

X-ray and FTIR μ -CTs for morphological and chemical characterization of eco-sustainable insulating foams

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Abstract

Here it is reported a multidisciplinary approach based on tomography and infrared techniques applied to the characterization of tannin porous rigid foams, potentially usable as new insulating materials in green building technology. With conventional x-ray tomography it was possible to preliminarily evaluate the homogeneity of the samples at low resolution, while then, thanks to the synchrotron source, it was possible to obtain more detailed information at a micro-scale level. At the same time chemical characterization was done through Fourier Transform infrared (FTIR) imaging. Conventionally, FTIR imaging is limited to a planar projection, not considering the 3D structure of the material. To avoid this limitation, a FTIR 3D-tomography setup was built and the foams characterized by a chemical point of view. The idea is to directly correlate these data with the 3D-structural information obtained with the x-ray computed tomography exploiting the synchrotron radiation as source, allowing a complete characterization of the material morphology and chemistry at the microscale.

Keywords: tannin foam, mesoscale, FTIR, computed tomography, tomoIR.

1 Introduction

Tannin-based and lignin-based foams are porous rigid materials made of inexpensive organic compounds, like tannin [1–5], or lignin [6]. These bio-foams, thanks to their relevant physical properties, as the low thermal conductivity and the high fire resistance, might be used as insulating material for eco-sustainable buildings (green building technology). Tannin and lignin polyphenols, the main components of these porous materials, are present in the so called “black liquor”, which is a side product of the paper and wood industry. The possibility to convert this unexploited matrix into a bio-compatible foam is a key point to reduce the production of insulating building materials which are highly demanding from a disposable point of view.

The polymeric nature of these rigid foams brings some problems as, for example, the homogeneity of the panels at the micro and nano-scale level. Although the chemical composition, the dimensions of the pores and their connectivity are averaged at a macro scale, this is not true as soon as the investigation is brought at a more detailed level. The correlation between structure and degree of pore connection, as well as the chemical nature of the skeleton and surfaces of the walls, play a fundamental role for steering the most appropriate applications[1–6]. In order to fill the gap between the molecular characterization of these bio-foams and their macro-behaviour, a deeper investigation of these materials at the mesoscale has to be addressed.

In collaboration with scientists of Salzburg University of Applied Science and Paris Lodron University of Salzburg, researchers from SISSI (Synchrotron Infrared Source for Spectroscopy and Imaging) and SYRMEP (Synchrotron Radiation x-ray micro-computed tomography, SR μ -CT) beamlines at the Elettra Synchrotron facility in Trieste are studying the porous material to better characterize it. With the μ -CT technique it is possible to understand the structure and the morphology of the pores and of the cell walls as well as their connectivity. FTIR spectromicroscopy, on the other hand, allows acquiring spatially resolved vibrational spectra with micrometric resolution, thus providing information on sample chemical composition. When using Focal Plan Array (FPA) detectors to collect the data, this technique is called FTIR imaging. Each pixel of the detector collects the whole IR spectrum in the Mid-IR spectral range ($4000\text{-}900\text{ cm}^{-1}$), and by the integration of the signal of choice, corresponding to some specific chemical moieties, it is possible to obtain heat maps representing its distribution in the sample. IR tomography is a new analytical approach, first presented by Martin et al. in 2013 [7]. It exploits the chemical imaging capabilities of IR bidimensional detectors and the vast knowledge in terms of setup and reconstruction algorithms of CT for achieving 3D chemical images of the materials. Albeit a one to one porting is not possible yet, due to some technical issues that will be discussed in the paper, the first published results demonstrate its feasibility and potentiality. By obtaining 3D chemical distribution of the inspected samples at micrometric lateral resolution can make possible studies that are not possible with conventional 2D IR imaging. Actually, in IR transmission measurements, light passes completely through the sample and the information obtained comes from the whole volume; this may be an issue, for example, when the sample is not homogeneous in the axial direction, as in the case of tannin foams. With IR tomography it is possible to reconstruct the whole volume of the sample and identify



chemical singularities otherwise hidden. This is mainly due to the hyperspectral nature of the acquired data, which contain the whole FTIR spectrum for each pixel measured. Thus, once reconstructed, it is possible to obtain a spectrum for each voxel and render a chemical volume for each IR spectral feature of interest. By reviewing the current state of the art, some main issues become evident. The first regards the developed setups. They were designed focusing on compactness and ease of use, but this may not guarantee 1) all the degrees of freedom needed for a controlled μ -CT measure, 2) the required stability and precision, 3) a complete automation to increase the speed and the repeatability of the measurements [8–10]. Another critical issue that we identified is in the pre-processing of the 2D IR projections after the acquisition. There may be spectral artifacts, due to scattering for example, that have to be corrected before the reconstruction. In addition, sometimes there is the need of an embedding medium (oil or paraffin) to anchor the sample to the support, and the spectral features are to be removed from the spectral map, especially if they 1) colocalize with the sample in space or 2) overlap over some of the IR band of relevance of the inspected sample (see Figure 3). The third and in our opinion the most critical point is the projection pre-processing to correct potential inconsistency of the dataset (for example sample out of focus or motion artifacts, zero signal). In the literature, several approximations have been taken in order to reconstruct the data, which may heavily affect the reliability and quality of the final result.

In this work we used the bio-foam as a model case to present our approach to tackle these three issues. Before the FTIR acquisitions, centimeter size samples were also acquired using both conventional X-ray and SR μ -CT, respectively, for 1) a preliminary screening of the foam at low resolution and 2) evaluate their homogeneity at micron scale. For the IR experiment, we first optimized the measurement setup, both in hardware and software, with respect to what already published, in order to obtain a more stable and precise system. With this setup we collect the first data on small piece of the tannin bio-foam embedded in paraffin oil and supported in a nylon loop. Optimized data pre-processing of the 2D IR images allowed us to separate the signals of the sample from those of the supporting loop, used as tomographic reconstruction tuning.

2 Material and Methods

2.1 Tannin foam synthesis

To prepare the tannin furanic foams at first 39 %_{wt} of the tannin extract is mixed with 14 %_{wt} of the distilled water, 25 %_{wt} of the furfuryl alcohol and 4 %_{wt} of the diethyl ether as blowing agent. Afterwards 17 %_{wt} of the diluted sulfuric acid (32%) is added and everything is thoroughly mixed [5,11]. The homogeneous blend is poured into a wooden mold. The mold is then covered and placed in a laboratory hot press at 90 °C for 5 minutes. During this time the blowing agent evaporates and simultaneously the formation of the tannin-furanic polymer occurs by self-polymerization of the tannin and the furfuryl alcohol, afterwards the curing and hardening of the material takes place [12]. This results in a porous, sponge like material called foam.

2.2 Tomography

A preliminary screening of the foams was done by means of X-ray μ -CT with conventional micro-focus sources at Tomolab [13]. The main source parameters for the scan were: 50 kVp high voltage, 160 μ A current and 8 μ m focal spot size. The emitted beam was also filtered for low energy components with 0.25 mm Aluminum. Considering the cone beam magnification, images were acquired with equivalent pixel size of 9 μ m and an acquisition time of 2 s/projections (1800 projections over 360°). Local area dimension sample 40x40x30 mm³ (final VOI field of view 18 x 11.7 mm²).

The higher flux of the SR source enables to acquire images at higher resolution and with shorter acquisition time, while the high spatial coherence permits to exploit phase-contrast effects that increase both the contrast resolution and the visibility of small details in reconstructed images when compared to conventional laboratory sources. Exploiting one of the Elettra bending magnets, a polychromatic X-ray beam (8-40 keV) is delivered to the experimental station. The detecting system consists in a water-cooled camera (with sCMOS chip) coupled with a high numerical aperture optics and a LSO:Tb screen. For the SR- μ CT experiments, the beam was filtered by means of 1 mm of Silicon (resulting average energy around 21 keV) to reduce the beam hardening effect. The pixel size was set to 2 μ m (final VOI field of view 4 x 4 mm²) and the sample to detector distance was 8 cm, sufficient to exploit phase-contrast effects. We acquired a set of 1800 projections over 180 degrees (parallel beam) with an exposure time of 200 ms/projection. The projections were pre-processed using a single distance phase-retrieval algorithm, based on the Transport of Intensity equation (TIE-HOM [14]) to exploit the phase effects.

2.3 FTIR 2D-imaging

FTIR 2D-images of the samples were acquired at the Chemical and Life Science branch of SISSI beamline, the infrared spectroscopy and imaging beamline of Elettra - Sincrotrone Trieste [15]. The sample, a thin tannin rigid foam fragment, was imaged with conventional global source in transmission mode using a 64x64 elements Focal Plane Array (FPA) detector equipped to the Hyperion 3000 IR/VIS microscope coupled with a Vertex70v interferometer (Bruker GmbH). The IR light was focused onto the sample and collected with two equivalent 15X Cassegrain objectives, with numerical aperture, NA=0.4. In this configuration, every detector pixel corresponds to ~2.6 microns. The images were acquired averaging 64 scans at 8 cm⁻¹ spectral resolution in the 4000-900 cm⁻¹ spectral range, in order to limit the acquisition time to 2 minutes per image. For the same reason, we recorded only the sample interferogram and did the Fourier Transform (FT) after the whole dataset acquisition, as well as the rationing with the air background in order to obtain the absorbance spectra. Spectral acquisition and FT (zero filling factor: 2;

apodization function: Blackman-Harris 3-Term; phase correction mode: Mertz; non linearity correction: 1) was done by using the Bruker proprietary software OPUS 7.5.

2.4 FTIR-Tomography

For the tomography setup, Mdrive (M), Corvus (C) and Standa (S) motors were used, thus enabling 5 degrees of freedom: rotation (S), translation (M), pitch (C), roll (C) and yaw (C) (see Figure 1a). A nylon loop (50 μm loop hole and 20 μm nylon wire diameter) was used as holder to anchor a small piece of the tannin foam exploiting the viscosity of a mineral oil (NVH Oil). The loop was then mounted on a goniometric head (See Figure 1b). The goniometric head has 4 more degrees of freedom (pitch, roll, and two translations). This allowed performing the fine alignment of the sample with respect to the objectives. Motor control and data acquisition procedures were assisted by an in-house procedure written in LabVIEW 2017 using both USB (for S) and TCP/IP (for M and C) connection protocols. Sample rotation was synchronized with the single-projection acquisition in the OPUS 7.5 software. Once a single FTIR-FPA image was acquired, using the same parameters used for the 2D-images, the sample was rotated by 5°, until acquiring 72 projections.

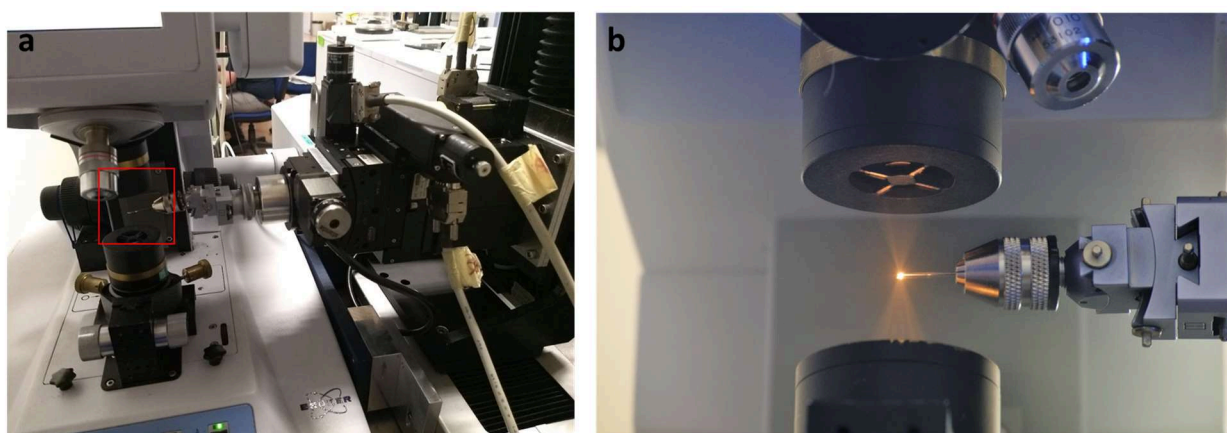


Figure 1 a) FTIR tomography setup; b) close-up of the sample area, highlighting the goniometric head used for the fine alignment and the focusing/collection of the light by the two 15x Vis/IR Cassegrain objectives.

2.5 2D-image pre-processing

Specific infrared absorption bands from each pixel image were selected in the following spectral ranges of interest: 3340-3560 cm^{-1} stretching mode of hydroxyl moieties, $\nu(\text{OH})$ – band indicative of the analyzed tannin foam; 3040-3120 cm^{-1} , amide B band associate to peptide N-H stretching – indicative of the nylon support loop; 1690-1730 cm^{-1} stretching mode of carbonyl group, $\nu(\text{C}=\text{O})$ – band indicative of the analyzed tannin foam; 1580-1635 cm^{-1} from the aromatic groups of the tannin foams and 1190-1260 cm^{-1} , bending mode of C-C linkage, $\delta(\text{C}-\text{C})$ – band to retrieve oil distribution. All the truncated spectra were then baseline-corrected with the linear baseline, and finally integrated with the basic trapezoidal method. Examples of pre-processed images are shown in Figure 4a-c for the aromatics, amide B and $\delta(\text{C}-\text{C})$ bands, respectively. The same data analysis workflow was then applied for each single FTIR-FPA projection image. All the procedures were performed with an in-house code written in Python 3.5 with the matplotlib, numpy, and scipy packages.

3 Results and Discussion

3.1 Tannin rigid foam

Tannin-based rigid foams are the product of the acid catalyzed self-polymerization between two main building blocks: the polyphenol of the mimosa tannin extract and the furfuryl alcohol. The blowing agent (diethyl ether), the catalyzer (sulphuric acid) and the solvent (water) complete the mixture necessary to obtain the final foam. Due to the several reacting groups of the polyphenolic component (Figure 2a), the polymerization might lead to different chemical products. The complete understanding and a precise characterization of the foam by a chemical point of view, as well as the chemical formula, are still under investigation and only some hypothetical structures might be drawn as reported in Figure 2b [5].

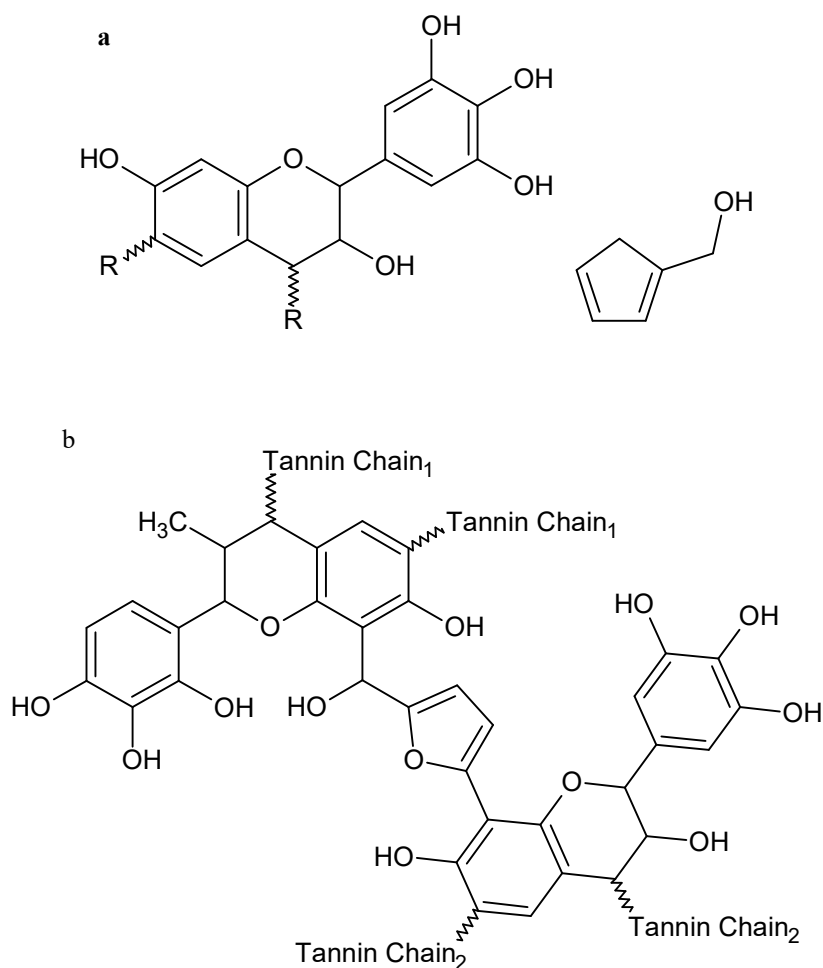


Figure 2: a) mimosa tannin polyphenol on the left and the furfuryl alcohol on the right; b) one of the possible polymerization products [5].

3.1 X-ray μ -CT

X-ray μ -CT results are presented in Figure 3. The final 3D reconstructions at low resolution allow a basic/rough characterization of the foams in terms of porosity and cell size distribution (see Figure 3a) and has been used to select specific sub regions of interest for the following high-resolution analysis at the SYRMEP beamline [15]. The obtained contrast enhancement allows a better detectability of the pore's walls (Figure 3b). The morphology of the foam can be accurately defined paving the possibility to perform size distribution analysis of cells and to evaluate their connectivity. Looking at the cell nodes (see Figure 3c) it can be noticed that they are characterized by an inner microstructure and, maybe, by a density or local composition variation. This point can be addressed by a chemical inspection of the same region using FTIR 3D-tomography.

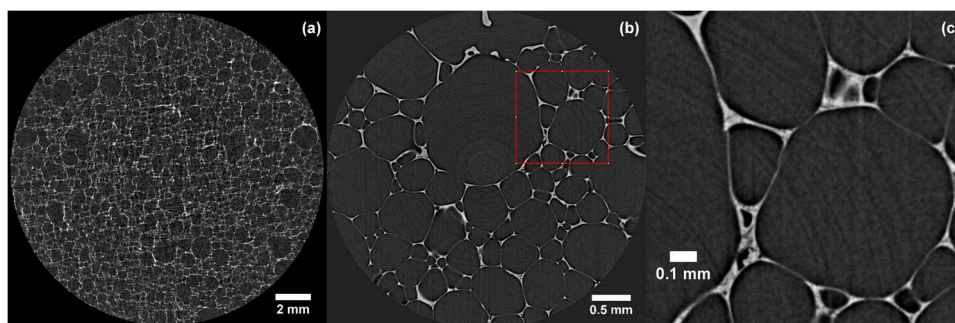


Figure 3: a) Cone-Beam XCT slice of the foam; b) SR μ -CT slice and c) related detail. Scale bars are also reported.

3.2 FTIR FPA 2D imaging

Figure 4 shows the results of a 2D FTIR measurement on a small fragment of a cell of the foam. By the examination of the optical picture in Figure 4a we can guess that we are analyzing a part corresponding to a corner of the cell (Figure 3c), this can be seen by the curvature of the sample and a thinning towards the lower end.

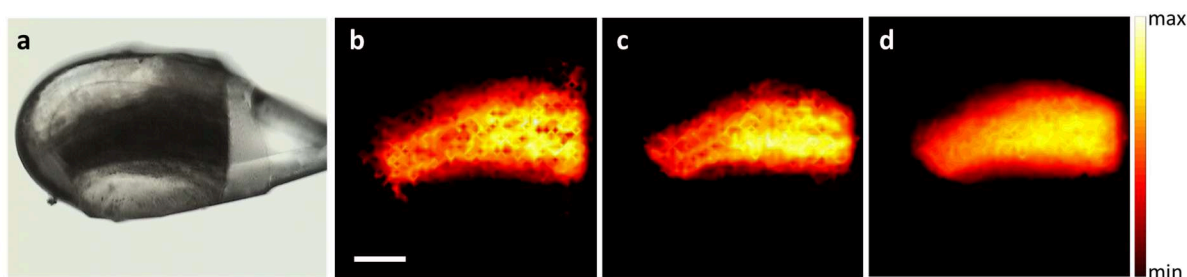


Figure 4: a) Optical image of the measured foam, and corresponding IR-images: b) 2D false color image of the spatial distribution of the -OH group inside the foam; c) 2D chemical image obtained integrating the band of the carbonyl moieties of the foam; d) 2D image of the aromatic chemical moieties in the foam. The scale bar is 20 microns.

The FTIR images show the 2D chemical distribution of three of the predominant chemical moieties present within the foam, the -OH from phenyl groups, the aromatic moieties from the tannins and the carbonyls due to any oxidative product formed during the polymerization reaction. The tannin signal is pretty homogenous, whereas the -OH and the C=O ones are more heterogeneous and seem to have a similar spatial distribution. Although informative, these maps cannot give us any information about the tridimensional distribution of these chemicals within the sample, thus we proceeded with the acquisition of the different projections of the same sample.

For imaging purposes, the 2D hyperspectral images went through a pre-processing pipeline to separate the spectral contributions of the foam (Figure 5a), the loop (Figure 5b), and the oil (Figure 5c). This process was necessary in order to remove any signal from the loop or the oil in the maps of the foam. As a matter of fact, there is a strong overlapping of the peaks of the three materials, as can be seen in Figure 5d, and the separation step was mandatory in order to have a reliable dataset to use as a base for the chemical reconstruction.

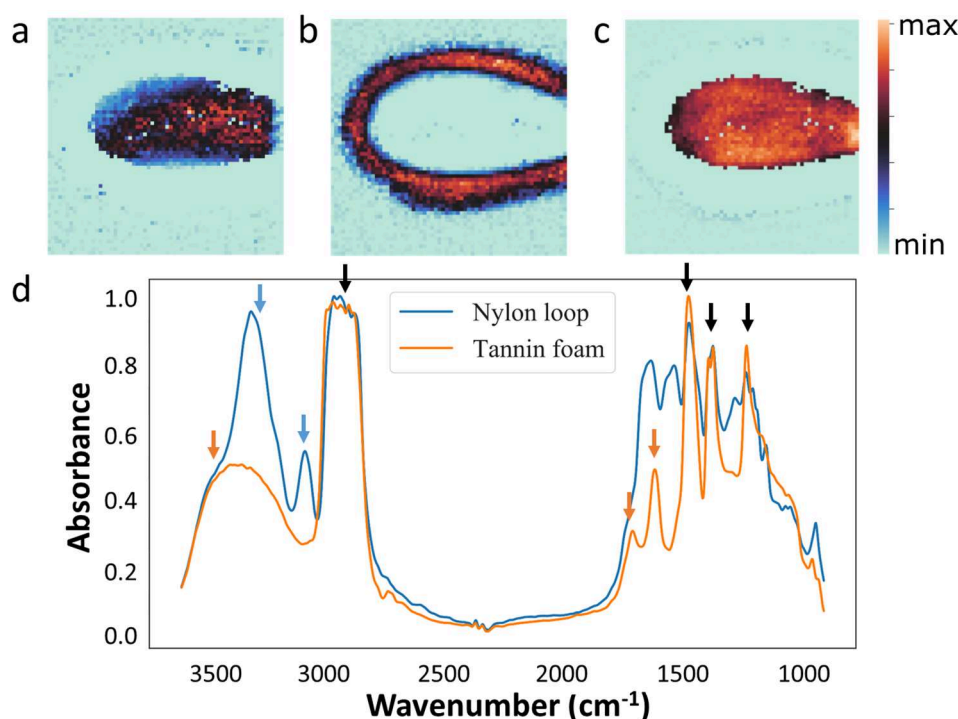


Figure 5. Total integrated intensity image for a) ν (OH) (the tannin foam), b) amide B (the nylon loop) and c) δ (C-C) (the oil) bands. d) Average min-max normalized FTIR spectra of the tannin foam and nylon loop. Blue arrows point to distinctive peaks of nylon loop, black ones to peaks mainly due to the oil (spectrum not shown), and orange arrows to the peaks used to identify the foam.

3.3 FTIR 3D Tomography

The 2D images (Figure 3a, 3b and 3c) give a good indication of the chemical distributions of the foam constituents, but do not take into account the three dimensional structure of the foams [16]. Therefore, FTIR 3D tomography was implemented in order to obtain the chemical compositions in terms of volume instead of the planar 2D images.

We verified that the treatment of the raw infrared data heavily affects the reconstruction process, leading to different outputs depending on the performed analysis. The procedure that we optimized in order to allow a correct 3D reconstruction first encompasses to pre-process the data as for the images in Figures 5a-c. Then, individual stacks of projections for the distribution of the functional groups of interest were normalized by their respective extinction coefficient, partially corrected for motion artifact and finally reconstructed using a standard Filtered Backprojection algorithm implemented in a built-in house software [15]. Volume rendering (imaged with Avizo® 9.3) of the extracted functional groups is shown in Figure 6a, while a zoom of the C=O group, with both oil and loop superimposed, is shown in Figure 6b.

The algorithm used for the reconstructions is the same applied for parallel-beam μ -CT. To make this assumption valid for the infrared technique, it is required to keep the sample always confined in a focused plane (thickness around 10 μ m for a 15X objective). This is not guaranteed during the rotation of our foam because of the dimensions of the sample (see Figures 6a and 6b). Moreover, the transition between in-focus and out of focus introduces a geometrical distortion in the sample geometry itself. These limitations need to be overcome, and we are working on this topic. Following the approach of Martin and co-workers [7], we can consider the waist of the beam in the focusing region as likely approximated by a parallel beam. The goodness of these assumptions can be observed in the reconstruction of the loop (used to find the best reconstruction parameters) that is surrounding the sample and so more sensitive to out of focus and object deformation artifacts.

By comparing Figures 4b-d and 6a, it is therefore possible to assert that by FTIR 3D tomography it can be better appreciated the non-homogenous distribution of foam moieties, at the level of the corner of the foam cell.

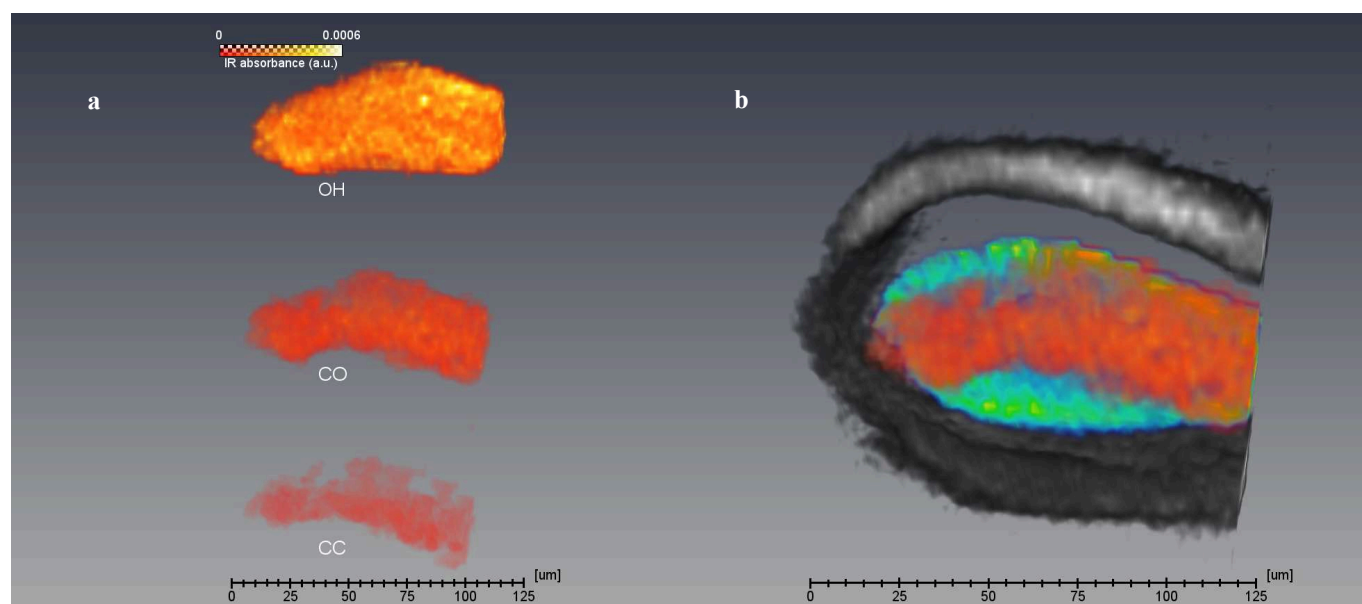


Figure 6: a) Volume rendering of the -OH, C=O and C=C functional groups obtained after the integration of the same bands used for the 2D imaging with a color bar (in arbitrary units) which intensity is proportional to the concentration; b) Volume rendering of the C=O band of the tannin foam (in red) superimposed with the oil distribution (in green-blue) and of the nylon loop (in greyscale). The rotation scan axis is oriented along the horizontal axis of the images.

4 Conclusions

In this paper we present our optimization of FTIR tomography: we addressed some of the critical points we deemed important in order to make this technique more reliable and faster. Our setup is more stable and precise of those presented so far, and the automation part we implemented allows for a fast data acquisition. The IR data pretreatment has been optimized in order to segregate sample, supporting loop and anchoring oil chemical signals, and we demonstrated that is possible to reconstruct 3D models for each chemical moiety of interest, and overlap them to show colocalization of the different components. By this analysis, we got interesting, despite preliminary, new insights on the 3D chemical distribution of the tannin foams that can help us to understand their actual/local chemical composition.

The final aim of our collaborative research activity is the complete integration of X-ray μ -CT and FTIR 3D tomography. By combining these two techniques, it will be possible to render the volume of the inspected sample with μ -CT and to associate it

to the IR absorption voxel by voxel. This will allow retrieving the local concentration of the selected chemical species by exploiting Beer-Lambert law. Nevertheless, at the actual stage of the FTIR tomography setup development, there is a mismatch in the dimension ranges of the two techniques. X-ray μ -CT can measure samples that are in the order of millimeters with micrometric resolution, while FTIR 2D individual images are limited to an area of about 170x170 microns square. In order to solve this limitation, we are planning to implement the IR microscope with objectives at lower magnification, thus increasing the field of view of a single image to several hundreds of microns. Moreover, the implemented setup, having the motorized translation, makes possible to collect mosaic images for each projection, thus increasing even more the field of view. Furthermore, new mathematical models need to be implemented in order to obtain more reliable FTIR CT reconstructions, able to model all the real physical processes during the scan. We believe that these efforts will be really worthy because they can lead a robust technique to obtain 3D chemical mapping at the microscale level integrated with the morphology from X-ray μ -CT.

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