



The effect of particle-scale dynamics on the macroscopic properties of disk-shaped colloid–polymer systems



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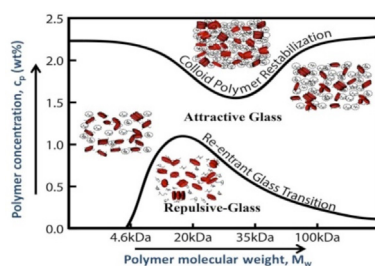
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HIGHLIGHTS

- Dynamics of polymer–clay dispersions are reported at varying polymer concentration.
- Colloidal re-entrant behavior is observed when the polymer medium is dilute.
- A second critical transition is observed at higher polymer concentrations.
- Dispersions at the second critical exhibit slower aging dynamics.

GRAPHICAL ABSTRACT



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ABSTRACT

Particle-scale rearrangements occurring in mixtures containing anisotropic disk-shaped colloids and polymers often lead to the development of unusual viscoelastic features that can play a crucial role in applications. Here, we report the early aging behavior of a series of mixtures containing laponite, a model disk-shaped colloid, and poly(ethylene oxide) (PEO) chains of three different molecular weights, 35 kg/mol, 20 kg/mol and 4.6 kg/mol. The concentrations of PEO were varied within their respective dilute and semi-dilute un-entangled regions. Rheological experiments were utilized to describe the effects of chain number and length on the macroscopic behavior of suspensions and dynamic light scattering (DLS) was used as a tool to establish a correlation between the macroscopic behavior and dynamics seen at smaller length scales. For dilute concentrations of PEO, the rheology is consistent with a glass–liquid–glass phase transition, a trend that resembles the re-entrant behavior observed in many colloid–polymer systems. However, in more concentrated PEO solutions, samples re-stabilize and remain stable for a longer period of time. Interestingly, at lower length scales the stabilization that is seen in the concentrated region is characterized by an increase in the first and second relaxation timescales, suggesting that tightly bound stable clusters diffuse through the medium. To our knowledge, this type of behavior in an anisotropic colloid–polymer system has not been previously observed.

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1. Introduction

Colloid–polymer mixtures are of interest for a range of conventional and emerging industrial applications. In recent years, the use of anisotropic colloids has gained attention, as their geometry facilitates tunable phase behavior and properties, oftentimes at lower particle volume fractions than in spherical colloids. Mixtures containing natural/synthetic clays with polymers are one amongst

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the many suspensions that are frequently used in industries that manufacture paints, cosmetics, food, and so on [1]. However, maintaining the stability of these mixtures still remains an industrial challenge, and the conditions under which they are manipulated and processed have a strong bearing on the effective interactions in the system. Therefore, it is critical to understand the rheological features arising from the complex interactions between the nanoparticles and polymers.

Laponite RD is a charged disk-shaped synthetic clay which is often used as a model to understand interactions within an anisotropic colloid–polymer system. This 25 nm wide, 1 nm thick disk has a negatively-charged face and an edge whose charge depends on the pH of the dispersing medium. Under more basic conditions, the edge is primarily negative, and when the pH is <9 the edge develops a small positive charge [2]. Aqueous dispersions of laponite exhibit a time-dependent phase behavior that is highly sensitive to conditions like pH, temperature, ion/particle concentration and the presence of other macromolecules in the system. These experimental conditions are known to change the interactions between particles in a way that leads to the formation of different arrested states like gels and glasses [3,4] yet the formation of these states and their physical behavior is not understood well.

The pH of the medium in which these particles are suspended plays a vital role in influencing particle interactions, and in turn their relevance in applications across different fields. At pH values below 9, the edges are positive and the particles form a house-of-cards structure as a result of face–rim attractions. This structure is widely exploited in the bioengineering field as they shear thin and self-assemble to form structures in aqueous media [5]. Recent experiments have shown that polymer hydrogels containing laponite also show enhanced mechanical properties when immersed in phosphate buffer saline (PBS), which is often used in studies involving cell growth [6]. Studies have also shown that the particles are compatible with stem cells and various animal cell lines [7,8] and laponite-based systems have been explored as vehicles for drug delivery [9]. At pH >9 and at very low ionic strengths, the interactions between particles are largely repulsive. The electrostatic repulsions in the system primarily dominate, and the system slowly evolves to form a repulsive glassy phase with structural and dynamic heterogeneities present across length scales [10]. However, in a more recent and detailed study conducted by Angelini et al., it was observed that the systems that exist as repulsive glasses at early waiting times undergo a glass–glass transition to behave like an attractive glass at longer time scales [11]. Upon increasing the ionic strength by adding salts, the electrostatic screening by the counter ion cloud changes the kinetics of aggregation, and this has a direct influence on the aging behavior of the system [12–15].

Besides salt/ion effects, polymer chains can alter the structure and macroscopic properties of a colloidal dispersion. A number of rich state transitions have been observed both through experiments and theoretical studies for dispersions containing either adsorbing or non-adsorbing polymers [16–18]. For polymer chains that adsorb onto surfaces of colloids, steric and bridging effects play an important role in deciding the effective interaction between particles, and this in turn influences the aging behavior of the system. However, the transitions in behavior will depend on fundamental polymer chain characteristics like chain length, concentration, and the nature of the polymer itself. PEO is a weakly adsorbing, neutral, hydrophilic homopolymer that is often used as a simple model polymer to observe colloidal behavior. The extent of adsorption of PEO on a surface depends not only on its length but also on the way chains arrange themselves on a surface. The chains assume a loop, train and tail configuration on a particle surface, as the adsorption of a polymer segment on one site dictates the steric configuration of the segment next to it. Numerical experi-

ments on spherical particles with weakly interacting polymers have shown that for long polymer chains the fraction of tails is greater when compared to smaller chains which predominantly form loops with multiple contacts close to the surface [19]. NMR, dynamic light scattering (DLS) and small angle neutron scattering (SANS) studies conducted by Nelson and Cosgrove on dilute solutions of laponite and PEO (20–986 kDa) reveal that the adsorbed polymer chains have a flat conformation with a thickness that agrees with the Scheutjens–Fleer theory [20,21]. This observation was found to be in agreement with the first SANS study conducted by Lal and Auvray [22,23]. They also observed that the thickness along the edge had a weak dependence on the molecular weight of PEO, which suggests that the chains begin to wrap around the edge and trail along the opposite face or extend in solution.

The presence of a weakly adsorbing chain like PEO in a colloidal suspension can either slow down or speed up the aging process of the system, and this typically depends on the chain length of the polymer. The impact of chain length on the kinetics of this aging behavior has been investigated by several groups. In an experimental work conducted by Baghdadi et al., the rheological behavior of laponite–PEO dispersions with PEO at two concentrations 1% and 2% and at different molecular weights (M_w : 13–700 kg mol⁻¹) was observed over a period of time [24]. In this study, two distinct features were observed: (1) retardation of aging behavior for PEO < 83 kg mol⁻¹ as a result of steric effects and (2) faster aging behavior for PEO > 83 kg mol⁻¹ due to polymer bridging effects. Concurrently, in another study by De Lisi et al., techniques like SANS and viscometry were used to understand the behavior of laponite with a range of low molecular weight PEO (M_w = 0.2–35 kg mol⁻¹) at a concentration of 2.2% [25]. Their SANS results indicate an attractive interaction in the system which increases with increasing laponite concentrations. The results also suggest that the gelation kinetics speed up for the low molecular weight case but this effect is reversed for chains larger than 1 kg mol⁻¹. Similar observations were also made in a study by Mongondry et al. where the aggregation kinetics of dilute Laponite dispersions with dilute concentrations of pyrophosphate and poly(ethylene oxide) was tracked using light scattering [26]. Though the qualitative observations may seem different, they bring out the importance of how different polymer and laponite concentrations could possibly influence the competing interactions between particles in the system.

There are studies which discuss the effects of concentration on the bulk and microstructural behavior of laponite with both high and low molecular weight PEO. The addition of a high molecular weight PEO results in the formation of a gel-like network predominantly due to polymer–particle bridging. This behavior was first observed by Schmidt's group who conducted a systematic study on the microstructure of systems with PEO at molecular weights greater than 1000 kg mol⁻¹ [27]. Shake gels were later observed within a narrow range of concentrations, at molecular weights between 200 and 600 kg mol⁻¹, and this state was attributed to bridging which was a consequence of partial saturation of a laponite surface [28]. A qualitative state diagram was later proposed by Can and Okay to define this shake gel region [29]. A dual aging behavior in a laponite suspension with 100 and 200 kg mol⁻¹ was recently proposed by Zulian et al. [30]. In this experimental work, the group investigated the aging dynamics of dispersions at a fixed laponite concentration of 2% and varied the concentration of PEO between 0.05 and 0.5%. Fast and slow aging dynamics were observed and the existence of a critical concentration (at 0.38%) marked the transition between the two physical features.

The behavior of laponite with shorter polymer chains is rather difficult to understand, as the polymers contribute to a variety of interactions depending upon their concentration and molecular weight. In a recent work by Sun et al., a universal scaling was

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