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Physical adsorption of anisotropic titania nanoparticles onto poly(2-vinylpyridine) latex and characterisation of the resulting nanocomposite particles

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ABSTRACT

Four poly(2-vinylpyridine) latexes with intensity-average mean diameters ranging between 246 and 955 nm were prepared by aqueous emulsion polymerisation. These latexes were characterised by transmission electron microscopy, field emission scanning electron microscopy, dynamic light scattering, aqueous electrophoresis, disc centrifuge photosedimentometry and thermogravimetry. The adsorption of rice grain-shaped nano-sized titania particles onto the surface of these latex particles from aqueous solution was investigated. It was found that the titania particles adsorb strongly at pH 10 and the optimal loading and packing density of titania was investigated for each latex. The resulting core–shell P2VP–titania nanocomposite particles were characterised in terms of their titania contents, surface coverages and colloidal stabilities. UV–Vis spectra were recorded for the titania nanoparticles, the original P2VP latexes and the poly(2-vinylpyridine)–titania nanocomposite particles. It was found that, for the larger nanocomposite particles, UV–Vis absorption was dominated by the latex core, whereas the smaller P2VP–titania nanocomposite particles exhibited UV attenuation to longer wavelengths compared to both the bare latex and the titania particles. The poly(2-vinylpyridine) cores were selectively removed by calcination of the nanocomposite particles and the resulting hollow titania structures were investigated by transmission electron microscopy.

1. Introduction

The preparation of inorganic/organic colloidal nanocomposite particles has been of great academic interest over the last two decades [1–4]. In particular, particles comprising a polymeric core and nano-sized silica shell have received much attention [5–14]. It has recently been shown that core–shell poly(2-vinylpyridine)–silica (P2VP–silica) nanocomposite particles can be readily be prepared by heteroflocculation between anionic 20 nm colloidal silica and poly(ethylene glycol) methacrylate (PEGMA)-stabilised P2VP latex particles at pH 10 [9,15]. The PEGMA-stabilised P2VP latexes were shown to have tuneable diameters between 210 and 970 nm using an aqueous emulsion polymerisation formulation with judicious selection of synthesis parameters such as initiator, stabiliser, surfactant and monomer concentrations [15,16]. The kinetics of silica adsorption and redistribution between various latex particles has been studied using techniques such as disc centrifuge photosedimentometry (DCP), X-ray photoelectron spectroscopy (XPS) and small angle X-ray scattering (SAXS) [17,18]. Calcination of these nanocomposite particles resulted in well-defined hollow silica shells, as judged by transmission electron microscopy [9]. Colloidal nanocomposites with inorganic particulate shells other than silica have also been reported with examples including Laponite or monmorillonite clays [19–22], magnetite [23,24] and titania [22,25,26].

In this work PEGMA-stabilised P2VP latexes with intensity-average diameters ranging between 246 and 955 nm were prepared and heteroflocculation experiments were conducted using commercially available ‘rice grain’ titania particles (Fig. 1). The packing of these anisotropic particles was examined and the resulting P2VP–titania nanocomposite particles were then characterised in terms of their colloidal stability, titania content and UV attenuation behaviour.

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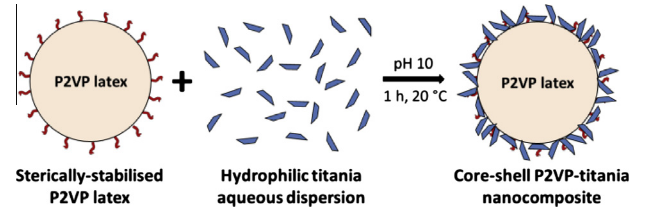

Fig. 1. Schematic representation of the physical adsorption of ultrafine titania 'rice grain' particles onto a sterically stabilised P2VP latex.

2. Experimental

2.1. Materials

2-Vinylpyridine (97%, 2VP; Aldrich, UK) and divinylbenzene (80 mol.% 1,4-divinyl content, DVB; Fluka, UK) were passed in turn through basic alumina columns to remove inhibitor and then stored at −20 °C prior to use. Aliquat 336 (Aldrich, UK) and 2,2′-azodiisobutyramidine dihydrochloride (97%, AIBA; Aldrich, UK) were used as received. Monomethoxy-capped poly(ethylene glycol) methacrylate (PEGMA) macromonomer ($M_n = 2000$; $M_w/M_n = 1.10$) was supplied by Cognis Performance Chemicals (Hythe, UK) as a 50 wt.% aqueous solution. Solaveil™ CT-30W titania particles [27] were provided as an 40 wt.% aqueous dispersion by Croda Europe Ltd. (Widnes, UK). These particles possess an alumina–silica surface coating to aid their dispersion. Deionised water was obtained from an Elgastat Option 3A water purifier.

2.2. P2VP latex synthesis

The synthesis of PEGMA-stabilised P2VP particles has been described in detail elsewhere [15,16,28–31] and therefore only one representative formulation is briefly discussed here. Aliquat 336 surfactant (20.0 g) and PEGMA stabiliser (40.0 g of a 50 wt.% aqueous PEGMA solution) were dissolved in deionised water (1.72 kg) in a 3 L double-jacketed reaction vessel equipped with a condenser and overhead stirring. A comonomer mixture of 2VP (198.0 g) and DVB (2.0 g) was added and the aqueous solution degassed for 1 h at ambient temperature using nitrogen. The solution was stirred at 200 rpm and heated to 60 °C; the initiator solution (0.30 g of AIBA dissolved in 20 g of degassed water) was added after 20 min. The copolymerising solution turned milky-white within 10 min and stirring was continued for 24 h at 60 °C. The latex particles were purified by repeated centrifugation–redispersion cycles, whereby the supernatant was carefully decanted during each cycle and replaced with fresh water. This protocol was used to remove residual 2VP monomer, excess Aliquat 336 surfactant, and non-grafted PEGMA stabiliser. Purification was continued until the serum surface tension was close to that of pure water (71 ± 1 mN m^{-1}).

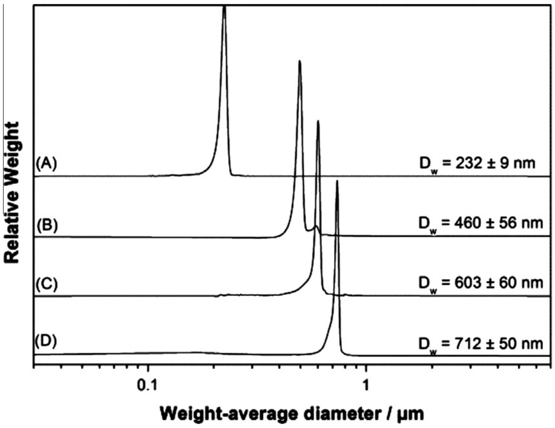

Fig. 2. Disc centrifuge weight-average size distributions obtained for PEGMA-stabilised P2VP latexes prepared by aqueous emulsion polymerisation at 60 °C. Traces A, B, C and D correspond to entries 1–4 in Table 1. The density of the PEGMA-stabilised P2VP latexes used for these measurements was taken to be 1.11 g cm^{-3}, as measured by helium pycnometry.

2.3. Adsorption of titania onto latex particles

Typically, the appropriate volume of aqueous titania dispersion was diluted with deionised water and the pH was adjusted to pH 10 using KOH. A dilute dispersion of latex particles was then added to this titania dispersion with stirring. These samples were allowed to equilibrate for >1 h either with stirring or using a roller mixer.

2.4. Calcination of nanocomposite particles

The nanocomposite particles were calcined using two different protocols. Firstly, nanocomposite particles previously prepared on carbon-coated copper TEM grids were heated in air up to 500 °C at 20 °C min^{-1} using a TA Instruments Q500. This ensured complete pyrolysis of the latex while still leaving the TEM grid usable for subsequent TEM studies. Secondly, the nanocomposite particles were calcined on a larger scale by heating pre-dried powder in a furnace above 550 °C. Full calcination was indicated by the absence of black char in the samples after removal from the furnace.

2.5. Dynamic light scattering

Studies were conducted at 25 °C using a Malvern Zetasizer Nano ZS instrument equipped with a 4 mW He–Ne solid-state laser operating at 633 nm. Back-scattered light was detected at 173° and the

Table 1
Summary of the initiator concentration, solids content, monomer conversion and mean latex diameter for sterically-stabilised poly(2-vinylpyridine) latexes prepared by aqueous emulsion polymerisation at 60 °C using a cationic AIBA initiator.

Entry number[a]	AIBA initiator (wt.%)	Solids (wt.%)	Monomer conversion (%)[b]	Number-average diameter (nm)[c]	Weight-average diameter (nm)[d]	Intensity-average diameter (nm)[e]
1	1.00	6.6	95	189 ± 10	232 ± 9	246 (0.025)
2	1.00	11.0	96	391 ± 12	460 ± 56	475 (0.039)
3	1.50	12.3	99	580 ± 40	603 ± 60	673 (0.120)
4	1.75	12.3	94	632 ± 17	712 ± 50	955 (0.299)

[a] Entries 1, 3 and 4 were carried out on a 2 litre scale using 10 wt.% PEGMA stabiliser, 10 wt.% Aliquot 336 surfactant and 1 wt.% DVB cross-linker (all based on monomer) at a reaction temperature of 60 °C. Entry 2 was carried under identical conditions but on a 100 ml scale with 12 wt.% PEGMA stabiliser.
[b] Monomer conversions were determined gravimetrically.
[c] Determined by TEM by counting at least 100 particles.
[d] As determined by DCP using a helium pycnometry density of 1.11 g cm^{-3}.
[e] As determined by DLS, the polydispersity index is given in brackets.