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MORPHOLOGICAL ANALYSIS OF CARBON-POLYMER COMPOSITE MATERIALS FROM THICK SECTIONS

Laurent Savary[1,2,3], Dominique Jeulin[1,2], Alain Thorel[2]

[1]Centre de Morphologie Mathématique, Ecole des Mines de Paris,
35, rue Saint-Honoré, F-77300 Fontainebleau, France
[2]Centre des Matériaux P.M. Fourt, Ecole des Mines de Paris,
BP 87, F-91003 Evry Cedex, France
[3]Laurent Savary was killed in a road accident on August 28th 1998

ABSTRACT

Transmission electron microscopy is used for observations of nanocomposite materials. Measurements from such micrographs can be affected by a bias error due to the thickness of specimens. A method of correction of volume fraction and covariance measurements is proposed. It leads to the description of the morphology of the composite in terms of random sets.

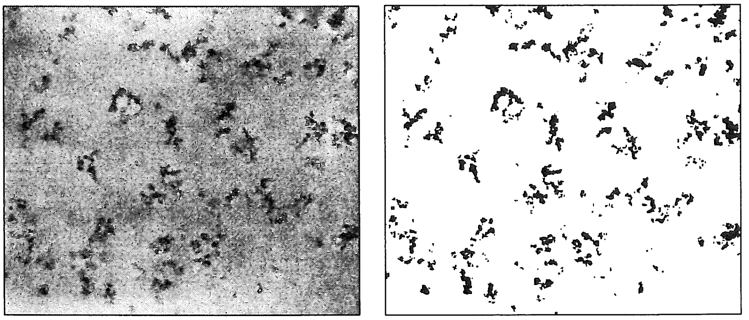
Key words: boolean model, composite material, covariance, morphology, random sets, thick section.

INTRODUCTION

The morphology of carbon polymer composites containing spheres with $38nm$ diameter (see Fig. 1a) has to be studied through transmission electron microscope observations by means of slices with a thickness close to $50nm$. To make a quantitative morphological analysis, we have first to correct measurements from the error introduced by the thickness of specimens, which cannot be neglected as compared to the size of the individual objects (a typical overestimation of 300% is achieved for an underlying volume fraction of less than 10%). A theoretical correction is proposed, assuming that the carbon aggregates builds a boolean random set. The validity of the procedure of correction is tested by means of simulations and by measurements on materials specimens. Finally, we generate simulations of 3D texture of the studied composites, starting from a random model of texture, the parameters of which being directly estimated from measurements made on thick specimens.

MATERIAL AND METHODS

The material investigated here is a carbon black (CB)/epoxy resin composite. The nom-



(a) (b)

Fig. 1. (a) TEM micrograph of the composite material; $5.0\mu m \times 4.4\mu m$. (b) resulting binary image after image analysis framework: CB particles are in black, resin matrix in white.

inal volume fraction of CB particles is 2.8%. Due to the size of the CB particles (Printex EX2, $38nm$ diameter), the composite observations were performed by transmission electron microscopy (TEM) (Philips EM 430 operating at 200 kV). Transmission microscopy requires preparation of thin sections. Sectionning was performed by a microtome at room temperature. An OmU2 Reichert-Leicart design ultramicrotome was used to obtain sections for TEM ($45 \pm 2nm$ thickness, as measured in the TEM). This thickness cannot be neglected as compared to the size of the CB particles. Therefore a correction has to be developped, based on a random set model. Seventy two TEM micrographs of the microtomed sections of the composite material were digitaly scanned. The images have a 1002×870 pixels size, and 256 grey levels (Fig. 1a). Then image analysis was performed to extract CB particles. The image analysis framework was the following : sequential alternate filter, top hat and threshold. Finally, binary images are obtained: polymer matrix in white and CB particles in black (Fig. 1b). On the binary images statistical measurements are performed (volume fraction p^*, covariance function $Q^*(h)$), and averaged over all of the images. The measured volume fraction of the studied material ($p^* = 0.0758$) has to be compared to the known value ($p = 0.028$); a theoretical correction of the overestimated value is proposed.

THEORETICAL THICKNESS CORRECTION

Principle of the thickness correction

Fortunately the handicap of working with thick sections can be overcome, at least for compact convex sets. Consider the section of a set X taken by a slice with thickness e, and the projection of this section on one of the faces of the slice, namely the plane Π. In Fig. 2 is shown that studying the projection of the thick section is equivalent to first dilate X with a segment of size e normal to the section and then studying the section of the dilate $X \oplus e$ by plane Π ($X \oplus B$ denotes the dilation of X by B). A correction can be developped, provided the volume fraction of $X \oplus e$ was calculated for the Boolean model (Miles et al., 1976; Matheron, 1976; Serra, 1982).

Thickness correction on measured volume fraction

In this section, we consider that CB particles build a boolean random set of spheres in the matrix. We call A' the spherical primary grain of radius R. The random set $A = \bigcup A'_{x_k}$ represents the CB particles with the volume fraction p, and the complementary set A^c represent the resin, with the volume fraction $q = 1 - p$. For a boolean model, q and the probability $Q(K) = P\{K \subset A^c\}$ are given by (Matheron, 1967),

$$q = \exp\left[-\theta_n.\overline{\mu}_n(A')\right] \tag{1}$$

$$Q(K) = \exp\left[-\theta_n.\overline{\mu}_n(A' \oplus \check{K})\right] \tag{2}$$

where θ_n is the Poisson density of the process in the n^{th} dimension, $\overline{\mu}_n(A')$ denotes the average Lebesgue measure of the grain A' in $\mathbb{R}^n$ (in practice, $n = 3$). On micrographs is estimated the apparent volume fraction $p^* = 1 - q^*$. Noting $A'' = A' \oplus e$, we have

$$q^* = \exp\left[-\theta_n.\overline{\mu}_n(A'')\right] \tag{3}$$

eliminating θ_n from equations (1) et (3), one gets:

$$q^* = q^{\frac{\overline{\mu}_3(A'')}{\overline{\mu}_3(A')}} \tag{4}$$

For a sphere of radius R,

$$\overline{\mu}_3(A') = \mathcal{V}(A') = \frac{4}{3}\pi R^3;\ \overline{\mu}_3(A'') = \mathcal{V}(A' \oplus e) = \frac{4}{3}\pi R^3 + e\pi R^2$$

Consequently,

$$q = q^{*\frac{1}{1+\frac{3e}{4R}}} \tag{5}$$

So, from the measured volume fraction q^*, one can estimate the real volume fraction q by a corrected volume fraction q_c (Eq. 5). This correction is subject to the assumption that the particles build a boolean model of spheres of known radius R, given the thickness e. In Fig. 3 is given the corrected volume fraction p_c depending on the measured value p^* and on the ratio e/R: the corrections due to the thickness of the microtomed section are significant. We have to point out that for a boolean model, it is theoreticaly possible to estimate the two values R and e from $Q^*(K) = Q(K \oplus e)$, using for K a segment with length l and a square with size a. Unfortunately, a small error on the two last measures involves significant instabilities on the estimated values (Savary et al., 1997). This method cannot be used in practice, and e is estimated from direct measurements.

Thickness correction on the measured covariance function

The covariance function $Q^*(h)$ is estimated from the images, starting from $K = \{x, x+h\}$ in Eq. 2. This has to be compared to the covariance $Q(h)$ of the boolean model:

$$Q(h) = \exp[-\theta_3\overline{\mu}_3(A' \oplus h)] \tag{6}$$

$$Q^*(h) = \exp[-\theta_3\overline{\mu}_3(A'' \oplus h)]$$

Table 1. Thickness correction on simulated thick sections of boolean random sets (BRS) of spheres.

Simulated Boolean Models	Parameters of the simulations	p	p^*	p_c	Relative error
BRS $n°1$	$p = 0.028$ $R = 4.5 pixels$ $e = 11 pixels$	0.0280	0.0788	0.0286	2%
BRS $n°2$	$p = 0.028$ $R = 8.5 pixels$ $e = 11 pixels$	0.0282	0.0551	0.0283	0.5%

We note $K_{A'}(h)$ the geometric covariogram of a R diameter sphere:

$$\overline{\mu}_3(A' \oplus h) = \overline{\mu}_3(A' \cup A'_h) = 2K_{A'}(0) - K_{A'}(h)$$

Since A'' is made of the union of two hemispheres and of a cylinder of radius R and of height e (Fig. 2), we have, noting $r(R,h)$ the reduced geometrical covariogram of the disk with radius R:

$$K_{A''}(h) = K_{A'}(h) + e\pi R^2 r(R,h)$$

$$r(R,h) = \frac{2}{\pi}[\arccos(\frac{h}{2R}) - \frac{h}{2R}\sqrt{1-(\frac{h}{2R})^2}] \text{ for } h \leq 2R, \text{ else } 0$$

and consequently, the covariance function $Q(h)$ can be estimated from the measured covariance $Q^*(h)$:

$$\begin{aligned} Q^*(h) &= Q(h) q^{\frac{3e}{4R}(2 - r(R,h))}, \text{ for } h < 2R \\ Q^*(h) &= Q(h) q^{\frac{3e}{2R}}, \text{ for } h \geq 2R \end{aligned} \quad (7)$$

VALIDATION AND GENERALISATION

Validation on simulations of a boolean model of spheres

In order to validate this thickness correction model, 3-D images of boolean models of spheres were generated. Parameters of the simulations are closed to experimental caracteristics of the material. Volume fraction and covariance measurements were performed on twenty images of thick sections of these simulations. Then a thickness correction is performed. Table 1 gives parameters of the simulations, the real volume fraction of simulations, p, the measured volume fraction on thick section simulations, p^*, and corrected volume fraction, p_c. The volume fraction correction is efficient; the relative error is rather low. In the same way, the correction applied to the covariance function is efficient; the corrected curves fit perfectly the theoretical ones.

Generalisation to more complex structures

These thickness corrections are tested on more complex structures. Two scale random sets are simulated ($A = A_1 \cap A_2$), in order first to describe more realistic microstructures, and to test the limits of the procedure outside the range of its elaboration. The intersection of two boolean random sets are simulated with different parameters given in Tbl. 2. The proposed thickness correction, developped for a simple boolean model, can be applied

Table 2. Thickness correction on simulated thick sections of the intersection of two boolean random sets (IBRS) of spheres.

Simulated two scale models	Parameters of the simulations	p	p^*	p_c	Relative error
IBRS $n°1$	$p_1 = 0.2$ $R_1 = 9.5 pixels$ $p_2 = 0.2$ $R_2 = 35.5 pixels$ $e = 11 pixels$	0.0420	0.0759	0.0414	1.5%
IBRS $n°2$	$p_1 = 0.2$ $R_1 = 4.5 pixels$ $p_2 = 0.2$ $R_2 = 35.5 pixels$ $e = 11 pixels$	0.0412	0.1049	0.0383	7%
IBRS $n°3$	$p_1 = 0.2$ $R_1 = 9.5 pixels$ $p_2 = 0.5$ $R_2 = 35.5 pixels$ $e = 11 pixels$	0.0990	0.1799	0.1007	1.5%

to the volume fraction in more general situations. The covariance correction cannot by applied, since its theoretical expression is unknown for multiscale models. We made the following simplification: the dilation affects only the smallest scale A_1. In that case, the measured covariance is given by:

$$Q^*(h) = 2q^* - 1 + (1 - 2q_1^* + Q_1^*(h))(1 - 2q_2 + Q_2(h)) \qquad (8)$$

with q^* , $Q^*(h)$, q_1^*, $Q_1^*(h)$, q_2 and $Q_2(h)$ deduced from Eqs 1, 3, 6 and 7. It turns out that eq. 8 gives a very good approximation of the measured volume fraction and covariance, at least when the ratio e/R remains low.

APPLICATION TO THE MORPHOLOGY OF A COMPOSITE

Application

The volume fraction correction (Eq. 5) allows us to recover the real volume fraction of the material ($p_c = 0.0280$). The experimental covariance function was compared to the covariance function of a boolean model of spheres A_1 of radius $R = 19nm$. This simple model only describes the beginning of the experimental curve. A better fit for the larger scales, is obtained from more complex models. In the first step, we introduce a second scale A_2 (a boolean model with a population of spheres), and we define $A = A_1 \cap A_2$ or $A = A_1 \cap A_2^c$. In a second step, a third scale A_3 (boolean model with a population of spheres) is added and combined in the same way to the other scales. Fig. 4 shows the comparison of the covariance function measured on the composite images with three models (Tbl. 3), obtained with the best fit. The three scale model is interpreted as follow: the first scale describes the CB particles; the second one builds the aggregates of CB; the last one describes the areas free of CB particles, and by complementarity, the aggregate network (Fig. 7).

Table 3. Description of some tested models and their fitted parameters (single radius SR, exponential law EL).

Theoretical models	Scales		Primary grains Sphere Populations		Volume fractions
Model 1	A_1		SR	$R_1 = 19nm$	$p_1 = 0.028$
Model 2	$A_1 \cap A_2^c$	A_1	SR	$R_1 = 19nm$	$p_1 = 0.368$
		A_2^c	EL	$E(R_2) = 38nm$	$q_2 = 0.105$
Model 3	$A_1 \cap A_2 \cap A_3^c$	A_1	SR	$R_1 = 19nm$	$p_1 = 0.352$
		A_2	SR	$R_2 = 60nm$	$p_2 = 0.520$
		A_3^c	EL	$E(R_3) = 65nm$	$q_3 = 0.153$

Validation of the correction from simulations

Twenty images of thick sections were simulated with model 3 parameters (see Fig. 5 and Tbl. 3). The proposed thickness correction is applied. The volume fraction is underestimated with a 10% relative error which is statistically correct owing to the number of simulated images. The covariance remains well described (Fig. 6), and the morphology of thick sections is well reproduced (compare Fig. 1b to Fig. 5).

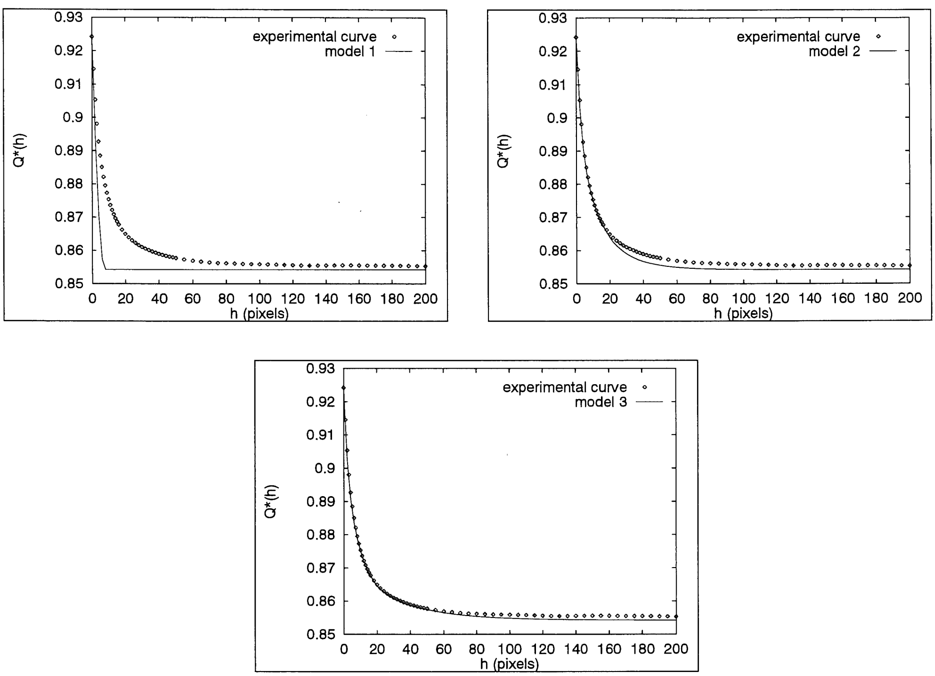


Fig. 4. Covariance function $Q^*(h)$: (◇) mesured covariance on composite binary images, (—) ajusted theoretical covariance function (see Table 3).

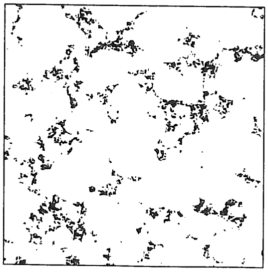


Fig. 5. Simulated thick section of model 3 (see Table 3).

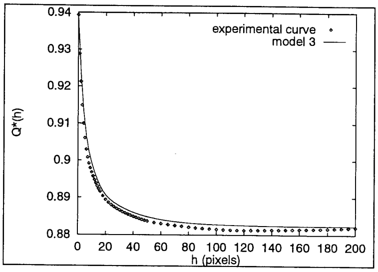


Fig. 6. Covariance function $Q^*(h)$: (⊗) mesured covariance on simulated thick sections of model 3 (Fig. 5), (—) covariance function of model 3 (see Table 3).

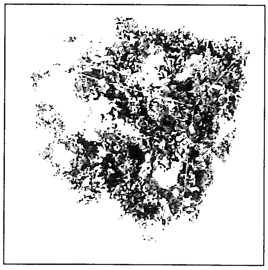


Fig. 7. Simulated 3-D image of model 3 (see Table 3).

CONCLUSION

We have proposed a theoretical procedure to overcome the handicap of working with thick sections. Based on boolean random sets, it allows us to correct measurements such as volume fraction or covariance from the error introduced by the thickness of the microtome sections. The proposed procedure can be used for more general textures than the boolean model, such as multiscale models. We applied this thickness correction to the experimental covariance of the composite material to caracterise its morphology in terms of multiscale random sets.
Modeling composite microstructures by means of random sets is a useful way to summarize microstructural information. Morphological models are available to simulate the 3D geometry of two phase composites (Fig. 7) and to predict their macroscopic physical behaviour (Jeulin and Savary, 1997).

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