

X-ray tomography as an estimation technique for wood consolidation by frontal polymerization

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Summary. — Polymers are often utilized in the restoration of damaged materials: their application to the restoration of wooden objects of artistic interest is of particular importance. However, their penetration is often limited by both their viscosity (even if in solution) and by their macromolecular size which can be larger than the matrix pores. Furthermore, the estimation of their penetration has been so far based only on weight measurements, thus the mapping of the restoring material inside the sample is not known. In this work, we have applied the frontal polymerization to the consolidation of wood samples and the Computer-Assisted Tomographic (CAT) technique in order to check the gradient of penetration of the monomer inside the sample.

PACS 61.41.+e – Polymers, elastomers, and plastics.

PACS 81.70.Tx – Computed tomography.

PACS 83.80.Mc – Other natural materials (*e.g.* wood and other vegetable materials).

1. – Introduction

The use of polymers in restoration is today finding an ever-increasing number of applications [1,2]. Dried and waterlogged stone and wood samples from cultural-heritage sites are some of the materials treated in this way [3-7].

The conservation and the restoration of such artworks is an ethical and mandatory challenge, which nowadays requires the cooperation of art historians, conservators, restorers, scientists and technicians from many fields.

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Organic consolidating products display an important advantage compared to those that are inorganic: if correctly chosen, they may also have a protective activity, thanks to their water-repellent properties.

However, the main problem of polymeric compounds is related to their macromolecular nature. For a polymeric compound it is difficult to penetrate the porous material due to pore size; in addition, the viscosity of a polymer solution is often too large in order to allow its deep penetration even if pore dimensions were not an obstacle. As a consequence, the penetration depth is generally limited to the superficial layers. This is acceptable for a polymer with only a protective action but not for a material that must also be consolidating; in this case, deep penetration is required.

These considerations are the starting points for the *in situ* polymerization. This technique, rather than using a pre-formed polymer, consists of introducing the monomer into the substrate and *in situ* polymerizing it in a subsequent step. Obviously, monomers (being small molecules) can reach also the smallest pores and at the end of polymerization the consolidating polymer is distributed more evenly and deeply.

On this respect, two different *in situ* polymerization approaches have been studied: the conventional thermal method [8] and frontal polymerization (FP). The first is carried out on samples which, after monomer sorption, are placed in an oven set at 60 °C for 24 h.

FP is a method that permits the conversion of monomer into polymer thanks to the exothermicity of the self-same polymerization reaction. If dissipated heat is not excessive, the residual quantity of energy can be sufficient to induce the polymerization of the monomer layer adjacent to the hot zone. The result is the formation of a hot polymerization front which propagates throughout the sample and is self-sustaining [9] without requiring any further supply of energy. In addition, FP process is complete only in a few minutes [10-16].

For both *in situ* polymerization techniques, the knowledge of the monomer distribution inside the sample is of obvious importance. This information is particularly important in FP runs. Indeed, as noted above, for FP to be self-sustaining the amount of released heat must be relatively large, while that which is dissipated (in the present case, mainly because of thermal exchange with the porous matrix) must not be excessive. Such requirements can be fulfilled only if a sufficient amount of monomer is present inside the sample. Consequently, in order to plan possible consolidating operations which take advantage of the FP technique, it is mandatory to obtain spatial (volumetric) information about the distribution of the filling material.

Until now, to the best of our knowledge, measurements of monomer penetration inside wood samples were mainly based on weight increments or on surface measurements [17]. Thus, only a rough estimation of the quantity of monomer material could be obtained, without any information about its localization.

Computer-Assisted Tomography (CAT) is a technique allowing the reconstruction of the internal structure of a sample without any destructive action on the sample itself [18]. This technique is based on the absorption of X-ray radiation. The X-ray photons going through the sample can be absorbed according to three principal effects: photoelectric, coherent scattering and incoherent scattering. Regardless of the type of interaction, a fraction of the initial photons will not pass through the sample and hence will not be detected. The tomographic measurement is based on the ratio between the number of photons passing through the sample and the number of photons emitted by the X-ray source. A CAT measurement is composed of a set of radiographies taken all around the sample. This set of radiographs can be used to reconstruct the transversal section of the

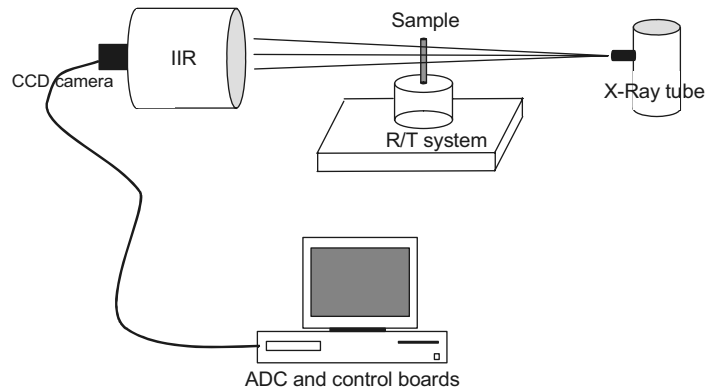


Fig. 1. – Schematization of a tomographic measurement.

sample, according to the well-known radon theorem. The contrast and the information contained in the reconstructed image mainly depend on the energy E of the X-ray photons used, which must be chosen according to the composition of the material. The best E value, from the contrast maximization point of view, is obtained when the product $\mu \cdot x$ falls in the range 1–6, where μ is the linear attenuation coefficient of the material at energy E , and x is the linear path crossed by the radiation. In the case of wood, it is composed of low- Z elements (so-called *light matrix*). The pores (air) are formed always by light elements. The monomer (or polymer) materials can be considered light. In this case, the matrix can be considered homogeneous enough, thus making the choice of energy easy.

On the basis of what written above, aims of the present work are: i) to check the feasibility of FP in the consolidation of wood and ii) to check the use of CAT as an effective non-invasive tool suitable for deeply visualizing monomer content and distribution and, subsequently, the content and the distribution of polymer inside the treated sample.

2. – Experimental part

2.1. CAT measurements. – The tomographic system was composed of an X-ray tube (0–80 keV, 5 mA), a CCD camera connected to an image intensifier, and a rotation stage. The maximum sample size allowed is about 7 cm and the spatial resolution is about 200 μm . A schematization of the experimental set-up for tomographic measurements is shown in fig. 1. If the X-ray source is distant enough from the sample and the sample is as close as possible to the detector, the X-ray beam can be considered as parallel and the sample needs only to be rotated from 0 to 180 degrees at uniform angular steps. At each angle, a line or a matrix of values (counts) is detected, according to the type of detector. The counts detected represent the number of photons passing across the sample without interaction. By generalizing the de Beer law to finite-size and non-homogenous sample, the number I of photons detected at each position can be expressed by

$$(1) \quad I(E) = I_0(E) e^{-\int_a \mu(E,Z) dl},$$

where: I_0 is the X-ray intensity irradiating the object; I is the X-ray intensity after crossing the object; μ is the linear attenuation coefficient depending on the energy of



Fig. 2. – Photograph of one of the wood samples reported in this paper. All the samples have the same size. The dimensions are $(5 \times 5 \times 2) \text{ cm}^3$.

incident radiation E and atomic number Z ; dl is the elemental path crossed by the incident radiation.

The detector (an image intensifier) may be considered as a surface detector, in the sense that each spatial position can be considered as a single smaller detector (a pixel). In this way, the parallel beam issuing from the X-ray source can be thought of as being formed by a set of elementary small X-ray beams, each of them going from the X-ray source to a pixel on the detector. Each line of pixels forms the so-called projection.

The composition of wood and that of the monomer are based on the same light elements, namely C, H, O. The size of the samples to be analyzed ranges from 2 to 7 cm. The optimization of the energy radiation led to an optimal voltage of 25 kV.

The use of a polychromatic beam and the different sensitivity and non-linearity of each pixel of the detector matrix to the same radiation intensity will produce some artifacts on the reconstructed image, where the most evident of them has the form of circular rings concentric to the rotation centre. In order to reduce such artifacts, a correction procedure has been implemented. The first step of this procedure performs a normalization of the intensities between the projections. This step is required because a temporal instability of the X-ray beam can be found. Then the procedure corrects for the pixel variable response. The beam hardening effect will be only partially cancelled by this procedure. The effect of the beam hardening on the images is evidenced by semicircular patterns visible in the resulting section. However, these patterns do not decrease the quality of the image to a significant extent and in any case the effect of monomer penetration is clearly visible.

2.2. Monomer sorption and frontal polymerization. – Monomer sorption has been carried out as follows: by operating at room temperature, wood (beech) samples ($5 \text{ cm} \times 5 \text{ cm} \times 2 \text{ cm}$) were allowed to absorb by capillarity a mixture composed of 20 ml of monomer (1,6-hexanediol diacrylate, HDDA), 1.0 g of azobisisobutyronitrile and, when specified, 1.0 g of 1-iodopentane (IP) (see fig. 2). The sample was immersed in a solution 0.5 cm high. After sorption was completed, the wood sample was tamponed with absorbing paper, and its $2 \text{ cm} \times 5 \text{ cm}$ base was put on a heated plate ($T = 200^\circ \text{C}$) until

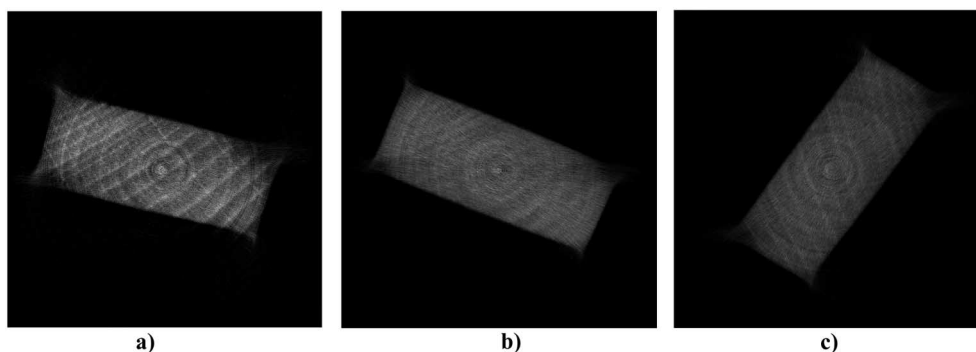


Fig. 3. – Reconstruction of a section of a beech wood sample: a) untreated sample. The natural structures of the wood (darker structures) can be observed; b) sample after monomer sorption; c) sample after frontal polymerization.

an ascending polymerization front was noted (after a few seconds). The sample was then removed from the plate and propagation proceeded without further supply of energy.

Conversion was determined as follows: the sample was cut in five slices (1 cm high each) parallelly to the heated 2 cm × 5 cm base. Every slice was then grounded and extracted in soxhlet for two days in boiling CH₂Cl₂ and desiccated in vacuum oven at 60 °C for 24 h. The wood-polymer powders were then analyzed by CAT thus finding that all IP was removed. However, a weight measurement confirmed that the grounded mater contained all the crosslinked poly(HDDA).

3. – Results and discussion

In fig. 3a, a tomographic reconstruction of a transversal slice of a beech wood sample is shown. The typical “anatomical” structure of the wood is visible. The poorly visible circular rings are artifacts due to reconstruction and to the polychromaticity. The wood rings show a different absorption coefficient with respect to the other parts of the sample, as evidenced by the white curved lines (white indicates high values; black, low values in this gray level scale). In fig. 3b, a slice reconstruction of the same sample is reported after monomer absorption. The wood rings are now less evident. This means that the differences in the absorption coefficient shown in fig. 3a have been compensated by the “introduction” of the monomer inside the sample. The wood sample was then placed onto a hot plate (~ 200 °C) until an ascending polymerization front started, that being clearly visible running along the vertical walls of the sample. Front velocity was 1.0 ± 0.1 cm/min. Several orientations of the wood samples with respect to the monomer bath were tested without any significative difference in the results.

In order to better visualize the monomer presence inside the wood and its local distribution, tests of partial sorption of monomer-IP solution into beech samples are reported (fig. 4). This additive contains a heavy atom (iodine), which is easy visible by X-ray CAT. Moreover, IP does not impart any undesirable color to the sample.

In fig. 4a, a reconstruction of this sample before being completely filled with the HDDA-IP mixture is depicted, showing the part submitted to the capillary absorption (on the right side of the sample) together with the untreated part. The former appears to be denser and, consequently, brighter than the rest.

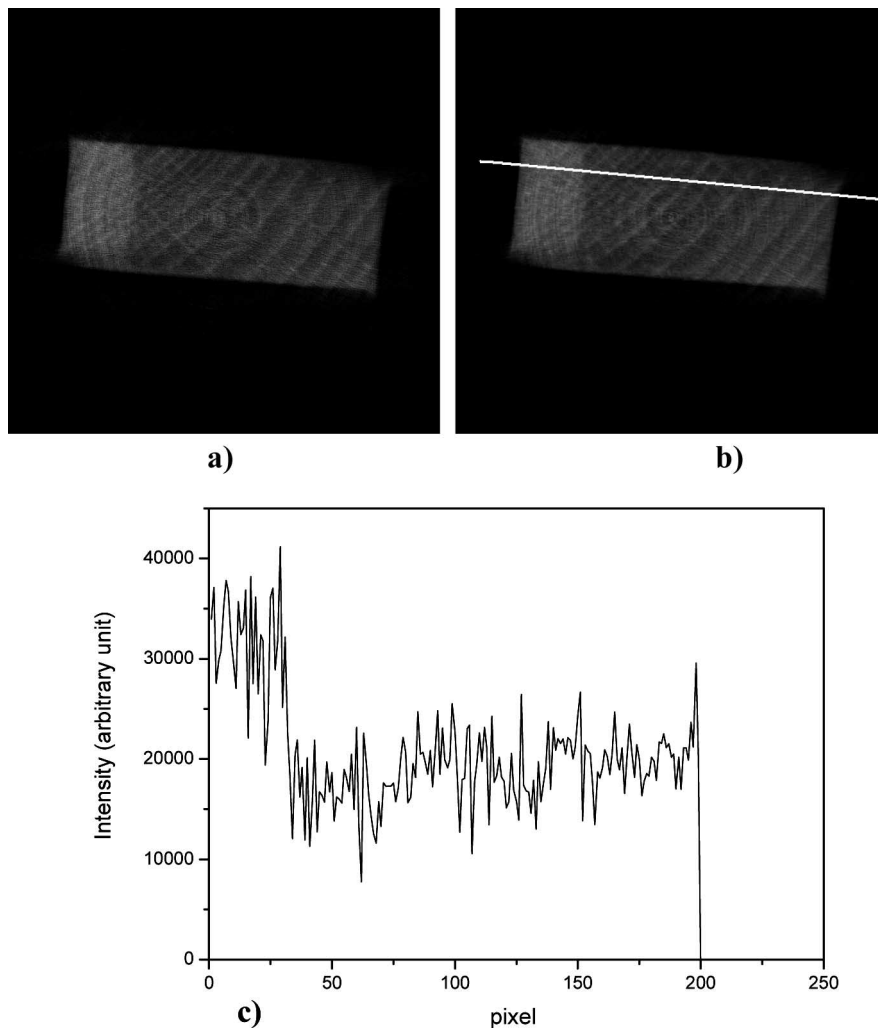


Fig. 4. – Reconstruction of a beech wood sample partially treated with monomer solution. a) Slice reconstruction; b) same sample, where the white line indicates the position of the section reported in c).

In order to understand the propagation of the monomer-IP mixture inside the wood it is useful to analyze sorption profiles. The white line represents a slice extraction along the gradient of penetration of the monomer. An intensity profile from fig. 4a is depicted in fig. 4b. A step-like behavior is visible, confirming the partial sorption of the monomer-IP solution. The oscillations are due to the natural rings of the wood having different X-ray absorption rates and to a large amount of noise.

By considering the thickness of each reconstructed slice and the time spent by the sample in the monomer bath, the velocity of sorption has been calculated as about 0.3 cm/min. This information will be of great help in the possible practical applications of the FP technique to the consolidation of beech samples.

4. – Conclusions

In this paper, a tomographic study of the sorption of a monomer in wood samples and its subsequent frontal polymerization have been described for the first time. CAT technique allows one to track the monomer and, after its reaction, the corresponding polymer inside beech materials with a spatial resolution of about 200 μm . This represents a big step forward in the study of the interaction of monomer and polymer compounds with woods which, so far, have been mainly based on weight measurements only. A study of the gradient of penetration has also been measured and discussed. In this way the time of exposition of the wood samples to the monomer bath can be determined.

Furthermore, it is noteworthy that FP has been confirmed to be a useful alternative method of polymer synthesis that is used in a growing number of practical applications. In particular, these results will pave the way of the careful use of FP as a wood consolidation method able to act also in depth, a result not achievable by any of the other common techniques. Its applications will be of great advantage in many fields such as those relating to cultural-heritage materials.

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