Visualization of monomer and polymer inside porous stones by using X-ray tomography

Antonio Brunetti [a,*], Elisabetta Princi [b], Silvia Vicini [b], Silvia Pincin [b], Simone Bidali [c], Alberto Mariani [c]

[a] *Dipartimento di Matematica e Fisica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy*
[b] *Dipartimento di Chimica e Chimica Industriale, Università di Genova and Local INSTM Research Unit, Via Dodecaneso 31, 16146 Genova, Italy*
[c] *Dipartimento di Chimica, Università di Sassari and Local INSTM Research Unit, Via Vienna 2, 07100 Sassari, Italy*

Abstract

Estimate of sorption of liquid materials inside porous stones is an important parameter in industrial material testing and cultural heritage conservation. In the latter case, a suitable polymer can be used for both consolidation and conservation, it being applied either in the final form or as its parent monomer, which is subsequently allowed to polymerize in situ by the classical method or by frontal polymerization. However, the sorption of such materials through the stone is often difficult because of their viscosity and/or stone porosity. For this reason, the amount of monomer (or polymer) is a parameter of great interest in order to determine the extent of protection reachable by the treatment. In this paper a new methodology based on X-ray tomography is presented. The methodology makes use of a contrast agent added to the monomer that does not interact with its propagation inside the stone and allows to increase the absorption coefficient and so to observe the monomer inside the sample, which is finally frontally polymerized.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Computed tomography is a widely used tool in non-destructive tests (NDT) [1–5]. It is based on a set of X-ray radiographs taken at fixed angular steps all around the sample to cover 180° or 360° depending on the kind of X-ray beam used. Each radiograph is a measure of the absorption of the X-ray photons due to the sample. Starting from this set of radiographs it is possible to reconstruct transversal section of the sample according to the well-known Radon theorem. Each reconstruction is a spatial map of the sample in terms of the absorption coefficient (μ) of the material composing the sample. The absorption coefficient depends on the energy, thus the quality of the image depends on the X-ray energy used and on material composition. From the point of view of the information contents, two important parameters

* Corresponding author. Tel.: +39-079-229483; fax: +39-079-229482.
E-mail address: brunetti@uniss.it (A. Brunetti).

of the reconstructed image can be evidenced: the spatial resolution of the system and the minimum observable variation of the absorption coefficient. Thus, a structure inside the sample will be visible only if its size is greater than the maximum spatial resolution and if its absorption, with respect to the neighboring zones, is greater than the minimum observable absorption difference. Only the first of these two parameters, the spatial resolution, is easily changeable. In fact, it is possible to obtain a magnification of the spatial resolution by using a fan beam scanning or making the beam thinner in parallel scan. In the case of poor resolution, in the sense of attenuation, it is not so simple to find a solution. Two ways can be followed: changing the kind of tomography, i.e. using fluorescence or scattering tomographies, or adding a contrast agent to the sample. The first option requires a strong modification of the setup and sometimes it is not possible. Moreover, the scan time increases by several orders of magnitude. The second option, adding a contrast agent, is normally used in medical measurements. It is based on the addition of a material which modifies the total absorption coefficient in those regions where it is present.

The subject of the present paper is a new application of this technique to a tomographic NDT test, namely aimed to the estimation of the extent of monomer sorption inside porous stones. The reason for such a work raises from the fact that polymeric materials are commonly used in stone consolidation and protection. However, polymers are large macromolecules having size of hundreds of Å. This feature and the high viscosity that they impart to their solutions often result in a poor penetration, especially in the case of stones characterized by small diameter pores. In order to overcome this drawback, we have recently proposed an alternative method which consists of soaking stones with the parent monomer and its subsequent in situ polymerization. The smaller dimensions and lower viscosity of monomeric compounds allow for an enhanced sorption inside the sample. We have suggested two alternative ways of polymerization inside stones. The first is the classical one in which the stone is warmed for a prolonged period in an oven [6]. The second is the frontal polymerization (FP) technique which is that used in the present work [7]. FP exploits the heat production due to the exothermicity of the reaction itself and its dispersion by thermal conduction. If the amount of dissipated heat is not too large, a sufficient amount of energy able to induce the polymerization of the monomer close to the hot zone is provided. The result is the formation of a hot polymerization front capable of self-sustaining and propagating through the reactor [8–12]. It is evident that for FP to occur through a stone sample, monomer must have filled its pores and they must be in contact each other to permit the hot front to propagate, thus obtaining polymer. For this reason, and in order to predict the possible efficiency of the consolidation treatment, it is mandatory to know in which extent monomer is able to fill stone pores and if the final FP allows for an optimal polymer dispersion inside the material.

Until now, monomer sorption has been studied only by NMR imaging [13–15]. However, it should be interesting to use X-ray tomography in order to extend the information about the monomer propagation inside porous materials.

From the point of view of X-ray tomography, observing the presence of the monomer requires a change of the absorption coefficient. This situation is verified because the monomer going inside the sample takes the place of the air. Unfortunately, common monomers are generally composed only by light elements such as H, C and N. Moreover, the energy of the beam must be high enough to pass the stone part of the sample. Thus, the variation induced on the absorption coefficient is too low to be observed. The solution to this problem might be the addition of a contrast agent to the monomer. The agent should be able to percolate inside the sample together with the monomer and should have a poor interaction with it. The chemical aspects of the present work, related to the FP inside stones, will be published elsewhere. Here, we are interested only to the estimation of the extent of monomer sorption and to that of final polymer content. The method used will be discussed in the next section.

2. Methods

A schematic of the experimental setup for tomographic measurement is shown in Fig. 1. The sample is rotated from 0 to 180° at uniform angular steps. At each angular position an image (radiograph) of the sample is acquired. The intensity recorded at each point of the image is proportional to the number and energy of photons passed across the sample without interaction. The number of photon after the sample is expressed by

$$I(E) = I_0(E) e^{-\int_d \mu(E,x)\,dx}, \tag{1}$$

where I is the detected intensity, I_0 is the beam intensity outsourcing the X-ray tube, $\mu(E,x)$ is the linear absorption coefficient, dx is the attenuation path length followed by the X-ray beam.

Reconstruction of the absorption map requires inverting the Radon Transform. There are several ways to do this operation; we use the widely applied backprojection algorithm. The reconstructed image in our case should report the differences in the μ values between the stone and the monomer filled regions. However, the acquisition system can introduce artifacts on the reconstructed image due to the spatial non-homogeneity of the X-ray beam, to its polychromaticy (multi-energies) and finally to the non-uniform response of the CCD detector used together with an image intensifier as X-ray detector. Thus, a set of correction procedures must be applied. The first and the third problems can be solved by using a flat field illu-

mination. This is an exposition of the CCD detector to the X-ray beam without the sample. In this way, spatial non-uniformity and variation of sensitivity of the CCD camera can be detected. A set of flat field images must be acquired and summed into one final image. In this way the signal to noise ratio is improved. After the sum of the images, the mean value of the final image is determined and every pixel of this image is divided by the mean value in order to normalize the image. After this step the correction image is ready and any reconstructed image will be corrected according to the following procedure:

$$L_{corr}(x,y) = \frac{L(x,y)}{L_{Flat}(x,y)}, \tag{2}$$

where L_{corr} is the intensity of the pixel (x,y) of the corrected image, L is the intensity of the pixel (x,y) of the uncorrected image, L_{Flat} is the correction values matrix.

The second problem, the polychromaticy of the beam, could be completely solved by using a monochromatic (monoenergetic) beam. Unfortunately, this approach cannot be used because making a beam monochromatic strongly decreases the number of photons. This results in circular artifacts on the reconstructed image.

An approximate correction for this problem is to apply a post-acquisition correction following the approach described by Mark Rivers [16]. This approach can solve also the non-uniform sensitivity of the pixels. The procedure is the following:
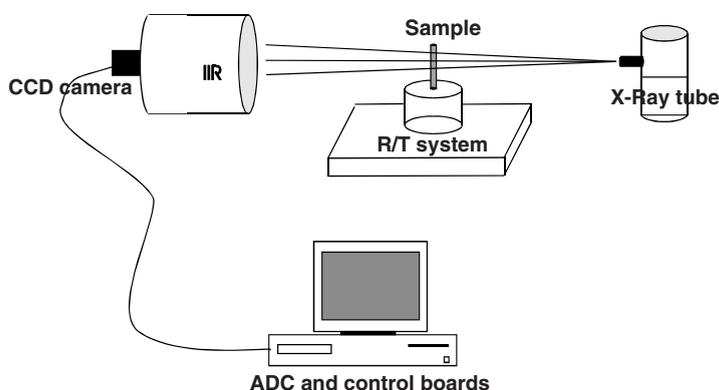

Fig. 1. Schematization of a tomographic measurement.

(a) The set of projections, called sinogram, are summed pixel by pixel. This sum will form a linear array of the same length of a projection. After this operation, the patterns due to the non-uniform response of the pixels will remain inside the array. This because these patterns are always at the same position in each projection and so they are summed. Therefore their effect will be enhanced. On the contrary the noise supposed to have zero-mean will be cancelled.

(b) A low-pass filter is applied to the array obtained from the step (a). The low-pass filtering will cancel the patterns leaving a smoothed sum of all the projections. The low-pass filter can be as simple as the sum of three pixel:

$$A(i) = \sum_{i=2}^{N-1} [A(i-1) + A(i) + A(i+1)]/3, \qquad (3)$$

where $A(i)$ indicates the ith pixel of the array.

(c) The low-pass filtered array (step (b)) is subtracted from the array obtained after step (a). In this way only the patterns will remain in the array. Let us call it *correction array*.

As a result of these operations, in the correction array the noise will be canceled and the fixed pattern exalted. Thus, the subtracted array can be subtracted from each projection. We have introduced some changes in this approach. Firstly, we normalize every projections in the sinogram for changes of intensity along the measurement. This can be done by calculation of the total number of photons in each projection that must be constant and then using this number as correction factor. Secondly, the steps (a)–(c) are performed iteratively, several times. The last step is important, in our opinion, because the values in the corrections array would not represent the true correction va-
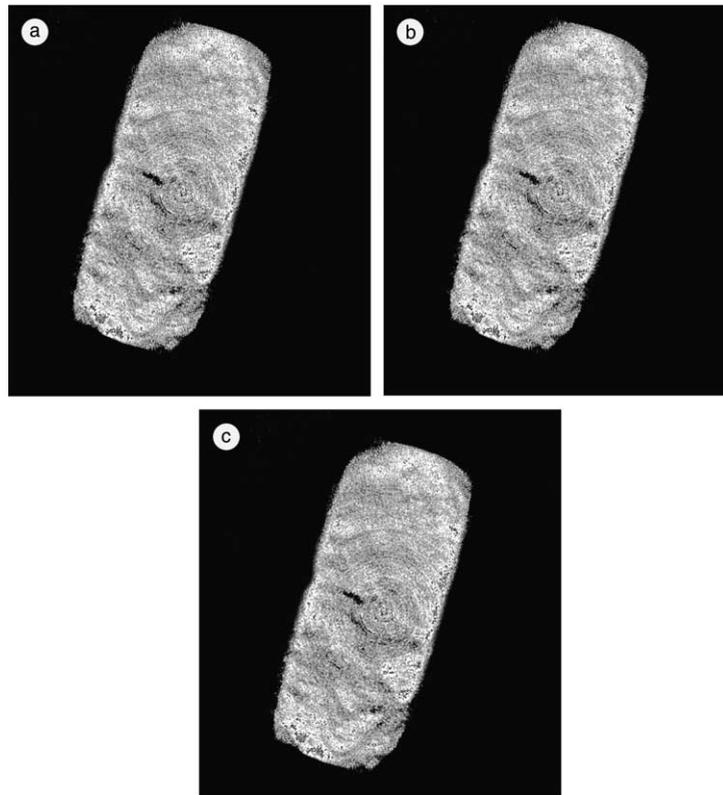

Fig. 2. Contrast effect of filling material on the reconstruction: (a) reconstruction of the sample without any filling material; (b) sample filled by water; (c) sample filled by monomer.

lue to be subtracted from the projection, because the response of the pixel can depend on the number of photons. In our experience, the modification introduced will improve the quality of correction.

The stone for the polymerizations has been chosen on the basis of the following requirements:

- high porosity, with the aim to reproduce a material degraded by chemical and physical agents;
- easily supplied in the standardized forms.

For these reasons, we have used a calcareous sedimentary stone of biological origin, easily available in Liguria, Italy, called "Pietra di Finale". This is found in four different formations, differing in the percentage of the components, impurities and fragments; they also have different colors (from white to rosé) and different physical characteristics. The dimensions of the used specimens are $5 \times 5 \times 2$ cm.

3. Results

The tomographic system used in this work is composed by an image intensifier by Thomson, a CCD camera by COHU, an acquisition board DT 2851 by Data Translation, a rotation–translation system by Contek and an X-ray tube (80 kV max, 5 mA max) by Gilardoni S.p.A. The system is controlled by custom software written in Modula-2 language and acquires images (radiographs) of 512×512 pixels. It is possible to add several images in order to improve the signal to noise (S/N) ratio. A set of options are available, such as selection of the part of the sample that must be reconstructed, correction procedure to be applied, false colors representation and so on.

In the reconstructions reported in this paper the samples were irradiated by a parallel X-ray beam at 50 kV peak with an aluminum filter 3 mm thick. The current was 5 mA.

A sum of 64 images for each radiograph (projection) was used. This procedure allows an improvement of the S/N ratio of eight times. Each

measure is composed by a set of 180 projections taken at different angles from 0 to 180°, at fixed step of 1°.

Monomer (1,6-hexanediol diacrylate), iodine and methanol were purchased from Aldrich, 2,2′-azobis(isobutyronitrile) (AIBN) was from Fluka. All chemicals were used as received.
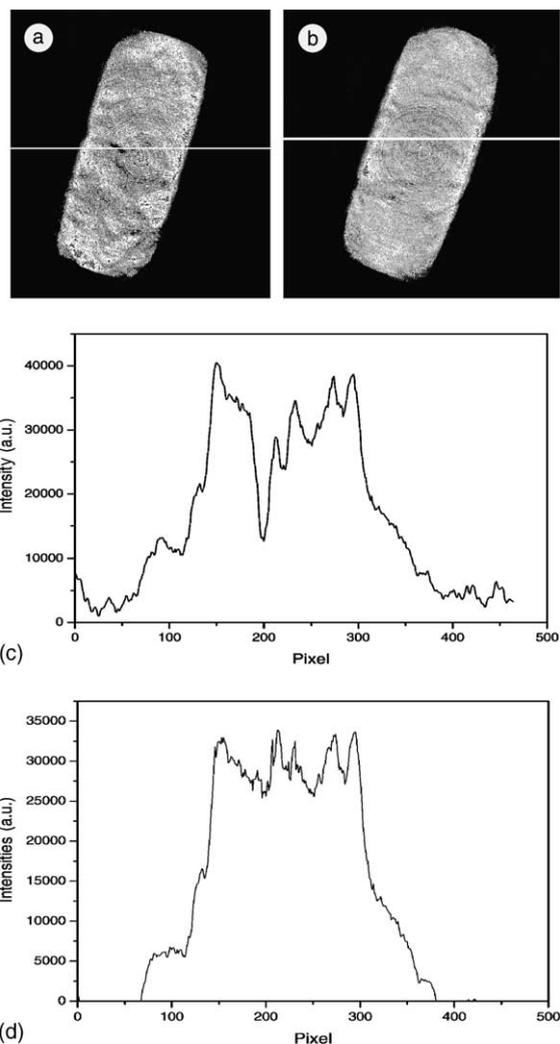

Fig. 3. Effect of addition of a iodine solution to the monomer: (a) reconstruction of the sample without any filling material. The white line represents the position of the profile reported in (c); (b) sample filled by iodine solution and monomer. The white line represents the position of the profile reported in (d); (c) intensity profile of reconstruction in (a); (d) intensity profile of the reconstruction in (b).
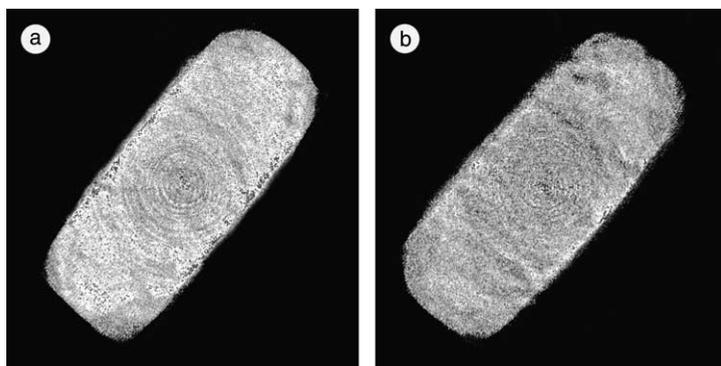
Fig. 4. Effect of frontal polymerization: (a) sample filled by monomer, i.e. before FP and (b) after the FP.

Regarding sample preparation, 0.5 g of I_2 (when present) were dissolved in 20 ml of a solution constituted by monomer and AIBN (5 wt.%). The resulting homogeneous mixture was allowed to penetrate into the stone by capillarity. This last procedure was carried out for 4 h, at 0 °C, in the absence of light. FP was started by placing one of the smallest stone faces onto a hot plate ($T \approx 200$ °C). Immediately after the formation of a hot polymerization front started, the sample was removed from the hot plate in order to avoid the occurrence of spontaneous polymerization simultaneously to FP.

In Fig. 2 a tomographic reconstruction of a porous stone sample is reported. In Fig. 2(a), the reconstruction is that of the sample before any treatment. In Fig. 2(b), the sample is placed in a water bath, so any cavity is filled by water. The sample in which water has been replaced by the monomer/tracer solution is reported in Fig. 2(c). In all the reconstructions of Fig. 2 there are no differences in the internal structure. This means that the monomer behavior is similar to that of water and air at the energy used for the measurement.

In Fig. 3, another set of reconstruction are reported. Namely, the sample without monomer is shown in Fig. 3(a), while the sample soaked with the monomer-iodine mixture can be seen in Fig. 3(b). In this case, the filling effect of the monomer is evident and the sample is completely loaded. This holds for the other transversal regions of the sample not reported here.

Fig. 4 shows the sample after the occurrence of FP. As a consequence of polymerization some of the pores that were previously completely filled (Fig. 4(a), before FP) exhibit some vacancies (Fig. 4(b), after FP). This fact can be attributable to the shrinkage undergone by the filling material, the polymer being slightly denser than the monomer. However, the extent of such a phenomenon is evident only in the larger cavities which show partially unfilled zones.

4. Conclusions

In this paper a new procedure for checking the sorption extent of a monomer and the filling degree of the corresponding polymer (obtained by in situ FP) inside stones is reported. It is based on a tomographic measurement using a contrast agent (iodine dissolved into the monomer) which does not affect the capability of the monomer to be absorbed into the stone and to be frontally polymerized. In this way the distribution of monomer or polymer inside the sample is visualized.

The instrumentation built for this measure represents the first application to this kind of measure and it should be more versatile and cheaper than the NMR apparatus usually used.

The good results obtained in this work will be helpful for the next application of such a technique on manufactured objects, namely those having an historical–artistic interest. Moreover, in order to adapt the contrast capability to other materials we

will test also other contrast agents with binding capability to the monomer.

Eventually, such a work presents a new practical application of the FP technique. Further details on this latter aspect will be reported soon.

References

[1] L.F. de Oliveira, R.T. Lopes, E.F.O. de Jesus, D. Braz, Nucl. Instr. and Meth. A 505 (2003) 573.

[2] R. Cesareo et al., in: Proc. SPIE, Vol. 3772, Denver, Colorado, USA, 22–23 July 1999, p. 292.

[3] D. Braz, L.M.G. da Motta, R.T. Lopez, Appl. Radiat. Isotopes 50 (1999) 661.

[4] W.A. Kalender, K. Engelke, S. Scaller, Proc. SPIE 3149 (1997) 688.

[5] G. Schneider, G. Denbeaux, E. Anderson, A. Pearson, W. Bates, S. Vogt, C. Knochel, M.A. Meyer, E. Zschech, J. Phys. IV 104 (2003) 607.

[6] S. Vicini, S. Margotti, E. Princi, G. Moggi, E. Pedemonte, Macromol. Chem. Phys. 203 (2002) 1413.

[7] A. Mariani, S. Fiori, S. Pedemonte, E. Pincin, S. Princi, S. Vicini, ACS Polym. Prepr. 43 (2002) 814.

[8] J.A. Pojman, Am. Chem. Soc. 113 (1991) 6284.

[9] A.M. Khan, J.A. Pojman, Trends Polym. Sci. 4 (1996) 253.

[10] A. Mariani, S. Fiori, Y. Chekanov, J.A. Pojman, Macromolecules 34 (2001) 6539.

[11] S. Fiori, G. Malucelli, A. Mariani, L. Ricco, E. Casazza, e-Polymers 57 (2002) 1.

[12] S. Fiori, A. Mariani, L. Ricco, S. Russo, Macromolecules 36 (2003) 2674.

[13] S. Capuani, M. Alesiani, F.M. Alessandri, B. Maraviglia, Magn. Reson. Imaging 19 (2001) 319.

[14] L. Appolonia, G.C. Borgia, V. Bortolotti, R.J.S. Brown, P. Fantazzini, G. Rezzaro, Magn. Reson. Imaging 19 (2001) 509.

[15] G.C. Borgia, V. Bortolotti, M. Camaiti, F. Cerri, P. Fantazzini, F. Piacenti, Magn. Reson. Imaging 19 (2001) 513.

[16] M. Rivers, private communication and http://cars9.uchicago.edu/software/tomography.html.