Mass-fractal nature of organic pigments

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Introduction

Mass fractal structures have been proposed for a variety of inorganic pigment materials, such as titanium oxide and fumed silica [1]. Organic pigments have rarely been considered in this context, although recent studies indicate that there may be a parallel morphological basis to these largely crystalline colloidal species [2]. We have recently completed a study at the UNI-CAT beamline using a unique small-angle x-ray scattering camera that targets the morphological scaling features of such colloidal scale structures. Two red pigments were used in this study, both of which are the C. I. Pigment Red 170 type. This is a non-toxic commercial grade of red pigment widely used to color plastics red. We found that in the powder state the particles are largely non-aggregated. However, when processed in a plastic part (polymethylmethacrylate or PMMA) a high degree of aggregation occurred (400 to 1000 primary particles per aggregate) with strong indications of a mass-fractal character. Importantly, it is not possible to sort out either the details of such pigment structures or their importance to coloring applications using conventional analytic techniques [e.g., high-resolution scanning electron microscopy (SEM) or light scattering] due to the high degree of overlap of structure and the sample preparation techniques necessary for such studies.

Methods and Materials

Two samples of C. I. Pigment Red 170 were prepared as nontoxic neat organic powders and at a 20% loading in PMMA of moderate molecular weight. The polymer sample was mixed in a 50 gram Brabender mixer and pressed to about 1 mm thickness in a Carver press at about 150°C for less than one minute. The dry powders were sprinkled on scotch tape in as close to a thin monolayer as was possible. The powder samples had a compacted density of 1.43 g/cc and a crystalline density of about 2.5 g/cc. The specific surface area of the powders was about 15 m^2/g for both. Figure 1 shows two typical SEM micrographs of the powders prior to milling them into the polymer.
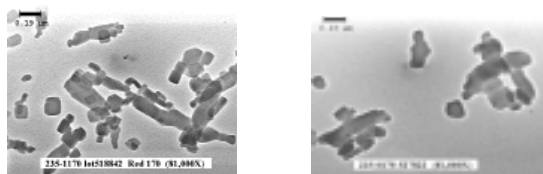

Figure 1: Micrographs of samples 1170 and 0170 Red Pigments.

Sample 1170 appeared very similar to 0170 as a powder. However, after being milled into PMMA and pressed, there was a noticeable and unexplained deeper red tint to the 1170 sample.

Results

Figures 2 and 3 show the ultra-small-angle x-ray scattering (USAXS) results from the two red pigments.
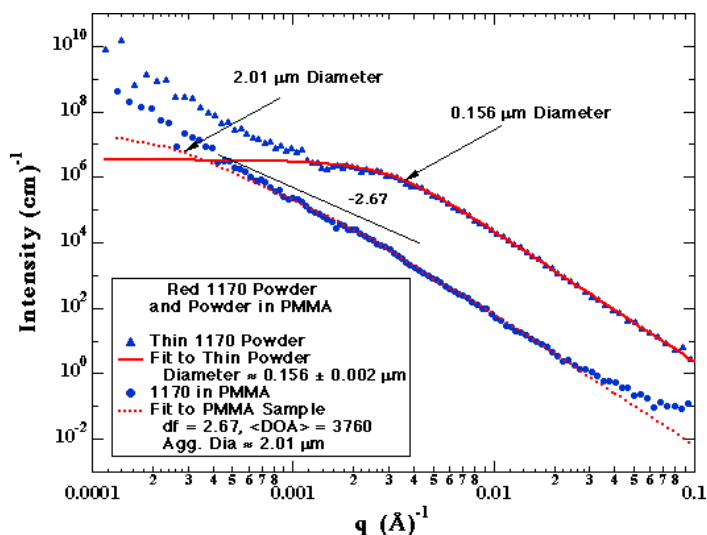

Figure 2: Scattering from 1170 powder and milled with PMMA with unified fits [1, 3, 4].
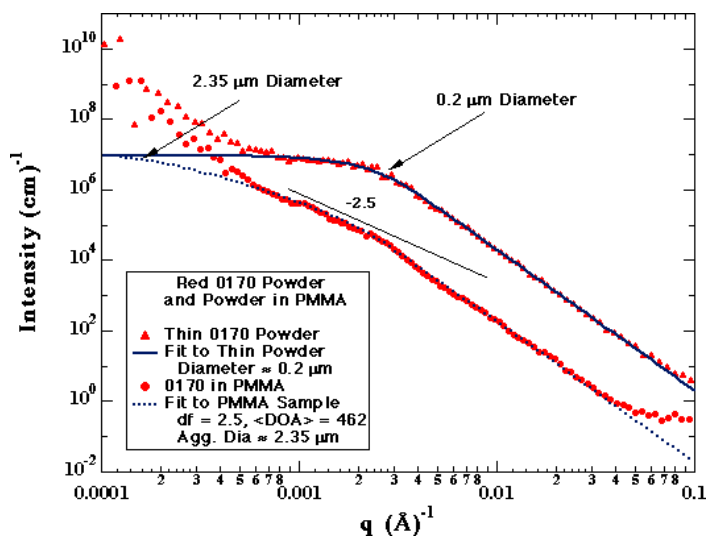

Figure 3: Scattering from 0170 powder and milled with polymer with unified fits [1, 3, 4].

In both cases (Figures 2 and 3), the dry powders display essentially non-mass-fractal scattering curves. The absence of a drop in the curve as it approaches the Porod regime indicates that the surface area is much higher than what is expected from spherical particles (i.e., that these are asymmetric particles as supported by the micrographs of Figure 1). The -2.5 slope (d_f = 2.5) in Figure 3 and the -2.67 slope in Figure 2 strongly support a mass-fractal aggregate model for the pigments when milled in polymer. We can propose a reaction-limited cluster-cluster growth process from these values [5]. From the fits to the data the number of primary particles in an aggregate (degree of aggregation) can also be estimated as indicated in the caption. The caption also reports the estimated diameter of an equivalent sphere from the radius of gyrations $D \approx 2.6\ R_g$. This is used as a rough indication of size comparisons with micrographs. All of the reported values agree with the SEM and TEM (transmission electron microscope) evidence available from Sun Chemicals. The surface area from the dry powder scattering data is 91 m^2/cm^3 and 63 m^2/cm^3 for the 1170 and 0170 powders, respectively. These values roughly agree with the values obtained by gas absorption and BET analysis.

Discussion

The colloidal scale structure of organic pigments can be elucidated using the unique USAXS camera developed by the National Institute of Standards and Technology (NIST) group on the UNI-CAT beamline at the APS. The information obtained is extremely useful in providing a morphological basis for industrially important features of organic pigments. For two red pigments that appear to be similar in SEM micrographs of dry powders and in USAXS patterns from the dry powders, dramatic differences in the mass-fractal dimension and degree of aggregation are observed that correlate well with industrial color comparisons and with visual observations of the pigments milled with polymers. We believe that there is a direct relationship between the coloring behavior of these pigments and the mass-fractal structure. Through our collaboration with NIST, UNI-CAT, and Sun Chemicals, we are pursuing these studies to understand the physical basis of color in organic pigments.

Acknowledgments

References

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