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Rheological investigations on the influence of addition of sodium polyacrylate to titanium dioxide suspensions

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ABSTRACT

The influence of addition of sodium polyacrylate (with 3 different molecular weights PA20 = 2500 g/mol, PA30 = 8000 g/mol and PA40 = 15,000 g/mol) on the stability of TiO_2 dispersions was investigated using particle size (determined by static light scattering), zeta potential and rheological measurements. Diluted dispersions as well as those containing 20% TiO_2 were dispersed by sonication for 5 min. The results show that without sonication and in the absence of NaPAA large aggregates with mean volume diameter of 3.89 μm are produced. On sonication for 5 min, the aggregates are broken down giving a mean volume diameter of 0.239 μm. Addition of NaPAA at low concentration (0.2 and 0.4%) resulted in a large increase in mean volume diameter indicating aggregation of the initially formed small aggregates on sonication. When the concentration of NaPAA was ≥1%, the aggregates became dispersed giving mean volume diameter of about 0.2 μm. These particle size measurements were confirmed by using SEM and TEM measurements. The zeta potential of diluted TiO_2 dispersion in the absence of NaPAA gave an isoelectric point of pH ~ 6. The effect of addition of sodium polyacrylate PA20, PA30 and PA40 on the zeta potential of TiO_2 dispersions at pH = 3 showed neutralization of the positive charge on TiO_2 particles reaching a zero charge at PAA concentration of 0.3–0.4% above which the particles acquired a negative charge that increase with further increase of PAA concentration reaching a plateau value of −45 mV when the PAA concentration was ≥1%. Steady state measurement showed that addition of PA20 to the TiO_2 dispersion causes a dramatic reduction in yield value when PA concentration is ≥1%. Oscillatory measurements were obtained for 30% TiO_2 suspension without any sonication. The frequency was kept constant at 1 Hz, and the stress was gradually increased till a critical value was reached above which the modulus showed a rapid decrease with further increase of the stress. In this way both elastic modulus G' and critical stress were measured as a function of PAA concentration. The results showed an initial increase in the elastic modulus reaching a maximum at critical PAA concentration above which there was a rapid reduction in both rheological parameters. These results indicated flocculation of TiO_2 dispersion at low PAA concentration which was accounted for/by charge neutralization and/or bridging. When the PAA concentration was ≥1% all dispersions showed low G' and critical stress indicating a highly deflocculated system. An attempt was made to correlate the rheological results with zeta potential measurements.

1. Introduction

High solid content titanium dioxide aqueous suspensions have a wide range of applications in the industry. Because of its high refractive index, TiO_2 particles are added to provide whiteness and opacity to products like paints, coatings, plastics, papers, inks, etc. [1]. In addition, titanium dioxide shows photocatalytic properties [2], and a great deal of research was carried out in this field [3]. In these applications a colloidally stable TiO_2 dispersion is required to produce primary particles with optimum size range. With paint applications the size range is 0.3–0.4 μm.

To produce a concentrated stable titanium dioxide suspension, it is necessary to add a polyelectrolyte as a dispersant [1,4–6]. Sodium polyacrylate (NaPAA) is the most common dispersant since it has strong adsorption affinity to the surface of titanium dioxide particles. By providing a high negative charge to particles surface, the electrostatic repulsion between particles prevents any flocculation. In addition, these molecules can also extend from the surface forming loops and tails which can provide an extra steric repulsion [1,7]. It is important to know under which pH, molecular weight and concentration range of NaPAA one can produce a colloidally stable

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TiO_2 dispersion. In particular it is well known that low concentrations of polyelectrolyte may induce flocculation (aggregation due to bridging) due to the incomplete coverage of the particles by the polyelectrolyte chains [1]. This occurs as a result of the simultaneous adsorption of the PAA chains on two or more particles.

For optimal applications, it is essential to obtain ultrafine and stable nanodispersions that can produce thin films with low surface roughness, haze and high transparency [7]. However, the most commercially available TiO_2 powders consist of large agglomerated particles about 1 μm in maximum dimensions that consist of primary particles with sizes ranging from 5 nm to 50 nm [7,8]. Ball milling, high shear mixing or ultrasonication are commonly used to break up the agglomerated nanoparticles, but none of the commercial powders are successfully broken to their primary particles [7]. This is due to the high surface energy of the TiO_2 which can induce aggregation of the primary particles during milling.

In this paper, ultrasonication and ball milling were used to break up the aggregates. However, only the big aggregates with weak bonds were successfully broken up into smaller aggregates with size range of about 200 nm. The particle size distribution was determined by static light scattering and transmission electron microscopy (TEM).

One of the most powerful techniques for studying the colloid stability of concentrated suspensions is rheology [9]. By carrying out steady-state (shear stress–shear rate) measurement and oscillation (amplitude sweep) test, one can obtain information on the colloid stability of the dispersion. These curves can be analyzed to obtain the viscosity of suspension as well as the elastic modulus (G') as a function of sodium polyacrylate concentrations. One would expect that a highly stable dispersion should give a lower viscosity and lower elastic modulus (G'), when compared with flocculated suspensions. By combining these results with zeta potential measurement, one can obtain a clear picture on the effect of polyacrylate on the stability of suspension and this is main objective of the present paper. The zeta potential is the most important parameter determining stability of electrostatically stabilized dispersions.

2. Materials and methods

Titanium dioxide powder was supplied by Evonik Degussa GmbH (Frankfurt am Main, Germany) with commercial name AEROXIDE® TiO_2 P25. The powder has specific surface area (BET) of $50 \pm 15\ m^2/g$ as provided by the supplier and average primary particle size of 21 nm. The suspension was prepared in 3 different ways to break up the aggregates: (i) Ultrasonication applied for 5 min using sonic probe UP200S (200 W, 24 kHz) (Hielscher Ultrasonics GmbH, Teltow, Germany); (ii) ball shaking in an aqueous solution using zirconium dioxide balls (diameter = 1 mm) for 2 h using SCANDEX® shaker (Fast & Fluid, The Tinting Company, Northbrook, USA); the suspension was separated from the beads by ultrafiltration. The latter did not cause any aggregation of the particles; (iii) ball milling in aqueous solution using zirconium dioxide balls (diameter = 1 mm) using DYNO®-MILL MULTI LAB (Willy A. Bachofen AG Maschinenfabrik, Muttenz, Switzerland).

Three types of sodium polyacrylate (NaPAA) were used as dispersants and these were supplied by BASF (Ludwigshafen am Rhein, Germany). They were PA20 (Molecular weight (Mw) = 2500 g/mol and polydispersity index (PDI) = 2.1), PA30 (Mw = 8000 g/mol and PDI = 1.9) and PA40 (Mw = 15,000 g/mol and PDI = 5.9). To 50 g titanium dioxide suspension, different amounts of 5% NaPAA solution were added to cover the concentration range from 0.1 to 2% NaPAA. The suspension was stirred for 10 min after NaPAA addition. The particle size distribution of each suspension was measured using static light scattering technique (Microtrac Inc. Montgomeryville, USA) with wavelength red 780 nm and blue 405 nm. The calculation was based on the modified Mie-theory for non-spherical materials.

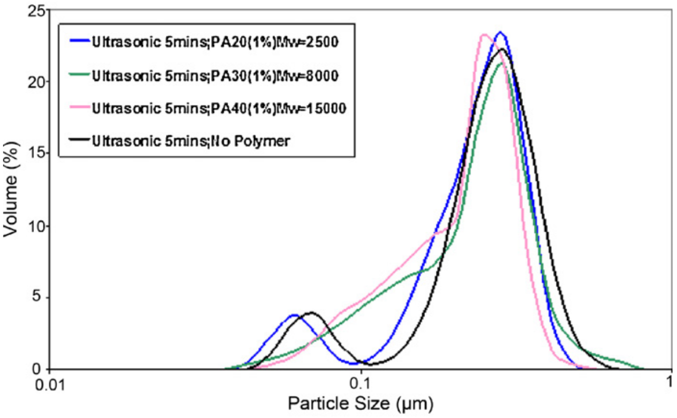

Fig. 2. Particle size distribution of TiO_2 various NaPAA molecular weight (PA concentration = 1%, ultrasonication 5 min).

Steady-state rheological measurements and oscillation amplitude sweep tests were carried out using a Bohlin CVO rheometer (Malvern Instruments Ltd., Malvern, United Kingdom). For the steady state measurements a 20% (w/v) suspension was used whereas for oscillatory measurements, the suspension concentration was 30% (w/v). In all cases the pH of the suspension was adjusted. Steady-state rheological measurements were carried out using concentric cylinder platens. The outer cylinder has a diameter of 26.5 mm and inner cylinder has a diameter of 25 mm. This means that the gap width is 1.5 mm (1500 μm) which is much larger than 10 times the particle size. All measurements were carried out at 25 °C. The suspension was left for 10 min in the concentric cylinder to reach a constant temperature. Thereafter, the shear rate was increased from 0 to 500 s^{-1} over a period of 1000 s and then decreased again from 500 s^{-1} to 0 over a period of 1000 s. Oscillatory measurements were carried out using a cone and plate measuring system. The cone has a diameter of 40 mm and 4° angle. Amplitude sweeps were carried out at a fixed frequency of 1 Hz and the shear stress was gradually increased until a rapid reduction occurs.

Zeta potential measurement was carried out using AcoustoSizer IIs™ (Colloidal Dynamics, LLC, North Attleboro, USA) after each addition of NaPAA to the 20 wt% TiO_2 suspension without dilution. For study the effect of pH on zeta potential, a diluted TiO_2 dispersion was used and the measurement was carried out using Zetasizer Nano Series (Malvern Instruments Ltd., Malvern, United Kingdom).

3. Results and discussions

3.1. Particle size distribution

Fig. 1 shows the particle size distribution of TiO_2 suspensions at various PA20 concentrations; the measurement was carried out after considerable dilution of concentrated TiO_2 suspension (which is necessary for static light scattering technique to avoid any multiple scattering) and the pH was always adjusted. The dilution process did cause any aggregation of the particles. In all cases a wide size distribution is obtained and a summary of mean volume diameter and standard deviation is given in Table 1. It seems from these results that the addition of low concentration of PA20 (at 0.2% and 0.4%) causes more extensive flocculation of TiO_2 suspension and even after dilution the flocs persisted. Ultrasonication is a powerful method for breaking up the big aggregates and this is indicated by the decrease of the mean volume diameter of 3.89–0.239 μm on sonication without addition of PA20. This result indicates that the