Journal of Colloid and Interface Science 336 (2009) 612–615

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

In situ USAXS measurements of titania colloidal paint films during the drying process

Bridget Ingham [a,b,*], Scott Dickie [c], Hiroshi Nanjo [d], Michael F. Toney [b]

[a] *Industrial Research Limited, P.O. Box 31-310, Lower Hutt, New Zealand*
[b] *Stanford Synchrotron Radiation Lightsource, 2575 Sand Hill Road, Menlo Park, CA 94025, USA*
[c] *Resene Paints Limited, P.O. Box 38-242, Lower Hutt, New Zealand*
[d] *National Institute of Advanced Industrial Science and Technology, 4-2-1, Nigatake, Miyagino-ku, Sendai 983-8551, Japan*

ARTICLE INFO

Article history:
Received 3 February 2009
Accepted 10 April 2009
Available online 21 April 2009

Keywords:
USAXS
Small-angle X-ray scattering
Synchrotron
Titania
Paint

ABSTRACT

Real-time ultra-small-angle X-ray scattering (USAXS) was used to follow the flocculation of titania particles in two paint systems as the paint films were drying. The inter-particle scattering was extracted by comparing the time series with diluted titania dispersion (having negligible inter-particle interaction). The paint system with pigment affinic groups showed considerably less flocculation than a pure acrylic emulsion. The results were confirmed by scanning electron microscopy (SEM) images of the dried film. The likely cause of this difference and utility of USAXS for such measurements are discussed.

1. Introduction

Titania (TiO_2) is a wide band-gap semiconductor with a high refractive index, which lends it to be used as a whitening agent. In powder form it is an effective opacifier. Titania colloids are used in many manufacturing industries, such as cosmetics, paper, coatings, foods, toothpastes and paint. The scattering power of individual titania particles for visible light (300–700 nm) is maximised when the particles have a diameter of approximately 300 nm [1].

One problem encountered in the paint industry is the flocculation or agglomeration of the titania particles, both in the colloidal liquid and while the paint film is drying. The flocculates can be microns in size. This is no longer optimal for scattering visible light and can cause loss of gloss and inferior durability. Flocculation of titania pigments can be retarded by applying moderate shear, although the flocculates typically reform quickly when the shear is removed. In the paint industry flocculation is commonly overcome by adding an excess of surfactant, although this is undesirable as it has a negative impact on other areas of paint performance, such as reduced gloss, tackiness (through leaching of the surfactants), and whitening or blooming of the film surface.

The mechanism of flocculation is not well understood [2]. It is suspected that the surfactant molecules preferentially bind to certain facets of the titania particles, and as the solvent is removed from the mixture (through evaporation), rearrangement of the titania particles occurs which presses the facets with fewer surfactants bound to them against each other [3]. The titania particle size is between 250 and 300 nm and the flocculates are up to several microns. While dynamic light scattering probes the same size range, this technique is not appropriate for the paint system due to its high opacity.

There has been some recent work using atomic force microscopy (AFM) to investigate the surface of dried paint films, and transmission electron microscopy (TEM) on cryo-frozen samples to obtain images of the wet state as well as dried paint films [4,5]. These were able to directly observe the presence and size of flocculates in the wet and dry states for various systems. Other techniques such as disc centrifugation and remission light spectroscopy (RLS) are able to imply the presence of different sized scattering objects [5] but are unable to provide further information such as the distribution of sizes.

While microscopy techniques are useful in that they give a direct picture of the actual film, they have limitations in that they only sample a very small area of the paint film and cannot be used in real time. AFM gives a picture of the surface only, and TEM requires the use of thin cross-sections. Both of these can sometimes give misleading results. Ultra-small-angle scattering is a technique that can probe the size range of interest (200–2000 nm). This samples much larger areas (the size of the beam, which is hundreds of microns to millimetres in size) and is a transmission measurement through the entire film, thereby sampling from the whole volume.

---

[*] Corresponding author. Address: Industrial Research Limited, Applied Mathematics, P.O. Box 31-310, Lower Hutt, New Zealand.
E-mail address: b.ingham@irl.cri.nz (B. Ingham).

0021-9797/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2009.04.035

Previous ultra-small-angle neutron scattering (USANS) experiments have been performed on the wet paint system under varying rates of shear [6]. This study showed the degree of flocculation was dependent on the shear rate, and on the polymer co-species. However due to the low signal, USANS measurements cannot be used to perform real-time experiments. Ultra-small-angle X-ray scattering (USAXS), on the other hand, has an advantage of high scattering signals and hence the potential for real time measurements.

Previous time-resolved SAXS studies have been performed on silica–titania/polymer composites during formation [7], and on silica/polymer gel systems during flocculation [8]. However, the inorganic particles in these systems are significantly smaller than in commercial paints (10 nm for Ref. [7] and 20 nm for Ref. [8]). Even so, these studies show that SAXS is useful for real-time measurements of flocculation and aggregation.

Here we report USAXS measurements on titania colloidal paint films to follow the drying process in two paints with the same grade titania, but different polymer systems. The goal is to explore and better understand the effect of the polymer on the degree of flocculation that occurs during drying.

2. Experimental

Two paint systems were studied, using the same ingredients (titanium dioxide, water, polyacrylic dispersant, non-ionic surfactant, coalescing solvent, antifoam, alkali swellable and associative thickeners, humectant and biocides) but different acrylic polymer systems. The millbase is a commercial grade titania with alumina and zirconia coatings and organic polyol treatment, combined with a commercial hydrophobically modified polyacrylate dispersant. The two paint systems using this millbase (henceforth called sample A) are an acrylic emulsion with pigment affinic groups (sample B) and a pure acrylic high solids emulsion (sample C). The pigment volume concentration (PVC) for both samples B and C was 20%.

Beam line BL-20-XU at the SPring-8 synchrotron facility, Hgoyo, Japan, was used for the USAXS experiments [9]. The sample-detector distance was 160 m and the wavelength was 0.539 Å (23 keV). The detector is a CCD, which enables scans to be taken in rapid succession, while the paint film dried (typically 1.5–2.5 h). Typical exposure times were 5–10 s. A simple controlled humidity cell was constructed, with X-ray transparent Kapton film windows, one of which acted as the substrate for the film. The paint sample was applied to the Kapton film at an average thickness of approximately 200 μm (wet), the humidity cell sealed, and the film dried under a constant airflow. In addition, a series of data were collected on the paint samples in the liquid state, at various dilutions with aqueous solvent. These were held in place on the beam line in pouches with a well-defined thickness (approximately 0.5 mm).

The raw CCD USAXS data images are radially averaged to obtain the intensity $I(q)$ vs. q, the magnitude of the scattering vector. An appropriate background signal was subtracted from all of the datasets: for the time series, the Kapton window signal, and for the dilution experiments, a pouch filled with distilled water.

Scanning electron microscopy (SEM) images were obtained of the dried samples using a Leo 440 microscope at 10 kV and 30,000× magnification.

3. Results and discussion

The scattering intensity $I(q)$ is given by the equation

$$I(q) = c\int_0^\infty n(r)[f(qr)]^2 S(qr)\,\mathrm{d}r \tag{1}$$

where c is a constant related to the sample properties and incident intensity, $n(r)$ is the size distribution of the scattering objects, $f(qr)$ is the form factor, and $S(qr)$ is the structure factor. The form factor is an expression describing the shape of the scattering objects (in this case, spheres of the titania particles). This term is assumed to be constant throughout the time series, since the individual titania particles do not change. The structure factor is an expression describing the X-ray scattering interference between neighbouring particles, including flocculation (particles coming together).

The dilution experiments are a system where inter-particle scattering is negligible (and hence $S(qr)$ in Eq. (1) is unity). During the drying process, solvent is lost due to evaporation which will lead to two strong effects in the time series: (a) particles moving closer together, but still separated by the surfactant shell, causing changes in the inter-particle scattering $S(q)$; and/or (b) flocculation. There are two ways to model flocculation. One is to add an additional term to Eq. (1) to account for the aggregated particles [10]. The other is to consider flocculation as a continuous variation in $S(q)$ as the individual titania particles come together. Given that: (a) we have a good measure of $n(r)[f(qr)]^2$ from the dilution measurements, (b) the data have a limited dynamic range, and (c) for the sake of simplicity (fewer terms), we have chosen to use the latter approach. Attempts were made to fit Eq. (1) to the data (using a log-normal size distribution, $f(\mathrm{qr})$ for spheres [11], and $S(\mathrm{qr})$ according to Pedersen's local monodisperse approximation for hard spheres [11]). However the results of the fitting were poor. This is most likely due to a broad and non-monotonic size distribution and the limited q-range of the data. It is less likely to be due to an incorrect choice for $f(qr)$ (e.g. for rods or core–shell structure), since the broad size distribution will smear out any effects due to particle shape/morphology.

Fig. 1 shows the dilution series for sample A (millbase) and sample B (paint) samples. As the systems become more dilute, the curves eventually develop the same shape (at dilutions below 12.5%). This shows that the inter-particle scattering is negligible for concentrations below 12.5%. We have chosen the 3% sample A curve as the 'reference' curve which shows the colloid SAXS when $S(\mathrm{qr}) = 1$. This is because this is the lowest dilution and it is the same at the 6% dilution. The other sample curves can be divided by this reference dataset to obtain an effective $S(qr)$ for those samples. The assumptions are that the particle size distribution, $n(r)$, and the form factor, $f(\mathrm{qr})$, are the same for all dilutions. Fig. 2, then, shows $S(\mathrm{qr})$ for the dilution series on the paint system.

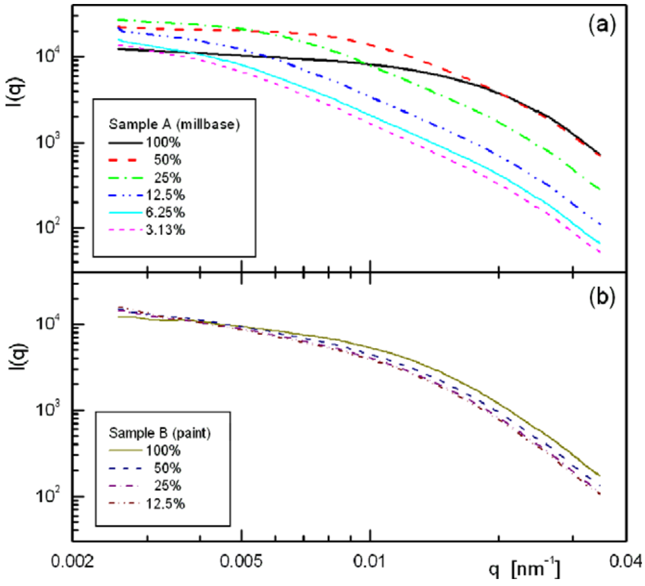

Fig. 1. Reduced data $I(q)$ vs. q for dilution series: (a) sample A (millbase), (b) sample B. The concentrations are shown in the figure legends.