Methodology for the characterization of the microstructure of nanocomposite polymeric foams using X-ray microtomography

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Aims

The past decade has witnessed a rapid increase in the number of laboratory X-ray microtomographs in material science department or industries. High resolution, small length scales, non-destructiveness, and shorter reconstruction times due to increasing computational power make X-ray microtomography (XRμT) a potentially fundamental tool for the understanding of many physical phenomena in materials, at the microscale. This is especially true for porous materials, for which generally the high contrast in the reconstructions eases the segmentation of the solid and porous phases, thus allowing rapid access to measurement such as porosity, and more interestingly, pore structure (size, distribution, connectivity).

Nevertheless, although quantification can be rapidly computed, there should remain the necessary scientific caution in the computation of such measures. The aim of this work is not to present the most robust algorithm for this application (explicit pore separation? using the medial axis or the skeleton, with a Chamfer or Euclidean distance map), but rather to evaluate fundamental aspects of the use of typical methods for quantification, namely representative volume and a measure of the error.

The examples given in this paper consist in nanocomposite polymeric foams with carbon nanotube reinforcements. These foams are becoming widely used in electromagnetic shielding applications, because contrary to steel plates they tend to absorb the energy rather than reflect it back on the electronic components[1]. Good shielding depends on a homogeneous cellular structure of the foam. Therefore, along with Electron Microscopy, XRμT is used to observe these micropores.

However, this material is not ideal for the use of XRμT, for several reasons. Firstly, polymers are poor X-ray absorbants, consisting mainly of carbon atoms (low atomic number), and the fact that they are foamed does not help to produce contrast in the radiograms. Secondly, the porosity is relatively small compared to the acquisition resolution: the pores are only a few pixels across, thus a one-pixel error can lead to significant measurement deviation. Thirdly, the wall of the cells can be extremely thin, and although Scanning Electron Microscopy (SEM) shows this is a closed-cell structure, as in figure 1, XRμT will show large connecting gaps between the pores, it being unable to identify the thin walls.
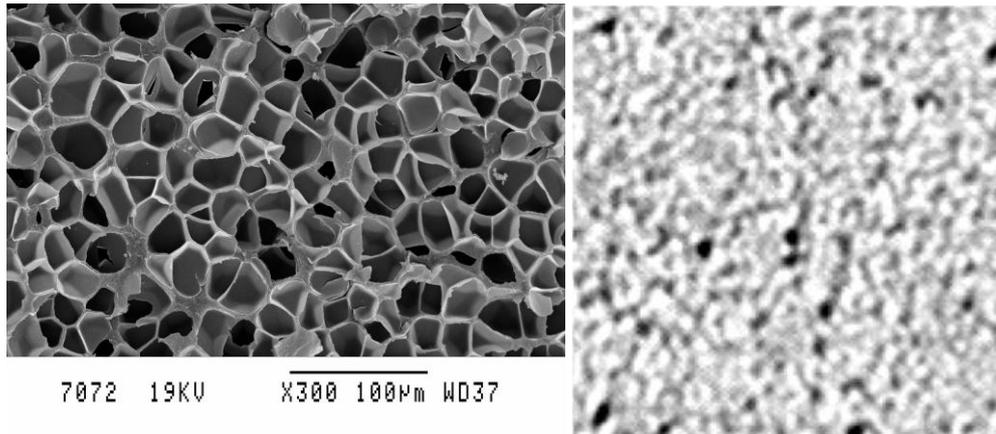
Figure 1: Left - A SEM image of a polymethyl methacrylate, or PMMA, nanocomposite foam studied. At this scale, the carbon nanotubes are not visible. Right - a cross-section of the same material from a tomographic scan at a resolution of 6.74 µm/pixel.

For these reasons, precise pore measurement is somewhat delicate. Because cell walls are not always identified, a statistical approach was preferred over direct pore separation.

Method

The algorithm uses the autocorrelation function, which determines correlation between intensities of all pixel pairs at a given distance, and in a given direction. This type of measurement is initially used in 3D imaging as an efficient tool to measure anisotropy[2]. By mapping the correlation values in all directions on a sphere, and distorting the shape of that sphere to account for the variation, we obtain what is called a rose of directions, an efficient visual representation of the anisotropy[3]. A simple example is presented in figure 2.
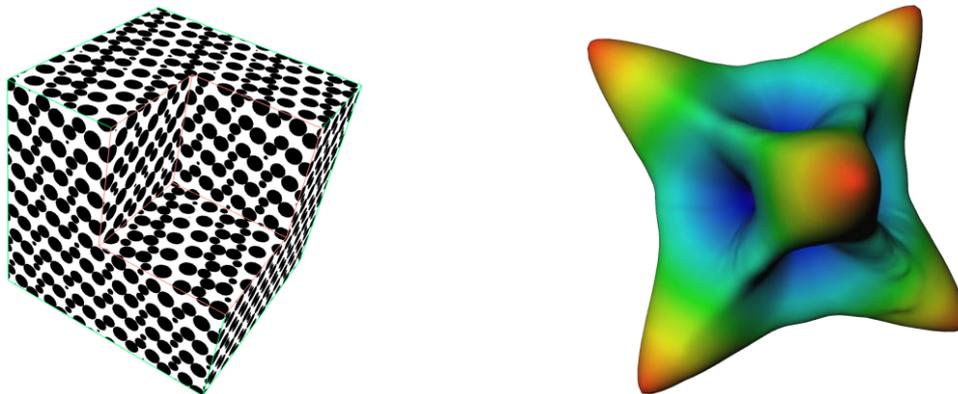

Figure 2: Left - a cubic sphere packing randomly oriented and digitised into a 500^3 image. Right – the resulting rose of directions, clearly showing that the maxima in the direction of the packing.

Furthermore, by integrating these values over all directions, we get an averaged measure of the diameter of the represented *features*. This is done by computing the maximum values of correlation at a given distance, and examining the deviation of this maximum from the average value. This deviation, plotted as a function of distance in figure 3 for the case of the cubic sphere packing, produces a curve which has peaks at distance where a more repeating pattern is found. On this graph, the first peak, at 34 pixels, corresponds exactly to the diameter of the digitised spheres.
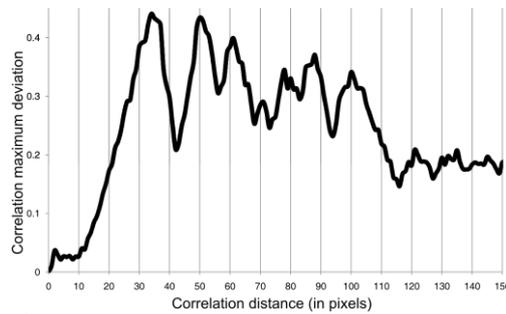
Figure 3: Deviation of the maximum correlation from the mean, as a function of distance.

In the case of foamed polymers, where wall thickness can be considered negligible, this measure could be a good indicator of the average pore diameters. This process was chosen because it shows low sensitivity to noise[2], the image needs not to be segmented, and since it is a global measurement the cells need not be explicitly separated.

Before directly using these extracted measures as truths about this material, two main aspects were studied: determination of a representative volume, and the measure of error. The latter was divided in two different tests, that are the influence of the tomographic scan and reconstruction, and the influence of the resolution (pixel size).

Results

The first aspect that was examined was the Representative Elementary Volume. In a homogeneous material, there is no need to calculate the autocorrelation over the entire image, a small subvolume containing sufficient features is preferable. In inhomogeneous materials, which is nearly always the case in reality, increasing the size of the volume of interrogation means smoothing out those inhomogeneities, making them undetected. In our case, this aspect is important for the subsequent physical properties and should not be overlooked. Therefore a compromise in the subvolume size has to be made between sufficient amount of information, and small enough size so as to detect heterogeneities within the sample. Several regions were examined, with increasing and concentric subvolume sizes. It was determined by examining both the peaks in the maximum deviation curves and the general shapes of the roses that for this structure, with cells roughly around 15 to 20 µm in diameter, a volume of over 0.003 mm^3 is representative. The maximum deviation curve shown in figure 3 shows the resulting curve shape, showing a peak at around 20 µm, which is encouraging in light of previous analyses on the SEM images.
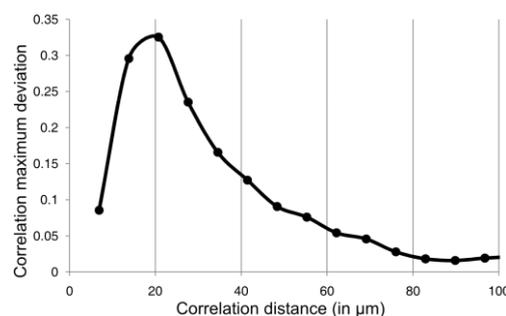

Figure 3. Deviation of the maximum correlation as a function of distance for the polymeric foam shown in figure 1.

The second aspect to verify is if the measure is intrinsic to the material, i.e. if only some features of the material is being measured and nothing else. An efficient way to verify this is to scan the same sample twice, but placing it differently on the sample holder in the microtomograph. After registering the volumes together (finding the translation and rotation that correctly superimposes the two volumes), as in figure 4, small subvolumes were extracted from each image, an example of which is shown in figure 5, at the same position.
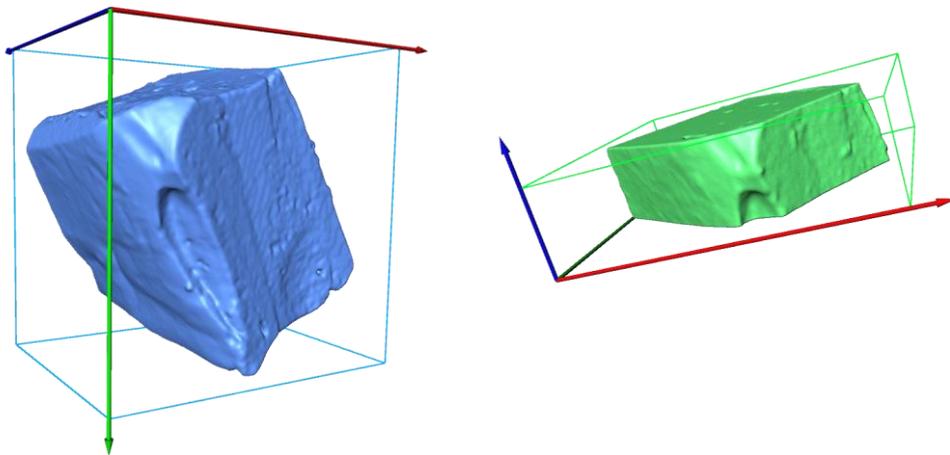

Figure 4: Surface views from the two reconstructions of the same sample (the bounding boxes is around 11.5 mm accross). The rotation and translation was applied to the green volume so as to coincide with the blue (the "dimple" in the foreground shows that this is the same object)
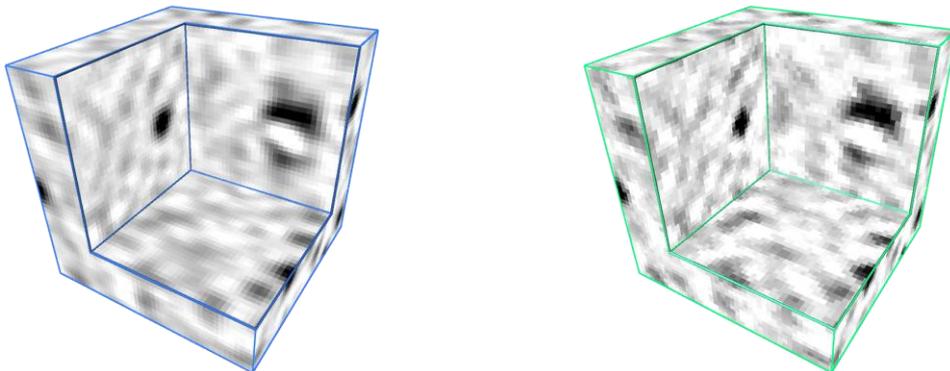

Figure 5: View of the 0.03mm3 subvolumes extracted from each reconstruction.

If the autocorrelations and roses of direction were identical, then the measure is independent of scanning conditions or reconstruction parameters. Unfortunately, the roses of direction proved to have considerable differences, as seen in figure 6. This was confirmed in all tested subvolumes, meaning that the conditions of the scan or the reconstruction is strongly influencing the resulting measure.
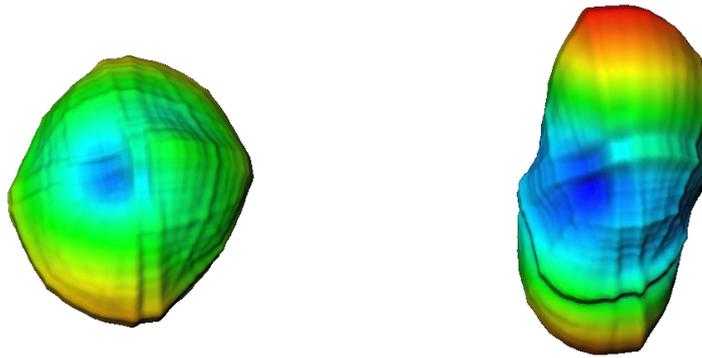
Figure 6: The rose of directions of the blue and green subvolumes, respectively.

A third aspect that needed verification was the influence of the pixel size on the measure. Another scan of the same material was performed, but at a higher resolution (4.49 µm/pixel instead of 6.74 µm/pixel). Again, the volumes were registered, subvolumes extracted, and autocorrelation calculated. The two graphs in figure 7 shows the curves for the previous green volume, and the higher resolution volume, for subvolumes near opposite sides of the sample. The left curves are fairly similar, detected peaks are in very good agreement, knowing the pixel resolutions. The second, however, shows strong variation not only in the amplitude of the deviation but the position of the peak, indicating again an influence from the imaging process.
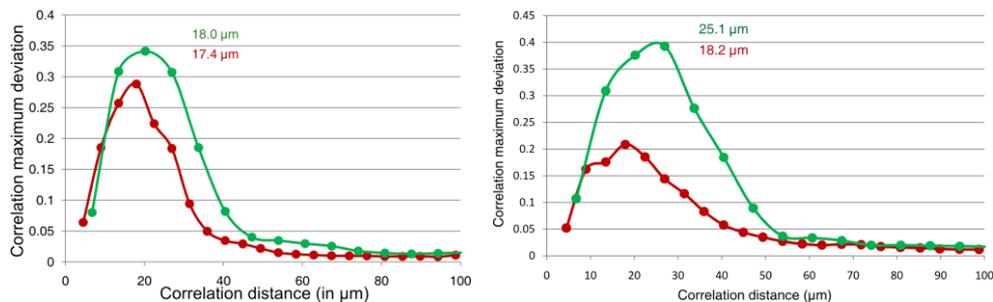

Figure 7: Curves from two scans of the same sample taken at different resolutions. The left and right curves were obtained from subvolumes at opposite sides the sample.

Conclusion

This work shows that although microtomography brings about a wealth of information on the internal microstructure of materials, and quantification can be quickly performed on 3D reconstructions, the scientific methodology requires caution and asks to verify the accuracy of any experiment.

In doing so for the computation of anisotropy of the cellular structure of polymeric foams, we have discovered that a factor related to the acquisition or to the reconstruction is responsible for significant errors in the measures.

An additional scan had been made, but was rejected due to strong artefacts seen on the cross-sections. Figure 8 shows a horizontal cross-section, with two zoomed portions. The blue region seems correct, with sufficient sharpness and contrast, while the red region show a doubling of the outer polymer layer, as if a shifted phantom image was superimposed. This type of artefact could be due either to a movement during the scan, or an incorrect alignment of the axis of rotation during the reconstruction.
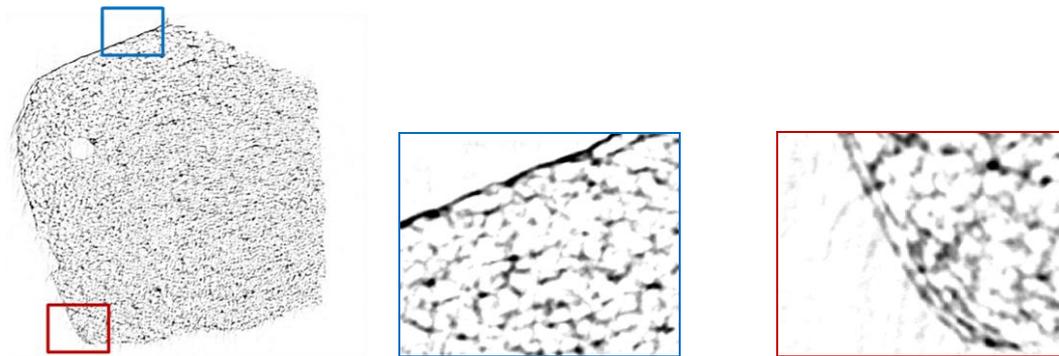
Figure 8: A cross-section of a reconstruction of the same material as in figure 1, that was rejected due to strong artefacts, seen in the zoomed red portion.

As a test, four subvolumes were selected along a line inside the sample, shown in figure 9, coming from the side with this artefact and going to the side that seemed clear of it. The resulting peaks in the curves clearly show a decrease when this artefact become significant. This is logical because the shift of the phantom image is smaller than the average cell diameter, thus artificially creating smaller features inside the image. Although more tests need to be performed, we can suppose that the errors that were seen in this study are the direct result of this type of artefact.
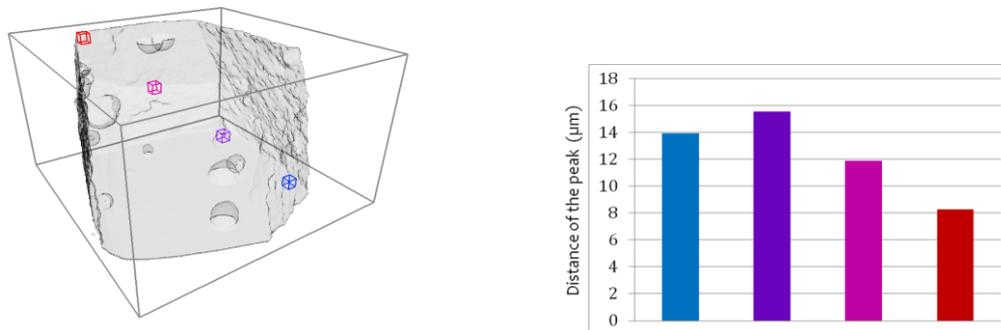

Figure 9: Left – the volume from figure 8, along with four 0.003mm^3 subvolumes extracted from one side to the other. The red subvolume shows the most phantom image shift. Right – the peaks computed on the correlation maximum deviation curves for the four subvolumes.

References:

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