



Frontal polymerization as a convenient technique for the consolidation of tuff

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Abstract: Frontal Polymerization was successfully exploited as an innovative technique for the consolidation of Neapolitan Yellow Tuff, the main volcanoclastic rock of Campania region (Italy). The protocol used and the full characterization in terms of mechanical properties of the resulting consolidated stone are presented here and discussed together with the data obtained by X-ray tomography as a non destructive analytical technique for determining the internal map of the consolidated material. The proposed treatment definitely succeeded from the technical point of view resulting in an enhancement of mechanical properties.

Introduction

The use of polymers for the conservation and consolidation of porous materials such as stone, cement and concrete is getting increasing attention [1-3].

Namely, the main efforts have aimed to the structural reinforcement of bridges and dams that are subjected to severe environmental conditions and the use of such techniques for the restorative consolidation of hand-made objects having historic and artistic interest, as well as for other kinds of structures, has been object of several studies.

In particular, it has been demonstrated that the impregnation of marble with polymers is a useful method for improving the physical and mechanical properties of the stone and to reduce the deteriorating effect of atmospheric agents [4, 5].

Generally speaking, in the past buildings were built up with native materials. In many Italian regions, and in particular in Campania, a large part of ancient houses and monuments were made of tuff that is a local porous stone of volcanic origin. Neapolitan Yellow Tuff (NYT) is the most used building stone in the historical architecture of the city of Naples (Italy) [6]. Its use dates back to the Greek period; but carved stones for tombs belonging to the Eneolithic age (4500 b.c.) were also found. Stone ageing, especially close to coastal zones, manifests itself as a worsening of physical properties which can even result in splitting. In order to avoid

the aforementioned erosion and deterioration drawbacks, one of the main methods used so far in the treatment of stony materials with macromolecular compounds is characterized by the use of thermoplastic polymers dissolved in suitable solvents. Such polymer solutions are spread on the stone surface and the solvent is allowed to evaporate, thus often getting unsatisfactory results that are due to the large polymer solution viscosity and to the consequent low penetrating ability. This penetration difficulty is also caused by the large macromolecular size, in many cases larger than that of the stone pores. Furthermore, the use of solvents has important disadvantages related to environmental pollution, costs and operational times.

In order to overcome the inconveniences cited above, one of the proposed alternatives is the in situ polymerization. Since this method uses liquid monomers, which are characterized by a viscosity much lower than that typically found in polymer solutions it permits also the consolidation of the deeper stone layers, not reachable by polymer solutions. The so-treated samples are subsequently heated in an oven in order to in situ polymerize monomers inside the stone [4, 5].

However, the use of an oven strongly limits the practical application of this method to little and easily movable samples only.

In the present paper, we propose Frontal Polymerization (FP), a facile technique which may represent a significant improvement of the above in situ polymerization methods. Indeed, FP: i) allows one to operate in times much shorter than those typical of all conventional polymerization methods; ii) requires a negligible energy amount; iii) can work also in absence of solvents; iv) is applicable also to large objects.

FP is a polymerization technique in which the reaction heat is exploited for the propagation and self-sustaining of the reaction itself. Indeed, due to an initial chemical or physical ignition, a hot polymerization front is generated. Front propagates throughout the monomer by converting it into polymer in a fashion similar to a reaction wave. It is noteworthy that no further energy supply is needed in order to self-sustain.

In 1972, Chechilo et al. [7] were the first who proposed FP as a new polymerization technique; in detail, they polymerized methyl methacrylate in “adiabatic conditions” under high pressure.

Since the nineties, a great deal of work has been done mainly by Pojman et al. who studied macrokinetics and dynamics [8-12] and new frontally polymerizing systems [13-15]; Morbidelli et al. suggested the application of FP to the preparation of copolymers [16] and blends [17]; Washington and Steinbock published on the preparation of hydrogels by FP [18, 19].

Since 2000, our research group has been active in this field [20-30]. Namely, we have studied the application of FP to the synthesis of polyurethanes [20, 21], polydicyclopentadiene [22], polyacrylates [23], interpenetrating polymer networks composed of polydicyclopentadiene and polyacrylates [24], polyester resins [25, 26] and epoxy resins [27]. Furthermore, polymer nanocomposites containing polyhedral oligomeric silsesquioxanes [28] and montmorillonite [29] as nanofillers were synthesized. Besides, we have proposed the application of FP to the consolidation of stone and wood with suitable polymers [31-33].

This work deals with the application of FP to the consolidation of NYT and the full sample characterization is also described.

Results and discussion

In the present work, FP technique have been used in order to consolidate NYT in a way that is easy, fast and very effective even in the deepest stone layers, those generally not reachable by the classical techniques which use polymer solutions instead of the corresponding monomers. The latter can penetrate the stone much better in that they are significantly less viscous than polymer solutions and are characterized by molecular size small enough to pass also through the smallest stone pores, which may have dimensions even smaller than those of a typical macromolecule.

HDDA was chosen as the monomer because it was found to be very reactive in FP runs by giving rise to self-sustaining fronts even in the presence of large amounts of inert material which dissipates heat. Indeed, one of the main FP features is that it can be successfully performed only if the amount of non dissipated heat is sufficient to induce the polymerization of the non reacted monomer which is in correspondence of the front.

NYT represents the product of one of the largest and most powerful eruptions of Campi Flegrei (Southern Italy). A substantial portion of this volcanoclastite (> 50 vol.-%) was involved in diffuse zeolitization processes that determined the crystallization of phillipsite and, subordinately, chabazite and analcime. The main content of these authigenic phases generally exceeds 50 wt.-% and sometimes can reach 70±80 wt.-% [34-37].

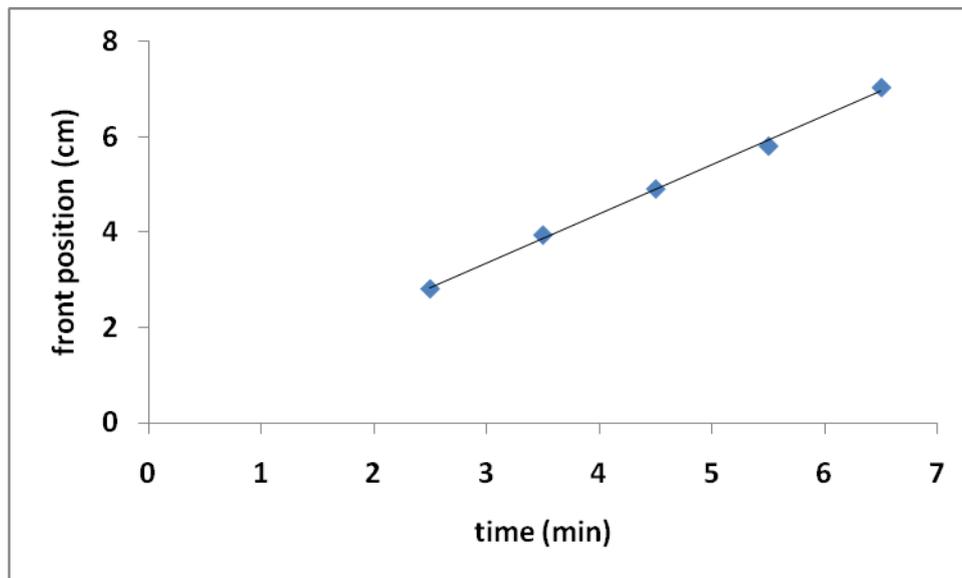


Fig. 1. Front position as a function of time for a typical FP run performed on a 7 cm edge cubic sample. Data have been recorded starting from the height of 2.5 cm. Time 0 corresponds to the start of the ignition period, which took 1 minute.

It owes its fame to the lithified facies that have been used as a building material since ancient times because of its color, light weight, and good insulating properties; at the same time, it is weak enough to be easily sewn into dimension stones.

Most of the building walls in Naples centre are composed of NYT which, before the advent of reinforced concrete, performed not only architectural but mainly structural functions, partly thanks to its good physical and mechanical properties [38].

High porosity, along with the abundant presence of zeolites (mainly phillipsite and subordinate chabazite) in the bonding matrix, makes this rock a good heat and sound insulator. According to NorMal 1/88 [39], the most frequent weathering typologies of NYT are: i) alveolization: mainly due to detachment of lithic clasts or disaggregation of zeolitized pumices; ii) scaling and exfoliation: both due to the action of damp waters through the stone and later recrystallization of soluble salts; iii) disaggregation: also due to infiltration of water and the consequent dissolution of the constituent stone phases (crystalline and/or amorphous); iv) patinæ, stains, efflorescences: extensively present on surfaces subjected to intense dissolution and evaporation of damp waters [40].

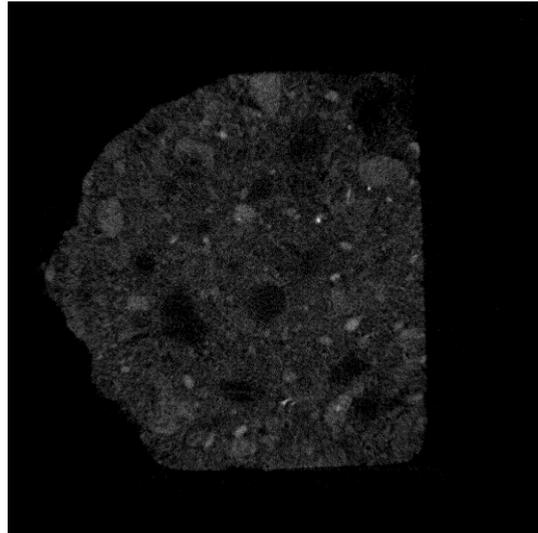


Fig. 2. Reconstruction of a transversal slice of an NYT sample before monomer absorption. The grey scale level represents voids (in black) and higher density zones (in white).

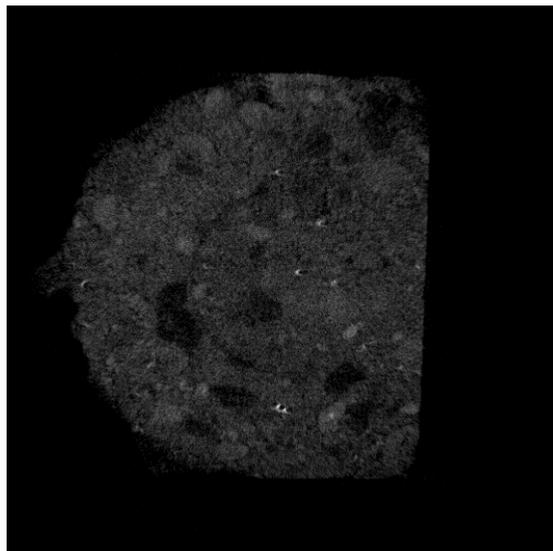


Fig. 3. Same sample as Figure 2 but after FP. At first glance, due to the rescale of the gray level scale in this reconstruction, the difference does not appear very evident. However, a higher X-Ray voltage was required, this being clear evidence that the object is now denser.

In Figure 1, front position as a function of time is reported for a typical FP run performed on a 7 cm edge cubic sample. By the analysis of these kinds of graphs, V_f s were calculated.

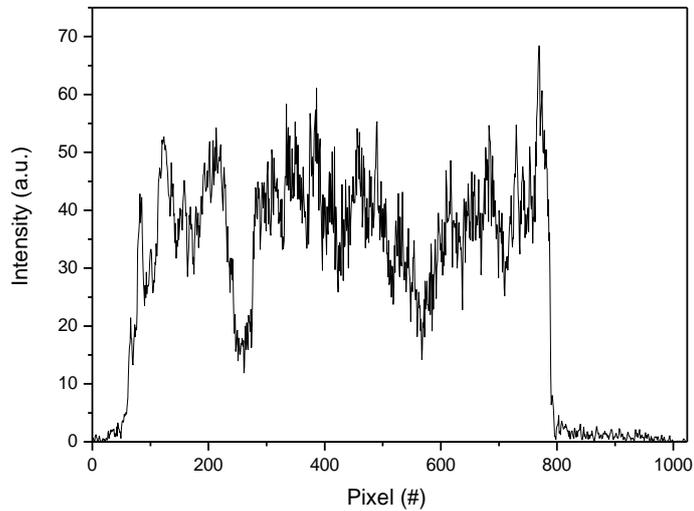


Fig. 4. Intensity profile of a central line of the reconstruction in Figure 2. Lower values correspond to a less dense material.

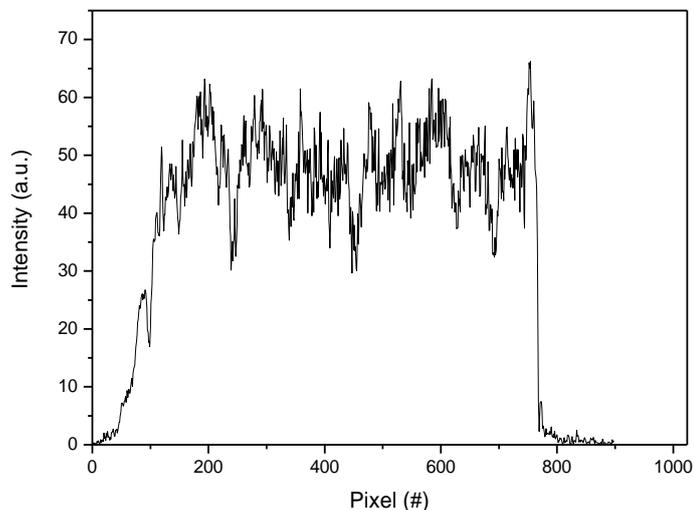


Fig. 5. Intensity profile of a central line of the reconstruction in Figure 3. Compared to the profile in Figure 4, a higher absorption (i.e. density) is visible. This effect is due to the presence of polymer inside the void of the untreated material.

In detail, polymerization times (1 minute heating period included) of 7 cm edge stones were between 6.0 and 7.5 min, corresponding to V_f s ranging from 1.2 and 0.9 $\text{cm}\cdot\text{min}^{-1}$. FP duration in 4 cm edge samples were 3.5 – 4.0 min corresponding to V_f s = 1.1 – 1.0 $\text{cm}\cdot\text{min}^{-1}$. T_{max} values ranged between 130 and 140 °C.

These values are in the same range of those typically found in FP runs, recorded also in absence of inert material such as a stone [7-32].

As mentioned before, X-Ray Tomography is a non destructive technique that allows reconstructing the internal map of a sample by analyzing the local variations of its absorption coefficient [41]. This can be related to the composition of the sample and thus, in our case, to the presence of the polymer which replaced air. Indeed, since these two materials have different absorption coefficient values, the increment of the latter can be easily related to the presence of the polymer, which is denser. For this reason, tomographic measurements can be successfully performed on NYT samples.

In Figure 2, a tomographic reconstruction of a transversal slice of an NYT sample of before any treatment is reported, while in Figure 3 the same slice after polymerization is shown. The 'polymerized' sample appears to be more homogeneous compared to the untreated one. However, the grey scale representation does not allow understanding well the quality of the filling. For this reason, in Figures 4 and 5 two intensity profiles, respectively extracted by the center of reconstruction reported in Figures 2 and 3, are depicted which confirm the above statement.

Physical-technical literature data of pristine NYT are reported in Table 1. Despite of material heterogeneity, those parameters are quite homogeneous. Apparent density ranges from 1106 to 1281 $\text{kg}\cdot\text{m}^{-3}$, whilst real density is comprised between 2246 and 2304 $\text{kg}\cdot\text{m}^{-3}$. Those values are coupled with very high porosity, on average slightly less than 50 wt.-%. The high porosity is also demonstrated by imbibition capacity, ranging from 31.28 to 40.85 wt.-%. 90 wt.-% of H_2O absorption took place in the first hour of test, and reached 100 wt.-% after 8 days. The same consideration can be drawn from capillarity absorption tests, which average value is $0.7581 \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1/2}$, and from water vapor permeability ($197.05 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$).

Tab. 1. Main physical parameters of pristine Neapolitan Yellow Tuff [38].

	samples ^a	average	Max	Min	Standard Deviation
Apparent density in $\text{kg}\cdot\text{m}^{-3}$	21	1198	1281	1106	0.05
Density in $\text{kg}\cdot\text{m}^{-3}$	21	2275	2304	2246	0.02
Open porosity in %	21	47.32	51.97	43.60	2.18
Imbibition capacity in %	18	35.49	40.85	31.28	2.86
Water vapor permeability in $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$	12	197.05	245.86	172.91	22.76
Capillarity absorption in $\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1/2}$	18	0.7581	0.8652	0.6623	0.0675
Dry ultrasonic velocity in $\text{m}\cdot\text{s}^{-1}$	57	2045	2437	1755	161.5
Wet ultrasonic velocity in $\text{m}\cdot\text{s}^{-1}$	57	2000	2311	1733	140.9
Uniaxial compressive strengths in MPa	3	3.99	5.89	2.87	1.66

^a number of considered samples

Ultrasonic velocity values are lower in saturated samples; this fact turns out to be a characteristic feature for high porosity materials. Ultrasonic dry velocities range from 1755 to 2437 $\text{m}\cdot\text{s}^{-1}$, while the wet ultrasonic ones are comprised from between 1733 to 2311 $\text{m}\cdot\text{s}^{-1}$.

Tab. 2. Physical parameters characterizing FP-treated NYT samples.

FP	samples ^a	average	Max	Min	Standard Deviation
Apparent density (Kg·m ⁻³)	6	1370	1400	1336	0.25
Density (Kg·m ⁻³)	8	1883	1892	1874	0.062
Open porosity (%)	8	25.86	27.78	23.62	0.017
Imbibition capacity (%)	6	9.57	11.96	8.04	1.71
Capillarity absorption (g·cm ⁻² ·s ^{-1/2})	10	0.0013	0.0014	0.0011	0.0001
Uniaxial compressive strengths (MPa)	10	15.75	17.52	13.83	1.48

^a number of considered samples

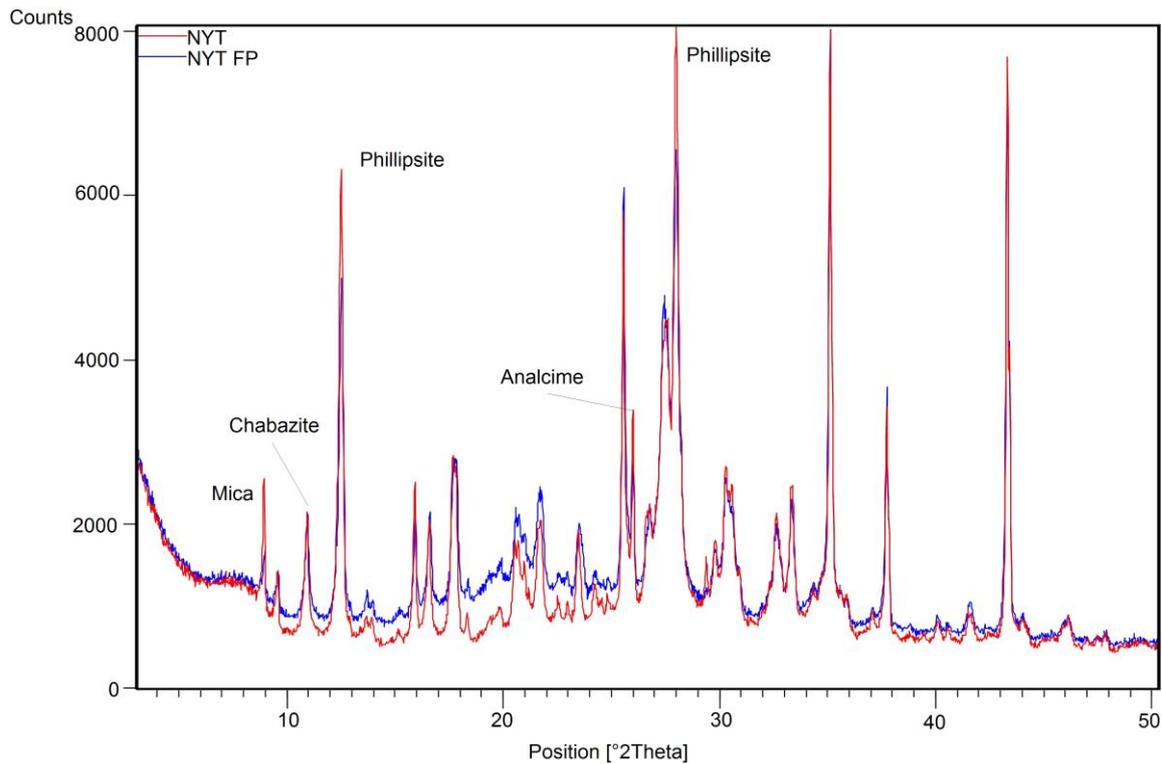


Fig. 6. XRPD for NYT samples: red= untreated; blue= treated.

Uniaxial compressive strengths (UCSs) allowed classifying NYT as a 'weak' rock [38] with good physical-mechanical properties and its values is around 4 MPa on average.

XRPD of NYT samples are reported in Figure 6. The comparison between treated and untreated samples evidenced the increase of the background in the treated one, due to the polymer X-ray scattering, but the crystal structure of the mineral phases was not affected, as confirmed by peak shape and intensity. SEM observations (Figure 7) were performed on both matrix and pumice constituents of NYT; as expected, the matrix of treated sample displays the embedding of crystal phases by the polymers (Figure 7B), whereas this fact is not so evident in the pumice (Figure 7D).

Apparent density on FP-treated samples revealed a substantial increase of this parameter (1198 Kg·m⁻³ vs 1370 Kg·m⁻³) and a sharp decrease in the open porosity (47.32 vs. 25.86 %) (Tables 1 and 2).

Hg porosity tests values confirmed this statement, mainly due to the reduction in micro- and meso-porosity range (Figure 8).

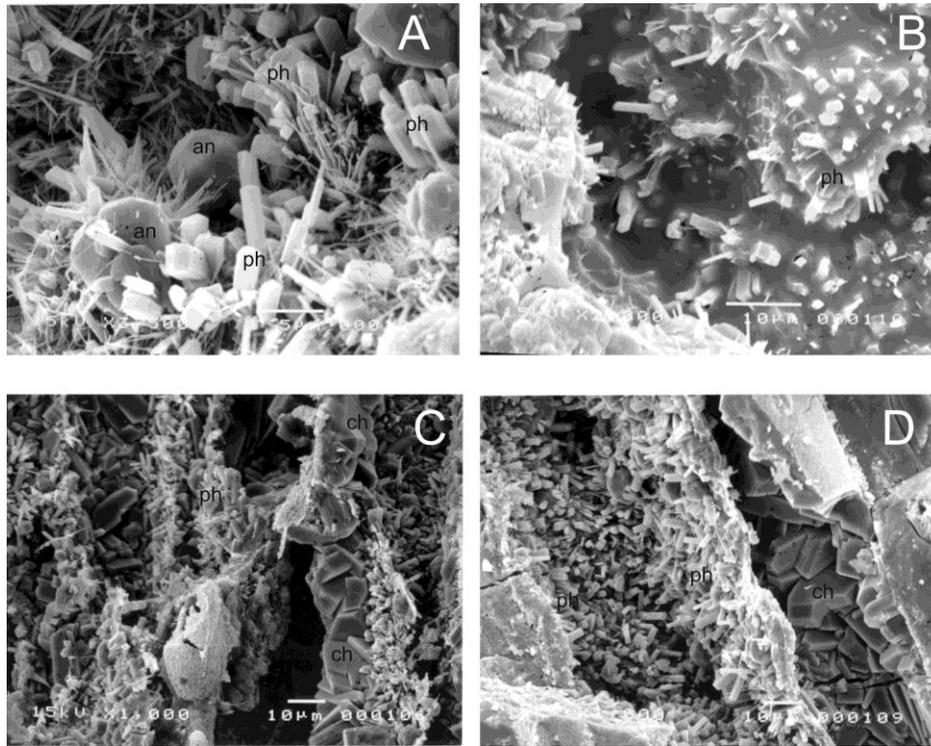


Fig. 7. SEM micrographs of untreated (A) and treated (B) matrix and untreated (C) and treated (D) pumice from NYT (an = analcime; ph = phillipsite; ch = chabazite). On the other hand, that involves a reduced capacity to absorb water (9.57 vs. 35.49 %) and a lowest coefficient of capillary absorption (0.0013 vs. $0.7581 \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1/2}$) (Table 2).

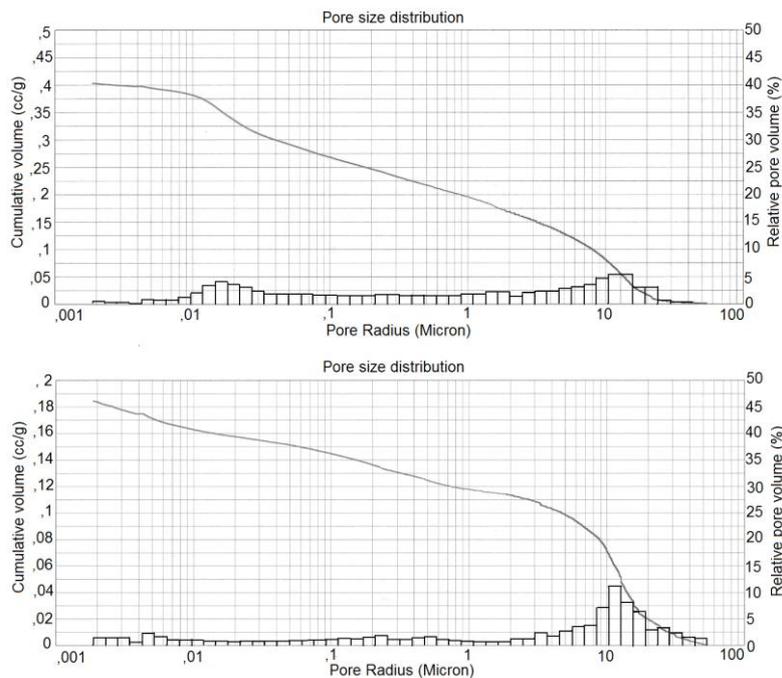


Fig. 8. Hg intrusion porosimetry test for NYT. Upper = untreated; lower = treated.

With regard to UCS tests, the results here obtained are the most striking features, since UCS values for treated samples are more than triple of those of the untreated (4 . 15.75 MPa, Table 2).

On the basis of the above results, the unique drawback for this kind of treatment seems to be the dramatic change in macroscopic aesthetical features of the rock, since its peculiar yellow color is totally lost during the frontal polymerization tests (Figure 1). However, such a feature cannot be considered a disadvantage in all those applications in which aesthetic appearance is not mandatory.

Conclusions

In the present paper, we have demonstrated once more that FP is a polymerization technique which may have great deal of practical interest. Initially studied for a laboratory curiosity, FP should now do enter the real application world by solving specific practical problems.

Namely, its use as a new consolidating technique of stone materials having historic-artistic or civil engineering interest looks now very promising.

Furthermore, by using the same method it is possible to prepare various polymer-based composites with other porous materials such as wood, paper, concrete etc.

For the above reasons, further studies on different kinds of materials are in progress and will be reported soon.

Experimental part

1,6-Hexanediol diacrylate (HDDA) came from Aldrich; 2,2'-azobis(isobutyronitrile) (AIBN) was from Fluka. All products were used as received.

X-ray powder diffraction (XRPD) data were collected on a Philips PW1730/3710 automated diffractometer (software Philips APD 3.6) with a curved graphite monochromator crystal, using the following operative conditions: CuK α radiation, 40 kV, 30 mA, 3 - 80° scanning interval; step size = 0.020° 2 Θ and counting time of 10 s per step; 20 wt.-% α -Al₂O₃ added as the internal standard. Scanning electron microscopy (SEM) was carried out with JEOL JSM 5310. Hg porosimetry was performed with Thermo Pascal 140 and 440 porosimeters, and uniaxial compressive strength tests were collected on a Controls MCC 82 control console, with a C5600 300kN compression frame.

Cubic NYT samples (coming from Marano quarry, near Naples) had the following dimensions: 4 x 4 x 4 cm³ and 7 x 7 x 7 cm³ (Fig. 9).

Each sample was previously dried in a vacuum oven at 80 °C for 12 h and weighed. For each of them, a proper HDDA solution containing 6.7 mol-% of AIBN was prepared. The total weight of the solution was always equal to 25 wt.-% of any single stone. Samples were then allowed to be soaked by capillarity until all the prepared solution was absorbed. Imbibition time (t_{im}) comprised between 320 and 330 min for the 7 cm edge samples. For the 4 cm edge ones, t_{im} was about 190 – 200 min. Therefore, in both cases, imbibition velocity (V_{im}) was about 0.02 cm·min⁻¹. At the end of the imbibition process, stone specimens were wiped with absorbing paper and placed onto a heated plate (T \approx 200 °C). Heating time was set at 60 s in order to ensure FP ignition and the subsequent ascending front propagation through the stone. After such a period, samples were removed from the hot plate, placed onto a

cork platform until the front reached the upper base and allowed to cool to room temperature. Front position and its velocity (V_f) were recorded by using several K-type thermocouples placed on the sample vertical surface at 1.0 cm one from each other; all thermocouples were connected to a digital thermometer used for the reading and recording of temperature. Front temperature (T_{max}) was measured by placing a thermocouple junction inside a hole obtained by drilling the stone specimen in depth, and after accurately covering it by using the resulting stone powder. This expedient was necessary in order to ensure an effective contact between the thermocouple junction and the sample.



Fig. 1. Untreated (left) and treated (right) NYT samples.

Polymer distribution inside the sample was obtained by tomographic measurements by using an experimental apparatus formed by an X-ray tube working at voltage of 50-80 kV and current of 5 mA, a translation-rotation stage and a 5 cm x 5 cm CMOS flat panel with spatial resolution of 50 μm . Each tomography was composed by a set of 180 projections (radiographies of the sample taken at different angles all around the sample). Each projection was formed by a 1024x1024 pixel image. Thus, up to 1024 internal absorption maps of the sample were reconstructed, one for each line of the image.

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