



Shaken but not stirred: The formation of reversible particle – polymer gels under shear



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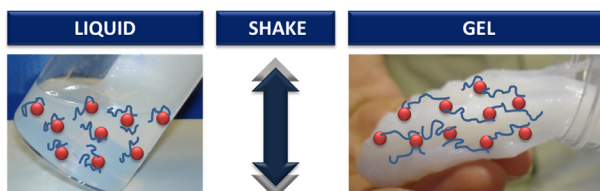
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HIGHLIGHTS

- Shake gels can be formed with particles with different shapes or sizes.
- Dispersions of poly(ethylene oxide) and laponite, montmorillonite or silica form shake gels.
- The shake gel formation depends on the nature of the applied shear field.
- The degree of particle coverage necessary for shake gel formation depends on particle shape.

GRAPHICAL ABSTRACT

Aqueous Ludox-PEO mixture contains 25% Ludox TM-50 and 0.4% PEO MV ~4,000,000. (LIQUID) before shake it; (GEL) after completion of shaking.



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ABSTRACT

Some dispersions of clay and silica particles in water in the presence of relatively high molecular weight polyethyleneoxide (PEO), which are fluid when at rest, become solid-like after a quick shake to such an extent that they can be held in the hand. On leaving the dispersions for a certain period of time, minutes to days depending on the polymer molecular weight and concentration, the dispersions become liquid-like again. These dispersions have been called “shake gels”, and a number of physical variables are determinant for producing the gel and controlling its behavior. In this work, we have studied the effect of the shape and size of the particles and of the PEO molecular weights. To that aim, we have mapped the “phase” behavior of silica (Ludox TM-50), montmorillonite and laponite dispersions in presence of PEO of different molecular weight. Shake gels are formed under certain concentrations of particles and PEO. The necessary degree of particle coverage for shake gel formation seems to depend on the particle shape. Whereas in the case of disc-shaped particles this limit is around the saturation concentration, in the case of spherical particles the limit is around 2/3 of the particle surface saturation. On the other hand, we observe some differences between montmorillonite (micrometer-size particles) and laponite (nanometric particles) dispersions. When we shake the former we find in some cases an important and irreversible phase separation; on the contrary, in the case of the laponite dispersions, the phase separation is far less frequent and extensive. Finally, we have found that the nature of the applied shear field has a profound effect on the sample behavior. When we place the dispersions in a conventional rheometer and shear them at moderate shear rate, for many minutes the gel is not formed. However, shaking it by hand or extruding it through a syringe brings about this effect in a matter of seconds.

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1. Introduction

Polymer adsorption to particles as a method of enhancing colloid stability, due the role of polymers in stabilizing particles against aggregation, has been extensively studied for at least the last 5 decades. It is also well known that under certain circumstances polymers can induce the aggregation of particles either by simultaneously adsorbing on two particles (bridging flocculation) or due to the presence of non-adsorbing polymer giving rise to depletion flocculation. Certain formulations where particles are dispersed in a relatively high molecular weight polyethyleneoxide (PEO) solution are perfectly stable for many days, giving a low viscosity solution. The important point is that a gel is formed upon shaking, reaching, in some cases, with the consistency of toffee. On standing the gel relaxes back into the liquid state over the course of seconds to days, depending on the formulation. This shear effect has been observed in watery mixtures of laponite and PEO [1,2] and silica particles in presence of adsorbing PEO [3,4]. As a possible explanation for this phenomenon, Pozzo and Walker [1] suggested that the PEO adsorbs on the particles; when the surface is not fully saturated, the PEO can bridge several particles causing the formation of aggregates. Application of shake can desorb some bonds of the PEO and reabsorb them onto other particles, causing the aggregates to grow substantially.

A number of physical variables are necessary for producing the gel and controlling its behavior. Liu et al. [3] and Cabane et al. [4] studied how depending on the adsorption of the number of silica particles per PEO macromolecular chain, and the free polymer equilibrium concentration, quite different rheological behaviors can be observed in the silica PEO mixtures such as rheopectic shear-induced gelation, Newtonian flow or thixotropic shear-thinning. Ye et al. [5] studied the effect of de particle polydispersity on the structure and dynamics of silica-PEO mixtures. They found that mixtures of PEO with polydisperse silica particles showed strong shear thickening upon shaking, while mixtures of monodisperse silica did not. In addition, there are some studies [1,2] about the “phase behavior” of laponite-PEO system. Shake-gels are observed for PEO concentrations slightly below the threshold of complete saturation of the laponite particles by the polymer. Can and Okay [6] investigated the effect of the molecular weight of PEO on the properties of laponite-PEO shake gels. They found that increasing molecular weight shifts the critical range of average number of polymer chains adsorbed by a laponite particle for the gel formation towards smaller values. Moreover, at high molecular weight PEOs only weak gels are formed. Saito et al. [7] studied the rheological behavior of silica-PEO suspensions. They found that suspensions of silica particles in PEO solution show shear-thickening profiles in steady shear, and highly elastic responses in oscillatory shear, under large strains.

The nature of the applied shear field has an important effect on the shake gel formation. When the samples are subjected to simple shear in Couette flow it is found that the gels are not induced up to shear rates of thousands of s^{-1} [3]. However, the gelation phase transition is observed with moderate manual agitation, which corresponds to a significantly smaller shear rate ($<100/s$) [1].

In this work, we study the effect of the shape and size of the particles on the shake gel formation. To that aim, we have mapped the “phase” behavior of silica (Ludox TM-50), montmorillonite and laponite dispersions in presence of PEO. Moreover, we also analyze the fact that extruding the dispersion through a syringe brings about the gel formation in a reproducible manner. We use these data to try to advance the understanding of the underlying mechanism that causing the shake gel formation.

2. Experimental

2.1. Materials

For our experiments, we have used colloidal silica, Ludox[®]TM-50 (Aldrich Chemical Company) with according to the manufacturer, specific surface area of $\sim 140\text{ m}^2/\text{g}$ and average diameter of 30–34 nm [8,9]. Laponite RD is a synthetic hectorite-like clay manufactured by Laporte Industries Ltd. (UK). It was used throughout this work without further purification. Laponite consists of small platelets of approximately $30 \times 1\text{ nm}^2$ dimensions [10,11]. Its surface area is approximately $350\text{ m}^2/\text{g}$, as determined by BET Argon adsorption measurements according to the manufacturer. Sodium montmorillonite was a commercial material supplied by Laporte Absorbents, sold under the trade name Gelwhite H-NF. The montmorillonite consists of plates of particles approximately $1\ \mu\text{m}$ in diameter and 0.5 nm thick. The surface area for montmorillonite, estimate by methylene blue adsorption was found to be $\sim 1000\text{ m}^2/\text{g}$ [12]. Poly(ethylene oxide), of average molecular weights 200,000, 300,000, 400,000, 900,000, 4,000,000 g/mol was purchased from the Aldrich Chemical Company.

Water was purified using a Milli-Q Academic System (Millipore Cooperation), USA.

2.2. Methods

Appropriate proportions of polymer solutions and particles were mixed and gently stirred in a bottle and let to stay for 24 h to ensure solutions homogeneity. They were then shaken, varying between a couple of shakes and 10 min.

Some samples were poured into a syringe and squirted through a hypodermic needle of dimensions 10 cm in length and 1 mm diameter.

Some samples were poured into the concentric cylinder geometry of a Paar Physica Universal rheometer (Austria) and the viscosity at different shear rates (from 200 to 1000/s) and the complex modulus (at 1 Hz and 1 Pa) were monitored as a function of time.

3. Results and discussion

3.1. Laponite suspensions

The “phase diagram” for laponite-PEO (average molecular weight 400,000 g/mol) dispersions as a function of clay concentration in weight percent and the mixture concentration given as Γ_t (total mass of PEO per total area of clay surface) is shown in Fig. 1. At low Γ_t no shake gel is formed, but as Γ_t increases, there is a narrow range of Γ_t , shake gel effect is observed. At higher Γ_t , shake gels no longer form. The critical value of Γ_t , below which no shake gel is formed is quite independent of the laponite concentration and seems to be related only to the available amount of PEO per total area of clay surface.

Phase diagram of laponite-PEO mixtures at lower PEO molecular weight ($\sim 300,000\text{ g/mol}$) has been presented previously by Pozzo and Walker [1] and Zebrowski et al. [2]. Their results agree fairly well with ours and it seems that there are no significant differences between the phase diagram of the two PEO molecular weights.

Fig. 2 shows how the complex modulus of laponite suspension (concentration of particles 1%) changes as a function of time for different PEO concentrations. As we can see, the complex modulus shows a maximum at 0.5 mg/m^2 and then decreases. This result is in accordance with Pozzo and Walker [1] discussion about the “phase diagram” of the laponite-PEO mixtures. At very low Γ_t we have found that the complex modulus is low and they suggest that, under those conditions, there is too little polymer to result

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