

A method to quantify the 3D microstructure of fibrous materials containing mineral fillers using X-ray microtomography: application to paper materials

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Abstract This article proposed and validated an original and automatic method based on synchrotron X-ray microtomography to characterise non-destructively, in 3D, the mineral fillers that may be present in fibrous composite materials. The approach consists of (i) obtaining the 3D internal structure of the sample in a non invasive way, (ii) identifying the fillers in the 3D microstructure using appropriate image processing tools, (iii) calculating the filler content on the numerical data, and (iv) validating the representativity of the data sets by evaluating the representative elementary volume. This method was successfully applied in the case of paper samples. The numerical filler content were in good agreement with standards. This method opens new perspectives in terms of characterisation of filler spatial repartition.

Introduction

Fibrous materials filled with mineral particles were analysed in order to characterise the amount, spatial position and size distribution of the particles. These characteristics are crucial for physical properties, such as permeability, mechanical resistance or optical properties. Composites consisting of fibres and fillers have been used extensively in various businesses such as public health, or in various industries such as automotive, aeronautic and paper production. Their composition and processing are tailored to the physical properties required for their use. Particles can be retained by the media during filtration process or introduced in the material during production. As an example, paper materials are constituted of fibres and mineral fillers which are mixed during the forming of fibrous webs. In this case, mineral particles are introduced to decrease the cost of materials but also to improve some end-use properties. For example, fillers improve optical properties such as brightness, opacity and printability [1]. Characterising such structures in 3D is a requirement to better understand the relationships between the fillers that are introduced in the material and the final product properties of the material. This can be achieved using synchrotron X-ray microtomography (SAXM). This technique, SAXM, is widely used in materials science [2, 3]. In fibrous materials [4–6], SAXM allows the 3D reconstruction of internal microstructure (at micron scale) in a non invasive manner. Coupled with appropriate image analysis tools, it allows for quantification of structural parameters such as porosity, or specific surface area of paper samples [7, 8].

In such a context, this paper details the possibilities brought by SAXM when interest is focused on filler characterisation. The main aim of this research is to quantitatively characterize the filler content in fibrous porous

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materials by SRXM and estimate the representative elementary volume (REV). Hence, in order to simultaneously evaluate the filler content and the filler distribution within the structure, SXRm tests were performed on paper samples containing different amounts of various fillers.

Materials and methods

Paper samples

Sheets of paper were lab-made using a Rapid Köthen type handsheet former. The furnish was 100 % Eucalyptus fibres with a mean length of about 2 mm and an average diameter of about 20 μm . During paper formation, fillers may agglomerate, as cationic starch was used for retention and alkyl ketene dimer (AKD) for sizing. We tested different fillers used in the pulp and paper industry, namely: ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), clay, talcum and titanium dioxide (TiO_2). Their average particle size was 3–5, 0.2–0.5, 0.5–1, 1–10 and 0.3 μm , respectively [9]. For each filler type, different amounts were introduced during paper formation. In each case, filler contents were evaluated using standards ISO 2144 [10] for comparison with structural results. This standard consists in weighting the sample before (m_{tot}) and after ashing it at 900 $^\circ\text{C}$ (m_{fillers}). The ash content or filler content is then defined as the ratio of m_{fillers} by m_{tot} . Ash rates were corrected for loss in ignition, considering a loss of 7, 14, 1 and 40 % for talc, clay, TiO_2 and GCC/PCC, respectively.

Obtaining 3D microstructure

During microtomography data acquisition, the sample was set on a rotation stage. A beam irradiated the sample. The transmitted beam was recorded for 1,500 angular positions. These images were then gathered to virtually reconstruct the internal sample microstructure using a filter back projection algorithm [11]. The obtained data sets represent a 3D map of the relative absorption coefficient of the sample constituents. Therefore, the different constituents (air, natural lignocellulosic fibres and fillers) were represented in the images by different grey levels as illustrated in the left column of Fig. 1 where the pores are in dark grey, fibres in grey and fillers are the brightest particles. The observation scale was chosen according to the different sizes of constituents. According to the typical sizes of paper constituents (cf. “Paper samples” section), the voxel which is equivalent to a pixel in 3D, had a size of $(0.7)^3$ microns³. Therefore, the total imaged volume was $(1.4 \text{ mm} \times 1.4 \text{ mm} \times \text{paper thickness})$ as the detector had 2048×2048 pixels.

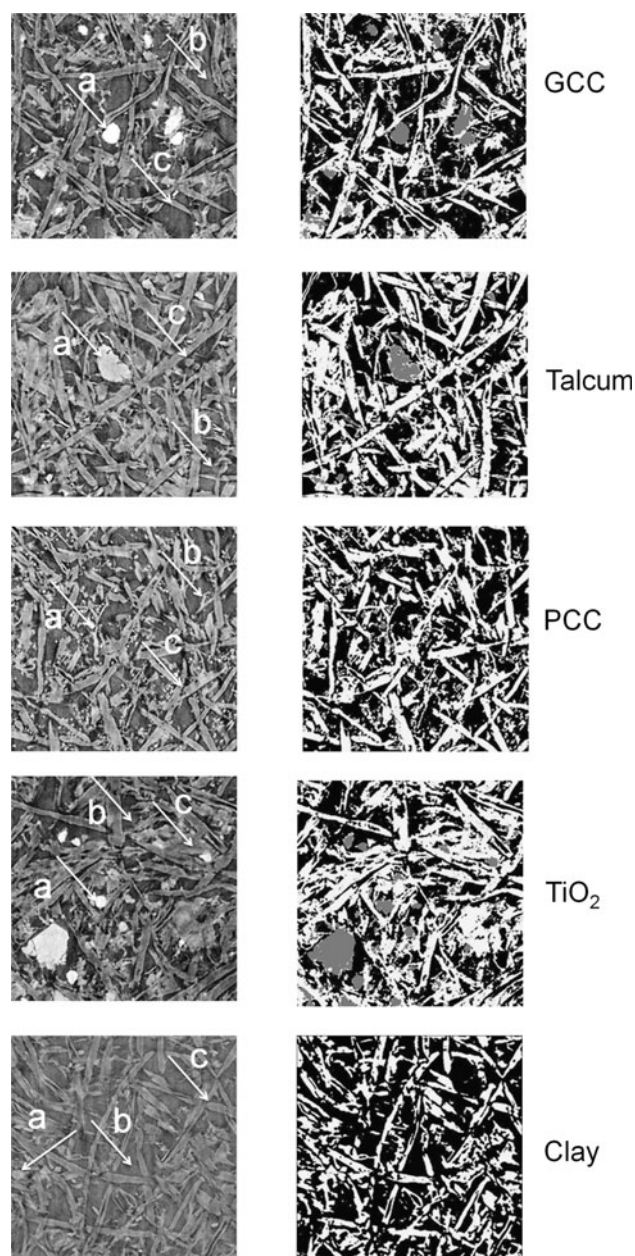


Fig. 1 Slices ($358 \times 358 \mu\text{m}^2$) extracted from imaged samples for different mineral fillers. The left column corresponds to the original images in grey levels. Arrows indicate the different constituents (a) fillers, (b) pores and (c) fibres. The right column represents the segmented corresponding slices

Segmentation: toward quantification of 3D data sets

To obtain quantitative parameters describing the local structure, the three main phases of the materials (air, fibre and filler) must be separated in order to obtain a new 3D data set where each constituent is represented by a single grey level. In order to reach this goal, an image analysis method was initially developed for paper samples [8]. This procedure was detailed in [9]. This is a two step procedure:

1. 3D data sets are denoised using a 3D anisotropic filter. It consists in smoothing homogeneous region while preserving edges of the sample constituents. As a consequence, the shapes of the pores, fibres and fillers are not modified in the resulting images.
2. A 3D region growing algorithm is then applied to separate one constituent of the paper from the other. It consists of (i) choosing starting regions using a thresholding technique and (ii) having grown these regions. When applied twice with different sets of parameters, this last step allows the separation of the different constituents: pores, fibres and fillers.

Evaluation of filler content

According to standards, the ash content is defined by the ratio of the filler mass to the total mass ($m_c/(m_c + m_f)$). In the case of tomographic images, considering segmented data, the filler content is deduced by counting voxels belonging to each phase. It is evaluated as: $(N_c d_c)/(N_c d_c + N_f d_f)$. In these relations, m , N and d represent the mass, the number of voxels and the density, respectively. The subscripts c and f , represent fillers and fibres, respectively.

Representativity of data sets

As the analysed volumes with SXRm are much smaller ($1.4 \text{ mm} \times 1.4 \text{ mm} \times \text{paper thickness}$) than the typical sizes on which standard measurements are carried out ($100 \text{ mm} \times 100 \text{ mm} \times \text{paper thickness}$), the representativity of such small volumes may be questioned. In other words, were the imaged volumes large enough for such filler content evaluation to obtain valuable quantitative results? If this is true, then the next step is to determine the size of the smallest volume that is necessary to carry out a reliable quantitative analysis. This smallest volume is called the Representative Elementary Volume (REV). It depends on the studied property and on its method of estimation.

In a previous study, we determined that the imaged volume ($1.4 \text{ mm} \times 1.4 \text{ mm} \times \text{paper thickness}$) was adequate to quantify both porosity and specific surface area of paper samples [12]. We also proposed [12] a systematic method to determine the REV which was initiated by the work of Drugan [13] and Kanit [14]. This method consists of evaluating the property of interest, for larger and larger volumes always centred on the same central voxel until stabilisation occurs. The volume for which the fluctuations become lower than a chosen error defines the REV. The criterion for the evaluation of the error here is defined by comparing the filler content in the REV to the one corresponding to the whole imaged volume. In this study, the same method for the characterisation of fillers was applied.

Results and discussion

3D microstructure of paper samples

The characteristics of the analysed samples in terms of filler types and standard ash content measurements are presented in columns 1–3 in Table 1. Tests were duplicated in the case of TiO_2 in order to demonstrate the reproducibility of the method. The left column of Fig. 1 exhibits in-plane slices of samples filled with one of the studied fillers. In each case, we can observe the three constituents of the paper samples namely pore, fibre and filler. It is possible to visually identify even the smallest fillers such as TiO_2 and PCC. This is due to the fact that these fillers agglomerate during the paper making process, which artificially increases their sizes. We now assume homogeneous clusters. Consequently, the scale of analysis can be considered adequate to the aim of this study from a visual point of view.

Segmentation

The right column of Fig. 1 presents the corresponding segmented slices where the pores are in black, fillers in grey and fibres in white. The segmentation reaches its goal as fillers are isolated from the fibres with the exception of clay: all fillers are identified and the morphological characteristics, such as shape and location, are close to the ones we can visually observe on the grey levels images (cf. Fig. 1, left). The failure of the segmentation process in the case of clay is due to the fact that in the experimental conditions, the coefficients of absorption in some parts of

Table 1 Filler contents (% in weight) obtained by both techniques (standard and SXRm). In the case of SXRm, both the bulk and the whole sample are considered

Filler	Ash rate without correction	Ash rate with correction	Numerical filler content in the whole sample (%)	Numerical filler content in the bulk (%)
TiO_2	18.4	18.6	19.5	18.0
TiO_2	18.4	18.6	17.9	15.5
TiO_2	8.2	8.3	8.9	9.7
TiO_2	8.2	8.3	8.9	8.5
PCC	9.8	13.7	11.4	13.7
PCC	6.0	8.4	6.9	6.1
Talc	13.8	14.8	13.5	14.2
Talc	9.1	9.8	8.9	7.1
GCC	10.2	14.3	12.4	14
GCC	3.4	4.8	4.4	4.3
Clay	14.5	16.5	–	–
Clay	8.8	10.0	–	–

the lignocellulosic fibres are of the same order of magnitudes as the ones corresponding to this filler. The initial starting regions for the segmentation of clay fillers are therefore located in both fibres and fillers. This thus precludes successful segmentation of these fillers. One solution to separate clay fillers from the fibre network would be to perform holotomographic scans [15]. In this study, clay filler were therefore excluded from the next analysis.

Numerical estimation of the filler content and representativity of the data sets

Table 1 summarises the filler content obtained using the standard gravimetric and tomographic methods. One can notice a good agreement between the standard method, taking into account the loss ignition, and microtomographic measurements. The repeatability was checked in the case of TiO_2 which indicated the reliability of these measurements.

As the tomographic results appeared to provide a viable method for determining filler content, we investigated the problem of the representativity of the imaged volume. We therefore evaluated the filler content for parallelepiped volumes of size $(l \times l \times h)$ where l and h represent the side length and the thickness of the considered volume, respectively. The thickness h was fixed to $35 \mu\text{m}$. This choice was justified in a previous study concerning similar handsheet papers [12]. The filler content in the bulk area are reported (Table 1). Figure 2 shows the evolution of the numerical filler content as a function of the side length l , for the handsheet filled with 8.2 % of TiO_2 . We call l_{REV} the length for which the stabilisation occurs. It equals $350 \mu\text{m}$ in this example. This length is representative of the in-plane structure. Similar curves were obtained for each analysed

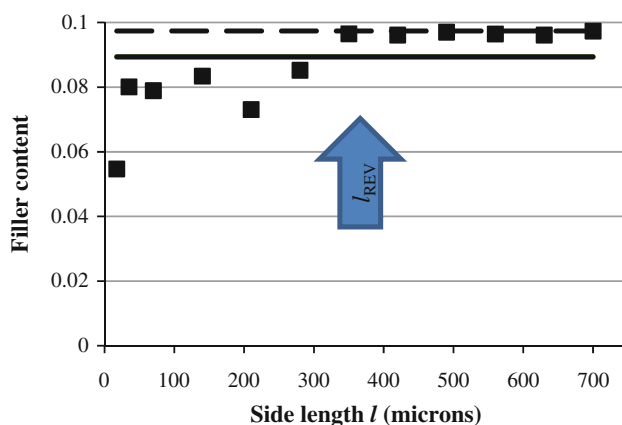


Fig. 2 Evaluation of the l_{REV} for filler content for the eucalyptus handsheet filled with 8.2 % of TiO_2 . The squares correspond to the filler content calculated on volumes of increasing side length l . The continuous line corresponds to the value measured on the whole microtomography volume and the dashed line to the final value of the biggest volume studied for REV evaluation

Table 2 Characteristics length (l_{REV}) of the REV for the different filler types and contents. Duplication of the measurements were carried out in the case of TiO_2

Filler	Ash rate (standard method)	l_{REV} (μm)	Error (%)
TiO_2	18.4	420	3
TiO_2	18.4	420	4
TiO_2	8.2	350	1
TiO_2	8.2	280	2
PCC	9.8	280	4
PCC	6.0	350	1
Talc	13.8	350	1
Talc	9.1	420	2
GCC	10.2	350	4
GCC	3.4	300	5

sample. Table 2 summarises the obtained values of l_{REV} for all the samples and the error made on the measurement. This table indicates that for filler content the REVs are then smaller or equal to $(400 \times 400 \times 35 \mu\text{m}^3)$ which was smaller than the imaged volume ($1.4 \text{ mm} \times 1.4 \text{ mm} \times \text{paper thickness}$) and the error made is always $<5 \%$.

In the thickness direction, both the bulk and the whole thickness were also considered in order to analyse the effect of the gradient of structure in the thickness direction. Differences were obtained, however, no trend concerning the spatial repartition between the bulk and outer layers can be deduced from results summarised in columns 4 and 5 in Table 1.

Application: 3D filler content and distribution in the thickness direction of industrial paper or handsheet paper samples

The results from the two previous sections indicate that quantitative measurements are possible on filler content regardless the filler type within the filler concentration range studied here. Different 3D properties of fillers can be studied such as the spatial repartition of the filler.

Figure 3a illustrates an example of 3D filler distribution of the binarised data where the fillers (GCC) and fibres were represented for a handsheet. Figure 3b shows the filler phase only. This sample presented a non-uniform distribution of fillers in the paper plane direction.

Moreover, filler content profiles were studied along the thickness direction (Fig. 4). Figure 4 illustrates results obtained on the eucalyptus handsheet filled with 18.4 % of TiO_2 . Two samples extracted from this handsheet were analysed to check for experimental variability. This example illustrates the spatial variation of the filler profile distribution.

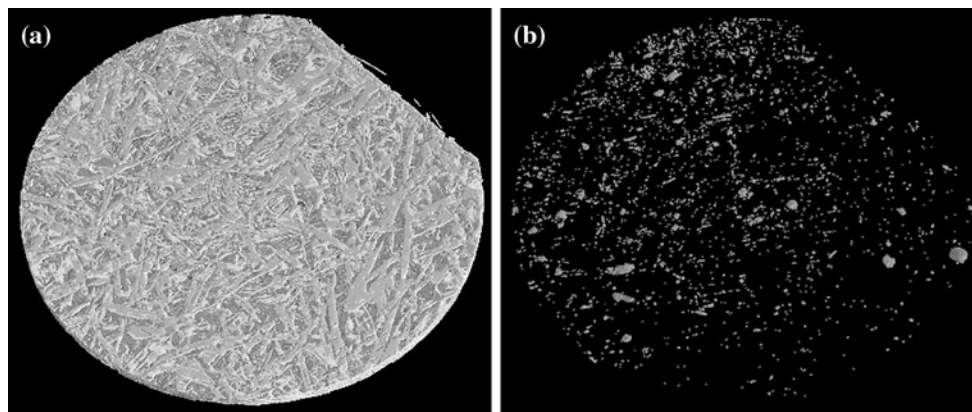


Fig. 3 3D visualisations ($1.4 \text{ mm} \times 1.4 \text{ mm} \times 150 \text{ }\mu\text{m}$) of the spatial repartition of fillers for a handsheet filled with GCC. The left picture (a) corresponds to the fibre and filler spatial distribution, whereas the right one (b) only refers to the filler distribution

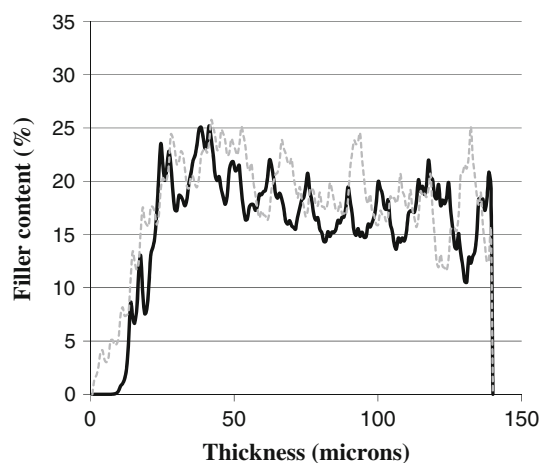


Fig. 4 Filler content profiles in the thickness direction. The solid and the dash lines correspond to two different samples of eucalyptus handsheet filled with 18.4 % of TiO_2 fillers

Conclusions and perspectives

An automatic non invasive method to quantify, in 3D, the mineral fillers present in a porous fibrous medium was presented. The approach consisted of (i) imaging in a non destructive way the sample of interest by SXRM, (ii) identifying the fillers in the 3D microstructure using appropriate image processing tools, (iii) evaluating the filler content on the numerical data and (iv) validating the representativity of the numerical data sets while evaluating REV. It was also validated quantitatively and compared to standard ash content method.

This method was successfully applied in the case of paper samples. It can be completed by 3D maps of filler concentration as well as their projection in the horizontal plane (2D distribution). Another perspective consists in analysing in a region the correlation between total mass and total filler mass.

The developed method opens new perspectives for characterising other porous and fibrous materials such as composites made of polymeric matrix containing mineral fillers and/or reinforced by glass fibres, for example.

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