Construction and Building Materials 187 (2018) 610–619

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

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

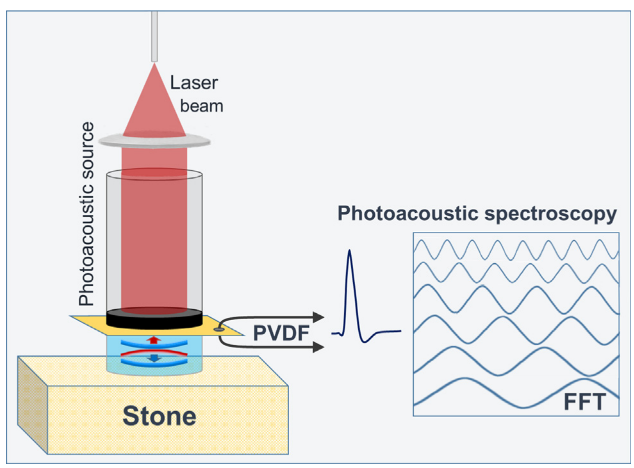
Daniele Ciofini, Andrea Azelio Mencaglia, Salvatore Siano *

Istituto di Fisica Applicata "Nello Carrara" (IFAC), Consiglio Nazionale delle Ricerche (CNR), Via Madonna del Piano, 10, 50019 Florence, Italy

HIGHLIGHTS

- A photoacoustic probe and method for surface characterization of stones are proposed.
- The approach allows quantifying surface stone deterioration and consolidation effects.
- Effectiveness in assessing the properties of consolidation treatments was demonstrated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 March 2018
Received in revised form 24 July 2018
Accepted 27 July 2018

Keywords:
Photoacoustic probe
Acoustic reflection
Pressure pulse
Laser
Stone consolidation
Ultrasound
Ultrasonic testing
Non-destructive testing

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 transients of amplitude around 1 MPa using a laser pulse fluence of about 8 mJ/cm^2. The probe provided an almost flat spectral response over a bandwidth of 7.5–30 MHz. Thanks to the high pulse-to-pulse laser emission 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.

* Corresponding author.
E-mail address: s.siano@ifac.cnr.it (S. Siano).

https://doi.org/10.1016/j.conbuildmat.2018.07.225
0950-0618/

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 (SO_x, NO_x, CO_2, 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 durability), organic treatments based on acryilic polymers, alkoxysilane-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 $CaCO_3$ 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