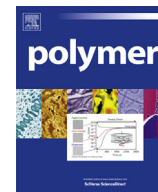




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Microstructure of colloid-polymer mixtures containing charged colloidal disks and weakly-adsorbing polymers

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ABSTRACT

Structural arrest in an aging colloid-polymer mixture of charged colloidal disks and weakly interacting polymers is primarily governed by the spatial arrangement of microstructural domains in the system. Here we present a detailed ultra-small angle x-ray scattering (USAXS) study of the polymer induced microstructural changes occurring in systems containing laponite[®] and poly(ethylene oxide) (PEO). Laponite[®] suspensions are known to transition from a homogeneous fluid to an arrested phase as a function of time. USAXS results show that when polymer chains are added to this colloidal system, the microstructural changes are found to depend on (i) polymer-colloid size ratio, (ii) particle and polymer concentration. Large length scale structures (300–1000 nm) of non-uniformly varying size appear with increasing concentration of high molecular weight PEO ($R_g/R \sim 2.4$). However with shorter PEO chains ($R_g/R \sim 0.5$), we observe the formation of intermediary structures with a characteristic length scale of 50–60 nm. With increasing particle concentration, we observe a more compact structure for the high molecular weight PEO and no signature of a percolating network in the case of the low molecular PEO. We believe that these results add to our understanding of the complex aging behavior of clay-polymer systems.

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1. Introduction

Particles in colloidal dispersions self-assemble under different conditions to form disordered, structurally arrested phases like colloidal glasses and gels. It is, thus of importance to understand the formation mechanism and the characteristic nature of these states as it helps in tuning material properties for a specific technological application and in determining the shelf life or long term stability of the material itself. Colloidal glasses and gels can form when the particle volume fraction is increased or when salts, surfactants or polymers are added to the system to modify interactions between particles. Hard-sphere colloidal systems are often used as simple models to understand the physics behind the formation of glasses and gels. For hard-sphere colloids at concentrations close to the fluid-glass transition ($\phi_c \sim 0.58$), the system transitions from a

homogeneous liquid phase to an arrested glassy phase primarily due to increasing excluded volume effects [1,2]. On the other hand, fluid-gel transitions can occur along a wider range of concentrations by increasing the range and strength of attractions between particles in the system. One way to achieve this is by adding salts to a charged repulsive colloidal system. The addition of salts increases attractions between particles by screening the electrostatic repulsive interactions. Fractal-like aggregates begin to form, and under certain conditions the fractal structure percolates to form a space-filling gel like network [3]. Colloidal gels can also form by the addition of non-adsorbing polymers to a hard sphere system, which causes a depletion attraction between particles. Recent studies have shown that the formation of this arrested phase is due to increasing strength of short-range attractions and can be precisely controlled by simply changing the length and the concentration of polymer chains in the system [4,5]. Experiments have also shown that the addition of non-adsorbing polymers to a glassy colloidal system can shift the effective fluid-glass transition to a higher volume fraction, thus making it feasible to work with a fluid phase at higher particle loadings [6]. Understanding the formation of these states in suspensions containing aspherical colloids is

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however not straightforward, as shape anisotropy and physical aging effects contribute to the existing complexities in the problem.

Laponite[®] is a model system that is often used to study the structure, phase behavior and dynamics of colloidal disks, as it exhibits a very rich physical behavior. Laponite[®] is a charged synthetic clay (~25 nm wide, ~1 nm thick) with an empirical formula of $\text{Na}^{+}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{22}(\text{OH})_4]^{-0.7}$. The particles carry a negatively-charged face which is counterbalanced with the Na^{+} ions present in between layers and a pH-governed charge distribution along the edges due to the formation of surface charges during hydration and swelling. Extensive studies have been conducted using techniques such as rheology [7], light, neutron and x-ray scattering experiments [8,9] to probe the structure and phase behavior of aqueous laponite[®] dispersions at different particle concentration, c_l , and salt concentrations. Bonn and co-workers used light scattering and conductivity experiments to classify dispersions of laponite[®] into three different arrested states; (i) Gels ($c_l < 1.5$ wt%), (ii) Repulsive glasses ($c_l > 1.5$ wt%) and (iii) Attractive glasses ($c_l < 1.5$ wt%, high salt conc.), based on the evolution of the relaxation time parameters [10].

Colloidal glasses and gels of laponite[®] both exhibit solid-like rheological behavior, and there are few experimental methods to distinguish between these two different arrested states. In comparison with spherical colloids, the formation of glassy phases in laponite[®] occurs at a much lower volume fraction of ~0.01. The formation of colloidal glasses in most cases is driven by dominant electrostatic repulsions between particles, and in other cases it is driven by weak inter-particle attractions. Many refer to the latter condition as an “attractive glass,” as long lived attractive bonds between particles exist in this structurally arrested phase, and the former state as “Wigner” glasses, although there is still a considerable amount of debate on whether these are gels or glasses [11–13]. Similar to the hard sphere system, colloidal gels in laponite[®] form when clusters begin to span the volume to form a space-filling network. In rheological experiments, glassy systems follow the framework of the SGR model [14] and gels can be identified by using the Winter-Chambon's criterion [15] where a single iso-frequency $\tan \delta$ point can be correlated with the fractal dimensions in the system. Neutron and x-ray scattering measurements are also used to identify these structures in the colloidal system. Colloidal glasses are homogeneous at larger length scales and correlations are restricted to the interparticle distances, whereas for the colloidal gel, correlations exist at larger distances with the structure factor profiles showing fluctuations at low values of the scattering vector q [11].

Laponite[®] gels and glasses have been studied extensively by several groups. However, there is still a considerable amount of debate on whether these systems are really gels or glasses. Several studies in the literature have reported the phase diagram of laponite[®] as a function of both particle and salt concentration. There seems to be a large consensus on the observation that laponite[®] particles phase separate at concentrations below 1% and when the salt concentration is above 20 mM [16]. It is also known that for concentrations between 1% and 2%, the suspensions largely evolve to form colloidal gels. However, the final state and microstructure in systems at and above 2% is largely unclear. Small-angle x-ray scattering experiments conducted by Ruzicka and co-workers have found that systems above a concentration of 2% form glassy phases where particles remain frozen and disconnected in the system [17]. Interestingly, results from a recent study by the same group have indicated that while these exist as repulsive glasses during the early aging period, the same system exhibited a repulsive glass – attractive glass transition due to increasing attractions as aging proceeds in the system [18]. On the contrary, studies conducted by Mongondry and Joshi have shown that the particles

exist as colloidal gels where attractive bonds do exist between particles [19,20]. Comprehensive set of experiments conducted by Joshi and co-workers have shown that structural arrest in laponite[®] systems is not driven just by repulsions but also by attractive interactions between particles [20].

The kinetics of structural arrest in laponite[®] can be modified by the addition of salts to the system. The addition of salts results in the screening of the electrostatic repulsions thereby increasing the van der Waals attraction between particles. The rate of particle aggregation under different salt conditions has been extensively studied by many groups. At very high salt concentrations and at low concentrations of laponite[®], the particles begin to aggregate and phase separate under the influence of gravity. Another way of modifying the interactions between the particles is by adding polymers to the system. Several techniques like NMR, reflectometry, x-ray and neutron scattering have been used to study the interaction of polymers with colloidal surfaces [21–24]. Polymers are expected to contribute to a variety of interactions depending on the nature of the polymer and on the way it interacts with the surfaces of a colloidal particle. While non-adsorbing polymers trigger attractive interactions based on thermodynamic effects, adsorbing polymers can contribute to both steric repulsions and, if chains are sufficiently long, a bridging attraction between particles. Adding short polymer chains to a laponite[®] system is known to slow down the aggregation process due to steric effects, and adding longer polymer chains leads to the formation of large-scale clusters and space-filling gels in the system [25,26].

Experiments using rheology were previously conducted to study the effect of chain length and concentration of polymers on the macroscopic properties of a laponite[®]-PEO system. Results from rheological experiments conducted for systems containing 2% laponite[®] with PEO have shown that two different behaviors exist when the polymer chain length is allowed to vary; (i) retardation in gelation kinetics for molecular weights below 83 kg/mol due to steric effects and (ii) accelerated gelation kinetics for molecular weights above 83 kg/mol because of polymer bridging [27,28]. Studies have also shown that by changing the concentration of small PEO chains, the system transitions through a re-entrant behavior because of increasing depletion attractions in the system. More recently our group has recently studied the effects of varying the concentration of PEO on the macroscopic properties of the system [29,30].

In this work, we have employed ultra-small angle x-ray scattering (USAXS) to investigate the microstructure of laponite[®] systems at particle concentrations of 2–3%, with poly(ethylene oxide), a weakly adsorbing polymer. In order to systematically examine microstructural changes, we consider two different polymer-colloid size ratios to highlight the effects of long ($R_g/R \sim 2.4$) and short ($R_g/R \sim 0.5$) polymer chains on the formation of structures in the system, where R_g is the radius of gyration of the PEO chains and R is the radius of the laponite[®] disc (~25 nm). In both cases, the concentration of PEO, c_p , was allowed to vary between 0.25% and 2.5% (w/w). For the longer PEO chain, this allows us to look at variations in the structure in the concentrated polymer regime. On the contrary, for the shorter PEO chains the range spans regions between dilute and semi-dilute polymer regimes.

2. Materials and methods

Laponite[®] RD was procured from Southern Clay Products (Gonzales, TX, USA) and poly(ethylene) oxide (PEO) with number-average molecular weight, M_w , of 20 and 300 kg mol⁻¹ were purchased from Sigma Aldrich and used without any further purification.

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