Journal of Colloid and Interface Science 417 (2014) 317–324

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Cracking in films of titanium dioxide nanoparticles with varying interaction strength

Alastair G. Mailer *, Paul S. Clegg

School of Physics and Astronomy, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

ARTICLE INFO

Article history:
Received 8 September 2013
Accepted 14 November 2013
Available online 1 December 2013

Keywords:
Titania film formation
Crack pattern
Gelation

ABSTRACT

We present an experimental investigation into how altering the inter-particle potential between colloids affects the cracking of a ca. 100 μm film deposited on a hard substrate. The colloidal material used was titanium dioxide ($r \approx 30$ nm) in an aqueous solvent with interaction strength being adjusted through alteration of the pH away from the isoelectric point. Stable suspensions were observed to form as surface charging increased. Drop casting was used to demonstrate the flow properties of the suspensions; doctor-bladed strips of suspension were subsequently imaged to capture the drying dynamics. Alteration of the pH between 3 and 4 resulted in significant changes in cracking patterns, with the normalised crack domain area $\alpha = \sqrt{A}/h$ increasing for unstable suspensions (pH 4) and the appearance of order in the initial crack pattern for stable suspensions (pH 3). These results can be unified in terms of the barrier to nucleate a new crack.

1. Introduction

Colloidal films, with thicknesses in the range of 10–500 μm are of technological interest in the areas of energy materials, sensors and catalysis [1,2]. As with larger ceramic bodies, the manufacture of these materials is complicated by various failure modes activated by strong capillary forces induced in the material during drying. Optimizing colloid–colloid and colloid–substrate interactions provides a means to influence film behaviour. The fundamental thermodynamic basis of fracture in solid materials was outlined by Griffith [3] in 1920, see also Lawn [4]. Subsequent developments have been reviewed by, for example, Brinker and Scherer [5] and Lewis [6].

Recent work on the drying of latex suspensions [7–9] and aqueous suspensions of inorganic oxides such as alumina and silica [6,10,11] has shown that the drying process depends on the stress/strain response of the suspended particles. Additionally, the effect of suspension/substrate interactions was established by Chiu et al. [12] by drying suspensions on a bed of mercury, and recently revisited by Smith and Sharp to investigate the effect of an elastic substrate [13]. The effect of substrate hydrophobicity and surface chemistry on adhesion and cracking have been investigated by Shorlin et al. [14] and very recently by Jing and Ma [15]. In addition, the importance of capillary forces in the later stages of drying to substrate–film adhesion and delamination has been highlighted by Pauchard [16]. Also pertinent here, the effect of colloidal cluster phases on cracking has recently been presented by Ma and Jing [17].

A previous study on the drying and cracking of charge-stabilised colloidal films focused on modifying the range of the interaction using salt screening effects [10]. The inclusion of salt in this study complicates the interpretation of the final stages of drying (including cracking phenomena) due to salt precipitation and bridging. A later study looked at the effect of suspension stability for alumina particles (through the modification of pH) and binder addition on the critical cracking thickness [18], but did not note a change to parallel crack formation when moving from a flocculated to a dispersed casting suspension. Our study looks at the effect of changing the electrostatic repulsion between particles on the cracking process and the resulting crack pattern. The interaction strength is varied by modification of the charge state of the particle surface through alteration of the solvent pH. Titanium dioxide deposited by both drop and tape casting was the material of choice due to its technological importance in soft energy systems [19]. Images and thickness data were gathered during and after drying to elucidate the effect of electrostatic stabilisation on the flow properties and the drying process. We find that the crack dynamics are different with more stable suspensions exhibiting more ordered initial crack patterns and smaller normalized domain areas.

2. Methods and materials

The colloidal particles used were 99% pure anatase titanium dioxide (Nanostructured and Amorphous Materials, Inc.; stock code 5425HT) with an average particle size of 10 nm. Dilute

---

* Corresponding author.
E-mail address: a.mailer@physics.org (A.G. Mailer).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.11.039

samples were prepared for transmission electron microscopy by dispersing titania powder at a volume fraction $\phi = 0.0026$ in deionised water using an ultrasonic probe (VCX 500, Sonics and Materials Inc.) for 30 s at 20% maximum tip amplitude. The pH was adjusted using hydrochloric acid.

Extremely dilute samples ($\phi = 0.00001$) were prepared as above to obtain the charge state of the titania in suspension. The zeta potential was measured for solution pHs of 3.1, 3.5 and 4.5 using a Malvern Nanosizer Z. Dilute suspensions were also prepared at a volume fraction of $\phi = 0.008$ to study suspension behaviour as a function of pH and salt content. The suspensions were imaged at various time intervals after dispersion and visually inspected to determine suspension stability.

Suspensions for casting were prepared by placing 3.2 g of titanium dioxide powder into 10.0 g of distilled water and dispersing using ultrasound. The mixture was then a highly viscous, white paste. Next, the pH of the mixture was adjusted with hydrochloric acid. Microscope slides were used as substrates; they were cleaned in 10% Decon solution for 15 min under ultrasonic agitation and then thoroughly rinsed with distilled water, ethanol and acetone. Following casting and drying, samples were profiled with a DekTak profilometer (Veeco Instruments) using a scan range of 1 cm (horizontal) × 131 μm (vertical).

2.1. Drop-casting

A plastic 5 mL Luer lock syringe (Braun Injekt) was filled with casting suspension. It was locked into a syringe pump (New Era Pump Systems Inc., NE-1010) and attached to a 5 μL glass micropipette (SupraCaps). The suspension/glass contact angle was increased to prevent the suspension from creeping up the outside of the capillary during deposition. The deposition procedure itself consisted of pumping 3 μL of suspension to form a pendant drop at the tip of the micropipette and slowly bringing a levelled stage with the substrate on it up to the drop. The droplets of suspension were then left to dry in ambient conditions, a process which usually was complete in 2–3 h, before being imaged.

2.2. Tape-casting

A casting mould was formed by affixing three layers of Kapton tape (3 M, 70 μm average thickness) to the slide and the pastes were spread using a PTFE doctor blade. Some cast tapes were imaged continuously during drying; once the films had dried they were all imaged before removing the Kapton tape moulds. Some damage to the edge of the ceramic tape was unavoidable, especially for tapes cast from lower pH suspensions. This had no visible effect on the parts of the film which were still well bonded to the slide. Representative regions of the film were then imaged using a microscope at low magnification (×5). These microscopy images were combined [20] for analysis purposes into one large image with dimensions of approximately 7 × 5 mm and a resolution of 1.12 px μm^{-1}. Higher magnification (×50) images were also taken when required to determine whether a crack truly bisected a domain.

The square root of the crack domain area divided by the thickness, α, is a material dependent parameter [8]. As the profilometer produces a line trace, it is necessary to use an interpolation scheme to calculate the thickness with which each domain area should be normalised. The traces were first smoothed to remove the crack discontinuities by fitting a fourth order polynomial to each. The mean thickness of these profiles was then used to normalise all measured crack areas. The maximum error introduced in this scheme, as defined as the ratio of the standard deviation of the polynomial to its mean, was 9%.

3. Results

3.1. Imaging of primary particles

Images of representative non-agglomerated particles were obtained via transmission electron microscopy (TEM, Zeiss). After capture, fourteen images containing 185 imaged particles were analysed to construct the particle size distribution. Characteristic lengths were extracted from measured particle areas by finding the equivalent circle radius, e.g. length $= \sqrt{\text{area}/\pi}$ see histogram, Fig. 1.

The zeta potential of the titania clusters in suspension was found to be +30 mV, +18 mV and −25 mV at pH 3.1, 3.5 and 4.5 respectively. Titania, like other metal oxides, exhibits surface charging in aqueous solution due to the presence of hydroxyl groups [5]. At low pH, the surface will be positively charged due to protonation and at high pH it will be negatively charged. The zeta potential data show that the titania surface is positively charged at pH 3.5 and negatively charged at pH 4.5, indicating that the isoelectric point lies between these pH values.

Fig. 2 shows the behaviour of low concentration titania suspensions at different pH. At pH 3.1, the suspension is charged and sedimentation occurs slowly after mixing. The interface between sediment and supernatant is diffuse due to the mobility of charged clusters. At pH 4.5 the suspension is unstable and rapidly aggregates. A sharp sediment/supernatant interface forms and the suspension sediments quickly. If salt is added to the charged pH 3.1 suspension, the rapid aggregation and sedimentation behaviour is exhibited once more, showing that the stable suspension must be formed from charged clusters of primary particles.

3.2. Drop-casting

Fig. 3 shows the transmission images and the height profiles of the dried droplets. As the pH increases, the drop characters change. These experiments demonstrate that changing the pH of the casting suspension modifies the strength of the flocculating potential and the resulting macroscopic flow behaviour of a cast droplet. At pH 2, the evaporation induced flow of material to the edge of the droplet (to make a ‘coffee ring’) indicates that the suspension is stable. At pH 4, the presence of a central ‘pile’ and ragged edge indicates gel-like behaviour of the suspension, i.e. an attractive interaction strong enough to generate a yield stress in the suspension that resists gravity. At pH 3, an intermediate regime is observed where the suspension still flows enough to form a defined droplet but the resistance to internal flow during drying is

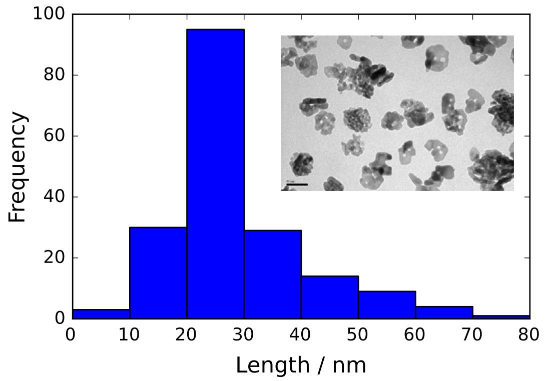

Fig. 1. Histogram of characteristic lengths for the 185 particles identified in all TEM micrographs. Inset: representative TEM micrograph of the titanium dioxide nanoparticles. Scale bar 50 nm.