Relation of the fractal structure of organic pigments to their performance

G. Skillas^{a)} Inst. f. Verfahrenstechnik, ETH Zentrum ML F24, CH-8092 Zurich, Switzerland

N. Agashe and D. J. Kohls Department of Material Science, University of Cincinnati, Cincinnati, Ohio 45221-0012

J. llavsky University of Maryland, College Park, Maryland 20742

P. Jemian University of Illinois at Urbana-Champaign, Illinois 61820

L. Clapp and R. J. Schwartz Colors Group, Sun Chemical Corporation, Cincinnati, Ohio 45232

G. Beaucage

Department of Material Science, University of Cincinnati, Cincinnati, Ohio 45221-0012

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Different pigments embedded in polymer matrices were examined by small angle scattering of x-rays over 3 wave number decades. The scattering intensities show differences both in the mass fractal dimension (varying between 1.4 and 2.67) and the size of the particles. The differences are pronounced between dry pigment powders and the same powders in a polymer matrix as well as between the pigments themselves. Further, a correlation of pigment geometrical configuration and pigment performance, as perceived by the human eye, shows how pigments with a maximum color brightness per pigment mass can be created. © 2002 American Institute of Physics. [DOI: 10.1063/1.1466524]

I. INTRODUCTION

Mass fractal structures have been proposed for a variety of materials which are used as inorganic pigments, such as titanium dioxide, fumed silica,¹ carbon black and soot.² Generally, primary particles with nearly spherical shape aggregate into quasifractal structures. Their fractal nature is often described by a scaling law, relating the aggregate mass M to the aggregate's radius of gyration R_g , $M \propto R_g^{d_f}$ where d_f is the quasifractal dimension. Organic pigments have rarely been considered in this context. However, optical properties such as the color and brightness of pigments consisting of aggregate particles in the range 0.02–0.5 μ m are intimately connected to the volume and volume structure of the pigment aggregate particles. In some cases an approach measuring the surface fractal properties of organic pigment particles was followed.³ Recent studies indicate that there may be a parallel morphological basis between the largely crystalline colloidal pigment particles⁴ and inorganic pigment materials. In order to overcome inherent limitations of two-dimensional techniques as, for example, various microscopy methods which usually yield correlations pertaining to the particle surface geometry, the pigment samples are analyzed by small angle x-ray scattering (SAXS).

II. METHODS AND MATERIALS

Three different pigments manufactured by the Colors Group, a division of Sun Chemical Corporation, are analyzed. In all cases both the pigment powder and the same powder mixed into a polymer matrix are analyzed. Two of the pigments are C.I. Pigment Red 170, 235-0170 and 235-1170. The difference between the two samples being the different size distributions of the pigment particles. The third sample is L64-3107, C.I. Pigment Green 7.

The two red pigments are embedded into poly(methylmethacrylate) (PMMA) of moderate molecular weight. Prior to mixing the PMMA is dried in an oven at 80 °C for 6 h. The polymer sample (20% pigment powder and 80% PMMA) is mixed in a tumble mixer for 1800 s. It is then added to the hopper of a twin-screw extruder reaching a maximum temperature of 230 °C. After extrusion, the PMMA dispersion is pelletized and then molded. The molding is done at 230 °C at 2000 psi. The resulting samples have a thickness of 1 mm. The heat stability of the red pigments is based on low-density polyethylene measurements, at low pigment loadings (<5%). The lowest maximum temperature measured for the pigments is 260 °C, while heating for 300 s. At that temperature the first measurable deterioration of the pigment occurred. So the process of extrusion and molding will not change the pigments chemically, as the process temperature chosen is lower than 260 °C.

For the green pigment (L64-3107), polyethylene (PE) is used as the matrix polymer, and the loading is 50%. Preparing the powder pigment samples for the small angle scatter-

^{a)}Present address: Degussa AG/VT-C, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang, Germany; electronic mail: skillas@ivuk.mavt.ethz.ch

ing analysis involves sprinkling a quantity of the powder on scotch tape. Care is taken to produce a layer as thin as possible.

The ultrasmall angle x-ray scattering measurements (US-AXS) are performed at the APS UNICAT beam line using a Bonse–Hart camera. The Bonse–Hart camera covers a q range from 10^6 m^{-1} or 10^{-4} Å^{-1} to about 10^9 m^{-1} or 10^{-1} Å^{-1} . The wave number q is defined as the magnitude of the wave number vector

$$q = |\mathbf{q}| = \frac{4\pi \sin(\theta/2)}{\lambda}.$$
 (1)

In Eq. (1), λ is the wavelength of the incident photons, while θ is the angle between the direction of the photon incident on the sample and the direction of the scattered photon. The data is de-smeared to be comparable to the SAXS data gathered with a pinhole camera at the University of Cincinnati. The q range covered by the pinhole camera is from 6 $\times 10^7 \,\mathrm{m}^{-1}$ or $6 \times 10^{-3} \,\mathrm{\AA}^{-1}$ to $10^9 \,\mathrm{m}^{-1}$ or $10^{-1} \,\mathrm{\AA}^{-1}$. The SAXS data presented are corrected for background radiation using standard correction procedures. Specifically, each Bonse-Hart measurement involves subtraction of a background run from the sample run. At low q, near to the main beam the intensities become nearly identical, after correction for transmission $(\lim_{q\to 0} \Delta I(q)/I(q) \rightarrow 0)$, and the error becomes large. All of the runs were corrected for background (scattering of the tape) prior to de-smearing. In the case of the pinhole camera each measurement involves a correction for the variation in detector pixel sensitivity as well as dark current and background subtraction. The data are then analyzed using a unified fit approach.^{5,6} From the transmission electron microscopy (TEM) images (Fig. 1) a two level structure can be seen, the first level being the primary pigment-crystal particles and the second organizational level being the aggregates formed by the primary particles. Both levels can be described in a similar way by a Guinier regime reflecting the characteristic radius R_g of the objects in this level followed by a power-law regime which describes the type of structures to which the Guinier regime pertains. The characteristic length R_g is defined as the radius of a sphere with the same mass and the same moment of inertia as the object under consideration.

$$R_g = \sqrt{\frac{\int \rho R^2 dV}{\int \rho dV}},\tag{2}$$

where ρ is the local powder electron density in the case of SAXS, V the object volume, and R the distance of the volume element dV from the center of mass of the object. Thus the intensity function can be approximated by^{5,6}



FIG. 1. TEM micrographs of samples 235-0170 (top), 235-1170 (middle) and L64-3107 (bottom). It can be seen that the size distributions of the two red pigments (samples 235-0170 and 235-1170) differ, while they are clearly larger than green pigment particles (L64-3107). The particles are nonspherical, in fact they can be approximated as rods.

$$I(q) = G_{2} \exp\left(-\frac{q^{2}R_{g2}^{2}}{3}\right) + B_{2} \exp\left(-\frac{q^{2}R_{g1}^{2}}{3}\right)$$

$$\times \left(\frac{\operatorname{erf}^{3}\left(\frac{qR_{g2}}{\sqrt{6}}\right)}{q}\right)^{p_{2}} + G_{1} \exp\left(-\frac{q^{2}R_{g1}^{2}}{3}\right)$$

$$+ B_{1} \exp\left(-\frac{q^{2}R_{g0}^{2}}{3}\right) \left(\frac{\operatorname{erf}^{3}\left(\frac{qR_{g1}}{\sqrt{6}}\right)}{q}\right)^{p_{1}}, \quad (3)$$

$$B_i = \frac{2G_i}{R_{gi}^2} \quad (i = 1, 2). \tag{4}$$

In our case $R_{g0}=0$, $p_1=4$ while B_1 and R_{g1} are fit parameters for the Porod regime, while B_2 , p_2 , and R_{g2} describe the mass-fractal behavior of the aggregates.

For the physical characterization of the samples the Brunauer-Emmett-Teller (BET) surface area, pigment chemical compound density (by helium pycnometry), and

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FIG. 2. Scattering from the 235-1170 sample as a powder and embedded in a PMMA matrix. The size distribution of the powder changes when it is mixed into the PMMA matrix. The solid curves shown are unified fits (see Refs. 1, 5, 6) performed on the data. The slope of the I(q) curve of the powder in PMMA displays a mass fractal behavior $(d_f=2.67)$ showing a rather compact structure, while at higher q a typical q^{-4} power law can be seen. The fit suggests that the average primary particle diameter, based on the radius of gyration, is $0.156\pm0.005 \ \mu$ m for the dry powder, while the powder in PMMA shows a characteristic length scale of D=2.01 $\pm 0.05 \ \mu$ m. The intensity slope of -4 suggests that the particle surface is smooth and sharply defined when measured on a scale corresponding to the q value at that point.

compacted powder density are measured. The procedure for measuring the compacted powder density is as follows: The powder is weighed and filled into a graduated glass cylinder. This cylinder is subjected to vibrations for 60 s. The compacted powder density is computed upon dividing the powder weight by the powder volume after vibrations. For the 235-1170 pigment the compacted powder density is 603 ± 25 kg m⁻³ and for the 235-0170 it is 416±10 kg m⁻³. The pigment chemical compound density is 1350 ± 10 kg m⁻³ for samples 235-1170 and 235-0170. BET analysis shows that the surface area is 15 $m^2 g^{-1}$ for sample 235-1170 and 14 $m^2 g^{-1}$ for sample 235-0170. In Fig. 1, typical TEM micrographs of the powders, prior to milling into the polymer, can be seen. The sample of the green pigment (L64-3107) shows a compacted powder density of 487 ± 30 kg m⁻³ and a chemical compound density of 2270±16 kg m⁻³. BET analysis shows that its surface area is $64 \text{ m}^2 \text{g}^{-1}$.

III. RESULTS

Figures 2–4 show USAXS and SAXS results for the three pigments. In all three cases the dry powders display essentially nonmass-fractal scattering curves. The absence of a drop in the curve as it approaches the Porod regime indicates that the surface area is higher than what is expected for spherical particles, consistent with the micrographs. Further, the absence of oscillations in the scattered intensity indicates a wide distribution of particle sizes, i.e., the particles are asymmetric of various sizes, as supported by the micrographs in Fig. 1. In the case of the embedded pigments two groups are formed. The red pigments seem to form mass-fractal aggregates when milled into the polymer matrix. This is suggested by the -2.5 slope ($d_f = 2.5$) in Fig. 3 and the



FIG. 3. Scattering from the 235-0170 sample as a powder and embedded in a PMMA matrix. The size distribution of the powder changes when it is mixed into the PMMA matrix. The solid curves shown are unified fits (see Refs. 1, 5, 6) performed on the data. The slope of the I(q) curve of the powder in PMMA displays a mass-fractal behavior (d_f =2.50) while at higher q a typical q^{-4} power law can be seen. The fit suggests that the average aggregate diameter, based on the radius of gyration, is 0.200±0.005 μ m for the dry powder, while the powder in PMMA shows a characteristic length scale of D=2.35±0.04 μ m, respectively. The intensity slope of -4 suggests that the particle surface is smooth and sharply defined when measured on a scale corresponding to the q value at that point.

-2.67 slope ($d_f = 2.67$) in Fig. 2. As the pigment particles do not easily bond with one another, the process leading to the observed mass-fractal dimensions can be seen as a combination of reaction limited monomer-cluster and cluster– cluster aggregation.⁷ Fitting the data allows for both the number of primary particles in an aggregate and the degree of aggregation to be estimated, as indicated in the figure



FIG. 4. Scattering from the L64-3107 sample as a powder (SAXS) and embedded in a PE matrix (USAXS). The size distribution of the powder changes only slightly when it is mixed into the PE matrix. The solid line curves shown are unified fits (see Refs. 1, 5, 6) performed on the data. The wealth of datapoints permits the inclusion of the low-*q* range in the fit. The slope of the I(q) curve of the embedded powders displays a mass-fractal behavior (d_f =1.4), and the fit suggests that the average aggregate dimension is D=0.767±0.005 μ m. At higher *q* a typical q^{-4} power law can be seen. The primary particle size of dry powder particles is 18.6±0.5 nm, while 36.5±0.3 nm is the primary particle size of the embedded powder, suggesting a more compact pigment particle structure in the PE matrix.

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caption. The estimated diameter *D* is the diameter of a volume equivalent sphere calculated from the radius of gyration $D \approx 2.6R_g$, which we use as an indicator for size comparisons with micrographs. All of the reported values agree with the TEM evidence available for the pigments. The specific surface area (SSA) from the dry powder scattering data is calculated by evaluating

$$\frac{S}{V} = \frac{q^4 I(q)}{2\pi Q},\tag{5}$$

$$Q = \frac{1}{2\pi^2 \phi(1-\phi)} \int_0^\infty q^2 I(q) dq.$$
 (6)

In Eq. (5), S and V are the surface and the volume of pigment particles probed at a wave number q in the Porod regime. The probing wave number q is smaller than, or equal to, the wave number corresponding to the characteristic length of a nitrogen molecule, so the value of S/V should correlate with gas adsorption measurements. The term ϕ is the pigment volume fraction, computed from the compacted pigment powder density and the pigment chemical compound density. The determination of the former is described in Sec. II, while the latter is measured by helium pycnometry. The massfractal structural model indicates that the surface area should be calculated from the scattering for the primary particles. This has been empirically demonstrated for inorganic massfractal structures.⁶ As a consequence, in Eq. (6) Q can be determined using the fit to the first structural level only. The dry powder surface area is 90 and 63 $m^2 cm^{-3}$ for the 235-1170 and 235-0170 powders, respectively. For the green pigment the specific surface area from the dry powder scattering data is $324 \text{ m}^2 \text{ cm}^{-3}$. The main error source stems from the limited accuracy with which the volume fraction ϕ can be determined by measuring it experimentally. To meaningfully compare the BET data with the Porod data the BET SSA (measured in m^2/g) has to be multiplied with the compacted powder density, $ho_{
m powder}$. Taking the ratio of $(SSA_{BET}*\rho_{powder})/SSA_{Porod}$ yields 0.0896, 0.0901, and 0.0962 for the red pigments (235-1170, 235-0170) and the green pigment (L64-3107), respectively. While the results are consistent, there is a difference of factor of 11 with the values obtained by gas adsorption and BET analysis. This indicates that the volume fraction of the powder on the tape is about a tenth the volume fraction of the compacted powder.

The color perceived by the human eye, for pigment particles of identical chemical composition, depends strongly on the size of the pigment particles. This is the case for every passive color element that relies on scattering incident light, which can then reach the eye. For the present pigments, where the light wavelength is comparable to the dimensions of the scattering pigment particles, the scattered intensity is a power law function of the particle diameter with an exponent varying between 6 and $4.^{8}$

The observations made indicate that, because both the red and green pigments are not soluble in the polymer matrices, the pigment particles are essentially pushed together in an effort to minimize the particle surface exposed to the matrix. While the tendency is the same, the red pigments behave in a much more pronounced way, and a shift of a factor of 11–15 in size can be observed. For the green pigment this shift is only a factor of about 2, going from 18.6 ± 0.5 to 36.5 ± 0.3 nm. The result is that the size range of the green pigment particles improves when they are added to PE, resulting in a more efficient pigment. The shift in the size distribution is so pronounced in the case of the red pigments that it is even noticeable by visual observation. Pigment 235-1170 has a bigger brilliance than pigment 235-0170 once both are embedded into the polymer matrix. In order to increase the pigment's brilliance one either has to increase its dispersability in the polymer, or to start with much smaller pigment particles (as is the case for the green pigment powder) which will then assemble into clusters of the optimal size for use as a pigment, once embedded in a polymer.

IV. CONCLUSIONS

We have shown that certain organic pigments, although dispersible in polymer matrices, display aggregation behavior leading to mass-fractal-like morphologies. With x-ray scattering the size change of the pigment particles and the formation of aggregates can be observed. This process is close to reaction limited aggregation. No chemical change in the pigments and no change in the crystalline phase is observed on mixing in the polymer. The size of the formed aggregates has a strong effect on the light scattering properties of the embedded pigments. Thus small differences in size have an effect noticeable by visual observation on the color brilliance (chroma). From this effect an optimum primary pigment particle size distribution can be deduced, so that a minimal amount of pigment will yield the most brilliant color possible. An alternative method would be to add surface active agents to control aggregation or particles with the same refractive index as the matrix, which can prohibit the pigment particles clustering together.

We find that the examined organic pigments can be described assuming a mass-fractal structure. The mass-fractal aggregation is intimately coupled with processing of these pigments in polymer matrices so that a large element of control over structural based properties is indicated. There is some evidence that the color displayed by these pigments in polymer matrices is linked to the development of aggregate morphologies in that two pigments of identical chemical composition displayed different color brightness when only the aggregation behavior differed. We plan to continue studies of these pigments through development of a theoretical basis for color brightness which incorporates mass-fractal structural models.

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