Study of Particle Aggregation in Organic Pigments and Polymer Composites

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Introduction, Methods, and Materials

Generally primary particles with nearly spherical shapes aggregate into quasi-fractal structures. Their fractal nature is often described by a scaling law that relates the aggregate mass M to the aggregate's radius of gyration R_g, that is, $M \propto R_g^{d_f}$, where d_f is the quasi-fractal dimension. Organic pigments have a rod-shaped primary particle shape and hence have rarely been found to form fractal structures. But it is the particle size and structural properties (such as mass and surface properties) of the primary particles or the aggregates and agglomerates that affect optical properties (such as the color and brightness) of pigments consisting of aggregate particles that range from 0.02 to 0.5 μm in size. Past studies have indicated that there may be a parallel morphological basis between the largely crystalline colloidal pigment particles and inorganic pigment materials. Usually a 2-D approach like microscopy is taken to evaluate the nature of fractal surfaces and substance. But there is a limitation to the accuracy of this procedure: While studying the surfaces in two dimensions, it is mostly the 2-D projection or a 2-D cross-sectional slice of a 3-D object that is actually examined. This difficulty was overcome by using small-angle x-ray scattering (SAXS) for the analysis of pigment particles.

Extremely small particles, about 100 nm in size, are seen to be present in large clusters. These clusters may be 1 to 2 μm in size and may contain about 10 to 1,000 particles each. In the physical sciences, these basic particles are known as primary particles, while the clusters are known as aggregates. Aggregation in colloidal systems has been studied for many years and is of great interest to various commercial industries. An important part of this study is the aggregation seen in organic pigments. It has been known since their discovery that organic pigments are present as aggregates of primary particles. The cause of aggregation, however, is a source of considerable debate. Some studies [1, 2] indicate that the aggregation in organic pigments is due to the surface roughness of the primary particles. The aggregates formed were reported to be surface fractal in nature, caused by the irregular surface. But there is evidence contradicting these findings; it suggests that the primary particles have a smooth surface and form mass fractal aggregates [3]. These aggregates are of two types: diffusion-limited and reaction-limited. The diffusion-limited aggregates have a fractal dimension of around 1.8, while those formed by reaction-limited aggregation have a fractal dimension of about 2.5.

Chemical groups, which display color because of selective absorption of visible light, are called chromophores. Groups that intensify or modify color are known as auxochromes. But because of the extremely small primary particle size of organic pigments, the perceived color of a pigmented material is determined not only by the pigment's chemical constitution but also by the size and shape of the pigment crystals. Also, because of their smaller size, pigment crystals have a marked tendency to cluster into aggregates. In the powder form, the organic pigments are generally made up of aggregates and agglomerates of fine crystalline particles. Aggregation in organic pigments is caused by fairly weak forces like van der Waals forces of attraction, forces arising from polar functional groups, surface-energy-driven forces, and static charge instead of chemical bonding between the primary particles. Because of this situation, it is possible to physically break up these aggregates easily while processing or by adding foreign agents like surfactants, additives, and other agents, which reduce surface energy.

Previous studies have taken into account only the aggregation caused by irregular, rough surfaces. They fail to explain how pigment particles having a smooth surface form aggregates. Previous studies have suggested that the organic pigment particles have rough surfaces, which cause them to aggregate. But our study clearly indicates that the organic pigment particles are smooth. This is evident from the SAXS scattering patterns. These patterns show a line having a slope of –4, corresponding to the Porod's law. We studied organic pigments produced by Sun Chemical Corporation and give results for selected pigments [4]. The pigments were mixed into polymers like PP, PMMA, and PE and were tested at the UNI-CAT beamline at APS.

Results and Discussion

Quinacridone pigments Red 122 and Violet 19 showed diffusion-limited aggregation. Here we discuss the results of Pigment Violet 19 only (Fig. 1). The primary particle of PV 19 is about 0.05 μm in size. It forms aggregates 0.5 μm in size. The data from the SAXS overestimated the size of the aggregate. This is because we assume that

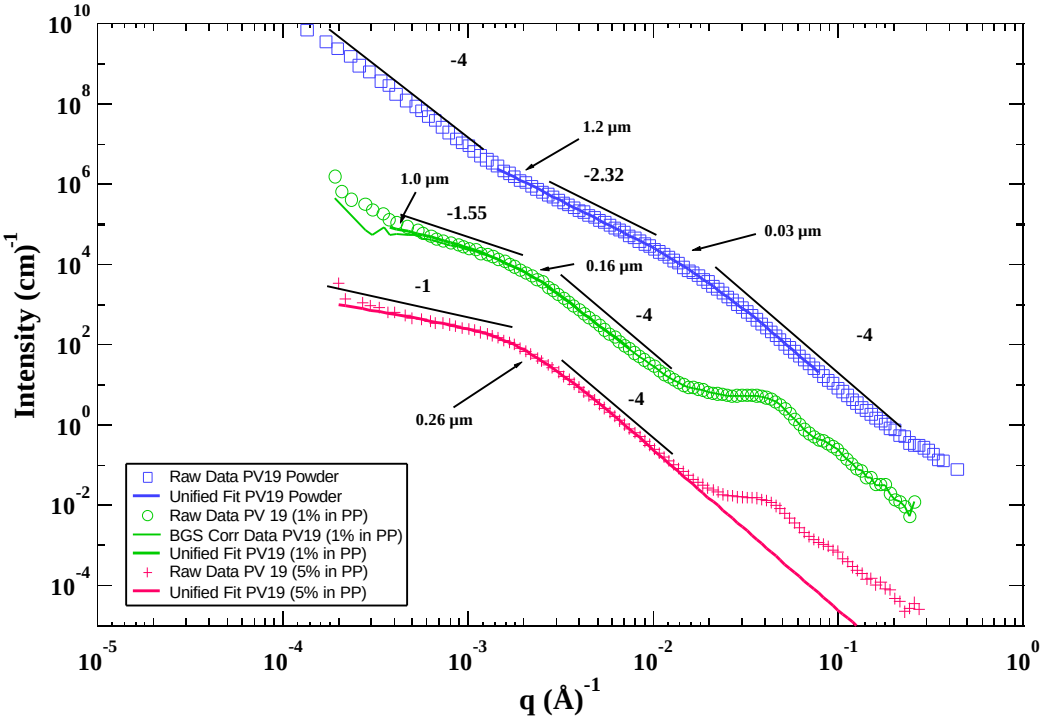

FIG. 1. Ultrasmall-angle x-ray scattering (USAXS) pattern for Pigment Violet 19.

the particle is spherical in shape, but it could be seen from the transmission electron microscopy (TEM) images that the shape of the particle is almost ellipsoidal. The powder aggregates form a mass fractal structure with a fractal dimension of 2.32. They show reaction-limited aggregation, forming big aggregates 1.2 µm in size. The primary particle of the pigment increases when mixed into the polymer. The 1% sample shows a primary particle that is 0.16 µm in size, while at a concentration of 5%, the primary particle is 0.26 µm in size. The aggregates in the 1% sample are 1.0 µm in size. The processing has an important effect on the formation of the aggregates. The fractal dimension of the aggregates is seen to decrease from 2.32 for powders to 1.55 for the 1% sample to 1.00 for the 5% sample. It is possible that the primary particles rearrange themselves to form rod-shaped structures. This might be the effect of the shear force exerted during preparation of the sample. The shear might also cause removal of the branches of the aggregates. The values for the fractal dimensions indicate that the dominant aggregation process in powders is reaction-limited aggregation, because the pigment particles do not react with each other while aggregating. In polymers, the aggregation is diffusion-limited because of the high viscosity of the polymer, which controls the probability of contact of primaries.

Pigment Red 122 had non-mass-fractal aggregates in the dry pigment powder, while, when mixed into PP, it showed mass fractal structures of dimension 1.91 at 1% and dimension 1.5 at 5% pigment concentration. The primary particle size was 0.13 µm.

Pigments of the disazo type, Pigment Yellow 13 and Yellow 14, formed reaction-limited mass fractal aggregates. We give here the details for Pigment Yellow 13 (Fig. 2).

The data obtained from TEM, LS, and SAXS show that the primary particle ranges from 0.05 to 0.1 µm in size and has a smooth surface. The TEM images of the powder indicated that the shape of the individual primary particle is not perfectly spherical, which supported the SAXS data. The aggregates are between 0.5 to 0.75 µm in size. But the absence of oscillations in the scattered intensity indicated a wide distribution of particle sizes; i.e., the particles are asymmetric of various sizes. The powder has a mass fractal structure because of the aggregation of the primary particles. The fractal dimension of 2.34 means that the aggregates are formed as the result of a reaction-limited process. In the polymer, the pigment forms aggregates that are slightly larger than those in the powder, with the aggregate size changing from 0.32 to 0.49 µm. As expected, there is no appreciable change in the size of the primary particle, because the particles do not react with each other to form a chemical bond but stick to each other only because of van der Waals forces. The pigment forms a mass fractal structure in the polymer, d_f = 2.7. The increase in dimension means that there may be branching of aggregates.

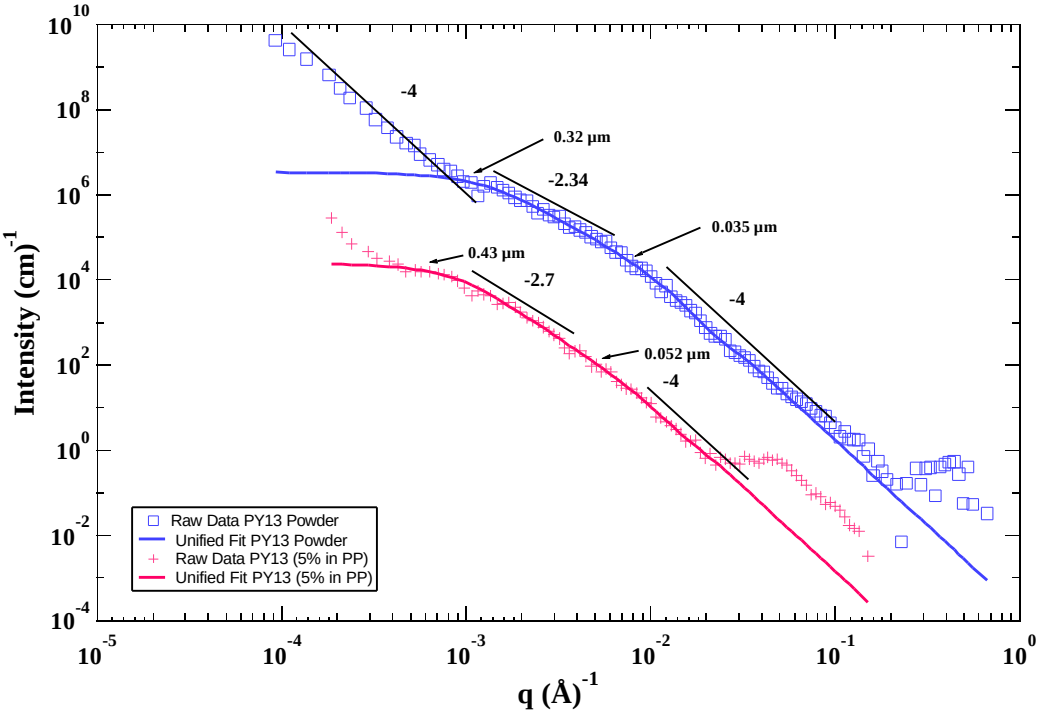

FIG. 2. USAXS pattern for Pigment Yellow 13.

Pigment Yellow 14 has a primary particle 0.1 µm in size, while the aggregates are 0.5 µm in size. It also exhibited mass fractal behavior with fractal dimension of 2.63 in dry powder and 2.77 when mixed into PP at a 5% concentration.

Acknowledgments

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