



	Experiment title: Structural Characterisation of Polymer-Silica Colloidal Nanocomposite Particles	Experiment number: SC-2789
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Shifts: 9	Local contact(s): Dr. Jeremie Gummel	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Oleksandr O. Mykhaylyk*, University of Sheffield Steve Armes, University of Sheffield Jennifer Balmer*, University of Sheffield Patrick Fairclough, University of Sheffield Anthony J. Ryan, University of Sheffield		

Report:

Small angle X-ray scattering (SAXS) is a powerful characterization technique for the analysis of polymer-silica nanocomposite particles due to their relatively narrow particle size distributions and high electron density contrast between the polymer core and the silica shell. Time-resolved SAXS is used to follow the kinetics of both nanocomposite particle formation (via silica nanoparticle adsorption onto sterically stabilized poly(2-vinylpyridine) (P2VP) latex in dilute aqueous solution) and also the spontaneous redistribution of silica that occurs when P2VP-silica nanocomposite particles are challenged by the addition of sterically stabilized P2VP latex. Silica adsorption is complete within a few seconds at 20 °C and the rate of adsorption appears to be strongly dependent on the extent of silica surface coverage. Similar very short time scales for silica redistribution are consistent with facile silica exchange occurring as a result of rapid interparticle collisions due to Brownian motion; this interpretation is consistent with a zeroth-order Smoluchowski-type calculation.

Adsorption of silica nanoparticles onto poly(2-vinylpyridine) latex

Time-resolved SAXS confirmed that the silica nanoparticles adsorb around a 616 nm diameter sterically-stabilized poly(2-vinylpyridine) latex to form a complete monolayer shell approximately 2.0 seconds after mixing the latex and silica dispersions. The lower time limit of our experimental set-up was just sufficient to observe the binary mixture of latex and silica sol before the silica particles begin to adsorb at the latex surface. The effective thickness of the growing silica shell increased rapidly, followed by a period of slower growth until equilibrium was attained after around 500 ms. The shell thickness was obtained by fitting the SAXS patterns using a two-population model.

Kinetics of exchange of silica nanoparticles between nanocomposite and latex particles

The redistribution of silica nanoparticles that occurs when a poly(2-vinylpyridine)-silica nanocomposite (prepared by the adsorption of 20 nm silica onto a 616 nm sterically-stabilized poly(2-vinylpyridine) latex, see above) is challenged by the addition of a 334 nm sterically-stabilized poly(2-vinylpyridine) latex was monitored by stopped-flow SAXS (see Figure 1). Here the latex diameters were deliberately chosen to be significantly different because this facilitates the data analysis (Figures 1b and 1c). Silica redistribution is

essentially complete approximately 3.5 s after mixing the nanocomposite particles with the sterically-stabilized latex (Figure 1a). For all subsequent scattering patterns, there is a rapid initial increase in the effective shell thickness, followed by a period of slower growth until equilibrium is attained after around 2.0 s. The effective thickness of the growing shell was obtained by fitting the SAXS patterns using a three-population model.

The experimental time-scales for the adsorption and redistribution of silica nanoparticles compare well with that estimated based on the Smoluchowski fast coagulation rate equation. This suggests that silica exchange is mediated by Brownian collisions. This seems reasonable because the silica nanoparticles are only weakly adsorbed via the steric stabiliser chains, rather than in direct contact with the latex surface (thus avoiding the primary minimum of the potential energy interaction curve).

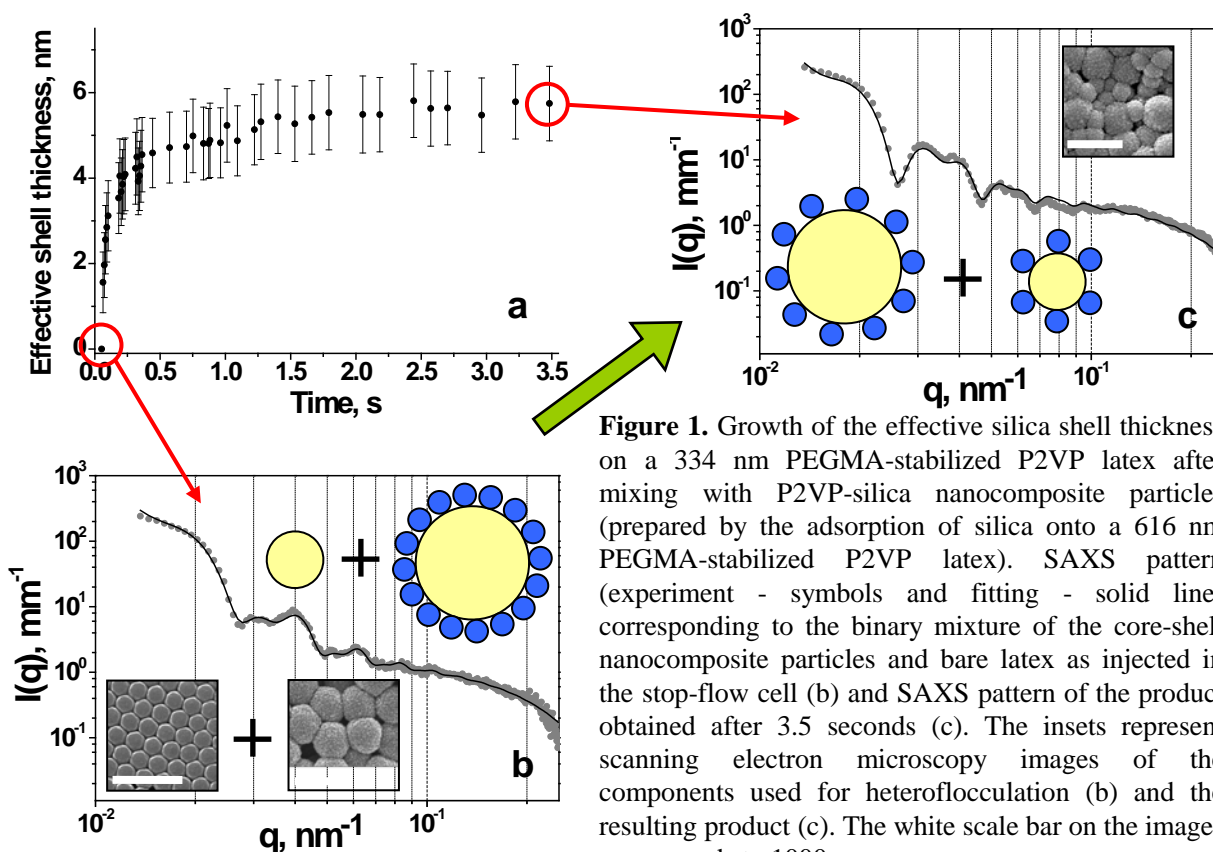


Figure 1. Growth of the effective silica shell thickness on a 334 nm PEGMA-stabilized P2VP latex after mixing with P2VP-silica nanocomposite particles (prepared by the adsorption of silica onto a 616 nm PEGMA-stabilized P2VP latex). SAXS pattern (experiment - symbols and fitting - solid line) corresponding to the binary mixture of the core-shell nanocomposite particles and bare latex as injected in the stop-flow cell (b) and SAXS pattern of the product obtained after 3.5 seconds (c). The insets represent scanning electron microscopy images of the components used for heteroflocculation (b) and the resulting product (c). The white scale bar on the images corresponds to 1000 nm.

Publications associated with this beam time:

1. Balmer J.A., Mykhaylyk O.O., Fairclough J.P.A., Ryan A.J., Armes S.P., Murray M.W., Murray K.A., Williams N.S.J., Unexpected facile redistribution of adsorbed silica nanoparticles between latexes, *Journal of the American Chemical Society*, vol.132, p.2166-2168, 2010.
2. Balmer J.A., Mykhaylyk O.O., Armes S.P., Fairclough J.P.A., Ryan A.J., Gummel J., Murray M.W., Murray K.A., Williams N.S.J., Time-resolved small-angle X-ray scattering studies of polymer-silica nanocomposite particles: Initial formation and subsequent silica redistribution, *Journal of the American Chemical Society*, vol.133, p.826-837, 2011.
3. Mykhaylyk O.O., Fernyhough C.M., Okura M., Fairclough J.P.A., Ryan A.J., Graham R., Monodisperse macromolecules - A stepping stone to understanding industrial polymers, *European Polymer Journal*, vol.47, p.447-464, 2011.
4. Holland C., Vollrath F., Ryan A.J., Mykhaylyk O.O., Silk and synthetic polymers: Reconciling 100 degrees of separation, *Advanced Materials*, vol.24, p.105-109, 2012.
5. Fielding Lee A., Mykhaylyk Oleksandr O., Armes Steven P., Fowler Patrick W., Mittal V., Fitzpatrick S., Correcting for a Density Distribution: Particle Size Analysis of Core-Shell Nanocomposite Particles Using Disk Centrifuge Photosedimentometry, *Langmuir*, vol.28, p.2536-2544, 2012.