



A study of structure and temperature-triggered breakdown of particle gels prepared by pH-triggered heteroaggregation

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ABSTRACT

Synthetic heteroaggregate particle gels are a relatively unexplored area of colloidal science. In our previous work pH-triggered formation of heteroaggregate gels prepared from mixed pigment/polystyrene (PS) dispersions were investigated [Hui et al., *J. Colloid Interface Sci.* 324 (2008) 110]. The pigment was β -copper phthalocyanine (β -CuPc). In this study that work is extended by investigating the structure of the heteroaggregates formed at room temperature in greater detail and also studying the temperature-triggered gel breakdown that occurs upon moderate heating for the first time. In this work the heteroaggregate structures were studied using TEM, atomic force microscopy (AFM) and also SEM. AFM showed the mesoscale structure to consist of highly branched space-filling heteroaggregates. They are proposed to be the building blocks of the heteroaggregate gels. TEM data supported our previous suggestion that the pigment particles act as a crosslink centre within the heteroaggregate gels. SEM images showed evidence for softening and partial coalescence of the aggregates at elevated temperatures which helped to explain the temperature-triggered gel breakdown that occurred upon heating. The temperature-triggered gel breakdown was directly correlated with the glass transition temperature of the PS particles. A study of the maximum storage modulus, G' , achieved just prior to gel breakdown, revealed a maximum at a volume fraction of pigment of 0.033. The data from the study are used to propose a conceptual model for the temperature-triggered breakdown of the pigment/PS heteroaggregate gels.

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1. Introduction

Heteroaggregation describes aggregation within dispersions containing more than one type of particle [1,2]. A number of fundamental studies involving heteroaggregation have been reported [3,4]. Many of these have involved oppositely charged silica and alumina particles [5–7]. Heteroaggregation is important in a number of areas which include waste water treatment [8]. Most of the reported work involving heteroaggregates has focussed on dilute dispersions or mixed polymer dispersions. Microgel heteroaggregates have also been studied [9]. Snoswell et al. [10] have shown that heteroaggregates with controlled porosity can be prepared using microgel particles. Whilst particle network gels formed from homoaggregation have been well studied and a clear understanding of the principles involved established [11,12], those formed as a consequence of heteroaggregation have received less attention [13]. In this study we focus on heteroaggregate gels comprised of latex and pigment particles.

In recent work [14] we reported studies on the pH-triggered heteroaggregation and gel formation within mixed dispersions of

polystyrene (PS) and β -copper phthalocyanine (β -CuPc) pigment particles. The PS particles and pigment particles were rendered pH-responsive by adsorption of a carboxylated alkyl ethoxylate surfactant. At low pH heteroaggregate particle gels formed due to pH-triggered electrostatic attraction between the positive pigment particles and the negatively charged PS particles. In this study we continue that work by examining for the first time the structure of the heteroaggregates in greater detail using TEM and atomic force microscopy (AFM). We also extend the work by exploring temperature-triggered breakdown of the gels. The aim of this study was to improve the mechanistic understanding of the heteroaggregate structural units present within the gels at room temperature and probe the changes that occur upon heating. This study is unique from the point of view of considering hybrid heteroaggregate particle gels (polymer and inorganic particles) that show two types of responsiveness. The mixed dispersions studied here exhibit pH-triggered heteroaggregate gel formation and the gels themselves show temperature-triggered breakdown.

The mixed PS/pigment dispersions investigated in this work show pH-triggered gel formation (fluid-to-gel transitions) at room temperature over a range of compositions [14]. This is shown in Fig. 1 where the pH for gel formation is plotted as a function of

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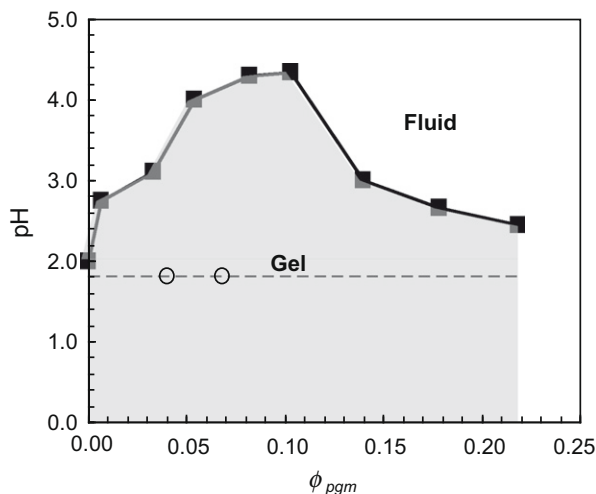


Fig. 1. Gelation phase diagram for mixed PS/pigment dispersions [11]. The dispersions contained a total of 15 wt.% pigment and PS particles. The dashed line shows the pH value used for this study. The open circles show the compositions used for the heteroaggregate size and imaging data presented later.

pigment volume fraction, ϕ_{pgm} , in the dispersion. (ϕ_{pgm} is the volume fraction of pigment with respect to total volume of pigment and PS latex particles present.) A maximum gelation pH was obtained (of about 4.2) which was attributed to an optimum composition in terms of pH-triggered network formation at room temperature [14]. The pigment played a role in increasing the gel formation tendency of the mixed dispersions, which was due to heteroaggregation. Selected dispersion compositions from the phase diagram are investigated in this work and are shown as open circles (Fig. 1).

It is well known that latexes can be added to pigment dispersions to improve storage stability and pigment compatibility [15]. Latex often provides the role of binder and film former in those mixed dispersions. Hence, it is important to study the interaction between pigment and latex particles. Islam et al. has discussed the importance of dynamics of particle–particle interactions [1]. They recognised the limitations of predictions from DLVO theory when dealing with a complex system containing more than one type of particle. There are a number of reports on the study of heteroaggregation involving the effects of particle size, zeta potential and viscosity [13,14]. In a series of seminal papers Vincent et al. investigated heteroaggregation of systems formed by opposite charged large particles with large differences in particle size [15–18]. This differs to the present study where the two components (pigment and latex) have comparable particle sizes and are gel forming.

Although temperature-triggered fluid-to-gel transitions of dispersions have been studied [12,13,16] there has been very little work reported involving temperature-triggered breakdown of latex heteroaggregate particle gels. Lazar and Hesp [17] studied aggregate growth of homoaggregated PS latexes triggered using temperature. For those dispersions aggregation was triggered by addition of a cationic surfactant. In the present work we focus on heteroaggregate particle gels which exhibit gel breakdown at temperatures close to the glass transition temperature of the latex.

The dynamic rheological behaviour of the heteroaggregate particle gels is also of interest because of the possibility of independently tuning elasticity using particle parameters [18,19]. Theoretical rheology data for model particle gels [11] have been reported which provided insights concerning the network elasticity and inter-particle forces. In the current study dynamic rheology is used to probe the temperature-dependent changes in elasticity and hence changes in inter-particle forces.

2. Experimental

2.1. Materials

Three PS latexes were used in this study (Table 1). They were prepared by emulsion polymerisation (initiated using ammonium persulfate) in the presence of Akypo RLM100. Details for latex preparation are provided elsewhere [14]. Akypo RLM100 (Laureth 11-carboxylic acid) is a carboxylated alkyl ethoxylate surfactant with an average molecular formula of $\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{10}\text{OCH}_2\text{COOH}$ [20]. The pK_a for this pH-responsive surfactant was previously determined [14] as 4.0. The pigment dispersion used for this study contained *CI Pigment blue 15:3* which consists of β -CuPc. Before use the pigment was milled in water using a bead mill with Akypo RLM100 and Solsperser 27000. The latter is a β -naphthol ethoxylate with a molecular formula [21] of $\text{C}_{10}\text{H}_7(\text{OCH}_2\text{CH}_2)_n\text{OH}$. It is a well known stabiliser for CuPc [22]. The value for n is proprietary information and has not been published to our knowledge. The latexes and pigment dispersion were supplied by FUJIFILM Imaging Colorants (Blackley, UK) and were used as received.

2.2. Particle gel preparation

Mixed particle dispersions were prepared using a Silverson LART high shear mixer. A total volume of 15 mL of mixed dispersion (15 wt.%) was added to a 25 mL glass beaker. The required amount of 2 wt.% sulphuric acid was added dropwise (ca. 2 mL) with high shear (7500 rpm) to decrease the pH to 1.8 and trigger heteroaggregation. This occurred over a 10 min period. An initial pH of 1.8 was used for all of the dispersions discussed in the work unless otherwise stated.

In the case of temperature-triggered gel breakdown the mixture was transferred to a 5 L water-jacketed vessel equipped with an overhead stirrer and temperature control. The initial temperature was 25 °C which was then raised ensuring thermal equilibrium was maintained. Samples were taken periodically for further study as required.

2.3. Physical measurements

Photon correlation spectroscopy (PCS) measurements were performed using a Brookhaven BI-9000 light scattering apparatus fitted with a 20 mW HeNe laser. The detector was set at a 90° scattering angle. A Coulter Multisizer II was used to determine the heteroaggregate size. Samples were diluted with Isoton II solution. SEM images were obtained using a Philips XL30 FEG SEM using an operating voltage of 8 kV. More than 200 particles were counted to obtain number-average diameters. For TEM, lacey carbon film grids (Agar scientific) were used. TEM data were obtained using a Philips CEM 200 operating at 200 kV. AFM measurements were performed using a Veeco CP-II scanning probe microscope

Table 1
Particle size and properties of PS or pigment particles.

| System | d_{SEM}^a (nm) (CV) | d_h^b (nm) | ζ^c (mV) | $\text{pH}_{\text{crit}}^d$ | T_g^e (°C) |
|---------|------------------------------|-----------------|----------------|-----------------------------|--------------|
| PS(90L) | 98 (17) | 87 (± 4) | –44 | 2.0 | 49.0 |
| PS(100) | 109 (18) | 100 (± 5) | –45 | 1.9 | 62.0 |
| PS(140) | 158 (16) | 140 (± 7) | –44 | 1.4 | 68.0 |
| Pigment | 135 (27) | 150 (± 8) | –16 | 3.5 | – |

^a Number-average diameter determined from SEM. CV is the coefficient of variation.

^b Hydrodynamic diameter measured using photon correlation spectroscopy.

^c Values in the presence of 10^{-3} M NaNO_3 . The pH was 7 for these measurements.

^d pH below which aggregation occurs.

^e Average value determined from the midpoint of the DSC data.

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