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Three-dimensional carbon black aggregate reconstruction from two orthogonal TEM images

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ABSTRACT: Current morphological characterization techniques extract the basic properties of Carbon Black aggregates from single bi-dimensional images, which are just planar projections of the real structures. Although widely used, this approach provides limited and inaccurate characterization of the aggregates. Several techniques have been proposed to achieve a full three-dimensional characterization of nano-structures, such as electron tomography and FIB-SEM. However, the capability of these techniques to characterize Carbon Black aggregates is still under study. In this work, we present a novel solution that aims to improve the characterization of Carbon Black aggregates by providing a fast, flexible and robust reconstruction method. The proposed method takes advantage of genetic algorithms to obtain a complete three-dimensional model of the aggregates from two orthogonal TEM images. Results were compared to an electron tomography reconstruction obtained from a full tilt series.

1 INTRODUCTION

Filled polymers are widely employed in many application areas such as paper, plastics, rubber and paint industries, where their polymer properties (e.g. density, conductivity, mechanical properties) and rheological properties are enhanced by means of mixing them with some filler. Different fillers have different effects on the material's chemical nature, particle size and shape, and therefore result in quite complex geometrical objects to which specific reinforcing properties can be associated. This is the case of carbon black where carbon black spherical units form three-dimensional aggregated structures s whose particular shape has an important impact on the reinforcing properties of the polymer. It is well known that stiffness, tensile strength, compression and tear strength, fatigue and wear resistance or dynamic performance significantly increase through these filler additions, but the mechanisms responsible for these effects are still under discussion (Kohls, & Beaucage 2002, Fukahori 2003).

Filler characterization is essential in order to state the relationship between the morphological characteristics of the fillers and their reinforcement effect on the polymer: the employment of Finite Elements Analysis (FEA), for example, requires a great amount of precise data. To this extent, it's clear that a greater precision in the filler characterization and a more complete characterization will lead to remarkable improvements in predictive models and FEA.

The filler characterization is standardized, and microscopic techniques are used for the characterization of the filler: a TEM/AIA procedure is well defined in the corresponding standard (ASTM D3849 – 07). This standard describes the procedure to characterize the carbon black's aggregates of each grade, but important parameters related to the reinforcing capabilities of the grade such as the aggregate's superficial area are derived from measurements based on TEM images, which are two-dimensional projections of the aggregate. It's clear that improvement of the morphological characterization is therefore an important issue, and that the three-dimensional characterization of the fillers could be a step forward.

Over the last years there have been several attempts to carry out a 3D reconstruction of fillers (Gruber et al. 1994). Electron tomography and FIB-SEM techniques are nowadays the most promising opportunities for achieving a complete 3D reconstruction of nanostructures. In the tomography area, Kohjiya et al. (2005, 2006 and 2008) have reported some 3D reconstructions of different fillers in rubber. The main difference between both techniques, apart from the microscopy technique itself (TEM for tomography and SEM for FIB-SEM) is that in the first case images are taken in a set of different tilts of the sample with respect to the incident electron beam and the volume is reconstructed later by means of some complex mathematic algorithms (Frank 2005), while in the FIB-SEM technique layers of the nanometer order are successively eroded from the surface of the sample employing a Focused Ion Beam (FIB) and a new SEM image of the surface is obtained, giving rise to a stack of images of the different layers of the sample, which can be reconstructed into a volume in a relatively easy way.

Both techniques are time-consuming and require a big amount of data (image stacks), and although after the volume reconstruction morphologic parameters such as the aggregate's volume or superficial area can be determined, the exact location and size of each of the carbon units in the aggregate can not be determined. Further work must be carried out upon these reconstructions in order to extract this kind of information. Monte Carlo methods could be an effective way of deducing the exact structure of the reconstructed volume (Eguzkitza et al., in prep.).

In this work we explore the possibility of reconstructing the same 3D TEM-images of the fillers by means of a less time demanding technique and, at the same time, obtaining exhaustive information about the morphology of the filler. A 3D model of a carbon black's aggregate will be obtained from two TEM images of the same aggregate at different angles. This model will be exhaustive enough to give all the details about the aggregate and its structure: the number, relative position and size of the carbon units and the volume and superficial area of the complete aggregate.

This technique is based on a genetic algorithm (Barricelli 1954), which applies a set of genetic operators to a group of possible solutions –called population–, in search for the fittest ones at each iteration –or generation–. These operators may include random mutations and crossover methods (i.e. forming an instance from two or more parents) (Koza 1995).

The result of this operation only provides us with the position and size of the particles in the aggregate. Therefore, in order to obtain more substantial information, a reconstruction process is usually achieved through the use of a three-dimensional volumetric field (a voxelization grid in which each of its elements, called voxels, contains the volumetric information at a given point). Furthermore, for the estimation of the superficial area, isosurface generation algorithms such as Marching Cubes (Lorensen & Cline 1987) are commonly used.

2 ALGORITHM'S DESCRIPTION

The algorithm proposed in this work can be divided into three main parts. The core is the 3D genetic algorithm where particles are randomly generated in pursue of an accurate three-dimensional aggregate structure determination. Initially, we need to process two TEM images captured at 90 degrees difference as shown in Figure 1 to obtain their height maps. Later we project the particles with the aim of obtaining similar height maps to the originals. Once we have the definition of the aggregate structure, that is, the position and size of its particles, we generate a 3D model with two main objectives: the visualization of the particles, and the estimation of their volume and superficial area.

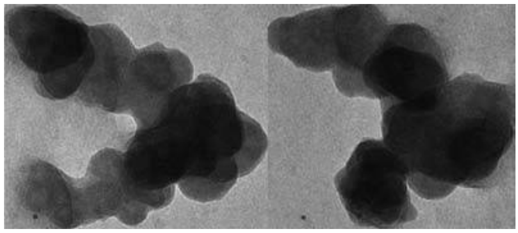

Figure 1. Original TEM images at $-45°$ and $+45°$.

2.1 *Image processing*

First, the aggregate from the two images is segmented with an enhanced version of a binarization algorithm we have previously published (López-de-Uralde et al. 2011). Afterwards, the images are transformed into height maps.

2.2 *Segmentation*

In order to be able to segment the aggregate we first have to binarize a noise-free image. To this extent, a Gaussian smoother is applied. This 2D convolution operator eliminates noise at the price of losing a bit of detail (Pajares & de la Cruz 2007). Then, a threshold for aggregate-background discrimination is estimated using Otsu's method (Otsu 1975). This threshold is adjusted to be more adequate for TEM images. We generate a binary image considering that pixels with a value below the threshold correspond to background and pixels above it are part of the aggregate area.

Moreover, we improve the edge quality by dilating and eroding it with a disk shape morphological structuring element.

2.2.1 *Height map*

A height map is a representation of the height of each point on a surface in a two-dimensional matrix. It is typically represented by an image indicating the surface height at each point by its corresponding pixel with its colour. In our case, this map represents the number of overlapping particles in each point of the initial image taken with a microscope. Our height map, as can be seen in Figure 2, is generated by the following steps.

2.2.1.1 *Image pre-processing*

First, the image is resized with a bicubic filter to reduce the processing time of all subsequent steps.

Then, with the aim of reducing the image noise, we apply the Median filter on the image obtained with the microscope.

To end this process, it is required to reverse the resulting image from the previous step, obtaining

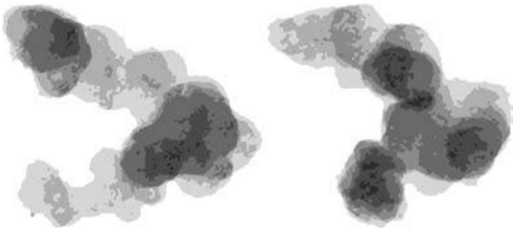

Figure 2. Height maps at $-45°$ and $+45°$.

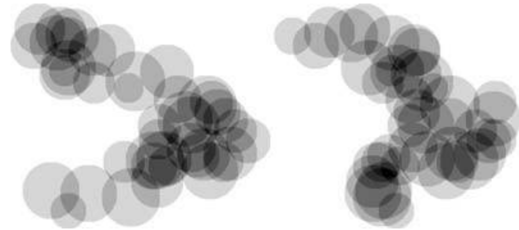

Figure 3. Particle projections at $-45°$ and $+45°$.

a predominantly black background with an aggregate whose accumulation of material in each pixel is directly related to the amount of white of that pixel.

2.2.1.2 *Background removal*
At this stage the objective is to completely eliminate the background colour, both the background itself and the white increase in the aggregate caused by the background material. In this way, the average value of the background pixels is calculated using the mask in the segmented image.

The final step of this section results in the aggregate obtained without any background. This will require painting black all the pixels marked as background by the segmentation image in the original image. It is also necessary to subtract the average value of the background obtained in the previous steps in all pixels of the aggregate image that the segmented image marks as not-background.

2.2.1.3 *Particle value detection*
To build the height map, the average amount of material of a single particle is needed. To do this we must normalize the heights from the above process by converting the maximum height into pure white and minimal height into pure black. By this step we get similar levels of white in all images.

Finally, to obtain the value of a single particle, it is necessary to recount the number of existing heights in the image and calculate a value for each level indicating the presence of this height in the image. With this value it is possible to discriminate the heights that do not have much presence in the image and keep the lowest height that exceeds a particular threshold.

2.2.1.4 *Height map generation*
Having calculated the height value of a single particle, we pass to the calculation of the height map. To do this we have to populate the array of heights with the value obtained by dividing the amount of white in that pixel by the amount of white that a single particle should have, therefore obtaining the number of overlapping particles in each pixel of the image stored in the height matrix.

The calculation of the value of a single particle is overly dependent on the original image, the original particles distribution and the segmented image. For that reason, the obtained value may be to be too low, generating too many particles at each point. To solve this problem it is necessary to make a normalization of the depth of the map. To make such standardization it is necessary to establish the maximum number of overlapped particles.

2.3 *3D genetic algorithm*

This algorithm is based on the theory of evolution, but is simplified in the way that there are only mutations and not crossover operators (i.e. mixing two intermediate solutions).

The goal that drives this evolution process is to obtain similar height maps from the TEM images projecting particles at -45 degrees and $+45$ degrees as shown in Figure 3. As they are orthogonal planes, the projection of a particle only requires to obviate one axis (e.g. (3, 8, 7) corresponds to (3, 8) and (7, 8).

First, the population is initialized. Then, an iterative process starts where each instance of the population suffers one mutation. Later, the mutated instances are compared with the previous ones by means of the defined fitness function and the best 30 instances are kept. Finally, when the best instance reaches the desired fitness a result is established and the algorithm terminates.

2.3.1 *Initialization*
The first step of the genetic algorithm is to initialize the population. Ten empty instances are created. Each instance will be an intermediate solution containing a list of particles that will form an aggregate.

2.3.2 *Mutations*
We have defined five types of mutations that are applied during the mutation process. One and only one of them is chosen randomly:

– Adding a particle: this mutation generates a three-dimensional point randomly. Its radius is established randomly between a minimum and maximum radius manually defined previously.
– Removing a particle: this mutation eliminates a particle.
– Moving a particle: this mutation changes the position of a particle.
– Moving a particle a little: this mutation changes the position of a particle only one pixel.
– Resizing a particle: this mutation changes the radius of a particle.

It is worth pointing out that when creating, moving or resizing a particle there are several constraints. Firstly, we ensure that the sphere is inside the square

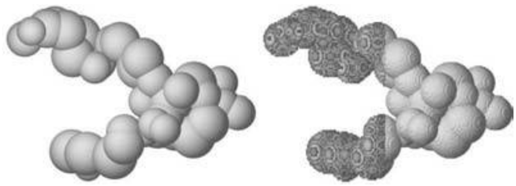

Figure 4. Sphere and volumetric mixed with isosurface representations of the aggregate at 0°.

prism formed by the two images. Secondly, we check that the centre of the particle is inside the masks of the two projections.

Moreover, when applying a moving or resizing mutation to an instance, the particle involved is chosen randomly.

2.3.3 *Selection*

To select between the instances of the population, we have defined a fitness function. This function computes the differences between the height maps of the two projections and their corresponding projections of the instance particles.

Furthermore, an instance is penalized for the portion of mask that is not filled by particles. Additionally, isolated particles harm the fitness function result proportionally to their radius and distance to the closest particle.

2.3.4 *Termination check*

There are two termination conditions: the best instance reaches a given fitness or a sufficiently good result is observed by manual inspection.

2.4 *Three-dimensional reconstruction and visualization*

The particle data obtained in previous steps enables us to faithfully recreate the original Carbon Black aggregate in a three-dimensional space. The resulting model not only provides us with a visual depiction of the aggregate (which can be used to further validate previous results), but also introduces additional volumetric and superficial information.

We provide the user with different representations. Each of them provides a different view of the model data so it can be perceived and understood more easily. In Figure 4 all the three representations are shown.

- Sphere-based representation: The simplest of the three, it utilizes spheres to display every particle of the aggregate. In this way it provides a fast and easy way for the graphic hardware to draw the surface of the aggregate. The user can check with this representation if the current best instance of the genetic is good enough.
- Volumetric representation: In this representation, only the volumetric information is shown. This is achieved through the creation of a voxelization grid, whose individual elements (called voxels), have a different value depending on the distance to the closest particle centre. This value is later translated into a colour through the use of an interpolable colour palette and drawn on screen. Furthermore, in order to show the inner section of the aggregate, additional clipping planes are introduced for the user to control.
- Isosurface representation: Taking into account the voxelization grid values established in the previous representation, a triangulated mesh is generated through our enhanced implementation of the Marching Cubes algorithm. By doing this, we obtain a surface that more accurately matches the original one.

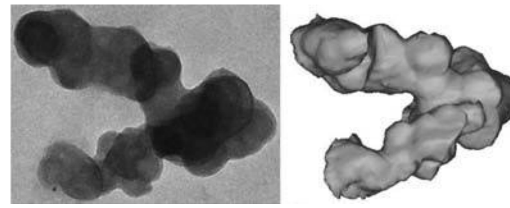

Figure 5. Original TEM image at 0° and its tilted tomographic reconstruction.

3 METHODOLOGY

In order to get the three-dimensional characterization of a carbon black aggregate, a stack of TEM images at different tilt angles has been obtained. The carbon black has been supplied by Cabot Corp. and is a CSX 691 commercial grade. Some specimens have been prepared to be analysed according to the ASTM standard procedure (ASTM D3849 – 07) employed for carbon black grades characterization. The microscope is a JEM-2200FS/CR transmission electron microscope (JEOL, Japan) equipped with an ULTRASCAN 4000 SP (4008×4008 px) and a cooled slow scan CCD camera (Gatan, UK). Tilted images have been taken in the $\pm 60°$ interval at every 1.5°, see Figure 5 for the image corresponding to 0° tilt.

The complete image stack has been used for a tomography reconstruction by means of the IMOD free software (Mastronarde & McIntosh 1996, IMOD Home Page). Once the whole tomogram is computed, the segmentation of the reconstructed volume gives rise to the carbon black aggregate's volume as can be seen on Figure 5. And the values for the superficial area and volume of this reconstructed volume are determined with the 3dmod program of the IMOD package.

At the same time, two images from the full image stack have been chosen for the calculation of the three-dimensional model deduced by means of the genetic algorithm presented in this paper. These images correspond to $\pm 45°$ tilted ones in the stack employed for the tomographic reconstruction.

After the images are processed as described in the previous section, the height map of each image is calculated and the 3D genetic algorithm is employed to calculate a 3D model according to these height maps.

The designed genetic algorithm predicts the position and size of the particles in three dimensions. An initial population of 10 individuals is created. Each individual contains a list of particles with their positions and radius, and the algorithm works with two projections in the $\pm 45°$ corresponding to that list of particles: it calculates a height map that estimates the quality of each individual at this stage and after the mutations that give rise to new individuals. To evaluate the quality of each individual we used a fitness function. This function returns a value calculated by comparison of the individuals' local height map and the previously calculated height map of the original image.

At each iteration, new descendants (individuals created by mutations) are generated using the entire population as well as 10 additional "children" of the 10 best individuals of the previous iteration. Then, the best 30 individuals of the population are selected and the rest are discarded from the population. We obtained this value of the population by an empirical validation with different configurations, maximizing the trade-off between accuracy and efficiency because a larger population can avoid the appearance of local maximum. However, such a population requires more overhead processing.

The possible mutations that may appear, as we aforementioned, include creation, removal, repositioning and rescaling of the particles. Both in the rescale and creation, it is mandatory to set a radius, whose maximum and minimum values are set manually.

Once there is a solution, the validation of the results is performed by extracting the volume from the voxelization grid and the superficial area from the reconstructed isosurface. These values are later compared to the same values obtained in the tomographic reconstruction of the TEM images.

In addition, we have performed another validation with an image taken at $0°$. With this purpose we have segmented it and generated its height map. Then we have projected the particles of the solution shown through this paper into the $0°$ plane. This projection is not as straightforward as the ones at $-45°$ and $+45°$. In this case, a change to the coordinate system by a rotation is needed. This third image, like the tomographic reconstruction is only used with validation purposes, so the number of images needed for the reconstruction is still two.

4 RESULTS

Values for the superficial area and volume of the re-constructed tomogram are $5.93 \cdot 10^5\,\mathrm{nm}^2$ and $1.69 \cdot 10^7\,\mathrm{nm}^3$ respectively. It must be pointed out that in order to perform these measurements, a segmentation task must be carried out on the orthoslices obtained after reconstruction. This manual intervention along with artefacts inherent to the reconstruction process itself (Frank 2005) induces errors in the quantification that should be kept in mind.

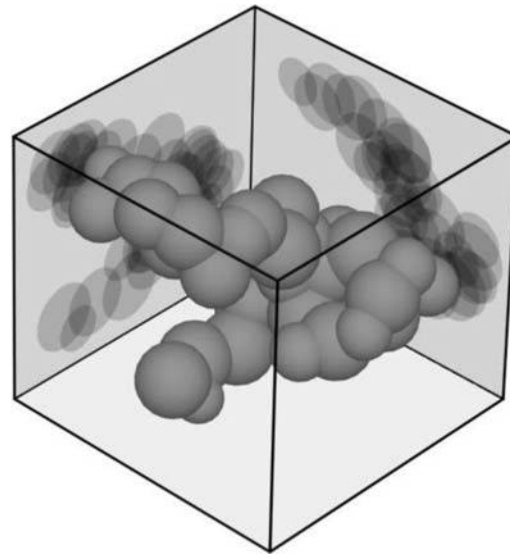

Figure 6. Reconstructed aggregate with its projections.

On the other hand, our algorithm has calculated the same parameters with only two TEM images and nearly no human aid, giving rise to a superficial area of $4.45 \cdot 10^5\,\mathrm{nm}^2$ and a volume of $1.21 \cdot 10^7\,\mathrm{nm}^3$. In the Figure 6 is shown their three-dimensional reconstruction.

It is obvious that further work must be carried out in order to improve the algorithm and draw final conclusions, but these results show a great concordance and confirm the validity of the proposed method.

5 CONCLUSIONS

We have presented a new and fast method for the three-dimensional reconstruction of carbon black aggregates. This study has led us to insightful conclusions; however, the research in this field is far from being completed. Since the global impact of carbon black aggregates on the mechanical properties has still a high degree of uncertainty, further study is required. In addition, it would be very interesting to validate it on more complex aggregates and other types of nanofillers such as nanoclays, graphene and so forth. In order to improve the algorithm, the following changes will be implemented in future work.

The projection method should be changed so that the centre of the particle projects more density than the outer area. Additionally, aggregate density is uniform across the aggregate so the fitness function should take this into account for particle intersections.

Different genetic techniques like crossover, drastic mutations and keeping randomly some elements despite having a bad fitness value. We expect to avoid getting stuck in local maxima.

These modifications will make the algorithm more computationally expensive, so we strongly suggest the study of a method to accelerate it by means of General-Purpose computation on Graphics Processing Units (GPGPU). In doing so, the higher resolution speed will increase dramatically enabling us to analyse more aggregates of the same sample.

Additionally, we propose the development of advanced skeletonization methods to correctly assess the internal structure of the carbon black aggregates. Since the exact location of each individual particle has already been calculated, the new skeletonization algorithm could achieve a faithful estimation of the internal structure of the aggregate. Subsequently, the resulting three-dimensional skeleton would provide several new features that, once processed by machine learning algorithms, could lead to a better classification of carbon black aggregates.

Finally, we suggest the creation of a User Interface based on Augmented Reality (AR) devices to properly visualize the different layers of three-dimensional information. Furthermore, by employing a stereoscopic device (e.g. a Head-Mounted Display) the new Human-Computer Interaction model should be able to provide a higher level of depth perception, allowing the user to easily understand the structure of the carbon black aggregates (even those with complex ramifications).

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