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Transient simulations of the particle size distribution during dispersion of inorganic pigments

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Abstract

The purpose of this work was to develop a mathematical model capable of mapping the full particle size distribution of inorganic pigments during a dispersion process. Three kinetic mechanisms, erosion, rupture, and re-agglomeration, were investigated. For model validation, particle size distribution measurements on TiO_2 and Cu_2O pigments were used.

The best agreement between simulations and experimental data, for both the transient volume-moment mean diameter and the full particle size distribution, was obtained with only the erosion mechanism active. Furthermore, by adjusting the erosion rate constant, the model was able to simulate experimental data from the high speed disk disperser or bead mill with perturbations in the coatings formulation and dispersion parameters.

In combination with particle size measurements, the mathematical model can, for a given pigment, suggest the dominant dispersion kinetics and point at relevant process improvements. The optimal dispersion time is of particular interest.

Introduction

Most performance properties of coatings, such as rheology, colour strength, hiding power, UV radiation resistance, and gloss, can be related to the degree (or lack) of dispersion [1,2]. When evaluating the presence of agglomerates in coatings or mill bases, the industry generally applies the maximum particle size (estimated from a grindometer reading). However, the entire particle size distribution (PSD) of pigments plays a role in the performance of coatings. On the other hand, excessive dispersion leads to energy waste and time loss, as well as a potential reduced weathering resistance [3]. Additionally, for some green and blue pigments, a loss in color strength has been observed [4].

Using the proper procedure, it is possible to measure the full PSD of pigments during a dispersion [2,5]. Furthermore, to supplement the measurements, a mathematical model, which describes the PSD changes during the dispersion process, can help to understand the kinetics and point at relevant process and formulation parameters. Wahl et al. [6] set up a model for the change of oversized particles in a high-speed disperser, and model predictions were compared to grindometer readings. Later, Winkler et al. [7] derived a pigment dispersion model based on probability functions. This model is empirically-based and does not explicitly include the size of agglomerates or dispersion kinetics. In the model of Kiil [8], the dispersion of organic pigments was quantified, and the entire PSD was taken into account.

The purpose of the present work is to develop a mathematical model, which can map the full PSD of inorganic pigments during a dispersion, while obtaining a detailed understanding of the dispersion process. From a comparison of simulations and experimental data, the dominant dispersion mechanism will be investigated. In addition, to predict the dispersion progress and evaluate potential dispersion failures, the model should be sufficiently simple for daily use in the coatings production industry.

Experimental

Four series of acrylic-based coatings with one of two volume concentrations (30 or 40%) of TiO_2 or Cu_2O pigments were formulated. For dispersion, a high-speed disk disperser (40 mm dispersion impeller) and a lab-scale, high-speed bead mill (45 mm parallel circular plates and 1 mm glass beads) were used. Table 1 shows the details.

The PSD of the coating samples was measured by laser diffraction (Malvern MasterSizer 3000, MV chamber). Eight samples were taken from the same dispersion batch at different dispersion times (i.e. 0 s, 15

s, 30 s, 1 min, 3 min, 5 min, 12 min, 20 min, 40 min). As an example, Figure 1 shows the transient overall development in the PSD and the volume-moment mean diameter ($D[4,3]$) of the TiO_2 HS sample.

Table 1. The critical pigment volume concentration (CPVC) and the reduced PVC (λ) of the coatings. HS=high-speed disk disperser, BM=lab-scale high-speed bead mill.

Experimental series	Pigment type	PVC	CPVC	λ (PVC/CPVC)
TiO_2 HS	TiO_2	30 or 40	54.55	0.55 or 0.73
TiO_2 BM	TiO_2	30 or 40	54.55	0.55 or 0.73
Cu_2O HS	Cu_2O	30 or 40	59.44	0.55 or 0.73
Cu_2O BM	Cu_2O	30 or 40	59.44	0.55 or 0.73

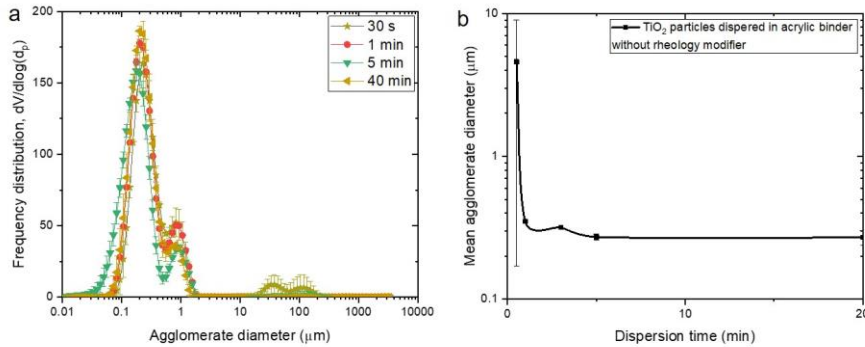


Figure 1: (a) Transient dispersion PSDs measured with laser diffraction. (b) The volume-moment mean diameter.

Mathematical model

A mathematical model for inorganic pigment dispersion, including an agglomerate population balance equation, was developed based on the organic pigment erosion model by Kiil [8]. Three mechanisms, erosion, rupture, and re-agglomeration, were included (Figure 2). The illustration in Figure 2a represents the erosion mechanism, which follows a so-called shrinking core model. During the dispersion process, primary pigment particles or small agglomerates (i.e. collections of primary particles held together by Van der Waals forces) are continually eroded from the surface of the parent agglomerate.

The rupture mechanism, on the other hand, shown in Figure 2b, assumes that the agglomerates, under sufficient shear stress, break into smaller agglomerates according to a Weibull distribution. Finally, the re-agglomeration of dispersed particles to form larger agglomerates was taken into account [9]. Figure 2c shows a schematic illustration of the re-agglomeration process between small agglomerates and/or primary particles.

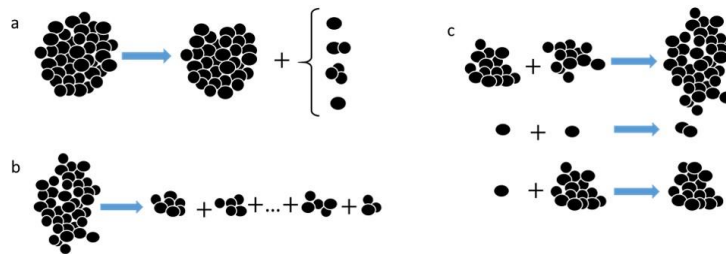


Figure 2: Schematic illustration of the dispersion mechanisms investigated. (a). erosion (shrinking core) (b). rupture (formation of several smaller agglomerates from a parent agglomerate). (c). re-agglomeration (formation of larger agglomerates from smaller)

To track the full PSD change during the dispersion process, population balance equations, including all three mechanisms, were set up [10].

$$\frac{\partial}{\partial t} V(d_{p,j}, t) = B(d_{p,j}) - D(d_{p,j}) + \text{net generation}(d_{p,j}) \quad (1)$$

where, $d_{p,j}$ is the current agglomerate diameter ($j = 1, \dots, N$, N being the total number of chosen size bins in the particle diameter interval of interest). V is the total volume of agglomerates of size $d_{p,j}$. B is the volume birth

term of larger agglomerates to agglomerates of size $d_{p,j}$. D is the so-called volume death term, accounting for smaller agglomerates or particles arising from agglomerates of size $d_{p,j}$. If the erosion mechanism only is taken as an example, eq (1) can be written, in discrete form, as

$$\frac{dV_{ero,j}}{dt} = R_{erosion,j+1}V_{j+1}\beta_{vol}\alpha - R_{erosion,j}V_j\alpha + \sum_{k=j+1}^N \alpha R_{erosion,k}V_k(1 - \beta_{vol})(F(d_{p,j}) - F(d_{p,j-1})) \quad (2)$$

where α is the fraction of mill base volume, where the stress applied can breakdown agglomerates. β_{vol} is the volume ratio of agglomerates with diameters $d_{p,j}$ and $d_{p,j+1}$, written as $\beta_{vol} = V_j/V_{j+1}$. $F(d_{p,j})$ represents the cumulative fragment PSD up to $d_{p,j}$.

Results & Discussion

The dominant mechanism during the dispersion process was determined by comparing various simulations with experimental as shown in Fig 3

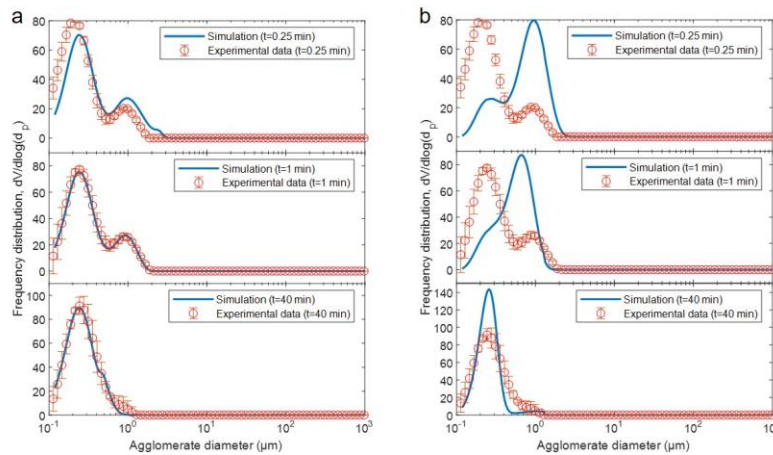


Figure 3: Comparison of simulations with experimental data when either the erosion or the rupture mechanism is included for three values of the dispersion time (0.25, 1, and 40 min). (a). Erosion only. (b). Rupture only. Symbols (with error bars) represent the experimental PSD of the TiO₂ BM sample, and the solid lines in Figure 3a and Figure 3b are simulations. Notice the logarithmic x-axis.

It is evident, from both figures, that when only erosion is taken into account, simulations are in a much better agreement with experimental data. At the beginning of the dispersion, rupture may play a part for the large agglomerates, but the effect is almost negligible relative to erosion. Erosion is therefore the dominant mechanism.

The next issue to consider was how well the full PSDs and volume-moment mean diameter are estimated when only the erosion rate constant is varied. Figure 4 presents the $D[4,3]$ value as a function of dispersion time. The mean diameter of TiO₂ went from 40 to 0.3 μm within 40 minutes, in good agreement with the experimental data.

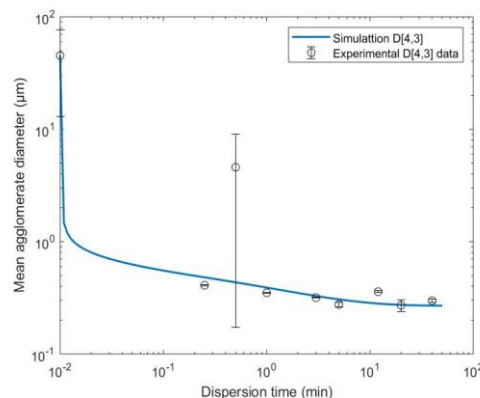


Figure 4: Comparison of a simulation with experimental data for the volume-moment mean diameter, $D[4,3]$, as a function of dispersion time. Notice the double-logarithmic axis.

Despite the $D[4,3]$ value, the full PSDs and accumulated volume percentage were quantitatively described. In Figure 5, simulations (full lines) are compared with the experimental data. From both figures, when varying the erosion rate constant, a good agreement between the experimental data and simulations was obtained.

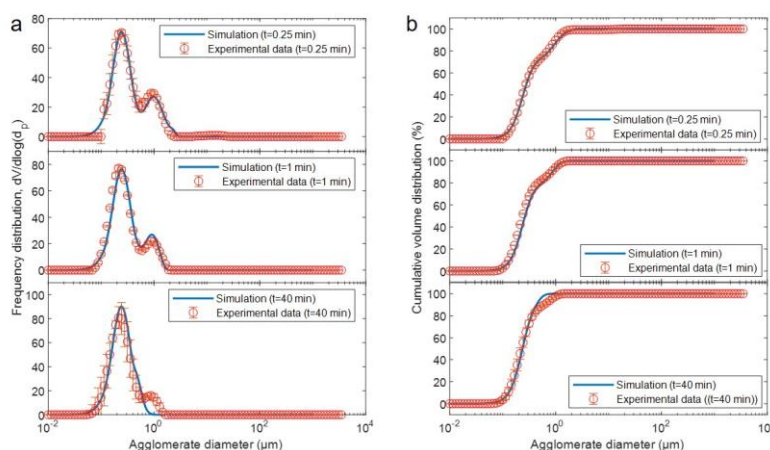


Figure 5: Comparison of simulations and experimental data for three values of the dispersion time (0.25, 1, and 40 min) for TiO_2 pigment in a lab-scale high-speed bead mill. a. The frequency distribution (full PSD). b. The accumulated volume distribution. Symbols (with error bars) represent the experimental data of the TiO_2 BM sample and the solid line in Figure 5a and Figure 5b represents simulations using only one adjustable parameter (erosion rate constant).

Conclusions

A transient mathematical model, capable of simulating the full PSD during a dispersion process with the three important dispersion mechanisms, was developed. When including the erosion mechanism only and adjusting the erosion rate constant, the model was able to simulate experimental data for TiO_2 and Cu_2O pigments. Results of the remaining coatings in Table 1 will be discussed in the presentation.

Acknowledgements

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