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Assessment of consolidation treatments: micro-CT as a potential tool for material's penetration detection.

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Abstract – **In the frame of an experimental study focused on structural reinforcement of wood by consolidation, developed during two master's theses in Conservation and Restoration of Cultural Heritage (Turin Universiy in collaboration with Centro Conservazione e Restauro La Venaria Reale), the potentials and limits of possible investigation techniques to verify the performances of the treatments, both superficially (optical and electron microscopy) and in terms of penetration (micro-tomography) were evaluated. This paper discusses the main preliminary results, with particular attention to the micro-CT measurements, carried out for detecting the penetration of consolidating materials into the wood. The results appear particularly encouraging in terms of potentialities of the diagnostic technique, taking also into consideration its non-invasiveness and, in perspective, of possible applications to real case studies, boosted in the case of addition of nanocomposites (metal particles) to traditional materials for consolidation.**

I. INTRODUCTION

Biotic infestation (basomycetes, ascomycetes, xylophagous insects), a common problem found on many wooden artefacts, entails deterioration in terms of erosion of cellulose and, in some cases, of both cellulose and lignin. Entomatic attacks in particular can also occur in seasoned and aged woods, frequently in sapwood or, more rarely, heartwood. For an assessment of the state of preservation of the wooden materials, it is important to evaluate the diameter, number and position of the porosities even if these are not directly connected to the galleries. In case of deterioration of the material, it is common practice to foresee treatments through the application of diluted products by capillarity inside the wooden mass to ensure the safety of the asset, boosting the durability of the material and, in general, recovering the physical-mechanical characteristics of the structure. An unsolved problem up to date is how to monitor the penetration of the consolidating materials in terms of diffusion within the wooden material and filling capacity. This issue is determined by the organic nature of both the wood and the consolidating agent, with consequent difficulty of discrimination, if not at the morphological level. A possible solution proposed in the literature consists in the addiction of a coloring substance in the tested material as a marker [1], although the evaporation of the solvent determines migrations highlighting areas where the consolidating agent is absent. In other cases microscopic analysis were performed in order to assess the presence of the materials into the wooden structure [2]. In this contest, an experimental study has been developed in the frame of two MA degree theses in Conservation and Restoration of Cultural Heritage (University of Turin in collaboration with the CCR La Venaria Reale) [3,4], aimed at evaluating the capability of specific diagnostic techniques in verifying the behavior of the materials, both superficially and at a bulk level. In particular, a multi technical approach was combined with micro tomography. This technique has been performed over the years on

different types of archaeological and anthropological finds [5], also by means of synchrotron equipment [6], in order to evaluate the state of preservation and to get a more detailed knowledge of ancient objects, but it has been applied scarcely to monitor conservation treatments, in particular on wood. [7-10].

II. MATERIALS AND METHODS

The research was structured in different steps, the first of which [3] had, among its goals, a possible identification of monitoring protocols, with a multi-technique approach aimed at measuring dimensional variations, mechanical properties and micro and macro-porosity of the wood, in the view of a possible mapping of the distribution of the materials in the matter. The second phase [4] allowed the integration of the results, as regards the selection of materials to be tested and the further verification of the limits and advantages of the analytical techniques for monitoring. To map the distribution of the treatment materials, in terms of penetration and variation of the micro and macro porosities, micro tomographic analyzes were carried out; the acquired data were integrated with the surface characterization in optical and electron microscopy to investigate the potentialities of the method. Optical microscopy made it possible to document any chromatic and textural variations; electron microscopy images, carried out by fully inserting the sample inside the instrumentation, investigated the transversal sections according to the direction of absorption of the consolidating material.

A. *Tested materials*

Traditional materials (organic materials of a synthetic nature: aliphatic resin, Regalrez® 1126, combined with acrylic resin, Paraloid® B72) and of the innovative ones that involved the modification of organic substances with the addition of nanocomposite filler materials (lamellar phyllosilicates nanocomposites, Laponite® RD) were tested. In details: Paraloid® B72 is a high molecular weight acrylic resin of methyl acrylate-ethyl methacrylate, soluble in ketones, esters and ethers, aromatic and chlorinated hydrocarbons; it is a material used in the conservation field mainly as a consolidant in increasing concentrations (3-10%) for gradually favor the penetration of the molecule into the system. The localization of the material occurs within the cellular lumen, reducing the micropores [11]. Regalrez® 1126 is a low molecular weight aliphatic resin (1250 u) soluble in mixtures of aliphatic and aromatic hydrocarbons. Given the low molecular weight, the resin in solution tends to enter in the cell walls of the wood, but the reinforcing effect conferred is not sufficient to solve medium-sized structural problems. For this reason, it is generally used combined with Paraloid® B72 [1]. Acrylic resin (Paraloid® B72) with the addition of lamellar phyllosilicates, nanocomposites (Laponite® RD) has been combined in the frame of a collaboration between the CCR La Venaria Reale and the Department of Applied Science and Technology, Politecnico di Torino), also in consideration of the best mechanical performances obtained with organic materials added with fillers with filling capacity (microcrystalline cellulose [12]). Laponite® RD is a clay mineral belonging to the montmorillonoid group; it is a lamellar phyllosilicate obtained by layering of magnesium hydroxide silicate [13]. Due to its synthetic nature, disk-shaped particles with an average diameter of 25 nm and an average thickness of 1 nm [14] are present, which are overall more homogeneous, smaller in size and free of inclusions than natural clays.

B. *Mock ups*

The dimensional variations in case of application of aqueous, hydro-alcoholic or polar solutions, as well as the absorption speed of the dispersing phase, led to discard the hypothesis of making sponge samples of vegetable origin (cellulose based) or balsa wood [15]. In the first step, deteriorated coniferous wood was selected for an assessment of the distribution of materials within existing xylophagous insect tunnels; in the second step analyzes were carried out on seasoned but not aged poplar wood (*Poplar* spp.), diffuse-porous wood, characterized by small pores in no specific arrangement, numerous to uncountable. In both cases, mock ups were conditioned at a temperature of 22 ± 1 °C and relative humidity (RH) of 50 ± 1 %. Treatments application was by capillary rising in order to evaluate the penetration capacity of the material. The duration of the treatment was preliminary defined by applying a colored hydro alcoholic solution containing mordant with a marker function on dedicated samples.

C. *Scientific analyses*

The X-ray micro-tomography analyzes were performed in the first research step at the Physics Department of the University of Turin and the National Institute of Nuclear Physics (INFN), acquiring tomographic images of a limited portion of material, before and after treatments. The apparatus used, developed inside previous projects, is consisting of: a Hamamatsu Microfocus L8121-03 X-ray source, anode voltage up to 150 kV, maximum current 0.5 mA (maximum power of 75 W), focal spot down to 5 μm, 43° emission cone, 0.2 mm beryllium window and 2 mm aluminum filter; a Hamamatsu C10650-321 TDI (time delay integration) CCD detector, coupled with a fiber optic plate and a scintillator, consisting of 4608×128 square pixels of area 48 μm × 48 μm, 4096 gray levels (12 bit).
Image processing takes place with software developed internally on the MATLAB platform, with ParRec software developed by the University of Bologna and with Imgrec software developed by Lawrence Livermore National Laboratory. In the second step of the research, the measurement of the penetration of the treatment materials was carried out with micro-tomographic analyses on a single, not deteriorated sample, before and after the

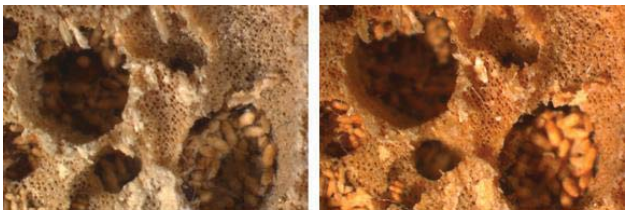

Fig. 1. Optical microscopy, magnification 16×. Before and after the treatment (Regalrez® 1126+Paraloid®B72)

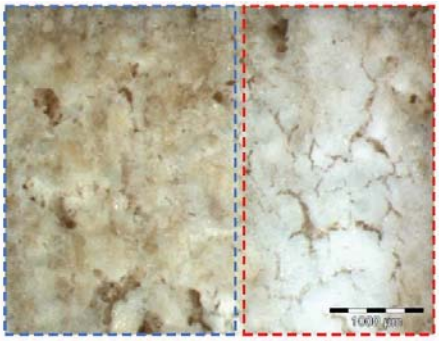

Fig. 2. Optical microscopy, after the treatment (Paraloid® B72+Laponite® RD). Different distribution on the saple of the nanoparticles. In blue: localized deposition; in red: compact layer of particles

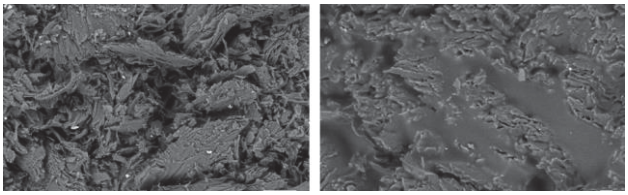

Fig. 3. Electron microscopy, BS images before (left, magnification 300x) and after (right, magnification 500x) the treatment

treatment, in collaboration with the Center of excellence for research, teaching and assistance in the field of dentistry - Dental School (University of Turin). A Micro-CT scan (commercial instrument: SkyScan 1172; Bruker, Billerica, MA, USA) was employed to recreate an accurate 3D model of the wood structure. High-resolution scan was performed using the following parameters: voltage = 59 kV; current = 167 µA; no filter; pixel size = 3.98 µm; averaging = 6; rotation step = 0.2°. NRecon software (Bruker, Billerica, MA, USA) was used to reconstruct the images and obtain DCM files (DICOM, Digital Imaging and Communications in Medicine) applying the following corrections: beam hardening = 0%, smoothing = 0, ring artifact correction = 15.

The obtained files were imported into a segmentation software (Mimics Medical ver. 24.0; Materialize, Ann Arbor, MI, USA) [16]. Thanks to the different radio density between the structures, it was possible to automatically create segments consisting of sets of pixels belonging to certain radiopaque structures within the wood mass representative of the radiopaque structures within the sample. The acquisitions were then aligned and compared with each other following the selection of the most representative slices.

Optical microscopy was performed perpendicularly to the fibers of the samples with an OLYMPUS BX51 optical (MO) mineropetrographic microscope, in visible and UV light, interfaced to a PC using an OLYMPUS DP71 digital camera and processed with proprietary analySIS Five software. Specific points have been selected for observation, at one of the corners of the section subjected to capillary rising treatment. Electron microscopy (images acquired in BSE) were carried out with a Zeiss EVO60 electron microscope in variable pressure mode (20 Pa) at the Scientific Laboratories of the CCR La Venaria Reale. The EDX investigations, aimed at mapping the distribution of Laponite® RD particles, were carried out at the National Institute of Metrologic Research (INRIM) electron microscopy and elemental microanalysis laboratory, using Hitachi TM4000 instrumentation on samples as they are, non-metallized, under variable pressure. The samples were investigated both on the surface and in longitudinal section with the aim of verifying the quantity of particles absorbed during the treatment. The longitudinal section was obtained by splitting the wooden matrix along the direction of the fibers.

III. RESULT AND DISCUSSION

Optical microscopy acquired on mock ups treated with the traditional application with organic materials (Fig. 1), allow observing a chromatic variation of the surfaces, whose natural color appears altered with a partial gloss increase. The products (more likely Paraloid® B72) seem to be localized without filling the micro and macro-porosities. The observation of the mock up treated with modified acrylic resin allowed to detect, in addition to the characteristic yellowing of the wooden material, already documented in the literature [11], the presence of a whitish layer, attributable to the particles of lamellar phyllosilicates, in proportion to the percentage dispersed in the resin. The stratification is formed above the surface, both in the form of a compact film and in single crystals, with a partial saturation of the micro porosities.

The phyllosilicate particles show a different behavior in relation to the observed section areas.

In the first case, the crystals are clearly distinguishable from each other and only partially placed within the porosity of the wood; on the contrary, where the saturation of the porosities is almost total, the formation of a compact layer is observed above the surface (Fig. 2). This behavior, observed on all the samples treated with modified Paraloid® B72, in all the tested concentrations of Laponite® RD, is believed mainly to be due to the method of application by capillary rising in correspondence with the cross sections.

Preliminary observation with Scanning Electron Microscopy (SEM) on the mock up test before and after

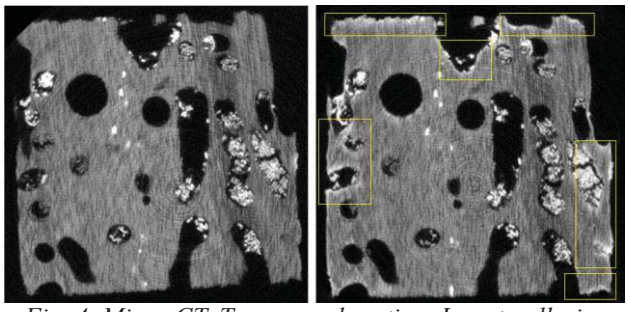

Fig. 4. Micro-CT. Transversal section. Insect galleries (macro porosities). Left: untreated wood; right: a thin layer of radio dense material is detectable after the treatment (Regalrez® 1126+®B72), as evident in the yellow areas.

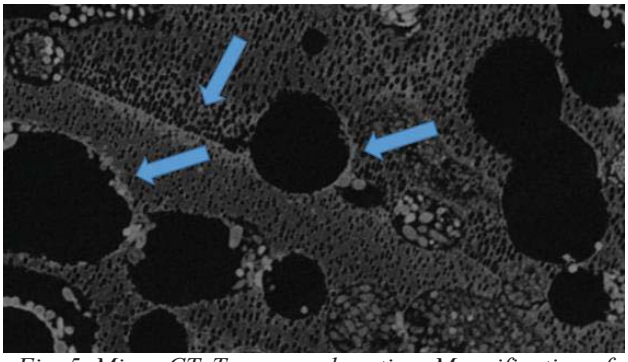

Fig. 5. Micro-CT. Transversal section. Magnification of an area of the treated wood (Regalrez® 1126+®B72)

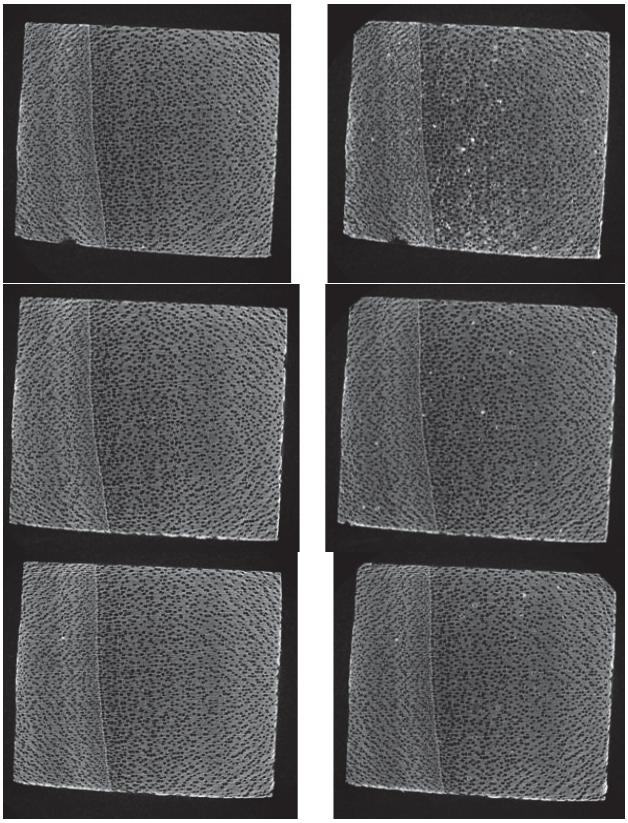

Fig. 6. Micro-CT. Transversal sections representative of three areas of distribution (around the contact area with the material to be absorbed, in the middle and in the last third of the sample)

the treatment, gave encouraging results due to the discrimination of consolidating products in BS images. (fig. 3)

The SEM-EDX analysis of the sample treated with modified materials highlighted the presence of characteristic elements of the nanostructured particles, in particular of silicon, sodium and magnesium, confirming their high surface concentration. On the contrary, the investigations carried out in the longitudinal section of the same sample did not reveal useful elements for identifying the presence of Laponite® RD particles penetrated inside the wood.

Concerning Micro Computed Tomography (micro CT), in the mock up treated with only organic materials, a difference in radiodensity is observed before and after the treatment: as expected, the impregnation face (and partly the side faces) is that with the greatest contrast, indicating the concentration of the products in those areas. Further differences can be seen in the visible macro porosities.

The filling of the cavities is not observed, although a thin clear deposit is detected (completely absent in the untreated mock up, Fig. 4). The images show a partial saturation of the wall around the cavities, measuring approximately 80 µm (Fig. 5).

Analyzing the different radio density in the longitudinal section of the treated mock up, traced back to the consolidant, it is possible to suppose its location: the upper part of the sample, from which the impregnation took place, is the one with the greatest concentration of product and more radiopaque.

As regards the samples treated with the modified organic material, the presence of elements with a greater atomic weight compared to the carbon one, constituting the wood, suggest its differential radiopaque response useful for mapping the distribution of the nanocomposite particles absorbed during the consolidation treatment. The protocol followed provided for the identification of the localized radiopaque particles relevant to the constituent materials of the wood in the mock up before the treatment and an evaluation, after localization of the same particles in the post-treatment, of the increase in radiopacity in the porosity

The presence of radiopaque particles absents in the wood as it is and referable to the particles of Laponite® RD is highlighted; they are more localized in the upper third of the specimen, impregnation section by capillarity. A progressive decrease is observed in the quantity of particles found along the direction of propagation of the consolidating product, distributed unevenly in the sample mass. (Fig. 6).

The images show a partial saturation of the porosities,

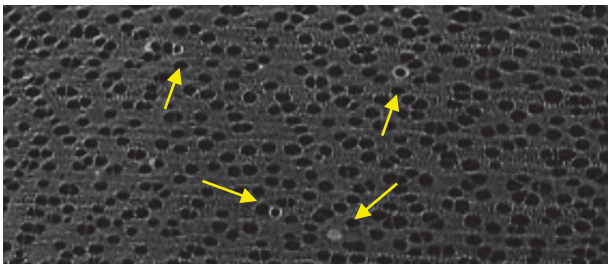

Fig. 7. Micro-CT. Transversal section: after the treatment (Paraloid® B72+Laponite® RD). Magnification of an area of interest, after the treatment. The yellow arrows suggest total and partial filling of macro porosities.

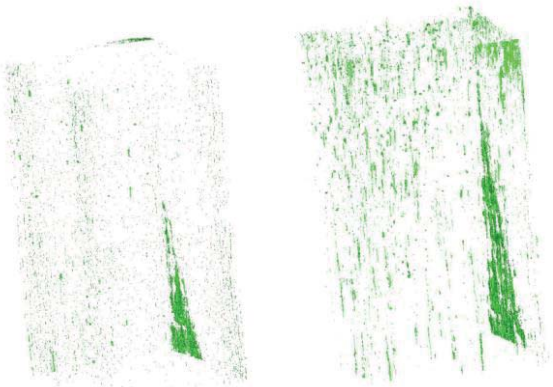

Fig. 8. Render before (left) and after (right) the treatment (Paraloid B72+Laponite RD). In green: material with higher radio density

obtained from the preferential deposition of the particles around the walls of the micro-cavities; in some cases, it was possible to observe the total filling of the pores, less widespread (Fig. 7).

We then proceeded with the digital creation of renderings representative of the distribution of radiopaque particles in the sample before and after the treatment (Fig. 8). The advantage of using a segmentation software that, having structures of different radio density, automatically offers the possibility of separating them from the total volume and picturing them immediately, allows to considerably streamline the analysis procedures, at least in a preliminary way [17].

In consideration of the same condition both for acquisition and for reconstruction, before and after the treatment, possible slight shift in the grayscale, especially for intermediate greys, should be considered negligible in terms of rendering reliability.

From the comparison of the two acquisitions it can be inferred that the substantial increase in the areas highlighted following the consolidation treatment is representative of the dispersion of the absorbed Laponite® RD particles, as already highlighted in the tomographic section.

As underlined before, the treatment product seem to be more concentrated in correspondence with the impregnation section. An evaluation of the reasons for an apparently random distribution must necessarily take into account variables such as the anatomy of the wood, the porosity, the direction of the fibers [18]. Is well known as wood shows a level of permeability related to its porous characteristics. Permeability reflects the wood's ability to be penetrated by gases and liquids and, obviously, is one of the most important physical properties of wood.

In particularly, hardwoods permeability in the longitudinal direction is mainly dictated by the vessels: vessel tissue ratio, length and diameter, and intervessel pit size were responsible for influencing the permeability in the longitudinal direction.

Regarding poplar wood this species exhibits an unusually high level of variability in permeability and treatability (EN 350) related to the portion of sapwood and heartwood [19]. In conclusion, the preferential distribution detected of the material could be correlated to the distribution of the porous in the wood samples and portion of sapwood and heartwood, further investigations seem necessary to ascertain this hypothesis.

IV. CONCLUSIONS

Optical and electron microscopy proved to be useful for the qualitative study of surfaces, without providing significant information on the penetration of the products; in addition to this, the impossibility of extensive analysis on a work of art must be considered, taking into account the invasiveness of the method. Acquisitions in high resolution CT scan have produced encouraging results in terms of the capability of discrimination between wood and consolidating products based on acrylic resin (with particular reference to materials modified with nanocomposites). The possible discrimination of the different materials would theoretically allow the monitoring of the penetration and distribution of the intervention material in a completely non-invasive way even on real case studies using local tomography. Being limited to the mapping of the elements with greater atomic weight, it determines only an indirect indication on the real dispersion of the acrylic consolidant, slightly distinguishable in tomographic investigation. The addition of a metal composition material inside the organic product has determined a considerable advantage in the monitoring of the penetration, in particular through high-resolution micro-CT tomographic acquisitions. The potential demonstrated through this technique can be considered as a first encouraging step for the definition of a diagnostic method to map the penetration of the treatments. As a next step of investigation, it could be interesting to hypothesize the integration of micro-CT data with the use of a thermal source in order to discriminate the impregnated areas (online, meanwhile treating) by analyzing the different heat response of different materials, which, theoretically, for synthetic resins should be possible.

V. ACKNOWLEDGMENTS

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