Consolidation of Tuff: In Situ Polymerization or Traditional Methods?

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ABSTRACT: Two monomers, flexible ethyl silicate and butyl methacrylate, have been tested on a pyroclastic rock (tuff) for evaluating the consolidating efficacy of in situ polymerization treatments. In the step polymerization mechanism, flexible ethyl silicate has given good yield, which is associated to high hydrophobic and cohesive properties, and remarkable chromatic changes of the treated stone surface. On the contrary, in the radical polymerization of butyl methacrylate low yields and poor performances have been usually obtained. Good penetration depth and high stone hardness have been obtained with traditional consolidating treatments using macromolecules with suitable molecular weight. However, an increase in stone brittleness has been observed in tuff samples treated with an acrylic polymer (Paraloid B72).

1 INTRODUCTION

The development of macromolecular chemistry and the increasing synthesis of new products have contributed to change the methodological approach of restoration of works of art: conservative repairs of sculptures and monumental buildings are preferred to replacement treatments. The conservative repairs, however, may be carried out only if the object recovers cohesion and suitable mechanical properties, without changing its superficial shape and chromatic characteristics. Moreover, an important requirement for conservative treatments is a good penetration depth and a homogeneous distribution of the product in order to avoid a superficial consolidation and protective effect, which produces discontinuity between the outer and the inner layers of the stone.

Macromolecular compounds usually have not only qualified chemical and physical-chemical characteristics (absence of colour, transparency, adhesive and cohesive properties) for restoring the required properties to decayed stones, but also protective properties because reduce the water absorption.

However the chemical composition and, in particular, the structure of the rocks, such as total porosity, pores dimension and pore size distribution, may contribute to the failure of the consolidating treatment with polymeric materials. A typical drawback of the consolidation with polymeric compounds is the low penetration depth of the macromolecules, due to their dimension sometimes higher than the pores diameter. For a better penetration, consolidation with monomers, small molecules able to react in situ, has been proposed since the second half of the last century, and silicon based compounds have been used for the consolidation of several monumental buildings (Ramiere and de Tassigny 1976, Amoroso and Camaiti 1997, Vicini et al. 1999).

In this work in situ polymerization of two monomers on tuff samples has been carried out, and performances of these treatments studied.

Tuff, a consolidated pyroclastic rock, widespread in central and southern Italy, has been extensively used as building material since the ancient time, due to its softness, easy workability

and fairly good mechanical properties. This rock can be found in Etruscan tombstones and subterranean tombs, in Roman Forum, in Palatine area and throughout Rome and Ostia Antica. In the campanian region, tuff has been also used as face bricks for monumental buildings. This rock has an extreme variability in geotechnical properties, as a consequence of its genesis (eruptive mechanism, deposition and lithification processes), also within the same lithological unit. The high porosity of the tuff, associated to its genesis and high non-homogeneity, is the cause of poor mechanical properties and low durability of this stone (Grissom 1990, De Gennaro et al. 1993). As a matter of fact, tuff, a highly hydrophilic rock because of the presence of zeolites, undergoes continuous volume changes that lead to cracks. Some archaeological tuff objects, in fact, recently laid bare and found in fairly good state of conservation, are now completely decayed in consequence of the sudden changes of hygrometric conditions.

Aim of this work is the evaluation of the efficacy of the consolidating treatment by in situ polymerization. Step and chain polymerization processes have been considered and two monomers have been studied: flexible ethyl silicate (step polymerization) and butyl methacrylate (chain polymerization). In the step polymerization the monomer, applied on the stone samples as organic solvents solution, has been polycondensed at room conditions, while in the chain polymerization some radical initiators have been tested in order to obtain good yield in mild conditions. The radical polymerization has been carried out by applying the monomer as ethyl acetate solution, emulsion or micro-emulsion.

Traditional consolidating treatments, using poly(butyl methacrylate) and poly(ethyl methacrylate-co-methyl acrylate 70/30) (Paraloid B 72), have been performed in order to compare the different application techniques.

2 MATERIALS AND METHODS

2.1 Stone materials

Two kinds of tuff were used: via Tiberina tuff (a yellow tuff of the central Italy, an area close to Rome) and Neapolitan tuff (a yellow tuff typical of Naples).

Via Tiberina tuff, a welded pyroclastic rock with 47% of water accessible porosity containing zeolite (mainly chabazite), was cut in prismatic samples of dimension 5x5x1 cm^3.

Neapolitan tuff, a fine grained pyroclastic rock having a cineritic matrix partially altered in zeolite (mainly phillipsite and chabazite) and 55% of water accessible porosity, was cut in prismatic samples of dimension 5x5x2 cm^3.

For both rocks, 12 samples for each treatment have been used.

2.2 Products and treatments

Butyl methacrylate (BMA), from Merk, and flexible ethyl silicate (FES), a 75% w/w 2-propanol solution, kindly supplied by Chem Spec – Milan, have been used for the "in situ" polymerization. They were applied by capillary absorption, through a 5x5 cm^2 face of the stone sample that was placed on a pack of 20 filter papers (Whatman n° 4) soaked with the mixture to be applied. The whole system was kept in a glass vessel for a fixed time. Butyl methacrylate was applied as ethyl acetate solution, emulsion or micro-emulsion, while FES as supplied by the producer. The composition of the treatment mixture, the capillary absorption time and the polymerization conditions are reported in Table 1. The absorption time was decided on the basis of the different capillary properties of the samples and the absorption was stopped only when the samples were completely wet.

Poly (butyl methacrylate) (PBMA) has been also synthesized "in vitro" by radical polymerization using 2,2'-Azobis(2-methyl propionitrile) (AIBN) or tert.Butyl-per-2-ethyl hexanoate (TBPEH) as radical initiator for polymerization of BMA in solution or emulsion and micro emulsion, respectively. The polymer has been purified by precipitation of its chloroform solution in methanol. In the case of the polymer synthesized in emulsion and micro emulsion, the chloroform solution of the product has been washed with water before the precipitation in methanol. The composition of the polymerization mixture and the reaction conditions are reported in Table 2.

Table 1 : Composition of the mixtures and application conditions used for the consolidation of Via Tiberina (VT) and Neapolitan (Np) tuff samples. Emulsion and micro-emulsions were applied only on Neapolitan tuff samples.

Product	Concentration	Application technique	Capillary absorption time	Curing conditions	Ref. N°
	w/w				
FES	75% 2-propanol solution	In situ polym.: solution	5 h	1 month at 80% RH and room temperature	1
PB 72	15% in ethyl acetate	Polymer solution	V T tuff: 5 h Np tuff: 24 h	Room conditions	2
PBMA	3 % in ethyl acetate	Polymer solution	6,5 h	Room conditions	3
BMA	60% in ethyl acetate, 1% AIBN (w/w$_{BMA}$)	In situ polym.: solution	3 h	In closed glass vessel for 8 days at 40°C	4
"	BMA:H$_2$O = 1:1 SDS = 1.2% (w/w$_{H2O}$) TBPEH = 5% (w/w$_{BMA}$)	In situ polym.: emulsion	2 h *	In closed glass vessel for 5 days at 40°C	5
"	BMA:H$_2$O = 1:1 SDS=4.0 % (w/w$_{H2O}$) BuOH=18.57 % (w/w$_{BMA,H2O}$) TBPEH=5% (w/w$_{BMA}$)	In situ polym.: micro-emulsion	7 days *	In closed glass vessel for: 12 days at 21°C 7 days at 25 °C 7 days at 26 °C 7 days at 28 °C	6
"	"	In situ polym.: micro-emulsion	3 days *	In closed glass vessel for 18 days at 28 °C	7
"	"	In situ polym.: micro-emulsion	3 h *	In closed glass vessel for 4 days at 40°C	8
"	"	In situ polym.: micro-emulsion	29 h *	In closed glass vessel for 5 days at 56 °C	9

SDS = sodium dodecyl sulphate; BuOH = n-butanol; * only one sample for each treatment was used.

Table 2 : Experimental conditions and yield of the "in vitro" polymerization.

Mixture Composition	System	Curing temperature	Curing time	Yield
w/w		°C		%
BMA 60 %, ethyl acetate 40 %, AIBN 1 % (w/w$_{BMA}$)	solution	40	4 days	94
BMA:H$_2$O=1:1, SDS=1.2% (w/w$_{H2O}$), TBPEH=5% (w/w$_{BMA}$)	emulsion	40	2 days	65
BMA:H$_2$O=1:0.5, SDS=1.2% (w/w$_{H2O}$), TBPEH=5% (w/w$_{BMA}$)	emulsion	40	4 days	84
BMA:H$_2$O=1:1, SDS=4% (w/w$_{H2O}$), BuOH=18.75% (w/w$_{em}$) TBPEH=5% (w/w$_{BMA}$)	micro-emulsion	40	38 h	nd*
BMA:H$_2$O=1:1, SDS=4% (w/w$_{H2O}$), BuOH=18.75% (w/w$_{em}$) TBPEH=5% (w/w$_{BMA}$)	micro-emulsion	28	7 days	nd*

* The polymerization occurred because the liquid phase became solid (highly viscous liquid).

Paraloid B-72 (PB 72), poly (ethyl methacrylate-co-methyl acrylate) 70/30 from Röhm & Haas, has glass transition temperature (Tg) = 43°C and average molecular weight (Mw) = 90500 amu.

The PBMA (Mw = 211500 amu, Tg = 35°C) obtained by polymerization of the monomer solution, and PB 72 have been used for the traditional consolidating treatments of the tuff samples. Both polymers, in ethyl acetate solution, have been applied by capillary absorption using the same procedure followed for the "in situ" polymerization. The treatment conditions are reported in Table 1.

The amount of polymer deposited on each sample was determined by weighing the sample after the cure of the products and evaporation of the solvent.

Average molecular weights and molecular weight distributions have been determined by a modular SEC system using a RI detector and two Gel mixed D columns 30 cm length, 5 μm particle size (Polymer Labs, UK) for the separation. Chloroform was used as mobile phase and standards of poly(methyl methacrylate) for the calibration.

2.3 Evaluation of performances

The effects of the treatment on the properties of the porous material have been evaluated determining the water repellence and the colour change achieved by the external surface of the rock, the permeability to water vapour and the resistance to drilling.

The water repellence was measured by the capillary water absorption, according to UNI 10859 (2000) and Borgia et. al (2000). The hydrophobic effect of the treatment, expressed as protective efficacy (PE%), was calculated from the amount of liquid water absorbed by the unit surface of the rock in 20 minutes (PE% 20 min) or in 150 hours (PE% 150h), before (A_0) and after (A_1) the treatment: $PE\% = 100(A_0-A_1)/A_0$.

The permeability to water vapour was measured by the "bicchierino" method, in accordance to the NORMAL 21/85 method (1986) and evaluated measuring the mass of water vapour passing through the unit surface in 24 hours at 25°C and 5% RH in equilibrium conditions. In a typical "permeability test" the equilibrium conditions are considered to be achieved when the mass of water evaporated in 24 hours remains constant or differs by less than 5% in two consecutive weightings. Typically mass changes are recorded every 24 hours for 8-10 days. The water vapour permeability was reported as Residual Permeability (RP%), calculated by the formula: $RP\% = 100(P_1/P_0)$, where P_1 is the sample permeability after the treatment and P_0 the average permeability calculated on 5 untreated samples.

The colour determination was carried out by a Minolta Chroma meter, using the reference source C. The colour data have been presented in the CIE-Lab* system where L* is the relative brightness ranging from 0 (black) to 100 (white), a* the hue ranging from -60 (green) to +60 (red) and b* the chroma ranging from -60 (blue) to +60 (yellow). The colour change (ΔE) has been evaluated by: $\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, where ΔL^*, Δa^* and Δb^* are the difference between the parameters before and after the treatment.

The consolidating efficacy has been evaluated by the Drilling Force Measurement System (DFMS), where the mechanical resistance to drilling is monitored vs the penetration depth. The equipment, described by Tiano (2001), was fitted out with Fisher bits (diameter of drill holes = 5 mm) using a rotation speed of 100 rpm, penetration rate of 40 mm/min and hole depth 10 mm.

3 RESULTS AND DISCUSSION

In spite of the high total porosity of tuff and the wide range of the pores size distribution, the diffusion and the distribution of macromolecules inside the stone is largely influenced by the molecular weight of the polymer. Preliminary tests of treatment carried out with PB 72 (average molecular weight Mw = 90500 amu) and PBMA (Mw = 211500 amu) have shown a different behaviour in the capillary absorption of the polymers solution: the application of PBMA was possible only as dilute solution (3% instead of 15% for PB 72). In this condition the stone samples were completely wet, even if different absorption times have been necessary (Table 3). Moreover, the amount of polymer retained by the stone, after evaporation of the solvent, was

lower than for PB 72: five times lower, as the polymer concentration in the ethyl acetate solutions.

Table 3 : Amount of polymer applied on Via Tiberina (VT) and Neapolitan (Np) tuff samples. The amount of polymer for each product tested is the average value determined on 12 samples.

Product	Ref. N°	Application technique	VT tuff		Np tuff	
			C A time h	Amount of polymer applied g/100g of tuff	C A time h	Amount of polymer applied g/100g of tuff
FES	1	In situ polym.	5	13.2 ± 0.5	5	21.8± 0.9
PB 72	2	Polymer solution (15% in ethyl acetate)	5	5.9 ± 0.8	24	7.8 ± 0.6
PBMA	3	Polymer solution (3% in ethyl acetate)	6.5	1.1 ± 0.1	6.5	1.4 ± 0.1
BMA	4	In situ polym. solution	3	0.3 ± 0.1	3	0.8 ± 0.1
"	5	In situ polym. emulsion			2	1.08*
"	6	In situ polym. micro-emulsion			7 days	12.4*
"	7	"			3 days	2.8*
"	8	"			3	0.41*
"	9	"			29	22.2*

C A = capillary absorption; * only one sample for each treatment was used.

However, Protective Efficacy determinations (PE%) (Table 4) and kinetics of capillary water uptake (Fig. 1) show good hydrophobic characteristic of the surface treated with PBMA for short time (20 min) of water absorption but not for long times (150 h). This may be justified with a poor penetration of the polymer and a preferential distribution of it on the first layers of the surface. The Residual Permeability to water vapour (RP%), on the other hand, seems in accordance with this hypothesis because significant reduction in the residual permeability (84-89%) is observed for PBMA, where low amounts of polymer were applied. On the contrary, PB 72 gives high PE% values both for short and long times of capillary water absorption (Table 4 and Fig. 1) and the RP% (62-64%) is lower than for PBMA but not so low considering that much more polymer has been applied.

Table 4 : Protective Efficacy (PE%) and Residual Permeability (RP%) of different treatments on Via Tiberina (VT) and Neapolitan (Np) tuff samples.

Product	Ref. N°	VT tuff			Np tuff		
		PE 20 min %	PE 150 h %	RP %	PE 20 min %	PE 150 h %	RP %
FES	1	98± 0	93±1	50±8	99±0	90±1	47±10
PB 72	2	98± 0	84±2	64±8	99±0	89±1	62±6
PBMA	3	91±1	15±12	89±11	98±1	8±13	84±8
BMA	4	12±7	0±6	nd	35±16	5±4	86±10

Drilling resistance measures, finally, show a very low improvement of the resistance (Force) in the first 2 mm from the surface for PBMA, while for PB 72 the hardness of the rock is increased more than 5 times and also concerns the inner zones (Fig. 2).

The strange profile of the curve obtained for PB 72 is due to the break of the stone sample during the drilling. The curve is drawn from the average values of the force obtained on three holes in the same sample: in consequence of the break at 4.5 or 6.5 mm a steps profile is observed.
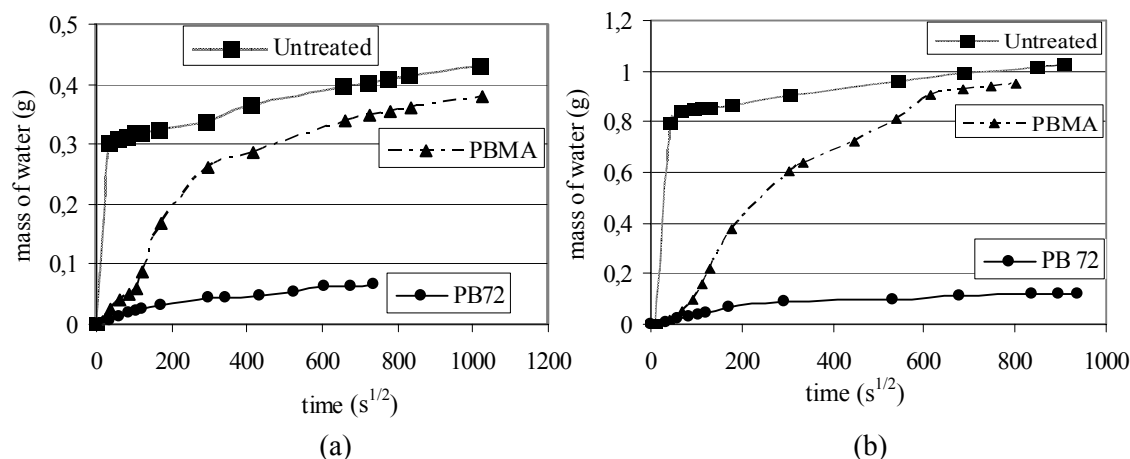
Figure 1 : Kinetics of capillary water absorption on (a) Via Tiberina and (b) Neapolitan tuff samples treated with PB 72 and PBMA. Kinetics of untreated stone samples is reported for comparison.
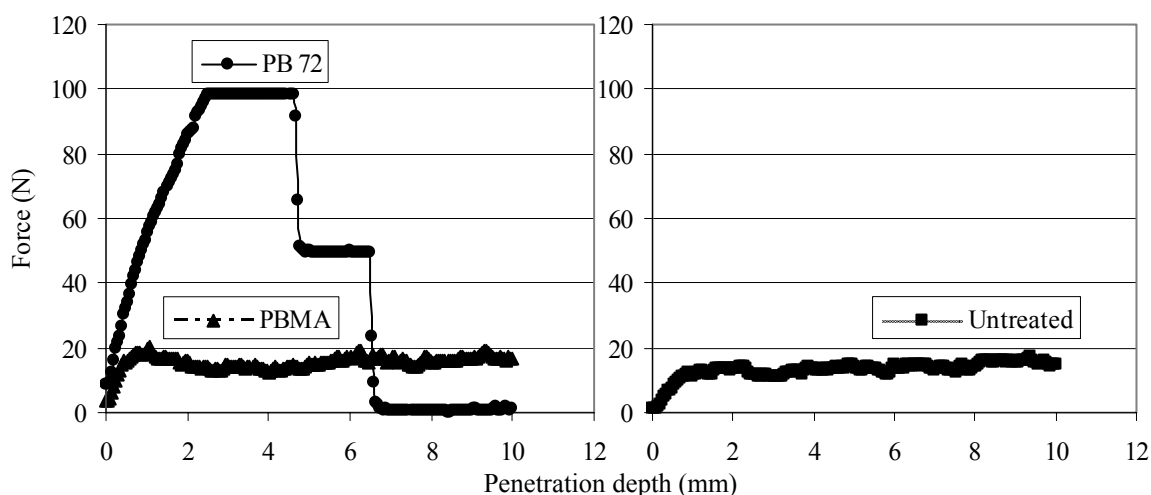

Figure 2 : Drilling resistance of Neapolitan tuff samples treated with PBMA or PB 72. Drilling resistance of untreated tuff is also reported for comparison. The curves are drawn from the average values of the force detected on six holes carried out on two samples for each group. For PB 72 only one sample was drilled.

The treatment with small molecules (monomers) helps the penetration of the active product and the amount of the treatment mixture absorbed by the stone is always high and may reach values near the water porosity value of the tuff (Table 5). However the amount of polymer obtained by radical polymerization (polymerization yield) greatly depends on the curing conditions. In any case longer curing times are necessary than "in vitro" polymerization where higher yields were always obtained (Table 2). However, the good yield obtained in the preliminary tests on Neapolitan tuff samples with the ethyl acetate solution (60% of BMA) has not been confirmed in the next treatments, both on Via Tiberina and Neapolitan tuff samples, where much lower amount of polymer was found (Table 3).

A different behaviour may be observed when flexible ethyl silicate (FES) was used as monomer (Table 3). In this case a step polymerization mechanism occurs: the reaction time is also long (approximately one month), however no controlled conditions for limiting the evaporation of the monomer are necessary, unless the first hours after the application, because the reaction involves, at the same time, all the monomers producing not volatile oligomers. The amount of active product inside the stone is higher than in all the other treatments (Table 3).

The performances of the two in situ polymerizations reflect the amount of polymer formed: higher protection efficacy is observed for FES both at short and long times of capillary water absorption (Table 4), while very low PE% is obtained for in situ PBMA also at short absorption

time. On the contrary a drastic decrease in Residual Permeability is detected for FES (RP% ≤ 50%), but not for PBMA (RP% > 85%).

Drilling resistance measurements show force values approximately three times higher for FES consolidated samples than for the unconsolidated ones (Fig. 3) and the consolidation concerns the whole depth investigated (10 mm). Contrary to the consolidation with PB 72 (Fig. 2), less brittleness was here observed: only three holes on nine performed caused the stone break.

Drilling resistance measurements carried out on tuff samples treated with BMA, does not show any consolidating effect in the whole thickness of the samples (Fig. 3).

Finally, colour change determinations have been detected because a good conservation treatment must maintain, as much as possible, the natural chromatic characteristics of the stone. Higher chromatic changes are observed for FES and PB 72 ($\Delta E \sim 15$), where higher amounts of products were applied (Table 6). The treatment with PBMA also shows high ΔE values in spite of the low mass of polymer applied. This result confirms the preferential superficial distribution of the PBMA.

Table 5 : Amount of the treatment mixture and yield in the preliminary tests of "in situ" radical polymerization of BMA. Neapolitan tuff samples (water porosity = 55% and density = $1.107 g/cm^3$) were used.

Treat-ment	Absorp time	Curing		Yield		PBMA/ tuff	Mixture$_{abs}$/ tuff
		Temp	time	PBMA/ BMA$_{abs}$	PBMA/ mixture $_{abs}$		
		°C	days	%	%	g/100g	g/100g
S_1	3 h	40	4	nd	nd	2.9	nd
S_1	3 h	40	8	nd	nd	5.0	nd
S_2	48 h	40	7	10.9	8.7	1.3	14.9
S_3	48 h	40	7	6.8	-	1.8	26.4
E	2 h	40	5	7.7	3.8	1.1	29.5
M_1	3 days	28	18	nd	nd	2.8	nd
M_2	6 h	40	3	-	0.1	0.04	30.3
M_3	4 h	40	14	-	3.6	0.94	26.2
M_4	29 h	56	5	-	47.1	22.2	47.2

abs = absorbed; S_1=BMA (60%), Ethyl acetate (40%), AIBN 1%; S_2=BMA (80%), Ethyl acetate (20%), AIBN 1%; S_3=BMA, AIBN 1%; E=emulsion (H_2O:BMA = 1:1), TBPEH=tert.Butyl-per-2-ethyl hexanoate.
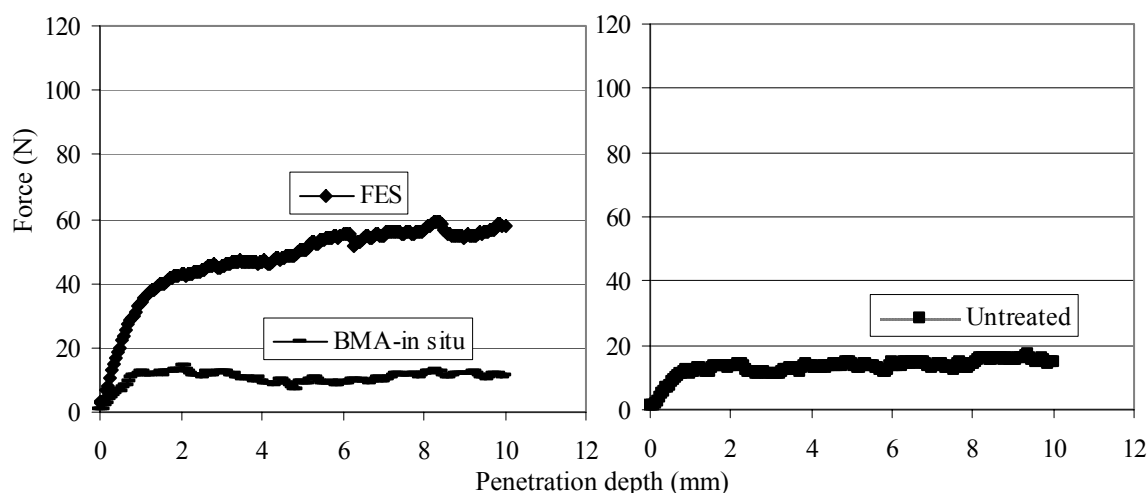

Figure 3 : Drilling resistance of Neapolitan tuff samples treated with FES or BMA. Drilling resistance of untreated tuff is also reported for comparison. The curves are drawn from the average values of the force detected on six holes carried out on two samples for each group. For FES nine holes were performed.

Table 6 : Chromatic change of Via Tiberina and Neapolitan tuff samples after treatment with different polymeric compounds.

Product	Via Tiberina tuff		Neapolitan tuff	
	ΔE	Amount of product g/100g tuff	ΔE	Amount of product g/100g tuff
FSE	15.3	13.2	14.9	21.8
PB 72	14.7	5.9	14.1	7.8
PBMA	9.2	1.1	11.0	1.4
BMA	5.9	0.3	1.9	0.8

4 CONCLUSIONS

The results obtained in this work show that tuff may be properly consolidated both by in situ polymerization and traditional methods using pre-synthesized polymers. The wide pore size distribution of tuff favours the penetration of small molecules, but a good penetration depth is reached if polymers with suitable average molecular weight are used: PB 72 (low Mw), in fact, show better performances than PBMA (high Mw). On the other hand, the consolidating efficacy of the in situ polymerization is greatly influenced by the polymerization mechanism and by the curing conditions. For the radical polymerization mechanism, in particular using BMA as monomer and AIBN or TBPEH as radical initiator, the yield of the in situ reaction is generally low. Only long curing time in a closed place and/or high temperatures (> 60°C) increase the amount of the polymer. The application of BMA as solution, emulsion or micro emulsions does not seem to influence the polymerization yield. This monomer seems not very suitable for the consolidation of tuff buildings.

For the condensation mechanism, using FES as monomer, high amount of polymer is obtained with reduced loss of monomer, which is limited to the first hours from the treatment. Even if the reaction time for this polymerization is also long (approximately one month), the room temperature and humidity are more practicable conditions in real treatments.

ACKNOWLEDGMENTS

REFERENCES

Amoroso, G.G. Camaiti, M. 1997. Scienza dei materiali e restauro- La pietra: dalle mani degli artisti e degli scalpellini a quella dei chimici macromolecolari. Firenze: Alinea Ed.

Borgia, G.C. Camaiti, M. Cerri, F. Fantazzini, P. Piacenti, F. 2000. Study of water penetration in rock materials by Nuclear Magnetic Resonance Tomography: hydrophobic treatment effects. Journal of Cultural Heritage 1, p. 127-132.

de' Gennaro, M. Fuscaldo, M.D. Colella, C. 1993. Weathering mechanisms of monumental tuff-stone masonries in downtown Naples. Science and Technology for Cultural Heritage 2, p. 53-62.

Grissom, C.A. 1990. The deterioration and treatment of volcanic stone: a review of the literature. In A.E. Charola (ed.), Lavas and volcanic tuffs, Proc. intern. Meeting, Easter Island, 25-31 October 1990, p. 103-122. Santiago de Chile: Direccion de Bibliotecas, Archivos y Museos.

Normal 21/85 – 1986. Permeabilità al vapor d'acqua. Roma:CNR-ICR Comas Grafica.

Ramiere, R. de Tassigny, C. 1976. Methode de conservation des calcaires par impregnation-irradiation gamma. In R. Rossi-Manaresi (ed.), The conservation of stone I, Proc. intern. Symp., Bologna 19-21 June 1975, p. 499-509. Bologna: Centro per la Conservazione delle sculture all'aperto.

Tiano, P. 2001. Una nuova metodologia per la valutazione in situ dei trattamenti consolidanti delle pietre monumentali – DFMS. ARKOS Scienza e Restauro 2, p. 42-49.

UNI 10859 -2000. Materiali lapidei naturali e artificiali, "determinazione dell'assorbimento di acqua per capillarità". Norma Italiana Beni Culturali.

Vicini, S. Princi, E. Moggi, G. Pedemonte, E. 1999. In situ polymerisation for restoration of stone manufactured objects. Chimica e Industria 81, p. 1013-1016.