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Investigating morphological changes in treated vs. untreated stone building materials by x-ray micro-CT

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Abstract Calcareous stones have been largely used to build historical buildings. Among these, the calcarenites are usually characterized by a high content of calcite and a high open porosity, which make them very sensitive to the weathering caused by physical and chemical agents. In order to prevent their deterioration and to retard their decay, different protective products—mainly polymers—are applied on the stone artefact surfaces. In this work we apply the methodology tested in a preliminary study to investigate the morphological changes of the internal structure of a biocalcarenite (Lecce stone) by micro x-ray computed tomography (μ-CT). The porosity and other morphological parameters of the rock before and after the conservation treatment were calculated on a significant number of samples. The Student's t test was applied for statistical comparison. The results reveal that the treatment with Paraloid B72 (PB 72) is homogenously distributed and causes small changes to the natural properties of the rock, whereas the application of a fluoroelastomer (NH) causes an appreciable decrease in porosity and variation in terms of wall thickness distribution, probably resulting from its inhomogeneous distribution.

Keywords Cultural heritage · Stone conservation · Calcarenite · Porosity · Morphological parameters · Protective treatments · μ-CT

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Introduction

Many of the historical buildings and other stone artefacts of old European cities were created using calcareous rocks. The high content of carbonates, usually calcite, makes these historical objects very sensitive to the action of chemical agents and, in particular, to atmospheric pollutants [1–3]. The combination of chemical composition and high open porosity, normally found in calcarenites, increases the decay processes due to the action of physical and chemical agents.

Water plays a major role in all of these weathering processes and reactions [4, 5]. In order to reduce the capillary uptake of liquid water by the stone, and thereby to prevent or at least reduce the deterioration of the historical buildings and objects, different protective products—mainly polymers—are applied on the repaired stone artefact surfaces.

Because of the variability of the rock characteristics, e.g., mineral composition, porosity, pore size distribution, and interconnectivity of the channels, a standard treatment procedure is hard to formulate. Every case should be

considered as unique and all the treatment parameters, such as choice of the conservation products, concentration of the solutions, and the application method, should be tested and optimized. The effectiveness of the protective treatments is normally evaluated by measuring the changes of some macroscopic properties of the stone samples induced by the application of the product, such as capillary water absorption [6], water vapor permeability [7], and superficial water repellence [8].

As the performance of the conservation treatments strongly depends on the penetration and distribution of the protective products inside the stone structure [9–11], it is essential to determine these parameters in order to assess their efficacy. An overview on the current methods, both direct and indirect, for the study of polymer penetration depth has been done by Casadio and Toniolo [9]: most of these methods are destructive, not very accurate or reproducible, and others require a complicated sample preparation or the use of markers to highlight the presence of the treatment.

The evaluation of the polymer distribution inside the stone material is more difficult. Magnetic resonance imaging (MRI), an indirect and nondestructive technique, has been successfully applied to visualize the diffusion of liquid water in treated (hydrophobic treatment) and untreated stone samples [12].

Micro x-ray computed tomography (μ-CT) is a possible alternative to these methods [13–15]. This nondestructive technique has already been demonstrated to be an important tool for stone conservation [16–18] and very useful for monitoring the changes of the morphological parameters induced in the stone structure by the application of the conservation treatments [11]. By analyzing a reasonable number of samples, this method allows one to estimate the penetration and distribution of the polymers. The calculation of the porosity by means of μ-CT has been found to be very repeatable: the maximum difference among five repeated measurements of the same sample has been estimated to be within 1% [11]. Further advantages of μ-CT are the easy sample preparation (no special procedures are required, other than preparing the samples to the appropriate dimensions to allow sufficient transmission of the x-ray beam and good magnification) and the possibility to access the full 3D structure. This latter aspect is very important to visualize and study the actual shape of the pores—very often modeled as spheres or cylinders—and their interconnectivity and network.

The present research aims to confirm, extend, and improve the preliminary results of a previous work [11] by means of statistical data analysis in order to (a) characterize the natural rock, measuring quantitatively its petrographic parameters, such as porosity and pore size distribution, (b) compare the distribution of two different conservation treatments, and (c) monitor the changes induced on the stone pores by the application of the protective product.

Experimental

Preparation of the samples

For this research, a biocalcarenite (Lecce stone) was chosen. This rock takes its name from the city of Lecce in the south of Italy. It is, however, an extensively used material in the entire Salento region. It has been used for a long time, especially during the Baroque period, for covering the façades of the most important and beautiful buildings of that area (e.g., the Basilica of Santa Croce in Lecce) as well as for sculptures. Nowadays, it is employed for the creation of decorative objects.

Petrographic examination of Lecce stone reveals that it is made of a grain mixture of microfossils, fossil fragments, and shells, with dimensions ranging between 100 and 200 μm, incorporated into the calcitic cement. Calcium carbonate is the basic component, with a total of 93–97%, while small amounts of granules of quartz, glauconite, feldspars, and clay minerals (i.e., kaolinite, illite, smectite) were detected by x-ray powder diffraction, using a Philips PW1729 diffractometer. The total open porosity determined by a Quanta Chrome helium Penta-Pycnometer is $47.4\pm 1.2\%$, whereas meso porosity (i.e., 3.5×10^{-3}–150 μm radius), determined by means of a Thermofinnigan mercury intrusion porosimeter, is $35.8\pm 2.1\%$. The porosity accessible to water, measured by weighing the specimen before and after saturation with water, is $39.0\pm 0.2\%$.

Twenty one samples with dimensions of 3 mm×3 mm× 10 mm were prepared and then divided into three groups: set 1 (samples 1–7), set 2 (samples 8–14), and set 3 (samples 15–21).

All the samples were initially scanned and analyzed with μ-CT prior to any treatment. Subsequently, set 2 and set 3 were treated with Paraloid B72 and a fluoroelastomer, respectively [5, 19]. PB 72 is poly(ethyl methacrylate-*co*-methyl acrylate) (70:30) with an average molecular weight (M_W) of 91,000 amu, whereas NH is poly(hexafluoropropene-*co*-vinylidenefluoride) with M_W 350,000 amu. Both protective products are widely used for stone conservation and they were applied as an acetone solution with a concentration of 2% (w/w) for PB72 and 1% (w/w) for NH.

The treatments were performed by impregnation under reduced pressure (10 mmHg): the specimens were put in a Schlenk flask and connected to a membrane vacuum pump for 2 h to eliminate air and moisture inside the pores. Afterwards, the treatment solution was added using an addition funnel, until complete immersion of the sample.

After 20 h, the samples were removed from the solution and dried at room temperature.

μ-CT measurements

The samples were mounted on a dedicated sample holder and scanned by a SkyScan 1172 x-ray microtomography instrument. The x-ray micro focus tube (tungsten reflection target) of the μ-CT system was set at a voltage of 100 kV and a current of 100 μA, applying a filter (Cu 0.038 mm+Al 1 mm), in order to obtain a better contrast and to prevent beam hardening artefacts. Radiographs, with isotropic resolution of 2.6 μm in terms of pixel/voxel size, were acquired by means of a CCD camera of 4,000×2,096 pixels binned to 2,000× 1,048. A frame averaging of 4 and a rotation step of 0.4° between individual radiographs, covering a view of 180°, were chosen. These instrumental parameters allow for a good balance between required scan time and quality of the tomographic results.

These projections were processed using a modified Feldkamp cone-beam algorithm and a stack of 2D cross section images of the samples were obtained [20].

The data set was analyzed with the "CTAn" software package in order to create a complete 3D representation of the internal microstructure of the stone and to calculate the main important morphometric parameters characterizing the samples:

- Porosity, as a percentage of the empty spaces on the volume of interest (VOI)
- Pore size distribution and pore size average, calculated as the weighted average of the pore dimensions
- Wall thickness distribution (i.e., the distribution of the thickness of the stone between two pores) and wall thickness average, calculated as the weighted average of the wall dimensions

All the parameters of the same sample were calculated in 3D and compared before and after the treatment in order to study the changes due to the application of the polymeric product.

Statistical treatment of the data

Lecce stone is a sedimentary rock which very often shows differences in porosity and composition from one block to another. For this reason the estimation of the porosity should be based on a sufficiently large number of samples. In our case, 21 samples were investigated to obtain a statistically meaningful average of all the basic morphological parameters. This data treatment was used for porosity, pore size distribution, and wall thickness distribution values.

A further statistical data analysis was carried out by calculating the differences in porosity (Δ_i) of the same sample before and after the treatment. The averages of the differences ($\overline{\Delta}$) of the same group (i.e., set 2 before and after treatment with PB 72 and set 3 before and after treatment with NH) were compared with a Student's t test for paired samples to determine whether the protective product caused significant changes at a given level of significance, α [21]. By means of the t test it is possible to verify whether the null-hypothesis is statistically valid. Indicating δ as the average of the population of the differences, the null hypothesis (H_0) is that there are no significant differences ($\delta=0$) in porosity values before and after treatment; on the contrary, the alternative hypothesis (H_1) is $\delta \neq 0$.

The standard deviation (σ_Δ) of the same set of samples is calculated as follows:

$$\sigma_\Delta = \sqrt{\frac{\sum_{i=1}^{n} \left(\Delta_i - \overline{\Delta}\right)^2}{n-1}} \tag{1}$$

The experimental value of t_{calc} calculated according to the following formula

$$t_{calc} = \frac{\overline{\Delta}}{\sigma_\Delta} \sqrt{n} \tag{2}$$

will be compared with that tabulated (t_{tab}): if $t_{calc} > t_{tab}$ then H_0 is rejected and there are significant differences between the two averages, i.e., the treatment does change the stone porosity; otherwise H_0 is accepted and the two averages come from the same population. If H_0 is rejected, it is
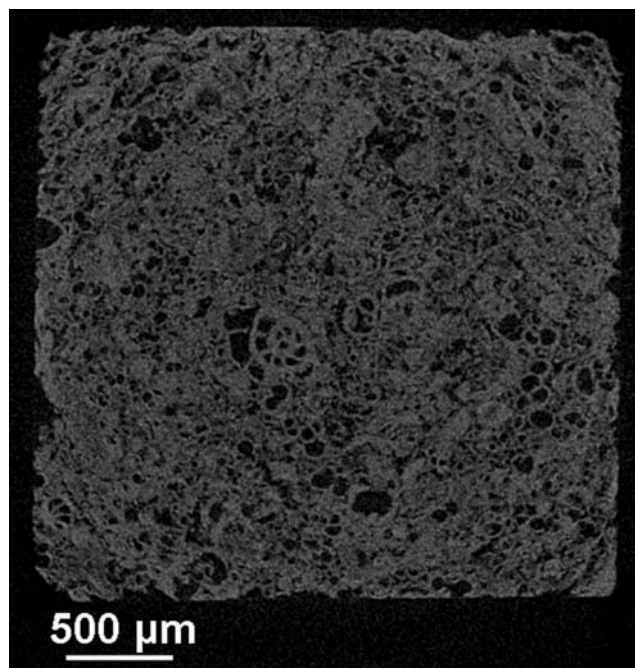

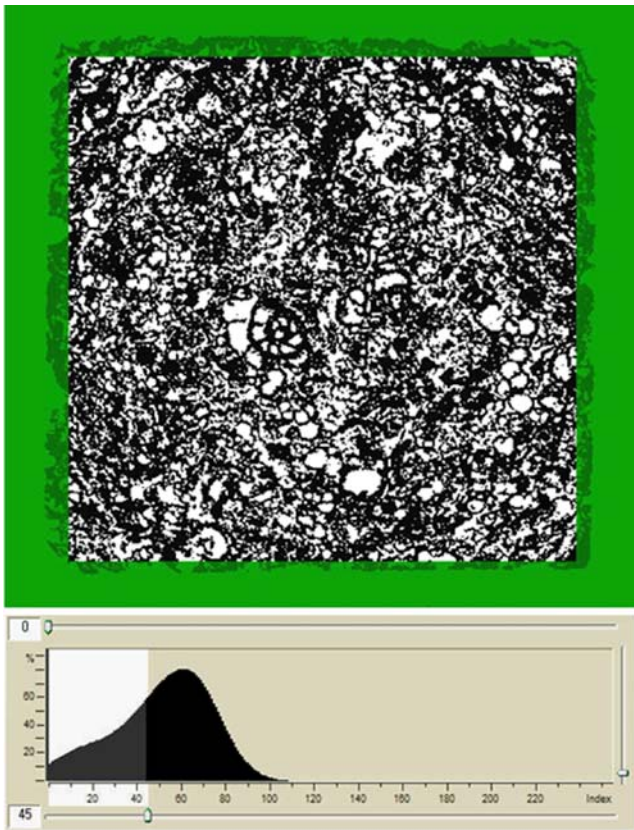**Fig. 1** Example of reconstructed cross section of Lecce stone sample

Fig. 2 Region of interest (ROI) within a reconstructed cross section, binarized by global thresholding, values 0–45

possible to calculate the averaged difference and its confidence interval as follows:

$$\delta = \overline{\Delta} \pm \frac{t_{\mathrm{tab}} \cdot \sigma_\Delta}{\sqrt{n}} \qquad (3)$$

Pore size and wall thickness distributions, as well as their average values before and after treatment, were compared in order to evaluate in more detail the changes
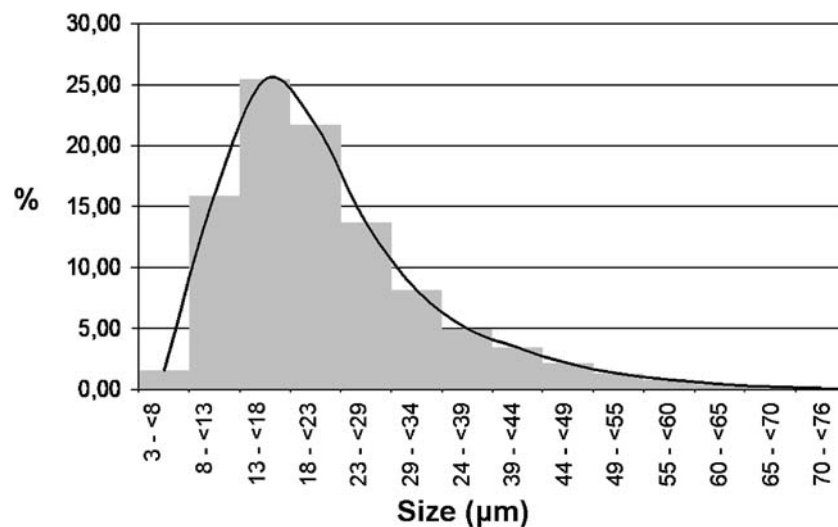
of the stone structure and properties induced by the application of the conservation treatment.

Result and discussion

Morphological characterization of Lecce stone

The images (Fig. 1) reconstructed from the projection images have an 8-bit depth: this means that the x-ray absorption of the samples is represented by a gray scale from 0 (black) to 255 (white).

The calculation of the 3D parameters is based on binary images in which the material and the pores are represented in black and white, respectively (Fig. 2). These parameters are obtained by selecting a threshold in the distribution of the gray levels, as shown in Fig. 2. The histogram corresponds to a certain area of the sample called the region of interest (ROI). The ROI should be as large as possible but completely inside the sample in order to avoid an overestimation of the porosity. The threshold should be chosen carefully, it can influence the calculated morphological parameters. The choice of a too low threshold can increase the noise, resulting in an underestimation of the porosity, a false visualization of pore/channel connectivity, and an unrealistic evaluation of the pore size distribution. On the other hand, a too high threshold would result in an overestimation of the porosity and a wrong visualization of the rock structure, with pore walls appearing thinner than in reality. In our case, an appropriate threshold of the gray values was 0–45. There is no standard procedure to select the threshold value. An optimal value is normally set by trying different values and by a visual inspection of the appearance of the cross sections.

If the aim of the analyses is to compare samples before and after treatment, it is important to keep the threshold

Fig. 3 Pore size distribution of untreated Lecce stone samples. The values were calculated by averaging 21 samples

Fig. 4 Wall thickness distribution of untreated Lecce stone. The values were calculated by averaging 21 samples
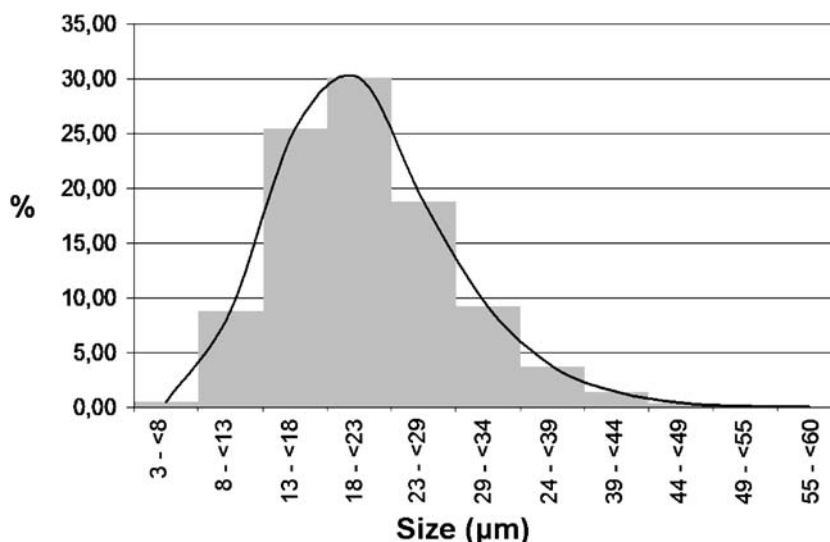
value fixed, so that all the 3D parameters are calculated under the same conditions and only a systematic underestimation or overestimation of the porosity affects the results always in the same manner. Thus all the 3D calculations were performed using first a global threshold [22] to obtain binary images; no additional filtering operation was performed on the reconstructed images.

The average porosity calculated for 21 samples is 39.5±1.1%, which is in good accordance with the results from other techniques (reported in Preparation of the samples). Pore size distribution (Fig. 3) indicates that the diameter of most of the pores ranges from 8 to 29 μm, which confirms our preliminary results [11]. The discrepancy that might be found between these results and those obtained by mercury intrusion porosimetry has been already discussed by Bugani et al. and Cnudde et al. [11, 23].

Wall thickness distribution (Fig. 4) shows that the thickness of Lecce stone walls ranges from 13 to 29 μm, and that thicker walls (up to 60 μm) can be found, probably corresponding to fossils and shells, visible in the rock structure. These results confirm that x-ray tomography can be used for the characterization of stone materials both qualitatively (i.e., study of morphology, internal structure, shape, and interconnection of the pores) and quantitatively

(i.e., estimation of porosity, pore dimension, and wall thickness) in a nondestructive manner.

Set 2: samples treated with PB 72

Porosity values obtained from set 2 (before and after treatment with PB 72) are presented in Table 1. The two averages, before (39.4±1.3%) and after (36.3±1.6%) the polymer application, were compared using a t test. The t_{calc} was 7.659, which is greater than 3.707, the t_{tab} for a two-tailed test with probability of 99% ($\alpha=0.01$). H_0 is therefore rejected, i.e., the two averages are significantly different, and we can conclude that PB 72 caused a decrease in porosity, estimated to be 3.1±1.5%, according to Eq. (3).

The porosity is not the only morphological parameter that changes. The wall thickness distribution in Fig. 5 shows that there is a small decrease in the thinner walls (arrow A) and a slight increase in the thicker ones (arrow B) after the treatment. By forming a protective film along the walls of the pores, PB 72 probably induced a wall-thickening effect. These slight changes were noted also in the average wall thickness, since the value after treatment increased from 21 to 23 μm: again the t test reveals that the

Table 1 Porosity values (%) and standard deviations of set 2 before and after treatment with PB 72

	Sample number							Average
	8	9	10	11	12	13	14	
Porosity before treatment (%)	38.5	38.6	41.0	38.1	38.9	39.5	41.3	39.4±1.3
Porosity after treatment (%)	37.1	35.1	36.4	33.9	36.3	36.7	38.8	36.3±1.6
Difference (Δ_i) before−after (%)	1.4	3.5	4.6	4.2	2.6	2.8	2.5	3.1±1.5

Fig. 5 Wall thickness distribution of set 2 untreated (*solid line*) and treated with PB 72 (*dashed line*). The profiles were calculated on average of seven samples and show a small decrease in the thinner walls (*A*) and a slight increase in the thicker ones (*B*) after the treatment
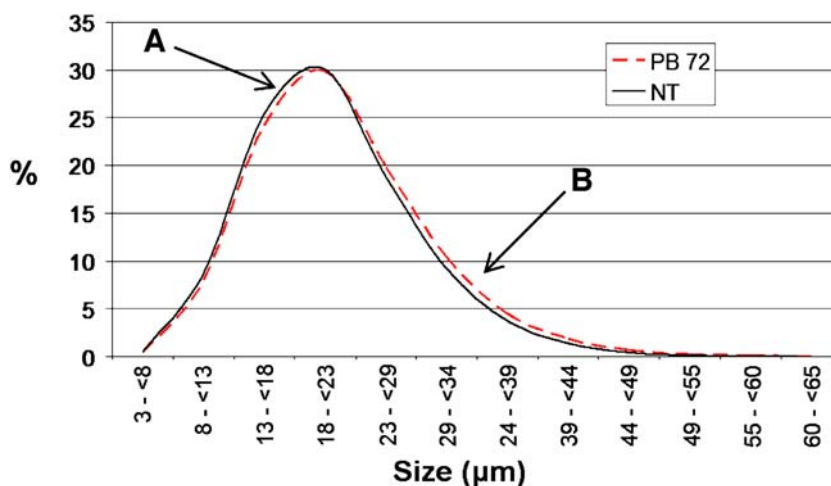
two averages of the wall thickness are significantly different.

Unexpectedly, only small differences were found in the pore size distribution before and after the treatment (Fig. 6). PB 72 is probably distributed in thin films around the grains or on the pore walls of the Lecce stone, inducing an increase in smaller pores (arrow A) and a decrease in the bigger ones (arrow B). Since the pore size is calculated as the diameter of the largest sphere that can be inscribed in the cavities [24], it is possible that the polymer in some cases fills small cavities and irregularities resulting in an increase of the wall thickness without changing the pore dimension.

The results obtained for PB 72 are in good accordance with those obtained during the preliminary study [11]. It should be taken into account, however, that these values are probably subject to an underestimation due to the distribution of the polymer in thin films around the grains of the Lecce stone and its low attenuation coefficient for x-rays in comparison to the rock.

Indeed PB 72 provides the stone with good water repellence without drastically changing the natural charac-

teristics of Lecce stone, so harmful effects due to the occlusion of the open porosity and/or to the formation of a continuous film on the surface of the artefacts should be avoided.

Set 3: samples treated with NH

Values of porosity of set 3 (before and after treatment with NH) are presented in Table 2. The two averages obtained before ($39.6\pm1.2\%$) and after ($31.2\pm1.8\%$) the application of the polymer were compared again with a t test. The t_{calc} was 22.114, i.e., much larger than 3.707, the t_{tab} for a two-tailed test with probability 99% ($\alpha=0.01$). In other words, the null hypothesis H_0 is again rejected, meaning that the two averages are significantly different and that NH caused a decrease in porosity, estimated to be equal to $8.4\pm1.4\%$, according to Eq. (3).

These results are not contradictory with the results of the previous study [11], in which the decrease in porosity, due to the treatment with the fluoroelastomer, was found to be around 3%. This quantitative discrepancy may be explained

Fig. 6 Pore size distribution of set 2 untreated (NT, *solid line*) and treated with PB 72 (*dashed line*). The profile shows a slight increase of the smaller pores (*A*) and a decrease of the bigger ones (*B*)
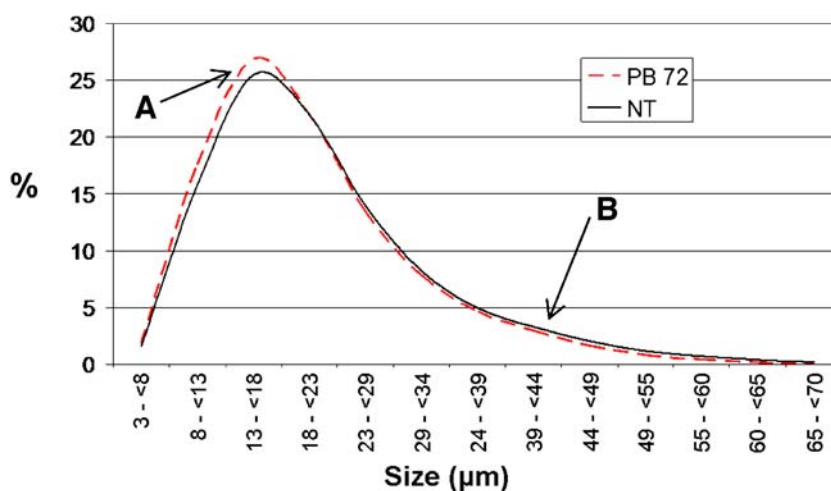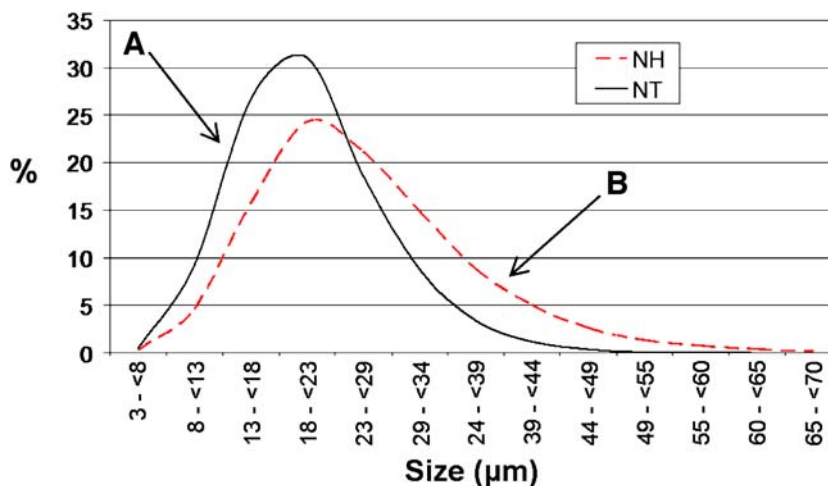
Table 2 Porosity values (%) and standard deviation of set 3 before and after treatment with NH

	Sample number							Average
	15	16	17	18	19	20	21	
Porosity before treatment (%)	39.7	37.7	39.6	40.9	39.9	38.4	41.1	39.6±1.2
Porosity after treatment (%)	33.3	28.9	30.3	32.4	31.7	29.1	32.9	31.2±1.8
Difference (Δ_i) before−after (%)	6.4	8.8	9.3	8.5	8.2	9.3	8.2	8.4±1.4

by the small changes in the treatment conditions, e.g., room temperature and sample dimensions, that occurred during the applications carried out in two different time points, which influence the evaporation rate of the solvent. On the other hand, the distribution of the polymers with high molecular weight, such as NH, may be more influenced by these small changes than polymers with lower molecular weight, such as PB 72. As a general trend, in fact, the solubility of polymers decreases as the molecular weight increases, while the viscosity of the treatment solutions increases as the molecular weight increases. Moreover, the acrylic polymer (PB 72), owing to its ester functional groups, has more affinity with the rock than the fluorinated one, and these interactions may improve the uniformity of distribution inside the pores. However, an average of seven specimens may be representative of the real behavior of Lecce stone subject to the studied NH application, especially considering that all the samples show a similar porosity decrease and it can be compared with the average value obtained for the samples treated with PB 72 under the same conditions.

The wall thickness distribution (Fig. 7) shows a strong decrease in the amount of the thinner walls (arrow A) and a considerable increase in the thicker ones (arrow B). The NH treatment induced a thickening effect due to the coating of the pores and the grains of the rock. The same behavior was not noticed in pore size distribution, where no appreciable changes of untreated vs. treated were observed.

It is possible that the product application changed the wall thickness distribution and the total porosity, inducing a very small variation of the distribution of the pores dimension, as in the case of the treatment with PB 72. This small variation, associated with the appreciable decrease in porosity, also suggests that part of the cavities could be completely filled by the polymer.

The natural average pore size was 22 μm and it did not change after the treatment, whereas the average wall thickness increased from 21 to 26 μm after the application of the polymer.

Conclusions

X-ray μ-CT has been demonstrated to be an important tool to assess the performance of the products used in the field of stone conservation. Its biggest advantage is the possibility to study the internal structure of the materials both in 2D (cross sections) and in 3D (reconstructed models) in a nondestructive way. Moreover, it is a technique with which it is possible to estimate the penetration depth/distribution of the stone conservation treatments, and it is even more powerful if coupled with appropriate image processing and calculation of the morphological parameters, such as porosity, pore size distribution, and wall thickness distribution.

The performed statistical analysis makes the results more representative and provides an essential estimation of the

Fig. 7 Wall thickness distribution of set 3 untreated (*solid line*) and treated with NH (*dashed line*). The profile shows a decrease of the thinner walls (*A*) and an increase of the thicker ones (*B*)

changes the material undergoes because of the conservation treatments and allows one to assess the errors connected with these changes.

The results obtained from this research show that the polymer distribution in the internal structure of the rock is influenced by the physical and chemical properties of the products (molecular weight and chemical affinity with stone). In fact, NH, having high molecular weight and low affinity with calcarenites, causes a significant decrease in porosity with partial or complete blockage of some pores and inhomogeneous distribution inside the stone. In this case differences in distribution may also be obtained with little changes of the application conditions.

On the other hand, PB 72, having lower molecular weight and a higher affinity for stone, causes small changes to the natural properties of Lecce stone with moderate variation of pore size and wall thickness distribution, suggesting a homogenous polymer distribution in the stone structure.

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