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Agglomeration of solid particles

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Abstract

We characterize the fractal dimension of the projection of carbon black aggregates and carbon black aerosol clusters by image analysis of transmission electronic microscopy (TEM) and optical microscopy (OM). The results are compared to a numerical model in order to determine the real three-dimensional fractal dimension and the lower cut-off of the different fractal domains observed.

Keywords: Carbon black; Aerosol; Fractal dimension; Numerical simulation

1. Introduction

The existence of a relation between the morphology of carbon black aggregates and the physical properties of the composite materials which include them was emphasized many years ago [1,2]. Since the introduction of the fractal concept [3], a powerful tool is nowadays firmly established to characterize the structure of such kind of solid particles: the fractal dimension. This intrinsic parameter links the mass or the number N of primary particles to the size R of the fractal aggregate by the relation

$$N \sim R^D, \tag{1}$$

where D is the mass fractal dimension, which is always less than the Euclidean dimension.

The image analysis allows the treatment of those types of solids with elementary particle diameters varying in a large range, but it suffers from two limitations.

First, the determination of the fractal dimension from the projection of a three-dimensional object is only valid if the fractal dimension of this object is less than 2 [3].

Second, the determination of the fractal dimension from the projection of a three-dimensional object is only valid for an infinite object (composed of a large number of primary particles). For small aggregates, the well-known effect of "finite size" can bias the result [4].

In the present work, we determine the mass fractal dimension of two different industrial carbon blacks by image analysis of transmission electronic microscopy (TEM) and the mass fractal dimension of aerosol clusters generated with those carbon blacks by image analysis of reflexion optical microscopy (OM).

The results obtained are compared to the one obtained by a numerical model, developed by Thouy and Jullien [5] in order to determine the real three-dimensional mass fractal dimension and also the lower size of the fractal domains observed (the lower cut-off).

2. Experimental

2.1. Carbon blacks

The two carbon blacks investigated are one furnace black: Printex 60 (PX) and one gas black: Colour Black S160 (GB) from Degussa. Before use, the carbon blacks are treated under argon at 950°C for two hours. The physical properties are given in Table 1.

2.2. Aerosols

The agglomeration of the carbon blacks was performed in a vertical tube 10 cm inside diameter and 80 cm height. The sample is deposited on a sintered glass disk, welded at the bottom of the cylinder. At the top of the tube is disposed a membrane of polycarbonate with

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Table 1
Physical properties of the carbon blacks

	Printex 60	Colour Black S160
Specific surface (m^2/g)	115	150
DBP number (cm^3/g)	1.16	1.50
Density (g/cm^3)	0.23	0.12
Primary particle size (nm)	26	23
pH	9	4

calibrated pores of 1.2 μm. The aerosol is generated by a nitrogen stream through the sintered glass. The nitrogen stream goes through the membrane at the top of the cylinder while the particles are retained. The parameters, namely the nitrogen flux and the duration of the experiment are adjusted to avoid multiple collisions in the surface of the membrane, which would increase the appearing size of the collected aerosol clusters.

2.3. Image analysis

2.3.1. TEM

The carbon black samples are dispersed in toluene in three successive dilutions (100, 10 and finally 1 mg/l) and ultrasons are used to ensure a complete dispersion of the primary aggregates without secondary aggregation. A drop of the suspension is then placed on a microscope grid covered with collodion. The magnification used is ×20 K.

2.3.2. OM

The polycarbonate membrane is directly observed by reflexion OM at a magnification of ×200.

For both analysis, the negatives are converted to a 512×512 digitized image, each pixel having 256 gray levels. The gray-leveled image is transformed in a binary one on which we measured the projected surface area (S), the length (a) and width (b) of the circumscribed rectangle. The characteristic size of a carbon black aggregate or an aerosol cluster is chosen to be its geometric mean length T.

$$T = \sqrt{ab}. \tag{2}$$

It was shown [5] that no significant changes in D are expected with other convertion for the mean size $(\sqrt{a^2+b^2},\ \sqrt{ab},\ (a+b)/2)$.

The results are obtained on the analysis of 50 aggregates (resp. aerosol clusters), each object was individually treated, verifying that the contour of the binarized image coincided with the original one.

3. Results and discussion

The results obtained after the analysis of the carbon black aggregates and the aerosol clusters are reported in Figs. 1 and 2, in which we plotted in a log–log scale the projected surface area S as a function of the size T (Table 2).

The points are well fitted by a straight line, the slope of which gives the fractal dimension, following the equation

$$S = KT^D. \tag{3}$$

The present values are compared to the fractal dimensions obtained from a numerical simulation [5]. Using the "D-variable" model, we generated three-dimensional aggregates of 8–128 particles with a chosen mass fractal dimension between 1.6 and 2.0. Those aggregates were projected on a plan (Fig. 3). Their bi-dimensional fractal dimensions were then determined, using the same image analysis procedure than the experimental ones. The surface S and the size T of each simulated aggregate were normalized to the projected surface area S_0 and size T_0 of the primary particles used to generate them.

$$\frac{S}{S_0} = K'\left(\frac{T}{T_0}\right)^{D'}. \tag{4}$$

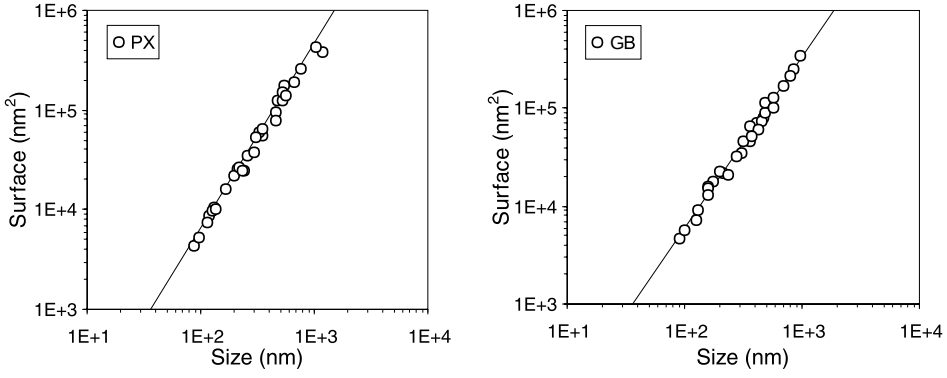

Fig. 1. Log–log plot of the projected surface area versus the size of the aggregates.

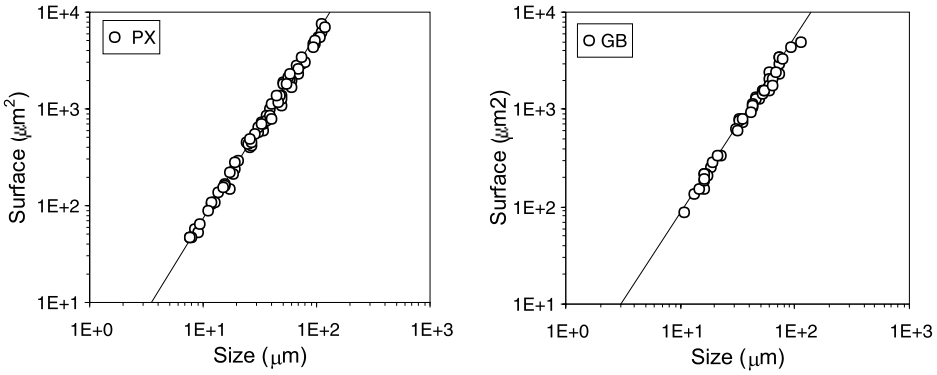

Fig. 2. Log–log plot of the projected surface area versus the size of the clusters.

Table 2
Fractal dimension of the projected carbon black aggregates and clusters

	Printex 60	Colour black S160
Aggregates	1.82 ± 0.05	1.74 ± 0.05
Aerosol clusters	1.85 ± 0.05	1.77 ± 0.05

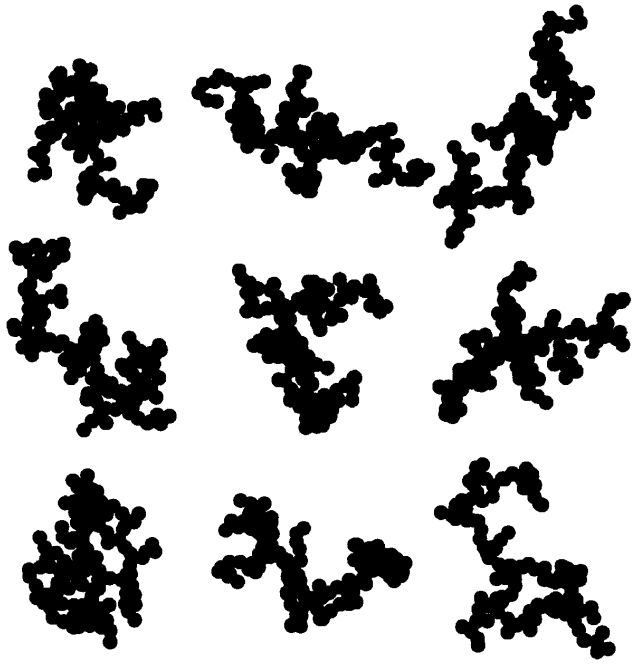

Fig. 3. 2D projections of 3D simulated aggregates ($N = 128$, $D_{3D} = 1.9$).

We could so apply the model to the carbon black aggregates (nanometric domain) and to the aerosol clusters (micrometric domain). See Table 3.

Combining Eqs. (3) and (4) and assuming that the primary particles and the agglomerates are spheres, we have calculated T_0, lower cut-off of the fractal domains observed. (Tables 4 and 5).

Table 3
Fractal dimensions of the simulated aggregates

D_{3D}	D' (± 0.02)	K'
1.6	1.67	1.16
1.7	1.66	1.15
1.8	1.70	1.10
1.9	1.74	1.04
2.0	1.77	1.01

Table 4
Simulated and experimental cut-off of the nanometric domain

	D	K	D′	K′	T_0 (nm)	Mean size (nm) MET
PX	1.82	1.42	2.0	1.01	25.4	26
GB	1.74	1.86	1.9	1.04	23.7	23

Table 5
Simulated and experimental cut-off of the micrometric domain

	D	K	D′	K′	T_0 (μm)	Mean size (μm) laser diffraction
PX	1.84	1.05	2.0	1.01	5.8	5.3
GB	1.76	1.37	1.9	1.04	8.6	7.7

The fractal dimensions calculated from the projection of the simulated three-dimensional aggregates are different from the real mass fractal dimension, even for D_{3D} less than 2. It is obvious that the direct treatment of projected fractal objects is much too sensitive to the effects of "finite size" in the range studied (aggregates of 8–128 particles). The fractal dimensions of the two carbon blacks studied are different, attesting to the two different processes employed to prepare them: furnace black and gas black. Nevertheless, the fractal dimension

of the aerosol clusters, generated by agglomeration of carbon black agglomerates, are nearly identical to the one obtained for each sample of carbon black aggregates. The property of auto-similarity is respected at the nanometric and micrometric range. The lower cut-off calculated for those two fractal domains, primary particle mean size and agglomerate mean size, are in good agreement with the experimental ones obtained by TEM and laser diffraction of carbon black agglomerates suspension.

4. Conclusion

The interesting result of this study is that the direct treatment of bi-dimensional projected fractal objects is much too sensible to the ''finite size effect''. This leads to an underestimated value of the fractal dimension, even for D lower than two. To calculate this relevant parameter unambiguously, to be able to determine the compacity of projected fractals, the use of numerical simulation is necessary.

Considering the values obtained, it is clear that the process conditions used to prepare the two carbon blacks studied have a relevant influence on their fractal dimension: the furnace black is more compact than the gas black.

The aerosol clusters formed by gas–solid dispersion and agglomeration of the two carbon blacks, exibit the same fractal structure as the aggregates. They are auto-similar from the nanometric range to the micrometric range. This result is in total agreement with the work of Sorensen and Feke on the morphology of carbon soot [6].

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