

Breakage of TiO₂ agglomerates in electrostatically stabilized aqueous dispersions

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Abstract

Nanoparticles of metal oxides have applications as additives in thin nanocomposite films. For optical applications that include transparent films and coatings, nanoparticles should be uniformly dispersed in the polymer film. Most commercially available nanoparticles are large agglomerates about 1 μm in maximum dimensions composed of primary particles with sizes ranging from 5 to 50 nm. The large agglomerates scatter light and are not directly suitable for optical systems. Ultrasonication of liquid suspensions was used to prepare stable dispersions from commercial titania nanopowders. The mean diameter of sonicated titania nanopowders was correlated inversely to the specific energy. After a rapid initial size reduction, continued ultrasonication lead to insignificant reduction and even reagglomeration of the particles. Both erosion and fracture mechanisms were observed. None of the commercial nanopowders were successfully broken to their primary particle sizes. Reagglomeration of the dispersion could be prevented by electrostatic stabilization with nitric acid or ammonium hydroxide when its zeta potential value was less than –30 mV or greater than +30 mV.

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1. Introduction

Due to its photocatalytic activity and high refractive index, titanium dioxide is an appealing additive in thin nanocomposite films for the optical industry. For the optical applications, it is crucial to obtain ultrafine and stable nanodispersions that will produce thin films with low surface roughness and haze and high transparency. To reduce the surface roughness of the optical films, the primary size of nanoparticles should be less than 20 nm. To insure transparency of the nanocomposite, the size of the agglomerates must not exceed 100 nm. Although the primary size of most commercial nanoparticles is quite small (5–50 nm), the high surface energy of nanoparticles causes them to agglomerate in the synthesis and post-synthesis processes. This leads to materials with primary particles in the nanometer range, but with variable and complex networks, shapes, and morphologies, all of which impact surface

roughness, haze and transparency. The actual morphology varies with the synthesis process and can have large batch-to-batch variations.

Ball milling, high shear mixing, or ultrasonication are commonly used to break up agglomerated nanoparticles. During ball milling, breakage occurs due to impact and high shear fields. The shape of produced particles is irregular and many defects are introduced into the grain structure. Also particles are often contaminated from milling media. Prolong milling, which is often required to obtain nanoscale particles, causes phase transformations of titania—from anatase to metastable TiO₂ to rutile [1,2].

High shear mixing of nanodispersions is conducted in rotor–stator systems or by forcing the dispersions through a nozzle. When the same amount of specific energy is applied, ultrasonication is more effective than rotor–stator systems [3].

Usually, ultrasonication is performed in a solvent. An energy transfer device, such as an ultrasonic horn, oscillates the liquid, causing nucleation and collapse of solvent bubbles. Bubbles initiating and collapsing on the solid surfaces can be

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very effective in fracturing the solids. The breakage of agglomerates is controlled predominantly by specific energy input (power, time and dispersion volume) [3].

Titania nanopowders are usually described as non-eroding particles [4] or aggregates. While it is not generally agreed, in this manuscript, the term agglomerates relates to powders with weak interparticle bonds that can be redispersed in a solvent and the term aggregates or hard agglomerates describes powders with primary particles held together by strong attractive forces [5]. Agglomerates break by erosion mechanism when bonds between primary nanoparticles are breached and nanoparticles or small agglomerates are separated one by one. Mechanical attrition of aggregates, on the other hand, occurs by fracture mechanisms [4,5]. Fracture of the aggregates initiates at surface flaws and imperfections. Large aggregates are broken down into smaller aggregates until there are no more defects to initiate the breakage. Further energy input results in no significant attrition.

In order to form stable dispersions, it is not enough to break nanoparticles apart. Stabilization of colloidal dispersions of several commercial and synthesized metal oxide nanopowders by electrostatic, steric or electrosteric interactions is documented [6–11]. Unless one of these methods is used, nanoparticles may adhere to each other, forming assemblies whose morphology or structure depends on the solvent, temperature, materials and other factors. In an electrostatically stabilized dispersion,

charges generated on the surface of particles prevent or control reagglomeration. Steric stabilization takes place when large molecules adsorb on to the surface of particles thus introducing physical barriers between them. A combination of electrostatic and steric mechanisms produces electrosteric stabilization. All three stabilization mechanisms prevent nanoparticles from agglomeration.

A common way to evaluate the stability of colloidal dispersions is by determining the magnitude of zeta potential. Zeta (ζ) potential is a function of the surface charge of the particles. In dispersions where value of the ζ potential is close to zero (isoelectric point), particles tend to agglomerate. At highly negative or positive values of ζ potential (more than 30 mV or less than -30 mV [12]) particles in dispersions tend to repel each other—no agglomeration occurs. The actual values needed to prevent reagglomeration are in dispute, and depend on the solvent, concentration of ions, effective pH, and the functional groups on surface of nanoparticles. Powders obtained from different manufacturers have dissimilar surface chemistries and as a result exhibit isoelectric points at different pH values.

As long-term stability of nanodispersions is important for producing high quality nanocomposites, breakage of the nanoparticles is also a critical issue for many processes. The purpose of this work is to study breakage of commercial nanoparticles in aqueous dispersions while controlling zeta potential.

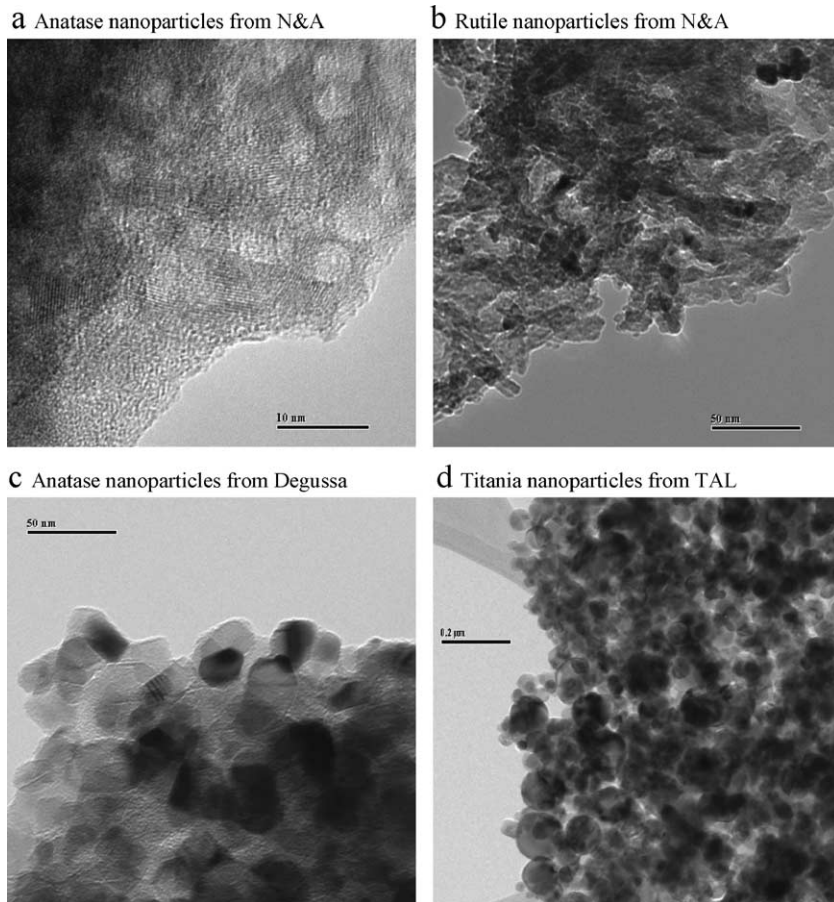


Fig. 1. Morphology of commercial titania nanopowders.

2. Experimental

Four titania nanopowders were purchased from three suppliers: Nanostructured & Amorphous Materials, Inc. (Los Alamos, NM), TAL Materials, Inc. (Ann Arbor, MI), and Degussa. The nanopowders were dispersed in deionized water. The pH of the aqueous media was adjusted with nitric acid or ammonium hydroxide to obtain suitable zeta potential values. The morphology of the particles was studied using transmission electron microscopy (TEM, Jeol 2010F). Changes in zeta potential with pH were measured on a zetameter Malvern 2000 (Malvern Instruments, Southborough, MA).

The ultrasonication was conducted using a Hielscher UP400S ultrasonic horn (Hielscher USA, Inc., Ringwood, NJ). The frequency of the ultrasound was constant (24 kHz). To keep the dispersions from overheating during the ultrasonication, the dispersions were sonicated in a cold-water bath maintained at a constant temperature (10 °C). The input of power was measured using electricity usage monitor (P3 International, New York, NY). Specific energy (kJ/m³) was calculated as a function of input power, time and dispersion volume. The efficiency of ultrasonication was evaluated by changes in mean diameters of sonicated titania nanoparticles. The particle size distributions were measured using a Beckman Coulter N4 Plus particle size analyzer (Beckman Coulter, Inc., Fullerton, CA) and verified by scanning electron microscopy (Hitachi FESEM S-900).

3. Results and discussion

3.1. Morphology of the nanopowders

Fig. 1 shows TEM micrographs of four commercial nanopowders—anatase and rutile materials from N&A, anatase material from Degussa and mixed anatase and rutile material from TAL. All these materials were received in the dry form, and all contained agglomerated particles. The primary particle size estimated by TEM analysis and the average agglomerate/aggregate size measured by photon correlation spectroscopy are shown in Table 1. Since the primary size of the particles of four samples varies from 5 to 100 nm, different magnification were used in TEM micrographs (Fig. 1) to better represent morphologies of the samples. The two samples from N&A had bimodal size distributions with one fraction having an average size much less than 1 μm and with the rest having an average size about 1 μm or greater. Anatase nanoparticles from N&A

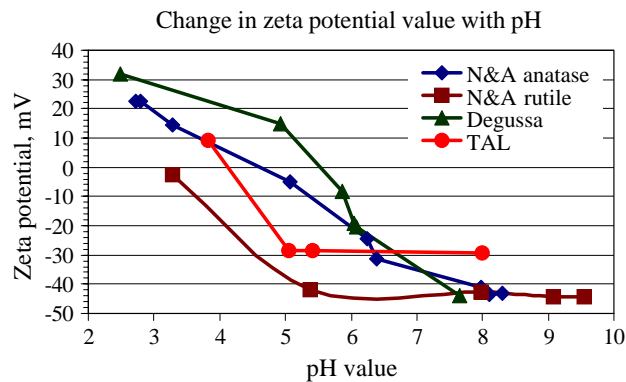


Fig. 2. Change in zeta potential with pH value for each powder.

have the smallest primary size of the tested nanopowders—about 5 nm; the nanoparticles are spherical and agglomerated into two fractions of 400 nm and 1500 nm. Anatase nanoparticles from Degussa (25 nm) form tightly packed agglomerates of about 1 μm. Titania nanoparticles from TAL are spherical and the primary particles varied from 20 to 100 nm. The particles are extensively agglomerated with an average size of 3 μm. Rutile nanoparticles from N&A are elliptical and their primary size is about 10 nm. These nanoparticles form two fractions of loosely packed agglomerates with the average size of 70 nm and 1500 nm.

3.2. Electrophoretic mobility of the nanopowders

The evaluation of the optimal dispersing conditions for titania nanopowders started with identification of the isoelectric point. Fig. 2 shows the change in zeta potential with pH value for each powder. The isoelectric point is defined as the pH at which the zeta potential is zero. The isoelectric points of the nanoparticles were: anatase—pH 4 (N&A) and pH 5.5 (Degussa), mixture of anatase and rutile—pH 4.1 (TAL), and rutile—pH 3.2 (N&A). The mixture of anatase and rutile nanoparticles had an isoelectric point intermediate between those of pure rutile (pH 3.2) and pure anatase (>pH 4.6). Another notable observation is that for the anatase nanoparticles (both anatase from N&A and Degussa), the change in zeta potential value with pH was almost linear. For rutile nanoparticles or mixture anatase and rutile (rutile from N&A and mixture anatase and rutile from TAL), the zeta potential was constant over a comparably broad range of pH values (from 5.3 to 8). Thus, for rutile particles, the isoelectric point was at the

Table 1
Estimated primary particle and average agglomerate/aggregate size for tested nanopowders

Crystalline phase	Manufacturer	Average primary particle size from TEM (nm)	Peak 1: average agglomerate size from PCS (nm)	Peak 2: average agglomerate size from PCS (nm)
Anatase	Nanostructured & Amorphous Materials, Inc.	5	~360	~1530
Anatase	P-25, Degussa	25	—	~1020
90% anatase and 10% rutile	TAL Materials, Inc.	50–100	—	~2760
Rutile	Nanostructured & Amorphous Materials, Inc.	10	~70	~1500

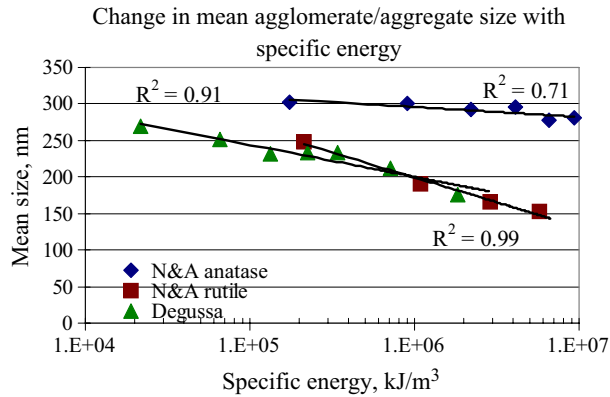


Fig. 3. Change in size of agglomerates/aggregates with ultrasonic input power.

lower pH value and the transition from positively to negatively charged particles was faster than for anatase particles.

The criterion for suspension stability is thought to be $|\zeta| > 30$. The TAL anatase sample did not reach the zeta potential stability limit over the measured pH range. However, its agglomerate particle size was about 3 μm , and it was unstable with respect to settling in any case. Rutile material would be stable at $\text{pH} > 4.5$, while the anatase materials would be stable at $\text{pH} > 7$.

3.3. Breakage of the agglomerates

Before ultrasonication, the aqueous dispersions of nanoparticles were modified with ammonium hydroxide. The disper-

sions were ultrasonicated at pH 8 to permit any newly formed particles to be stably dispersed. After ultrasonication, none of the powders was broken into their primary particle size. The mean size of agglomerates/aggregates (Fig. 3) followed the typical power law relation between average particle diameter and specific energy: $(dd/dt) = -kd^1$, where d is an average diameter, t is time, and k is a rate constant determined by materials characteristics.

According to their breakage behavior, the powders were differentiated as agglomerates or aggregates. For anatase from N&A, no significant change in size was observed for specific energies up to 10^7 kJ/m^3 . While this sample has the smallest primary particle size of all commercial materials, it was very difficult to break using ultrasonication. It broke via a fracture mechanism and produced essentially no satellite particles in its primary particle size range. Light scattering intensity vs. particle size before and after ultrasonication (Fig. 4) showed similar trends, which suggests that the attractive forces between primary nanoparticles are strong and the breakage started on surface flaws and defects.

Mechanical attrition of rutile from N&A and anatase from Degussa took place by an erosion mechanism—small aggregates consisting of few primary nanoparticles broke away from the agglomerates. For TAL nanopowder (ζ potential of -29 mV), attractive forces among the dispersed particles were stronger than repulsive forces and initial size of the agglomerates was from 3 to 4 μm range. The ultrasonication caused the breakage of the agglomerates (Fig. 4), but shortly after the end of ultrasonication, the particles reagglomerated back the 3 to 4

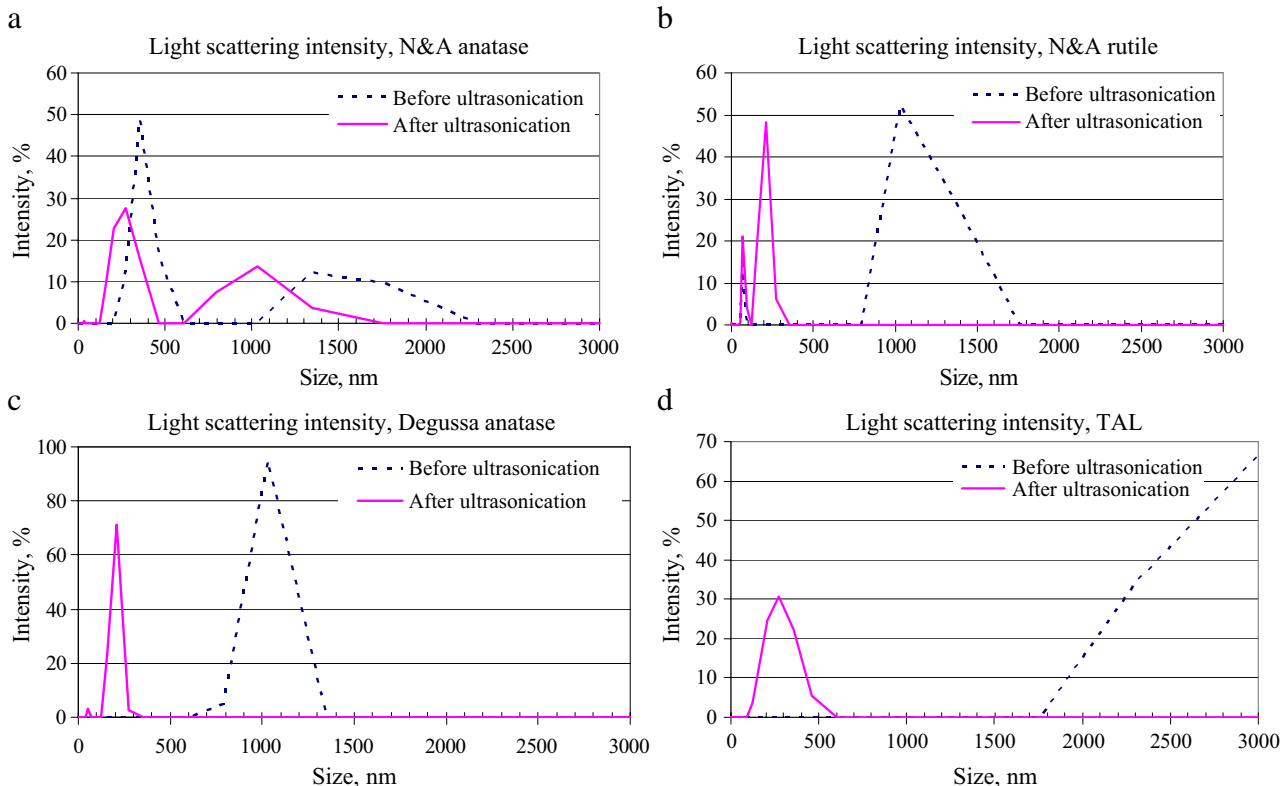


Fig. 4. Intensity analysis results for TiO_2 nanopowders before and after ultrasonication: (a) intensity distribution for anatase aggregates from N&A; (b) intensity distribution for rutile agglomerates from N&A; (c) intensity distribution for anatase agglomerates from Degussa; (d) intensity distribution for agglomerates from TAL.

μm range. Breakage of the powder was evident only when the size distribution analysis was conducted immediately after cessation of ultrasonication.

Regardless of the small primary size of the tested nanopowders, none of them was successfully broken to their primary particles within reasonable energy levels ($5.7 \times 10^6 \text{ kJ/m}^3$) and time frames (2 h). Similar to results reported elsewhere [13,14], after rapid initial size reduction, continued ultrasonication leads to insignificant reduction and even reagglomeration of the particles. Fig. 5a and b show SEM images of the anatase powder before and after 120 min of ultrasonication (the samples for SEM analysis were prepared by drying a drop of dispersion on a sample holder). Fig. 5c shows cumulative distributions of particles before, after 10 min and after 120 min of ultrasonication. Even after 2 h of mechanical breakage, none of the powders was completely deagglomerated to its primary particles.

The extent of agglomerate breakage depends on its strength which in turn depends on the nature of inter-particle bonds. Even

small adjustments to manufacturing process results in considerable changes in particle properties and size distribution [14–17]. Once agglomerates or aggregates are formed in the synthesis process it is very difficult to break them back to their primary particles.

Additionally, dark sediment was noted on the bottom of the ultrasonicated dispersions. The sediment is due to an erosion of the ultrasonic probe. Thus, long ultrasonication times were not only inefficient but also resulted in contamination of the samples.

4. Conclusion

Both erosion and fracture mechanisms were observed in the ultrasonication of commercial titania nanoparticles. In no instance was the ultrasonic power sufficient to break the commercial materials to their primary particle size range. Prolonged ultrasonication (60–120 min) resulted in contami-

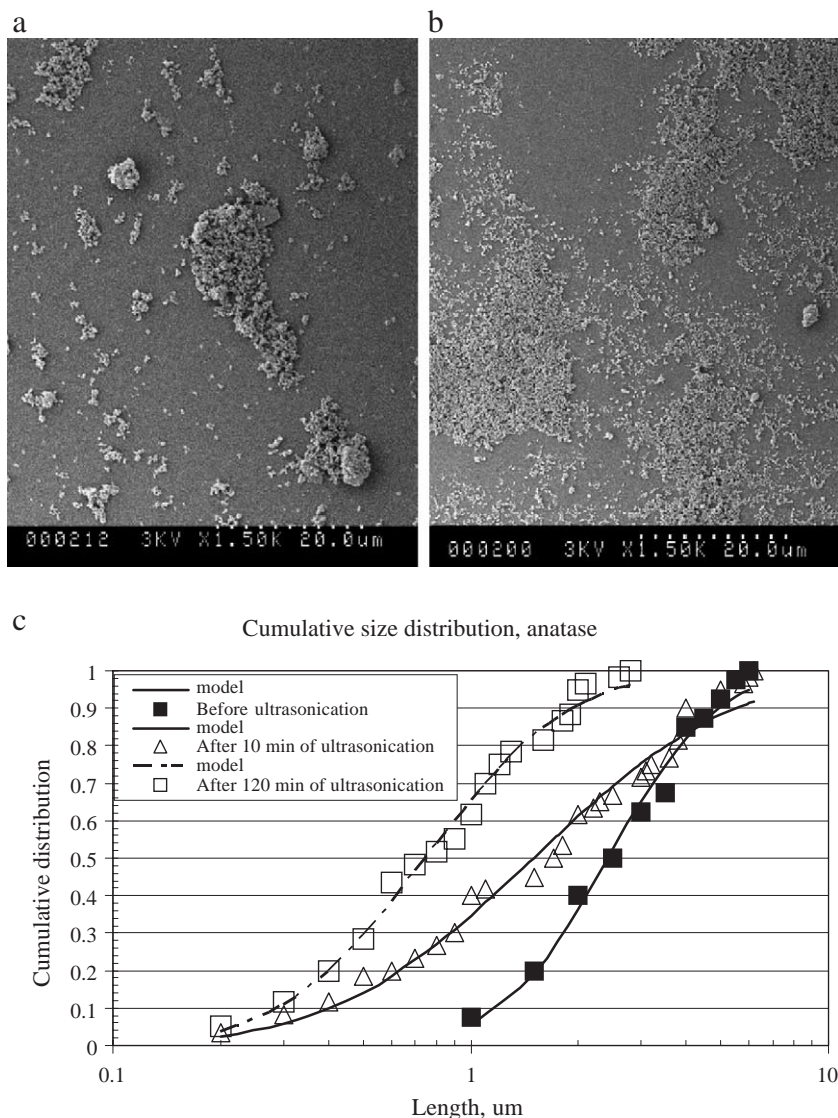


Fig. 5. SEM images of anatase powder (a) before and (b) after 120 min of ultrasonication. (c) Cumulative distributions of titania nanopowder before and after ultrasonication.

nation of the dispersion due to ultrasonic horn erosion. During the ultrasonic breakage, electrostatic stabilization of aqueous dispersions ($\zeta = -40$ mV) prevented newly formed particles from reagglomeration. Almost immediate agglomeration of mechanically broken particles was observed when magnitude of zeta potential was -29 mV.

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