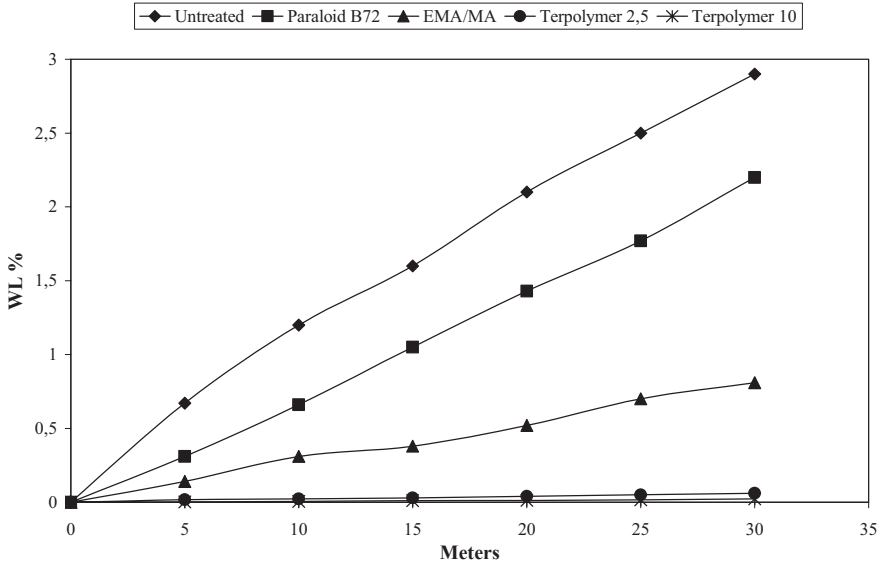

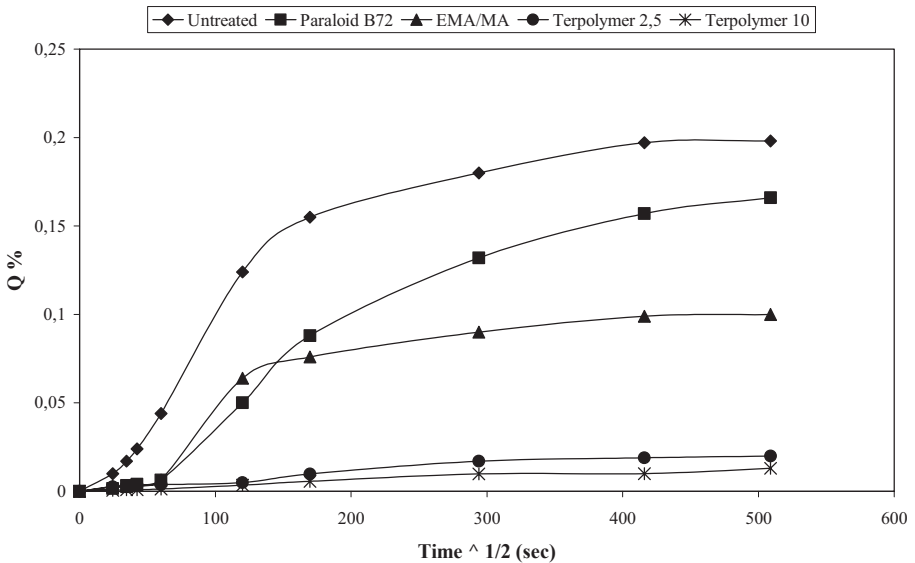*Figure 1.* Results of abrasion test concerning the experiments A.

Figure 2. Results of capillary absorption test concerning the experiments A.

The aggregation efficiency is particularly high for the terpolymers (EA= 90%) which penetrate deeply in the stone and low for Paraloid B72® (EA= 30%), which forms just a thin polymer layer on the surface. For the copolymer EMA/MA polymerized in situ EA is good (50%), but it probably could reach higher values increasing the monomers conversion, since the reaction time is limited to 24 hours.

The capillary absorption test shows that the presence of TFEMA largely improves the water repellence of the in situ polymerized copolymer, owing not only to the higher amount of polymer in the stone pores, but also the presence of the fluorinated repetition unit.

Comparing the behavior of Paraloid B72® with that of the in situ polymerized copolymer, the latest shows better performances for long time of exposition to the liquid water. In the short time Paraloid B72® supplies good water repellence; actually it forms a continuous layer on the stone surface, which hinders the penetration of the liquid water, but the layer is too thin to hold out: after about 1 hour, water gets over the polymer and penetrates deeply into the stone.

Finally, it is underline that, both in the abrasion and in the capillary absorption tests, the behavior of the two terpolymers is similar. This remarkable result leads to the conclusion that, since the price of the fluorinated monomers is high, the amount of TFEMA in the terpolymer can be limited to 2.5%, without changing the performances of the polymeric material.

As far as the experiments B are concerned, attention is focused only on the capillary absorption test, since the main purpose of the addition of the Tecnoflon TN® to the copolymerizing monomers is to improve the resistance to water penetration. The data are reported in Table 3.

These results show that Paraloid B72® and EMA/MA copolymer polymerized in situ have the same behavior, independently of the amount of polymer present into the stone. Obviously one must realize that the capillary absorption coefficient and the corresponding protective efficiency refers to the initial period of exposure of the treated stone to liquid water. Later on the performance of the EMA/MA copolymer improves, as stated in the experiments A, and its capillary absorption becomes smaller than that of Paraloid B72®.

Table 3. Capillary absorption data for the experiments B.

TREATMENT	CA $g/cm^2\ sec^{1/2}$	EP %
None	4.2×10^{-3}	-
Paraloid B72®	2.4×10^{-3}	45
EMA/MA copolymer	2.4×10^{-3}	45
EMA/MA + Tecnoflon 2	1.1×10^{-4}	96
EMA/MA + Tecnoflon 5	4.3×10^{-4}	90
EMA/MA + Tecnoflon 10	2.8×10^{-4}	93
Commercial mixture	4.3×10^{-5}	99

The addition of Tecnoflon TN® doubles the protective efficiency. It is noteworthy that the behavior of the polymer does not improve increasing the amount of Tecnoflon TN® and therefore only few percent of fluorinated ter-polymer are sufficient in order to have good protective characteristics.

Finally, the highest value of EP is obtained with the commercial mixture of Paraloid B72® and Tecnoflon TN®. This is probably due to the formation of a film on the stone surface which, owing to Tecnoflon TN®, is more adhesive and flexible than the one obtained with Paraloid B72® alone; it provides an excellent hindrance to the penetration of liquid water.

The last data, reported in Tables 4 and 5, concern the permeability test and the reduction of permeability after the application of the polymer. The permeability of the untreated stones follows their porosity: actually the Pale variety has porosity higher than that of Mascia variety (40% vs. 27%) and consequently the permeability increases from 28 to 56 g/(m^2.24h). The treat-ment with the polymer reduces the permeability but the experimental values are still acceptable. The reduction is larger in experiments B due to the high porosity of the stone, whose pores are more easily filled up with the polymers.

It is worth to note that the largest reduction of permeability is found for terpolymer 10 in the experiments A and EMA/MA + Tecnoflon 10 in the experiments B. These results support the conclusion that only few percent of fluorinated compound are enough to give the best performances.

Table 4. Results of the permeability test for the experiments A.

TREATMENT	Permeability (g/m^2 24h)	RP (%)
None	28	-
Paraloid B72®	19	33
EMA/MA copolymer	20	29
Terpolymer 2.5	20	29
Terpolymer 10	12	57

Table 5. Results of the permeability test for the experiments B.

TREATMENT	Permeability (g/m^2 24h)	RP (%)
None	56	-
Paraloid B72®	28	50
EMA/MA copolymer	30	46
EMA/MA + Tecnoflon 2	23	59
EMA/MA + Tecnoflon 5	20	64
EMA/MA + Tecnoflon 10	18	68
Commercial mixture	22	61

4. CONCLUSIONS

The experimental results presented in this paper support once again that the in situ polymerization is a technique more favorable than the traditional one, since the polymerization of acrylic monomers inside the stone pores

allows putting into the rock an amount of polymer larger than that obtainable by the application of a preformed polymeric material. This improves the consolidating and protective properties of the treatment.

On the other hand, it is well known that the protective efficacy of a polymer can be made better if fluorinated compounds are used. The present experiments show that either fluorinated monomers can be added to the co-polymerizing mixture or a fluorinated polymer can be dissolved in the acrylic monomers. In both cases the data lead to the conclusion that only few percent of fluorinated compound is enough to largely improve the protective properties. This is remarkable since it reduces the cost of the restoration.

REFERENCES

1.   P. Rota Rossi Doria, *Bollettino dell'Arte* **41**, 37 (1997).
2.   P. Rota Rossi Doria, in *Proceedings of the International Symposium on "Principles and applications of pore structural characterization"* (J. M. Haynes, P. Rossi Doria Eds., Arrowsmith, Bristol, 1985).
3.   G. Amoroso, V. Fassina, *Stone decay and conservation* (Elsevier, Lausanne, 1983), ch.13.
4.   J. P. Flory, *Principles of polymer chemistry* (Cornell Univ. Press, Ithaca, NY, 1962), ch.10.
5.   S. Vicini, E. Princi, G. Moggi, E. Pedemonte, *La Chimica e l'Industria* **81**, 1013 (1999).
6.   S. Vicini, S. Margutti, G. Moggi, E. Pedemonte, *J. Cultural Heritage* **2**, 143 (2001).
7.   S. Vicini, S. Margutti, E. Princi, G. Moggi, E. Pedemonte, *Macromol. Chem. Phys*. **203**, 1413 (2002).
8.   S. Vicini, E. Princi, E. Pedemonte, M. Lazzari, O. Chiantore, *J. Appl. Polym. Sci.* **91**, 3202 (2004).
9.   D. M. Brewis, *Int. J. Adhes. Adhesives* **13**, 251 (1993).
10. J. Hopken, S. Shieko, J. Czech, M. Moller, *ACS Polym. Prepr*. **33**, 937 (1992).
11. V. Castelvetro, M. Aglietto, L. Montagnini di Mirabello, L. Toniolo, R. Peruzzi, and O. Chiantore, *Surface. Coat. Intern*. **11**, 551 (1998).
12. F. Ciardelli, M. Aglietto, L. Montagnini di Mirabello, E. Passaglia, S. Giancristoforo, V. Castelvetro, and G. Ruggeri, *Progr. in Org. Coat.* **32**, 43 (1997).
13. G. Alessandrini, M. Aglietto, V. Castelvetro, F. Ciardelli, R. Peruzzi, and L. Toniolo, *J. Appl. Polym*. *Sci.* **76**, 962 (2000).
14. 11. R.F. Brady, *Chem. Brit.*, **26**, 427 (1990).
15. G. Mohad, D. H. Solomon, Azo and peroxy initiators, in *Comprehensive Polymer Science* Vol. 3 (G. C. Eastmond, A. Ledwith Eds, Pergamon Press, UK, 1989, p. 97).
16. O. Chiantore, M. Guaita and M. Lazzari, *Int. J. Polym. Anal. Characterization* **2**, 395 (1996).
17. D.R. Paul, and J. Wbarlow, *J. Macromol. Sci. Rev. Macromol. Chem*. **C18**, 109 (1980).
18. J. Mijovic, H. L. Luo, and C.D. Han, *Polym. Eng. Sci.* **22**, 234 (1982).
19. www.rohmhaas.com/coatings/.
20. F. Carpene', Le meraviglie della Pietra di Finale, Ed. Bacchetta, 1997.
21. G. Alessandrini, A. Pasetti, Arkos, **14**, 26 (1991).
22. G. Alessandrini, A. Pasetti, Arkos, **21**, 50 (1993).
23. UNI 10859 Cultural Heritage – Natural and Artificial Stones – Determination of water absorption by capillarity, UNI Milan, Italy, 2000.
24. Normal Protocol 21/85, Water vapor permeability, ICR-CNR, Rome, Italy, 1986.