

# *In Situ* Study of the Dynamics of Erosion of Carbon Black Agglomerates

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**ABSTRACT:** With the help of a counter-rotating transparent rheometer equipped with an optical microscope, the erosion of single, commercial carbon black agglomerates suspended in a polyisobutylene fluid was accurately recorded *in situ*. We observed that clouds of very small aggregates were leaving the agglomerate at 45 and 225° in the shear gradient-flow direction plane, where the stress is maximum. The distribution of the arrached aggregates is more efficient when the carbon black agglomerate is more asymmetric. A spherical agglomerate of critical radius  $R_0$  will reach a radius  $R_t$  at time  $t$  following  $R_0^3 - R_t^3 = at$ ,  $a$  being a constant. This implies that the rate at which the number of aggregates is leaving the agglomerate is a constant, independent of the size of the agglomerate. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1627–1629, 2001

**Key words:** carbon black; dispersion; erosion; optical rheometry

## INTRODUCTION

The dispersion of carbon black agglomerates is a fundamental process during the manufacturing of reinforced elastomers. It is only recently that the mechanisms transforming a porous agglomerate into a dispersion of aggregates by the action of a flow have been identified and described. Three main mechanisms are active, rupture, erosion, and collision. Rupture occurs when the hydrodynamic stress that is imposed on the agglomerate exceeds its cohesive stress.<sup>1,2</sup> It is the most obvious dispersion mechanism and its effects are well documented, even if the calculation of the cohesive stress is not very easy. We have recently studied collision; it is an active mechanism as soon as the concentration is large.<sup>3</sup> Erosion is a much slower process than rupture that occurs at

a smaller applied hydrodynamic stress.<sup>4</sup> It consists of the removal of small particles or aggregates from the surface of the agglomerate. Erosion has been recognized quite recently, Shiga and Furuta<sup>5</sup> observing an “onion peeling” mechanism in 1985. The precise mechanisms that control erosion are not well understood.<sup>6</sup> Before the erosion mechanism was clearly recognized, Kao and Mason<sup>7</sup> observed how a spherical concentrated suspension of polymethylmethacrylate spheres dispersed into a silicone oil. They found that the rate of size decrease of their suspension followed a simple equation:

$$R_0^3 - R_t^3 = at\dot{\gamma} \quad (1)$$

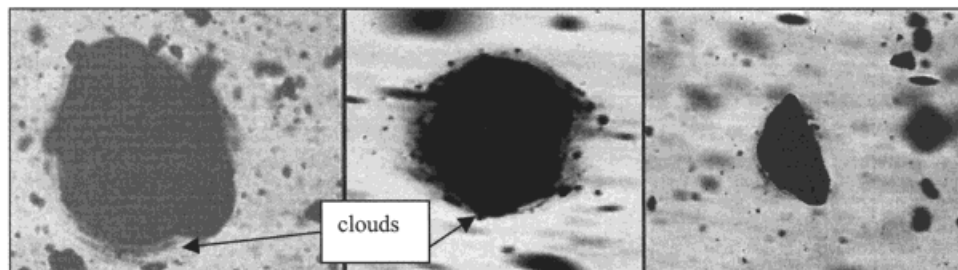
where  $R_0$  is the radius of the initial concentrated suspension,  $R_t$  is its radius at the time  $t$ , and  $a$  is a constant.

Kao and Mason<sup>7</sup> explained their results by considering that the rate of particle detachment at time  $t$  is proportional to the stress  $\eta\dot{\gamma}$  ( $\eta$  is the viscosity of the silicone oil and  $\dot{\gamma}$  is the macroscopic shear rate). Integrating this from time zero

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**Figure 1** Erosion of a carbon black agglomerate seen in the counter-rotating rheometer. The initial size of the agglomerate is about  $270\ \mu\text{m}$ .

gives the number of detached polymethylmethacrylate (PMMA) spheres which is proportional to the decrease of particle radius. This gives eq. (1), without any other assumption than that the rate of detachment is a constant. Later, Rwei et al.<sup>8</sup> studied the dispersion of large, artificially compacted carbon black and silica agglomerates in low viscosity fluids. Rupture and erosion were both present. By removing the fluids, and sedimenting the eroded particles, they were able to estimate the diameter change as a function of the dispersion time. They empirically fitted  $(R_0 - R_t)/R_0$  by a logarithm law that agreed with the result of Kao and Mason<sup>7</sup> at small dispersion times:

$$\ln(R_t/R_0) = kt\dot{\gamma} \quad (2)$$

A third law was postulated by Powell and Mason<sup>9</sup>:

$$R_0 - R_t = kt\dot{\gamma} \quad (3)$$

We recently built an optical rheometer that allows the direct observation of a single object under shear. To be able to keep this object in the field of view of the microscope, the rheometer is based on two 40-mm glass plates rotating in opposite directions. With such a counter-rotating optical rheometer, a sheared particle is fixed in the framework of the laboratory. The erosion of a single carbon black agglomerate can be studied in real time, without the need of destructive tests.

The objective of this study was to show how a carbon black agglomerate is dispersed by the erosion mechanism.

## EXPERIMENTAL

The carbon black agglomerates that were used are produced by Cabot (Boston, MA) (N134, spe-

cific area  $131\ \text{m}^2/\text{g}$ ). They have a diameter in the range of  $50\text{--}200\ \mu\text{m}$  with 70-nm aggregates. Agglomerates were suspended in a Newtonian polyisobutylene fluid of 1000 Pa.s viscosity. Very dilute suspensions were observed by optical microscopy while subjected to a shear, in the shear rate range of  $1\text{--}5\ \text{s}^{-1}$ . Owing to the use of a counter-rotating optical rheometer system described elsewhere,<sup>3</sup> it is possible to observe a single agglomerate while it is eroding, due to flow.

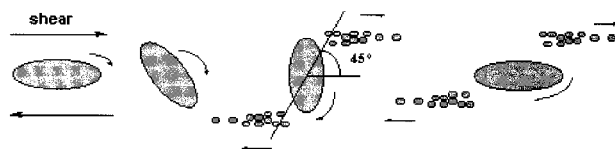
## RESULTS AND DISCUSSION

When subjected to shear, a carbon black agglomerate rotates over itself as would any similar particles. The center of mass of the agglomerate being fixed in space owing to the counter rotation of the two plates, this rotation is the only movement of the agglomerate that is observed under the microscope. The first important result that is obtained while shearing is that dark clouds are leaving the agglomerate (Fig. 1). They are the aggregates that are eroded from the agglomerate surface. Looking carefully at where it was occurring, we observed that it was happening at the angles of  $45$  and  $225^\circ$  about the flow direction plane. This is where the stress is maximum, and a similar result was obtained by Kao and Mason<sup>7</sup> for their PMMA sphere agglomerates. The detachment at  $45$  and  $225^\circ$  in the gradient-flow direction plane has an important consequence. Because of this erosion, an initially spherical particle should be gradually transformed into a particle elongated in the vorticity direction. The question is why we do not see this effect. The orientation of an asymmetrical particle in a shear is a complex matter that depends primarily on the elasticity of the matrix.<sup>10,11</sup> With polyisobutylene, we observed that elongated particles always aligned in the flow direction. As will be shown in a forthcoming report, this is due to the Newtonian character of the

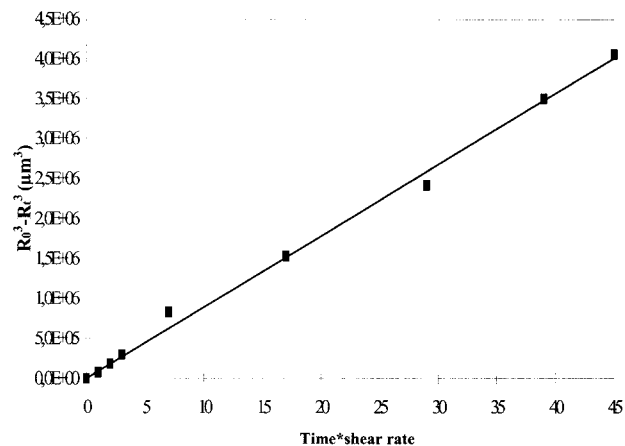
fluid. The fact that the long axis tends to align along the flow direction is probably giving a very smooth rotational movement of the particle around the gradient axis which always brings back the long axis along the flow direction and thus erodes it. This subtle drift was not possible to observe, but we noted that the agglomerates were always keeping their original spherical shapes.

We observed all sorts of initial agglomerate shapes, from nearly spherical to fairly asymmetrical. When the agglomerate was originally in the shape of an elongated ellipsoid, it was easy to observe its orientation in the flow direction. In addition, we looked at the way the detached aggregates were distributed. The more asymmetrical is the particle, the more efficient is the aggregate distribution. This has been previously noted by other authors.<sup>1,12</sup> This can be easily explained by considering the rotation of the agglomerate, as schematically drawn in Figure 2.

The erosion kinetics was studied by measuring the rate of decrease of the radius of a given spherical carbon black agglomerate. It was impossible to fit the data with eqs. (2) and (3). The result is given in Figure 3, fitted with eq. (1). The decrease of the radius is expressed as  $R_0^3 - R_t^3$ , with  $R_0$  being the initial radius and  $R_t$  the radius at a time  $t$ . It is plotted against time multiplied by shear rate. This gives a straight line with a slope of  $8 \cdot 10^4 \mu\text{m}^3$ . This slope is the constant of eq. (1), expressing how many aggregates are leaving the agglomerates as a function of shear deformation. In this constant are obviously hidden two parameters, the local external stress which is the active mechanism of detachment (this must be proportional to  $\eta\dot{\gamma}$ ) and the cohesive stress that is keeping the aggregates glued to the agglomerate. In absence of a more refined model, these stresses are difficult to estimate. The fact that eq. (1) is



**Figure 2** Schematic illustration of the distribution of the eroded parts of an elongated particle. When the long axis of the particle is lying along the flow direction, the eroded parts are far from it in the gradient direction, and have thus a large relative velocity compared with the particle. This pulls apart the eroded fragments from the particle and increases the distribution efficiency.



**Figure 3** Dynamics of the erosion of a carbon black agglomerate at a shear rate of  $1 \text{ s}^{-1}$ . Plot of  $R_0^3 - R_t^3$  as a function of time multiplied by shear rate.  $R_0$  is the initial radius ( $162 \mu\text{m}$ ).  $R_t$  is its radius at time  $t$ .

valid for describing the erosion of carbon black agglomerates is an important step to further understand the erosion mechanisms.

## CONCLUSION

The use of counter-rotating transparent devices should allow precise visualization of dispersion mechanisms in agglomerates. The observation of how these agglomerates are behaving in shear as a function of parameters like impregnation or agglomerate structure can help to optimize or devise better dispersion techniques.

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