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Evaluation of nanoparticle aggregate morphology during wet milling

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ABSTRACT

Recently developed wet mills (bead mills) have been shown capable of dispersing nanoparticle aggregates into primary particles in suspension, even with nanoparticles with primary particle radii as small as 5 nm and at high nanoparticle volume fractions (>1%). However, to date what has not been examined is the change in aggregate morphology during milling itself, i.e. it is not clear if wet milling simply fragments aggregates into smaller, similarly structured entities, or if milling can simultaneously lead to aggregate restructuring. Here we develop and apply methods to examine the change in morphology in titania and alumina nanoparticle aggregates (primary particle radii of ~8.25 nm and 7.20 nm, respectively) during wet milling with a Kotobuki Industries UAM-015 wet mill. Specifically, via nanoparticle tracking analysis (NTA) with a Nanosight LM-14 and simultaneous viscosity measurements, we characterized the hydrodynamic radius distribution functions and average intrinsic viscosities of both titania and alumina aggregates milled at 1% volume fraction in water. With NTA we found that for both particle types, milling led to a reduction in hydrodynamic radii. Conversely, the average intrinsic viscosity of titania decreased, while it increased for alumina with increasing milling time. By assuming aggregates were quasifractal in morphology (and hence characterized by the number of primary per particles per aggregate, the pre-exponential factor, and the fractal dimension) and by using Monte Carlo based techniques to link quasifractal aggregate descriptors to both the hydrodynamic radius and the intrinsic viscosity for an aggregate, measured hydrodynamic radius distribution functions and average intrinsic viscosities were used to infer titania and alumina aggregate quasifractal descriptors as functions of milling time. Through this analysis we found that both particle types were initially dense aggregates (fractal dimensions >2.9), and for titania milling did not alter aggregate morphology (i.e. titania aggregates remained dense). However, alumina aggregates were found to decrease in fractal dimension with increasing milling time, reaching a value near 1.6 after 180 minutes of milling. Such chain-like structures give rise to an increase in suspension viscosity despite the fact that alumina aggregate size decreased with milling. Overall, we show that depending on the particle material (and surfactant employed), milling may simultaneously lead to aggregate size reduction and restructuring, and may be a viable approach to the production of controlled morphology aggregates.

1. Introduction

Most industrial and medical applications of inorganic (metal and metal oxide) nanoparticles require that the particles remain stable (i.e. do not aggregate) in a particular solvent [1–5]. However, nanoparticles are rarely synthesized in the solvent in which they will be later dispersed for application, and subsequent to synthesis (either via liquid or gas phase processes) nanoparticles are frequently stored as dried powders [6–9], wherein van der Waals interactions bind nanoparticles together as aggregates. Upon introduction to a given solvent, dried powder aggregates are not necessarily immediately dispersed (even if surfactants which stabilize suspensions are added), as there remains a van der Waals energy barrier to aggregate breakup. The creation of stable nanoparticle dispersions hence typically requires the use of a high energy grinding process, such as wet milling [10–13]. Along these lines, a number of advances have been made in the development of wet bead mills in the past decade. In particular, recently devised bead mills [14–22] can utilize micrometer sized ZrO_2 beads in a slurry to disperse aggregates into individual primary nanoparticles with characteristic sizes as small as 10 nm. With proper suspension conditions, milled nanoparticles can remain dispersed over the course of days, even with nanoparticle mass fractions as high as 10%. Key to the development of such mills has been the addition of a centrifuge downstream of the bead vessel (where bead-bead collisions occur) which is capable of separating out beads as small as 15 μm from suspensions flowing through the milling system [14].

The efficacy of such bead mills when proper milling conditions are applied and reaggregation is mitigated is not in question. However, lacking are studies which examine changes in the morphologies of aggregates as milling proceeds, both under conditions where a stable nanoparticle dispersion is produced, and under conditions where

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complete dispersion is not achieved. Aggregate characterization during the milling process is not only of fundamental interest, but could also further aid in advancing milling technology; stable dispersion production can require 6–10 hours [15] and determination of the appropriate surfactant type and concentration needed to maintain suspension stability is often performed with a trial-and-error approach. Additionally, certain applications may benefit not from having stably dispersed primary particles, but rather stably dispersed aggregates where the extent of aggregation is controlled [23–28]. Therefore, techniques to evaluate aggregate morphology during milling would save substantial time in milling protocol design.

In this study, we develop and apply methods to quantitatively characterize aggregate morphologies during bead milling processes for aggregates in the sub-100 nm size range, which are difficult to structurally analyze by static light scattering [29]. Specifically, we used a Kotobuki Industries ultra-apex mill (UAM 015) with 50 μm ZrO_2 beads to disperse commercially produced titania (TiO_2) and alumina (Al_2O_3) nanoparticles in water. The former was chosen as a model system as stable primary particle dispersions have been produced with it previously [14], while studies show the dispersion of the latter is much more challenging [30]. To characterize aggregate morphology during milling, hydrodynamic radii distribution functions and suspension intrinsic viscosities were measured periodically, and by modeling the aggregates as quasifractal structures [31–34] (described by the number of primary particle per aggregate, the primary particle size/radius, the fractal dimension, and the pre-exponential factor), the fractal descriptors of particles were inferred from measurements. In the sections that follow, the results of titania and alumina dispersion experiments are described in greater detail as is the procedure we have developed to infer aggregate morphology in suspensions. We show that in these two instances aggregate morphologies were initially quite similar, but as milling proceeded, the titania aggregates, while decreasing in size, changed little in morphology, while alumina aggregates both fragmented and underwent substantial restructuring into chain-like aggregates.

2. Materials and methods

2.1. Materials

Metal oxide nanopowders of anatase titania (TiO_2,CAS registration # 637254) and gamma-phase alumina (Al_2O_3, CAS registration # 544833) were purchased from Sigma-Aldrich (Saint Louis, USA). Titania and alumina nanoparticles were added to ultrapure water (SpectraPure, Tempe, USA) at a volume fraction (V_f) of 1% and a total suspension volume of 500 ml. Sodium hexametaphosphate (Sigma-Aldrich (CAS # 71600)), an ionic surfactant often used to stabilize metal oxide nanoparticles in water, was added to each suspension at a concentration of 50% the mass concentration of nanoparticles. Specific information on the compositions of suspensions is provided in the Table S1 of the supplemental information.

2.2. Bead milling

A schematic of the UAM 015 bead mill is provided in Fig. S1, and is also presented in detail in earlier studies [14,15,35]. Briefly, the bead mill is composed of a 500 mL suspension reservoir, where samples are initially loaded, a peristaltic pump to facilitate the recirculation of suspensions through the mill, a vessel wherein the beads remain, and a centrifuge to remove beads at the vessel outlet. As milling proceeds, suspensions are recirculated from the reservoir to the vessel and centrifuge and back to the reservoir. For the presented experimental results, the vessel volume of 170 mL was loaded with highly monodisperse ZrO_2 beads with a diameter of 50 μm (obtained directly from Kotobuki Industries) at a volume fraction of 60%. The bead mill functions by harshly agitating beads within the vessel, such that during bead-aggregate-bead three-body collisions, aggregates break at nanoparticle-nanoparticle contact points. As described subsequently for nanoparticle aggregates, beads were periodically imaged via transmission electron microscropy; visible wear of beads subsequent to experiments was not evident in such images. The rotation speed settings of the vessel and the centrifuge region as well as the peristaltic pump must be controlled to ensure that (1) bead impacts do not fragment primary particles and (2) beads are separated from the flowing suspension in the centrifuge region. Such speeds are determined empirically; for the presented results the vessel and centrifuge speed setting was level “4” (out of 5, corresponding to rotation speed of 10 m/s for the centrifuge outer cylinder) and the peristaltic pump speed setting was 1.5 (out of 10). To maintain the vessel at a constant temperature, a sealed cooling water jacket was employed. During all experiments the water temperature was set to 7.5 °C via use of a recirculating chiller (Kodiak® Recirculating Chiller, Lytron, Woburn, USA). For both test suspensions milling was carried out over 180 minute periods, and 5–15 mL samples were extracted at time periods of 0, 5, 15, 30, 60, 90, 120, & 180 minutes for either hydrodynamic radius distribution function or intrinsic viscosity measurements. Milling experiments were performed twice for titania suspensions and three times for alumina suspensions to ensure that results were repeatable. For all suspensions, after milling for 15 minutes or more, sedimentation of particles from suspension was not observed for at least two weeks subsequent to experiments.

2.3. Nanosight™ and hydrodynamic size distribution

Aggregate hydrodynamic radii (R_H) distribution functions (i.e. the number concentration of aggregates per unit hydrodynamic radius) were measured using ‘Nanoparticle Tracking Analysis (NTA)’[36] with a Nanosight™ LM-14 (Malvern Instruments). In NTA, the Brownian motion of aggregates is monitored, yielding the scalar diffusion coefficient (D) for each aggregate. Via application of the Stokes-Einstein equation, $D = \frac{kT}{6\pi\mu R_H}$ (k: Boltzmann constant, T: temperature, μ: solvent dynamic viscosity), the hydrodynamic radius of each aggregate can be inferred, and entities with hydrodynamic radii as small as 5 nm may be directly observed with the LM-14. From measurement results, a fitting procedure can be used to reconstruct a probable hydrodynamic radius distribution function, or alternatively the hydrodynamic radii of all detected particles/aggregates may be directly output. For LM-14 measurements samples taken from the bead mill at specific times were diluted with ultrapure water by a factor of 10^2–10^3. The LM-14 temperature was set to 23 °C. Prior to sample measurements, for calibration NTA was performed on citrate stabilized near-monodisperse 80 nm gold nanoparticles (Nanocomposix, USA). NTA was performed 4 or more times for each sample, and rather than use a fitting procedure to determine the hydrodynamic radius distribution function, we elected to output directly the hydrodynamic radii of all examined particles at milling times of 15, 60, 120 and 180 minutes for both titania and alumina suspensions.

2.4. Viscosity measurement and intrinsic viscosity calculation

A glass ubbelohde viscometer (CANNON Instrument Company, PA, USA) was used to measure the kinematic viscosities of both titania and alumina suspensions after selected milling times. The viscometer employed has four measurement bulbs, enabling viscosity measurement at four different shear rates, and further enabling evaluation of Newtonian behavior via comparison of kinematic viscosities measured with different bulbs. We elected to use the first and second bulbs, which had viscosity constants of 0.003412 mm^2/s^2 and 0.0031496 mm^2/s^2, respectively, and corresponding shear rate constants 415687 and 219720, respectively, and in which measurement times varied between 300–800 seconds (the kinematic viscosity is calculated as the product of the viscosity constant and the residence time in the bulb, while the wall shear rate is the ratio of the shear rate constant to the residence time in the bulb). The temperature during