DISTRIBUTIONAL ANALYSIS OF CARBON BLACK AGGREGATE ANISOMETRY

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I. INTRODUCTION

Carbon black aggregate structure affects many of the properties of its end-use compounds. For example, raising bulk aggregate structure level generally increases modulus, tensile strength, and electrical conductivity of carbon black-containing polymer materials. Bulk aggregate size is typically measured using the dibutyl phthalate absorption (DBPA) technique, which yields the volume (cm$^3$) of DBP oil required to fill the three-dimensional (3D) voids between the branches of the aggregates in 100 grams of carbon black.

The 3D structures of individual carbon black aggregates have recently been determined$^5$ by acquiring multiple aggregate projections at different orientations and applying a reconstruction technique to calculate the three-dimensional distribution of mass in the aggregate. This and other 3D-based techniques$^6$ have been used to show that individual aggregates can be quite anisometric, with their longest dimensions generally aligned with the plane of the TEM sample grid. In this study, a TEM-based technique was used to reconstruct the particle positions in aggregates of three different shape types - ellipsoidal, linear, and branched - as defined by Herd et al.$^8$

Aggregate specific measurements using TEM with automated image analysis (TEM/AIA)$^9$ yield detailed information on aggregate structure and enable the assessment of size and shape distributional properties of entire aggregate populations. The TEM/AIA technique has been extended in this study by measuring aggregate populations at three different goniometer angles, allowing the determination of distributional aggregate anisometry via the analysis of changes in morphological size and shape parameters with rotation.

II. EXPERIMENTAL

Aggregates of the three shape types mentioned above were imaged in the TEM at multiple goniometer angles. The positions of particle projections were noted and correlated, and this data was input to the reconstruction algorithm. Visualization and image analysis software was subsequently used to interactively view and measure the 3D aggregate model at any desired projection angle.

The TEM/AIA method was used to measure aggregate size and shape distributional properties of 2000 aggregates of each of seven furnace carbon black grades at three goniometer angles (0° and ±45°). These grades differ widely in structure level within each of two mean particle size ranges (N300 and N600 series).

III. RESULTS

Figure 1 depicts three TEM projections of a very high structure carbon black aggregate. The nearly spherical particles are seen to be extensively coalesced into a tortuous, branched structure, which exhibits different projected properties at each angle. Figure 2 depicts projections of the aggregate model reconstructed using an algorithm similar to that previously described elsewhere$^9$. The model projections duplicate the TEM aggregate projections at the same angles, and display a very different structure at the ±90° orientations, which are unreachable using conventional goniometer-based techniques. The breadth of the aggregate perpendicular to the plane of the sample grid can be seen to be much less than in the direction parallel to that plane.

Figure 3 shows aggregate area data for the actual TEM and model projections. These two curves agree very well, which reinforces the accuracy of the model in reproducing the true aggregate structure. In addition, they show the extreme change in projected area (approaching 40%) near ±90°. Similar anisometry was also observed in other spatially reconstructed aggregates.

Many morphological parameters were calculated from the basic measurements acquired via TEM/AIA. Selected data are given in Figures 4 and 5. The ±45° data have been averaged in each graph. Figure 4 displays the dependence of change in average length (maximum Feret diameter) and perimeter of aggregate projections upon rotation versus DBPA for all seven carbon black grades studied. Linear trends are observed, with higher structure grades exhibiting more anisometry (larger changes with rotation). Figure 5 depicts the weighted average values of the non-dimensional shape parameters $V'/V$ (aggregate absorptivity index, which correlates linearly with DBPA) and $P^2/4mA$ (roundness), measured at 0 and ±45°, as a function of DBPA for all grades. Linear relationships are again observed. The degree of change of these shape parameters with rotation may be inferred from the graphs.

IV. SUMMARY AND CONCLUSIONS

A methodology for the determination of anisometry in populations of nanoscale colloidal materials has been demonstrated. Carbon black aggregate anisometry was quantified in individual aggregates, thereby confirming previous and current work in this area. Anisometry was demonstrated in carbon black aggregate populations for the first time, with anisometry found to correlate approximately linearly with aggregate structure level. These findings raise questions about aggregate formation processes and the possibility of preferential aggregate orientation in carbon black-containing compounds.
REFERENCES