A photoacoustic pulse-echo probe for monitoring surface stone mechanical properties: validation tests in consolidation of Carrara marble

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Abstract

The present work focuses on the development and validation of a laser-based photoacoustic sensor for non-destructive monitoring of surface stone mechanical properties. The sensor is constituted of a carbon black target excited by fiber-coupled Q-Switched Nd:YAG(1064 nm) laser with variable pulse duration between 10 and 50 ns, a superimposed PVDF film transducer, and gel coupler. The high optical absorption of the target and its relatively large lateral size allowed generating planar longitudinal pressure waves of amplitude around 1 MPa using a laser pulse fluence of about 8 mJ/cm². The probe provided an almost flat spectral response over a bandwidth of 7.5-30 MHz. Thanks to the high pulse-to-pulse laser power stability, the pressure transients were highly reproducible in amplitude and waveform. These features and the FFT analysis of the back reflected signal were exploited to characterize the surface mechanical properties of decayed Carrara marble upon consolidation. Treatment tests were carried out using three commercial products: acrylic-siloxane polymer, a fluoroelastomer-acrylic polymer, and ethyl-silicate. The acoustic reflection and then surface sound speed spectra were measured and analyzed for the first time within a spectral window of 1-30 MHz. Surface speed spectra and dephasing derived from reflectance measurements resulted to be essential parameters for characterizing and monitoring stone consolidation. The results achieved provide evidence that the technique proposed offers significant advantages with respect to traditional approaches and can represent an effective tool in conservation-restoration of stone artifacts, wall paintings, and other.

Keywords: photoacoustic probe; acoustic reflection; pressure pulse; laser; stone consolidation; ultrasound; ultrasonic testing; non-destructive testing.

1. Introduction

Weathering produces a slow and continuous decay process that affects natural stones exposed to the atmosphere [1]. Among physical and chemical processes, water transport, environmental pollutants (SO₂, NOₓ, CO₂, soil), salt crystallization, heat and freeze-thaw cycles and biodeterioration are the main causes of stone decay, which irremediably produces erosion, encrustation, flaking, spallation and granular disintegration [2–4]. In particular, Carrara marble, which was widely used in the past to craft architectural elements and execute sculptural masterpieces, is rather sensitive to thermal variation because of the anisotropic properties of calcite crystallites, which cause inelastic microstrains [5,6]. This, along with concurrent sulphation phenomena can produce serious microstructural damages up to the granular disintegration of the marble matrix (sugaring) [7]. With the aim of mitigating such a destructive environmental impact and prolonging the long-term mechanical stability, several types of consolidating products have been developed and applied so far.

In relation to consolidation treatments for marble (and in general for carbonate stones) latest research trends in conservation of cultural heritage are increasingly oriented towards the development of nanoparticles (NPs) based products. Among those tested on marbles, nanolimes, which represent an improvement of the traditional limewater treatment, stand out [8–10]. Nanosilica formulations have been proposed as promising treatments, even though compatibility, depth of penetration, durability, and other variables are still being evaluated [11,12]. Nanostructured materials represent the most advanced frontier of the inorganic approach to the consolidation of carbonate stones, which were thoroughly investigated along the last decades using various treatments based on barium hydroxide, ammonium oxalate (AmOx), and more recently, di-ammonium phosphate (DAP) [13–16]. Regardless to their well-known limitations (i.e. shrinkage, cracking, low chemical compatibility, inefficient chemical bonding and hence limited long term durability), organic treatments based on acrylic polymers, alkoxyisilane-based formulations,
specially methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS), and ammonium oxalate are still widely used for consolidating decayed marble, limestone, and sandstone [7,17,18].

Although it is not the main focus of the present work, the brief state-of-the-art mentioned above underlines that marble consolidation (and in general stone consolidation) is definitely a complex open problem in conservation and further research is required to find suitable products and to standardize the application procedures. Seemingly, reliable and precise evaluation and monitoring methods are increasingly required in the field. These primarily involve direct methods including a combination of various analytical techniques and microscopies, which are usually exploited for detecting surface and in depth consolidation performances either on stratigraphic stone fragments (containing surface and subsurface layers) or on powdered samples. In particular, the consolidation performance of hydroxyapatite (HAP)-based treatments of naturally weathered marble samples has been investigated by combining scanning electron microscope (SEM), mercury intrusion porosimetry (MIP), ultrasonic pulse velocity (UPV) measurement, and Fourier transform infrared spectroscopy (FTIR) [7]. The latter performed at different depths has resulted to be useful even to obtain indications of treatment penetration depth as well as of newly formed phases and metastable calcium phosphate, which can be eventually harmful for the stone [19]. Recently, a multianalytical approach based on XRD, FTIR, TGA techniques and SEM micrographs has been successfully adopted for monitoring compositional and microstructural evolutions of powdery archaeological limestone surfaces upon DAP treatment followed by in-situ precipitation of HAP [20]. Likewise, a Raman investigation on the extent of penetration provided by a combined use of AmOx and DAP has been carried out on tablets of pure CaCO₃ as well as on deteriorated marble samples [16]. The results have demonstrated greater penetration depth (down to 2.5 mm) and hence better bulk consolidating properties of DAP with respect of AmOx. Basically, if on one hand these techniques reveal effective and decidedly supportive to understand consolidation mechanisms on laboratory samples, on the other hand, the in situ non-destructive assessment of stone mechanical properties using reliable approaches is still far from being accomplished. As widely accepted, compressive and tensile strength, bending strength, modulus of elasticity, ultrasonic pulse velocity, abrasion loss, surface hardness and surface cohesion are considered as crucial parameters for assessing weathering as well as short- and long-term performances of a consolidation product.

Currently, available methods to measure surface cohesion are those based on the so-called Scotch Tape test or peeling test [21], whereas scratch width (Martens sclerometer), rebound hardness testing (Schmidt Hammer), Shore durometer [22], Drilling Resistance [23] and more recently, an Acoustic Energy Meter [24] have been used for field measurement of rock hardness. Moreover, it was shown as Leeb probes, conceived as hardness test for metals, may be exploited for assessing the variation of surface hardness of stone materials upon consolidation treatments [25]. Another distinctive class is represented by Ultrasonic Testing (UT), one of the most attractive Non-Destructive Testing (NDT) for characterizing building material [26] and stone artifacts of cultural interest [6,7]. UT is a widespread NDT approach exploited in various fields ranging from the well-known diagnostics of the living tissues [27] to the characterization of polymers and other materials [28]. It is useful for detecting surface and bulk defects (cracking, delamination, flaws), measuring the thickness of multilayered materials, and other.

UT has been widely exploited in conservation of stone artifacts for assessing the bulk mechanical properties through the measurement of the speed (v) of the longitudinal wave (P-wave) using both direct (i.e. transmitter and receiver positioned on opposite sides) [29–31] and indirect methods [32]. This allowed showing as increasing degree of weathering is associated with a lower ultrasonic speed [6]. According to the Köhler’s speed-porosity correlation function, five classes of material alteration were proposed, where v decreases from about 5 km/s of the quarry marble to values lower than 1.5 km/s of deeply altered marble [33]. The most advanced version of such a direct transmission method is
represented by U-tomography, which is increasingly applied for determining speed variations inside stone, distribution and depth of cracks, and weathering layers as well [6,31–34]. Besides the study of P-waves and S-waves (i.e. shear waves) velocity, Rayleigh waves have been also used in order to characterize the surface weathering effects of marble [35]. As the travel time of the propagated P-waves does not offer a complete evaluation of the wave transmission process it was proposed spatial attenuation as highly sensitive, more than v, to the petrographic characteristics (e.g. crystal size) of rocks as well as individual defects [36]. These applications typically exploit a frequency range of 50-500 kHz (central frequency) in order to achieve penetrations around tens of centimeters or more. The use of frequencies higher than 1 MHz is limited by their strong attenuation in marble [35,37]. Thus, in direct transmission measurements it is desirable to find a compromise between spatial resolution and penetration, mainly due to the need of recording pulse-echo signals from the back surface. However, in the conservation field, the precise determination of the consolidation performances requires the application of analytical techniques providing higher spatial resolution and accuracy, as weathering and consolidation effects in stone and mortars mostly concern the uppermost layers (~10 µm-1 mm) [38]. Moreover, the variety of microstructures and inhomogeneity (crystal sizes, porosity and degree of weathering) encountered do not make always possible in-situ detection of ultrasonic signals from the back surface. At the same time, the use of indirect methods poses several constraints because of the difficulty in the positioning of the transmitter and receiver transducers. In this regard, the assessment of surface stone weathering and consolidation could potentially be better performed using high-frequency spectral acoustic reflectometry, an approach extensively investigated in the biomedical field for tomographic purposes [39,40].

In the present work, a novel laser-based photoacoustic (PA) sensor probe, which was designed for back reflection measurements, has been developed and successfully tested in characterizing the surface mechanical properties of incoherent and porous (“sugared”) Carrara marble samples before and after different consolidation treatments. Basically, such an approach exploits the advantages of laser-generated pressure transients, which provide higher signal amplitudes (up to MPa), broader bandwidths (e.g. ranging over several tens of MHz for laser pulse durations of 5-10 ns) and superior spatial resolution (few tens of microns) in detecting inhomogeneity with respect to conventional piezoelectric sources.

2. Material and methods
2.1 Design and development of the PA probe

Schematic and real views of the PA probe developed are displayed in Fig. 1. As shown, pressure pulses were generated by irradiating an absorbing target with a fiber-coupled Q-Switched Nd:YAG (1064 nm) laser (variable pulse duration between 10-50 ns) and measured using a broadband piezoelectric polyvinylidenefluoride (PVDF) film (9 µm-thick uni-axially oriented and Al-coated). The latter has been widely used in many fields, for investigating the photoacoustics of the laser ablation [41,42], the laser-assisted cleaning methods [43], and for fabricating multi-layered PVDF piezoelectric ultrasonic sensors for PA tomography [44].

As mentioned above, the laser beam was homogenized using a 550 µm core optical fiber and a top hat laser beam profile at the target was achieved through the collimating lens L. The target consisted of carbon black powder (10-90% w/w, 1-10 µm particle sizes) pre-impregnated with polycarbonate (C-PC: 200 µm thick, 9 mm), which was glued to a Polymethyl methacrylate (PMMA) rod (10 mm, 2 cm height) using epoxy resin. As the optical properties of the absorbing target are crucial for PA generation, the optical penetration depth was measured (21.7±0.4 µm) using Kubelka-Munk according to a well-established procedure we reported in previous works [45]. These features allowed generating intense single-phase compressional pulses, as foreseen for the present rigid boundary condition [46]. The PVDF
transducer was glued on the other side of the C-PC target using cyanoacrylate. Once the sandwich was
dried, the PVDF film was re-sized to the target area (\(\Phi 9 \text{ mm}\)) and two small flaps (5\times3 \text{ mm}^2) were left
for electrical connections of its Al-coating to the oscilloscope through a short coaxial cable (about 20
cm). These components were assembled in a suitable cylindrical casing of a few centimeters,
which allowed easy handling of the PA sensor probe (Fig. 1b).

In the configuration described above, the voltage \(V(t)\) measured by the oscilloscope set in high
impedance coupling is proportional to the pressure \(p(t)\) at the PVDF film, according to the well-known
scaling law [41]:

\[
V(t) = \frac{d_{33} \cdot A \cdot p(t)}{C_{\text{tot}}}
\]

(1)

where \(C_{\text{tot}}\) is the total capacitance of the circuit, \(d_{33}\) is the PVDF piezoelectric coefficient and \(A\) is the
area of the pressure front of the travelling wave through the transducer, by assuming the latter is not
larger than the area of the PVDF film. In the present configuration (Fig. 1a) the area \(A\) can be assumed
to be the same as that of the laser spot at the target, since the thickness of the absorber (200 \(\mu\text{m}\)), i.e. the
distance between the source and the transducer, was much lower than the radius of the laser spot itself
(about 4 mm). The calculated \(C_{\text{tot}}\) was around 1.21 nF, which was essentially determined by the
capacitance of the PVDF transducer (1.18 nF), while those of the cable and of the oscilloscope were
almost negligible (20 pF and 10 pF, respectively). Thus, the scaling law for converting the electrical
signal into pressure signal was: found to be proportional at \(p(t) = 1.5 \cdot V(t)\).

2.2 PA measurements and data processing

The photo-acoustically generated pressure wave, after travelling across the PVDF film and the
coupling medium (in this case GG hydrogel, see section 2.4), encountered the marble surface, where it
was specularly reflected back to the PVDF sensor (pulse-echo configuration). It is worth mentioning that
the high repeatability of generated PA source was assured by the reduced pulse-to-pulse energy
fluctuations of the laser pulse energy. A standard measurement method was defined for PA signal
acquisition. Basically, the reflection peak of the surface was considered reliable whenever its full-width-
half-maximum (FWHM) corresponded to the shortest time and its amplitude to the maximum. This
condition assured the best mechanical coupling to the target and the parallelism of the marble and
transducer surfaces.

The first step towards the analysis of the reflected waveforms was the calculation, in the time
domain, of the fraction of the incident pressure pulse that is reflected back, namely the acoustic reflection
coefficient, which is given by:

\[
R = \frac{Z - Z_0}{Z + Z_0} = \frac{\rho v - \rho_0 v_0}{\rho v + \rho_0 v_0}
\]

(2)

where \(Z_0\) and \(Z\) are the acoustic impedances of the first (i.e. GG hydrogel) and second (i.e. marble)
medium traversed by the pressure wave, \(\rho_0\) and \(\rho\) the corresponding material densities, and \(v_0\) and \(v\) the
the corresponding longitudinal speeds, respectively.

For calculating the reflectance spectrum, \(R(\omega)\), amplitudes of the incident pressure pulse, \(p_0(t)\), and
the first reflected pulse at the gel-sample interface, \(p(t)\), were transformed to frequency domain data by
using the Fast Fourier Transform (FFT). Then, from the amplitude spectra (magnitude of the FFT) the following ratio was calculated: $R(\omega)=p(\omega)/p(\omega)$, where $\omega$ is the angular frequency ($\omega=2\pi f$). Afterwards, in order to make the measured acoustic reflectance independent on the gel thickness, $R(\omega)$ was re-normalized to the reflectance of the quarry Carrara marble, $R_{\text{ref}}(\omega)$: $R_{\text{ref}}(\omega)=R(\omega)/R_{\text{ref}}(\omega)$. More information about the surface mechanical properties of the stone sample were inferred by calculating the acoustic impedance, $Z(\omega)$, and the surface speed, $v(\omega)$. Variations of these parameters upon consolidation are mainly associated with changes of the surface bulk modulus, $B$, and then surface stiffness, being: $v=(B/\rho)^{1/2}$. Conversely, density variations are often negligible when considering marble consolidation. The surface impedance, $Z(\omega)$, and speed, $v(\omega)$, as a function of the measured reflectance $R(\omega)$, were calculated as follows:

$$Z(\omega) = \frac{Z_0[1+R(\omega)]}{[1-R(\omega)]}, \quad (3)$$

$$v(\omega) = \frac{Z(\omega)}{\rho} . \quad (4)$$

Lastly, the dissipative penetration depth along the back-scattering path as a function of the frequency, $\delta(\omega)$, was calculated as follows:

$$\delta(\omega) = \frac{\Delta \varphi(\omega)v(\omega)}{2\omega} \quad (5)$$

where $\Delta \varphi(\omega)$ is the dephasing spectrum obtained by the phase difference $\Delta \varphi = \varphi_2 - \varphi_1$ between the input signal and first reflected pulse, the factor 2 was introduced in order to take into account that dephasing is determined by the path length $2\delta$. A dissipative penetration is expected in those cases where the continuity and coherence of the outer material layer is not sufficient in order to produce a straight reflection at the sample surface.

2.3 Samples

Carrara marble samples were taken from a strongly deteriorated tortile column removed from a Florentine historical façade (Italy) and replaced for safety reasons. A stretch of this column was cut in order to produce six quasi-rectangular fragments, which included the original surface. The lateral faces of these samples (i.e. the cutting sections) exhibited a completely deteriorated marble matrix with the typical sugar-like crumbling of calcite grains. Sample surfaces measured about 5 \times 4 cm$^2$ and their thickness was about 3 cm. Conversely, a fresh quarry Carrara marble slab (2 cm thick) was used as acoustic reflectance reference. All the samples had a flat surface on which the various consolidation treatments were applied.

The consolidation treatments listed in Table 1 were selected in order to evaluate effectiveness of the novel PA probe in collecting information on the associated changes of the surface mechanical properties.

They are ready-to-use consolidating/protective materials commercially marketed by CTS s.r.l. (Italy). Among the selected products, the ethyl-silicate treatment (labeled as ESTEL 1000) is
characterized by a distinctive curing and drying mechanism in comparison to the others. Basically, hydrolysis-condensation reactions of ethyl silicate produce the formation of amorphous silica within the intergranular boundaries. Consolidants were applied at 5% v/v by brushing iteratively until complete impregnation was achieved. The treatment consisted of up to 5 brush application in standard laboratory conditions (T = 20 ± 2 °C, RH = 50 ± 5 %), and a 1 month drying period was waited before a further application, according to the technical data sheet recommendations. The procedure was repeated for three times. During brush applications, contrarily to FLUOLINE CP and ACRISIL 201/O.N, ESTEL 1000 was appreciably more absorbed by marble. According to the literature [30], indirect tests to assess water repellency upon consolidation have shown the two organic products imparted more hydrophobization properties to the surface than ESTEL 1000. Figure 2 reports representative SEM images of the quarry sample and of deteriorate marble, before and after consolidation with FLUOLINE, where the low porosity of the fresh marble, physically separated grains of the deteriorated one and its compactness recover after consolidation can be observed, respectively.

2.4 GG preparation

Tests were carried out in order to optimize the mechanical contact between the outer surface of the PVDF film and the surface of the sample under investigation. A low-acyl gellan gum (GG), a biotissue-mimicking material used in high-intensity focused ultrasound therapy [47], was found to be an effective coupling medium for acoustic reflection measurements. GG was prepared in deionized water (2% w/v) by heating up to 90°C under vigorous magnetic stirring for 10 minutes and then poured in Petri dishes prior to be used. To have a regular peak-to-peak delay, the measurements were carried out using a constant GG layer thickness of 1 mm.

2.5 Peeling test

Peeling test was used to evaluate the increase of surface cohesion strength upon consolidation treatments. Measurements were carried out by using a 3M double-sided pressure-sensitive modified acrylic tape (adhesion to stainless steel: 15 N/cm). It was cut into test strips of about 10 x 10 mm (1 cm² contact area) and glued by hand pressure on the clean and dry marble surface. As the binding strength increases as a function of time and temperature, each sample was kept under controlled laboratory conditions (T=22 °C, R.H.= 45-55 %) and 1 min. of adhesion time was used before peeling off the test strip. The amount of material pulled off by the tape, expressed as tape removal rate in mg/cm², was measured by weighting the test strip before and after peeling. A Sartorius Research balance with a sensitivity of 10⁻⁵ g was employed during the test. To estimate the surface cohesion about 15 peeling measurements were repeated exactly on the same test area. Despite the literature indicates that the results of the peeling test poorly depend on attaching pressure and the speed of detachment, a peeling angle of 180 °C and a speed removal rate of 10 mm/s were kept constant as much as possible during the tests.

3. Results and discussion

3.1 PA probe response

For NDT applications, signals of higher amplitude are preferred for improving the S/N ratio and the performance in detection. Therefore, the optimal laser beam intensity was accurately determined for
exciting as long as possible high and repeatable pressure pulses. The operative fluence at the C-PC target was between 8–12 mJ/cm², well below the occurrence of detachments at PMMA/C-PC interface, which was observed around 40 mJ/cm². The travelling pressure wave measured by the transducer by irradiating the target at 8 mJ/cm² and pulse durations of 10 ns and 50 ns, along with the associated frequency spectra, are displayed in Fig. 3, which represent the reference of the following reflection measurements.

As shown, the amplitude increased almost linearly with the laser intensity, I, as expected for highly absorbing targets. In this condition, the maximum pressure can be approximated by [48]:

\[ P_{\text{max}} = \beta \nu c_p \]

where \( \beta \) is the volumetric expansion coefficient, \( \nu \) the sound speed, and \( c_p \) the specific heat of the target at constant pressure. Using the physical parameters of polycarbonate (\( \beta = 70-80 \times 10^{-6} \text{ K}^{-1}, \nu = 2286 \text{ m/s} \) and \( c_p = 1.17 \text{ kJ/kg K}^{-1} \)): \( P_{\text{max}} \approx 1.2 \text{ MPa} \), which is congruent with the peak values measured (Fig. 3a). However, it should be taken into account that the latter represents the superposition of the compressional wave crossing the transducer and the corresponding rarefaction wave produced by the reflection at the PVDF/GG hydrogel interface. A rough estimation of the latter can be achieved by considering the reflection coefficient between two media provided by eq. 2, where \( Z \) is the acoustic impedance of the GG hydrogel (\( \sim 1.55 \times 10^{12} \text{ kg m}^{-2} \text{s}^{-1} \) at room temperature 20°C), \( Z_0 \) that of the C-PC target, since the thickness of the PVDF film is much lower than the shortest acoustic wavelength (\( \lambda_{\text{ac}} \)) generated. The latter can be estimated as \( \lambda_{\text{ac}} = 2 \nu c_{\text{t}} \tau_2 = 45 \) or 250 \( \mu \text{m} \) for \( \tau_2 = 10 \) and 50 ns, respectively. Thus, the pressure measured by the transducer is reduced by a fraction of 0.25 with respect to the incident wave due to the higher acoustic impedance of C-PC target.

In any case, the pressure transient measured (Fig. 3a) represents the actual pressure wave coupled to the gel layer and propagated towards the sample surface under characterization. Thus, as shown in Fig. 3a, the PA probe realized has an acoustic efficiency of about 0.12 MPa/(mJ/cm²). It is worth noting that the present pressure amplitudes compare favorably with those reported on the literature using carbon black-PDMS mixture, which is known as the polymer with the largest thermal expansion coefficient (\( \beta = 310 \times 10^{-6} \text{ K}^{-1} \))[49,50]. Here, the maximum pressure achieved was about 3–4 times smaller, but it was produced in a PC composite (\( \beta = 70-80 \times 10^{-6} \text{ K}^{-1} \)).

The FFT of the reference pressure transients measured are shown in Fig. 3b. Broad and rather flat spectra were achieved over a spectral range of some tens of MHz. At -3dB bandwidths for short and long \( \tau_2 \) were 22 MHz and 5 MHz, at -6dB, 30 MHz and 7.5 MHz. By considering that \( \nu c_2 = 2270 \text{ m/s} \) in the C-PC target (as estimated through independent time of flight measurements), \( \lambda_{\text{ac}} \) ranging between 75 and 300 \( \mu \text{m} \) may be roughly estimated from frequency spectra (at – 6dB level), which is in good agreement with \( \lambda_{\text{ac}} \) derived from the wave propagation during the laser pulse duration (\( \lambda_{\text{ac}} = 2 \nu c \cdot \tau_2 \)).

3.2 Gel attenuation

In order to verify whether the influence of the GG hydrogel could be neglected during PA detection, its attenuation coefficient was measured through the analysis of multiple reflections. For this measurement, an AISI 4340 alloy steel was used as a reflectance reference standard. Fig. 4 displays the attenuation per unit length (in dB/cm), which was expressed by the following relation:

\[ \alpha(\omega) = \left( \frac{1}{L} \right) \times \log_{10}[p_1(\omega)/p_0(\omega)] \]
where \( p_0(\omega) \) and \( p_1(\omega) \) are the FFT spectra of the first and second reflected signals and \( L \) the path length (twice of the thickness) \([51]\).

In the calculation, to account for deviations induced by the reflections at GG/steel and GG/PVDF interfaces, being \( R = 0.9 \) and 0.28, respectively, \( p_0 \) was multiplied by a correction factor of 0.25. The calculated \( \alpha \) of the present GG hydrogel has an approximately linear frequency dependence and does not differ significantly with respect to that of water over 1-30 MHz range. Differences in the slope among water and gel are within the uncertainty of the measurement. At higher frequencies, the calculation of \( \alpha \) was not reliable due to the low S/N ratio, even though it is reported that for water \( \alpha \) is greater than 5 dB/cm at 50 MHz \([52]\). Therefore, the variation of \( \alpha \) suggests that measurements performed on stone samples shown hereby are not drastically affected by attenuation using gel thickness of a few millimeters. For instance, at 10 MHz, an acoustic wave passing through 1 mm GG layer is reduced of 1.2 \%, whereas at 20 MHz of 3.6 \%.

3.3 Peeling testing

Comparative results of the peeling tests are displayed in Fig. 5. The constant rate achieved for decayed Carrara marble (non-treated) have to be considered a saturation value. Starting from the initial test the whole surface of the tape resulted completely covered by detached calcite grains. For sugary Carrara marble an average value of 30 mg/cm\(^2\) is consistent with value reported in the literature \([21]\). Regardless to the type of consolidating product, the peeling tests performed in consolidated areas underlined a strong decreasing of released material, which in turn means increased surface cohesion at grain boundaries level. Samples treated with ACRISIL and FLUOLINE CP showed a different trend as compared to ESTEL 1000 treated samples. As shown in Fig. 5, for ACRISIL and FLUOLINE CP, the tape removal rate started to increase after the fifth peeling test, up to about 10 mg/cm\(^2\). This suggests that the consolidation effect was non-homogeneous in depth as the surface showed a higher cohesion than the inner layers. Finally, the highest cohesion was observed for the samples consolidated with ESTEL 1000, as after 12 tests no grains were peeled out from the stone surface. Owing to its different nature and consolidating mechanism, one could notice that the binding strength of the adhesive tape on samples treated with ESTEL1000 was lower than the surface cohesion strength.

3.4 PA reflection measurements

Following the preliminary characterization of the PA efficiency and gel attenuation, a set of validation measurements were carried out on the Carrara marble samples presented above before and after applying the three different consolidating products. Input exciting signals and pulse-echo amplitudes for 10 and 50 ns laser pulse duration as recorded by the oscilloscope are shown in Fig. 6.

As shown, pulse-echo signals from the marble surface were remarkably different upon consolidation treatments. A very low signal was detected on decayed samples, as consequence of its high porosity. Instead, reflection properties of consolidated samples resulted significantly improved and closer to those quarry marble. To infer more about mechanical properties pressure pulses were Fourier Transform and then \( R_{rel} \) was calculated, as reported above.

The analysis of the reflectance spectra shown in Fig. 7 returned an immediate evidence of the degree of deterioration of not treated marble and its partial recovery after consolidation. The probed
surface of decayed Carrara marble acted as a low-pass filter with cutoff frequency of 1 MHz, whereas the spectral response of the consolidated samples showed a significant improvement over the investigated frequency range. FLUOLINE CP and ACRISIL 201/O.N, showed a clear reflectance maximum at circa 4 MHz, with that of ACRISIL 201/O.N higher than that of FLUOLINE CP up to 30 MHz. Conversely, the reflectance profile of stone treated with ESTEL 1000, showed a distinct profile, to be attributed to the different consolidation action. A relative improvement in the reflection of the low-frequency components and a decrease in the high-frequency components was observed.

It is noteworthy that spectra relating to 10 and 50 ns laser pulse duration, respectively, differed slightly in 1-2 MHz range and then they were almost coincident at higher frequencies. Considering the corresponding significant bandwidth differences (Fig. 3b), this behavior demonstrates the acoustic wavelength used were longer than the surface roughness of the samples under study and then supports the reliability of the present measurements.

In Fig. 8 the corresponding surface speed (longitudinal component of the sound velocity through the outer stone layers) spectra (see eqs. 3-4) are reported. For this calculation, $\rho \approx 2.7$ g/cm$^3$ was used for quarry Carrara marble, whereas for decayed and consolidated samples an average value of 2.5 g/cm$^3$, which was experimentally measured by gravimetric method. For quarry Carrara marble, $v_{\text{max}}(\omega)$ of about 5.22 km/s was achieved in the range 1-4 MHz, and then the speed dropped down due to the frequency-dependent wave attenuation.

For decayed marble (Fig. 8a) $v(\omega)$ approximates to zero at 5 MHz and had a maximum at 1 MHz of 1700-2600 m/s, which is in between the class III (progressive granular disintegration) and class IV (danger of breakdown) according to the Kohler’s velocity-porosity correlation [33,34]. The decrease of $v$ is ascribable to the porosity and reduction of the surface stiffness ($v = (B/\rho)^{1/2}$), produced by the loss of cohesion among calcite grains. Conversely, the relative increase of $v$ upon consolidation can be mainly associated with the reduction of the open micro-porosity (improved mechanical continuity) and binding effect of the consolidation treatment. At the lowest frequency investigated (1 MHz), marble treated with ESTEL 1000 exhibited a slightly higher speed with respect to that treated with the acrylic-based products. Conversely, at increasing frequencies the speed of the latter was higher.

The behaviors of Figs 7-8 represent fingerprints of the different state of consolidation of the marble samples. Despite such acoustic spectra cannot be strictly interpreted in terms of degree of consolidation and durability of the treatment, they can certainly be exploited in monitoring applications. Spectral changes along the time can objectively evidence the initial surface strengthening and then the following re-weakening due to the weathering actions.

Further information about the state of consolidation can be extrapolated using the spectra of the dissipative penetration depth, $\delta(\omega)$, displayed in Fig. 8. As explained above (see eq. 5), $\delta(\omega)$ represents an estimation of the marble depth, which contributes to the reflected signal. In the case of quarry marble, the behavior of $\delta(\omega)$ is flat over the whole frequency range, which means almost ideal surface reflection. Contrarily, $\delta(\omega)$ of the untreated deteriorated Carrara marble samples exhibited broad variations (not reported in Fig. 8a) due to the strong intergranular porosity (FLUOLINE CP and ACRISIL 201/O.N. treated samples provided similar results each other but different with respect to ESTEL 1000. In the low-frequency range (1-3 MHz), the observed phase delay up to circa 60$^\circ$ indicates the pressure pulses lose part of their energy through a sub-surface material layer. Wave dissipative penetration depths up to 350 µm for FLUOLINE CP, and up to 150 µm for ACRISIL 201/O.N. were estimated. Thus the slightly better performance of the latter with respect to the former is supported by both higher speed and lower
dissipative penetration. This difference was not evidenced through the peeling test because of the low sensitivity of the latter, which “flattened” the behavior (Fig. 5), whereas it was effective in pointing out the filmogenic behavior of the present polymeric materials. \( \delta(\omega) \) for the sample treated with ESTEL 1000 was almost negligible, which suggested a good degree of mechanical continuity and of immobilization of the calcite grains was achieved, although the sound speed decreased more rapidly at increasing frequencies than those of the samples treated with the polymeric materials. This result along that provided by the peeling test show that, in the present case, ethyl-silicate provided better strengthening performance.

4. Conclusions

A novel PA probe using a QS Nd:YAG laser (1064 nm, 10-50 ns), an optically absorbing target, and a PVDF piezoelectric film was developed and successfully tested for measuring the surface mechanical properties of marble samples. Intense and reproducible pressure transients (several tens of bar) were generated and used to investigate the reflectance properties of decayed Carrara marble, before and after a set of consolidation treatments. The novel tool showed high sensitivity, repeatability, and reliability in characterization of the surface mechanical properties of the stone samples. Amplitude and phase of reflected pressure waves were analyzed in the frequency domain using FFT, which allowed deriving surface impedance and sound speed spectra within the spectral range of 1-30 MHz. The surface sound speed and dephasing of the pressure pulse represent the key parameters for assessing the surface effects of the consolidation treatments and to easily monitor changes over the time. In particular, the characterisation of the marble samples treated with acrylic-based polymers showed a significant amplitude and spectral recover of the surface sound speed, whereas that produced by ethyl-silicate was spectrally limited to the lower frequency limit. Conversely, relevant wave dephasings were observed for the former treatments while these were not present for the latter, which indicate the relative higher surface hardness of the sample treated with ethyl-silicate, within the present spectral region. This conclusion was coherent with the results of the tape test that evidenced the mechanical improvement provided by the polymeric materials was limited to the outer stone layer, in agreement with their filmogenic behavior, whereas the tensile strength of the surface consolidated with ethyl-silicate was higher than the maximum strength exerted through the tape.

In conclusion, the novel PA probe provides objective evaluation parameters for the mechanical characterization of surface weathering and stone consolidation, soon after the treatment and for monitoring long term changes. Furthermore, we are presently exploring the possibility to use it for simultaneous surface and bulk measurements, which could offer some advantages with respect to conventional NDT ultrasonic testers by overcoming drawbacks associated with the positioning of the receiver and transmitter. Further investigation will be devoted to improve the efficiency and broad the spectral band of the PA tool introduced in this work and to extend its testing to other stone materials and consolidating products. At the same time, efforts will be dedicated to its engineerization by exploring different development perspectives. In particular, a very low cost solution (some hundreds Euro for components) can be achieved by devising the present tool as an accessory of laser cleaning systems. Alternatively, a dedicated low cost (some thousands Euro) miniaturized diode pumped solid state (DPSS) laser should be used as excitation source, which can allow compacting the whole system in a handheld device.
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Fig. 1

Fig. 2

Fig. 3
Figure captions

Fig. 1 Scheme (a) and real view (b) of the photoacoustic probe. OF: optical fiber. L: plane-convex lens.

Fig. 2 SEM image showing the cross section of a deteriorated Carrara marble sample.

Fig. 3 Laser generated pressure waveforms, $p(t)$, for 10 and 50 ns laser pulse durations, respectively (a) and corresponding frequency spectra (b). For comparison, frequency spectra were normalized to the maximum amplitude in dB of the recorded PA signal (the inset show the corresponding non-normalized plot).

Fig. 4 Pressure pulse attenuation spectrum for GG hydrogel and water.

Fig. 5 Comparison of peeling test carried out on sugary Carrara marble samples before and after different consolidation treatments.

Fig. 6 Pulse-echo signals obtained using 10 ns (a) and 50 ns (b) laser pulse duration on non-deteriorated Carrara marble and deteriorated before and after consolidation treatment.

Fig. 7 Relative acoustic reflectance of treated and untreated deteriorated Carrara marble samples. Solid and dashed lines refer to spectra achieved using 10 (solid line) and 50 ns (dashed line) laser pulse duration, respectively.

Fig. 8 Surface speed (black, $v(\omega)$) and wave penetration depth (red, $\delta(\omega)$) associated with the dephasing: a) quarry and deteriorated Carrara marble; b) ESTEL1000 treated; c) FLUOLINE CP treated; d) ACRISIL 201/O.N. treated. Wave penetration depth for untreated deteriorated marble is not reported because of the broad variations it exhibited. Solid line and dashed line refer to measurements carried out using 10 and 50 ns laser pulse duration.