

Shake-gels: shear-induced gelation of laponite–PEO mixtures

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This paper is dedicated to our colleague and friend, Kees de Kruif, in celebration of his 60th birthday.

Abstract

Suspensions of clay particles (laponite), mixed with poly(ethylene oxide) (PEO) undergo a dramatic shear thickening when subjected to vigorous shaking, which transforms them from a low viscosity fluid into a ‘shake-gel’, a solid with elasticity sufficient enough to support its own weight. The shake-gel is reversible, relaxing back to a fluid with a relaxation time that is strongly dependent on PEO concentration. Shake-gels are observed for PEO concentrations slightly below the threshold for complete saturation of the laponite particles by the polymer. Light scattering measurements confirm that the PEO is adsorbed on the surface of the laponite particles, and suggests that shear induces a bridging between the colloidal particles, resulting in a gel network which spans the system. Desorption of the polymer reduces the bridging and thus relaxes the network.

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Keywords: Laponite; Poly(ethylene oxide); Adsorption; Gelation; Relaxation

1. Introduction

Suspensions of colloids and polymers are widely encountered in many different applications, including biological fluids, drilling muds, cosmetics, food and pharmaceuticals. In addition, many manufacturing processes utilize colloidal suspensions, since liquid dispersions can be transported much more easily than the bulk solids themselves.

The stability of colloidal suspensions is strongly influenced by solubilized polymer; it alters the interactions between the colloidal particles in solution, and thus can be used to fine-tune both the phase behavior and the rheology of the colloidal suspension. There are extensive studies elucidating the role of polymer in stabilization or flocculation of colloidal suspensions [1–3].

The primary reason for adding polymers to colloidal suspensions is to achieve desired rheological properties. Typically, polymers are used to control the viscosity, often being added to induce shear thickening; sometimes the addition of polymers can even lead to shear-induced gelation, a highly non-Newtonian behavior. The most dra-

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matic examples are solutions containing long-chained polymers, such as ionomers [4], amphiphilic polymers [5] and mixtures of polymer and colloids [6]. In all these systems, the solution at rest and under low shear-rate deformation flows readily with a constant viscosity. Upon non-linear levels of deformation, these solutions shear-thicken and form gels. The resultant gel is typically quite weak, and has been described as having the consistency of ‘a half-cooled gelatin dessert [4].’ However, it is also possible to obtain significantly greater shear thickening, leading to much more elastic gels. In this paper, we present a study of a new system where the resultant gel is surprisingly strong. It is a solution of nanometer-sized clay particles mixed with a long-chained, linear polymer. If a jar containing a sample of this mixture is shaken vigorously, a highly elastic gel is formed; which is rigid enough that when the jar is inverted, the gel supports its own weight. The abrupt change in stiffness is reminiscent of electrorheological fluids rather than the shear-thickening typically observed in polymer solutions. More surprisingly, this flow-induced gelation is reversible; if the sample is left at rest for some time, ranging from minutes to days, the gel relaxes back into a slightly viscous liquid.

A similar behavior has been reported for mixtures of nanometer-sized silica spheres and polyethylene oxide (PEO); however, the silica–PEO gels were not observed to be as rigid as those studied here, nor were the relaxation times reported [6]. Nevertheless, the silica studies provide important insight into the basic mechanism leading to gelation: at rest, the PEO is weakly adsorbed to the clay particles, forming small aggregates comprised of several clay particles. When a sufficiently strong shear is applied, the polymer chain segments near the clay disk deform exposing additional clay surfaces to the bulk solution, thus making it possible for additional polymer monomers to adsorb onto the clay disk. As the shear proceeds, an increasing number of polymer–clay adsorption sites are created, a fraction of which involve adsorption of a polymer chain onto clay particles belonging to different aggregates, thus forming polymer bridges between the particles. In the case of silica, the larger aggregates have been

called ‘necklaces’ [6]; they correspond to multiplets in the ionomer literature [4], or ‘flowers’ in the amphiphilic polymer literature [5]. For appropriate polymer and laponite particle concentrations, these bridges rapidly form a network that spans the entire solution, giving rise to a gel that persists while the shear is applied. However, once the shear stops, the polymers desorb, reducing the bridging and attaining their original configuration; this causes the gel to relax back to a fluid.

This mechanism requires that the monomer–clay bond is weak and the energy associated with adsorption is much less than that associated with the entropy of the polymer coil. In this limit, moderate shear can increase the number of bonds between the polymer–clay without significantly altering the configuration of the polymer. This is the opposite limit from that of shear-thickening in ionomers and telechelic polymer solutions, where the bonds formed between ‘stickers’ [4], ionic side groups or hydrophobic heads which play a role analogous to clay particles for our solution, are strong and form the dominant contribution to the free energy of the aggregate. In these systems, moderate shear will significantly alter the polymer chain configuration without altering the number of bonds between sticker particles.

In this paper, we report measurements of the phase behavior of laponite–PEO mixtures subject to flow, and we determine the range of concentrations of polymer–colloid mixtures that exhibit shake-gel behavior. Static and dynamic light scattering measurements on the mixtures at rest are used to characterize the adsorption of PEO polymer on the clay particles. Relaxation times of the shake-gels are measured to gain insight into adsorption energies. We use these data to characterize the behavior of the shake-gels, and to develop a physical picture of the underlying mechanism that causes their formation.

2. Experimental procedures

2.1. Materials

The clay used in this study was Laponite-XLG (Southern Clay Products, Inc., Gonzales, TX). The

laponite particles are synthetic disc-shaped crystals, 25 nm in diameter and 0.92 nm in width, with an empirical formula given by: $\text{Na}_{0.7}^+[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{0.7-}$. The unit cell of the crystal is comprised of six octahedral magnesium ions sandwiched between two layers of tetrahedral silicon atoms, with these groups balanced by 20 oxygen atoms and four hydroxyl groups. When laponite is dispersed in water, the Na^+ ions are released into solution, creating a double layer that causes the particles to repel each other, initially stabilizing the particles. The suspensions are stable up to concentrations of 2.5–3% by weight, above which they form an irreversible gel. However, even at low concentrations, these solutions age slowly in time, ultimately forming gels; this suggests a weak driving force for the formation of the gel structure. The polymer used in the study is PEO, a linear chain polymer, (Sigma-Aldrich Co., Milwaukee, WI) with a molecular formula, $-\text{[CH}_2\text{--CH}_2\text{--O]}_n-$. The molecular weight of the polymer used is $M_w = 300\,000\text{ g mol}^{-1}$, with an approximate radius of gyration $R_g = 32\text{ nm}$ [7], so the polymer in solution is comparable in dimension to the clay particles.

2.2. Sample preparation

The laponite powder is added to deionized water and mixed at high speeds with a magnetic stirrer. The solution is initially turbid, but becomes clear in 15–20 min, indicating that the particles are fully hydrated. The laponite concentrations used for the stock solutions are typically 2.5 wt.%, and the pH 10.0. Since laponite at such high concentrations demonstrates aging characteristics [8], all samples are prepared within a few hours of use, and the measurements are performed before any significant aging of the stock Laponite solution occurs. The stock solutions of polymer are prepared by adding PEO to water and allowing it to dissolve for a few days; typical polymer concentrations are 1.5 wt.%. Prior to our experiments, the laponite and polymer stock solutions are mixed together by adding the polymer stock to the laponite stock with a pipette and then gently tilting the mixture back and forth to ensure complete mixing. This

sets the individual concentrations of laponite and PEO in the final mixture, enabling the phase space to be explored. All measurements are performed at room temperature, $T = 22\text{ }^\circ\text{C}$.

2.3. Light scattering measurements

Static and dynamic light scattering measurements are performed on laponite solutions, PEO solutions and unshaken laponite–PEO mixtures using a laser light scattering instrument (ALV-Laser GmbH, Langen, Germany), at a wavelength of $\lambda = 514.5\text{ nm}$ in vacuo. Static light scattering measurements are performed at angles ranging from $\theta = 15$ to 150° . Dynamic light scattering measurements are also performed on laponite solutions, PEO polymer solutions, and unshaken mixtures of the two components at $\theta = 90^\circ$.

2.4. Phase diagram and relaxation times

Measurements for the phase diagram and relaxation times are performed by observation. The laponite and PEO stock solutions are mixed in varying ratios and total concentrations, enabling a wide section of the phase space to be explored. Initially, the samples have viscosities that are not significantly different from pure water, as expected for a suspension of dilute colloidal particles [9]. The samples are shaken vigorously, several times per second for 15–20 s, and inspected visually for increased viscosity, increased turbidity, and the appearance of bubbles suspended within the sample. If the samples become elastic, and bubbles remain suspended in the solution, we consider them to have gelled. Measurement of the relaxation time begins immediately upon completion of shaking, and ends when the sample has totally relaxed, and becomes clear with all of the bubbles suspended in the sample having risen to the top. Samples that ‘relax’ according to these criteria have final viscosities not significantly different from their initial values.

3. Results and discussions

3.1. 'Phase behavior' of laponite–PEO mixtures

Laponite particles dispersed in an aqueous medium form many different phases such as gels, viscous fluids or phase separated flocs [10,11]. Well-defined phase diagrams exist for these dispersions, where the phases are determined as a function of the laponite concentration and the concentration of added counterions. Our experiments are performed in the absence of added counterions. However, when a non-associative, linear chain polymer such as PEO is added to the suspension of laponite discs, the situation is more complicated. PEO is known to adsorb on clay particles [12–14], with the amount of adsorbed polymer depending on the equilibrium concentration of polymer added. We present results on mixtures of PEO and laponite, where the concentrations of both components have been varied. At rest, all suspensions are clear and show low viscosity Newtonian-fluid-like behavior, where the viscosity is not a function of applied shear rate. However, when shaken vigorously by hand, some of the samples exhibit an intriguing behavior. The non-linear shear created by shaking the samples causes some of the mixtures to form macroscopic, heterogeneous gels. In fact, these gels are so elastic that even upon inverting the vials the samples remain stationary¹. If left undisturbed, the gels relax back to the fluid state in time scales that range from a few seconds to many hours, and sometimes even days. Once the gels return to the fluid state, gelation can be caused by shaking again. All samples that form shake-gels are reversible.

To explore this phenomenon, we vary the relative concentrations of PEO and laponite in the mixture, and determine when the shake-gels are formed. The results are summarized in Fig. 1, where we show the phase behavior of the samples that have been prepared using the same flow

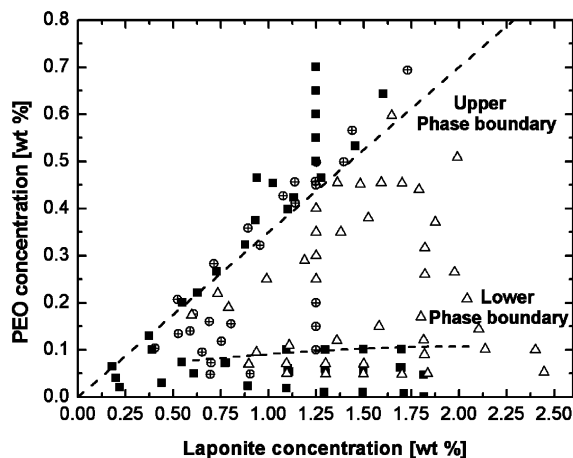


Fig. 1. Phase behavior of laponite–PEO 'shake-gels', formed by vigorous shaking. The open triangles represent mixtures that form shake-gels upon application of shear; the circles represent mixtures that shear-thicken and show an increase in viscosity but do not gel; and the solid squares represent mixtures that do not gel even when subjected to large shear. The molecular weight of PEO used is $M_w = 300\,000\text{ g mol}^{-1}$, with a radius of gyration $R_g = 32\text{ nm}$.

history. Three distinct phases are observed, as characterized visually: (1) the shake-gel phase (triangles), where the samples show bulk elasticity. This phase is characterized by increased opacity of the sample, and macroscopic heterogeneities resulting in a 'lumpy' gel. (2) The shear-thickening phase (circles), where the suspensions show a substantial increase in viscosity, but no visible elasticity, as the suspensions can still flow. This phase is also more turbid than the unshaken mixture. (3) The liquid phase (squares), where even the most vigorous shaking causes no visible gelation or shear thickening. This phase is characterized by the absence of any apparent rise in the viscosity of the sample, although a foam forms at the surface of the samples. The turbidity of this phase also remains unchanged from the fluid state at rest. The observation of foam suggests the presence of free PEO in solution, since PEO is somewhat surface active while laponite is not.

As seen in the phase diagram shown in Fig. 1, for very low concentrations of polymer, no shake-gels are formed, irrespective of the laponite concentration. For a fixed laponite concentration, we observe shake-gel like behavior for a finite range

¹ Images of the shake-gel can be viewed at <http://www.deas.harvard.edu/projects/weitzlab/research/lappix/index.html>.

of polymer concentrations. This range seems to increase as we increase the laponite concentration. However, beyond a certain polymer concentration, shake-gels no longer form. To account for the behavior of the phase diagram, we use the physical picture developed to explain shear thickening in mixtures of silica and PEO [6]. The surface chemistry of the silica and laponite are similar; when clay particles are dispersed in water, sodium ions are released into solution, leaving many bare silica sites on the surface of the discs. The main difference in the two systems is the geometry of the particles; however, this does not make a significant difference in the general phase behavior. The essence of this physical picture is illustrated schematically in Fig. 2, which shows different configurations of polymer adsorption on the

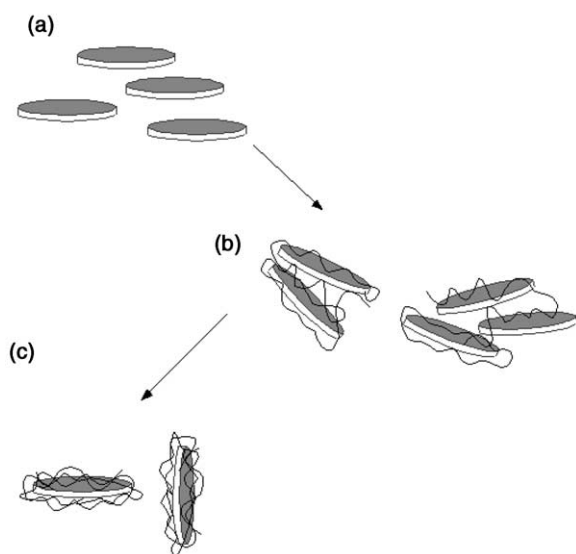


Fig. 2. Schematic representation of different configurations seen in laponite–PEO mixtures in the absence of shear, for increasing PEO concentration (a) when there is no polymer, the laponite discs are stable in solution due to the charges on their surfaces; (b) with increasing amounts of PEO, the laponite surfaces are unsaturated, and the polymer can bridge different discs to form small aggregates; (c) as the PEO concentration increases still further, the laponite surfaces become saturated with polymer, which forms a steric stabilization layer that prevents discs from aggregating. Only when the surfaces are not completely saturated can shear cause desorption of the polymer and readsorption onto neighboring particles, increasing the bridging and hence increasing the size of the aggregates, and ultimately leading to the formation of the shake-gel.

laponite surfaces, in the absence of shear. In the absence of polymer, Fig. 2(a), the laponite discs are stable in solution due to the charge on their surfaces. As the PEO concentration is increased, polymer adsorbs on the laponite surfaces. The most likely explanation for this adsorption lies in the displacement of water molecules immediately adjacent to the clay surfaces by the ethylene oxide segments on the PEO backbone [14]; the ether oxygens of PEO act as Lewis bases and have a high affinity for the silica on the clay surface, which act like Brönsted acids. Since the pH of the laponite suspension is quite high (pH \sim 10.0), there is competition between the hydroxyls and the polymer for the silica on the surface of the clay particle. This suggests that the adsorption energy is of the order a few $k_B T$ [14], with a finite probability for desorption (for silica–PEO, the adsorption energy is about $1.2 k_B T \text{mol}^{-1}$ of segment [6]). At low PEO concentrations, the surface coverage is incomplete, as illustrated schematically in Fig. 2(b); this allows for the formation of PEO–laponite complexes or aggregates, with a single PEO macromolecule bridging more than one laponite disc. The aggregates themselves remain stable, and equilibrated. As the PEO concentration is increased still further, the polymer completely saturates the clay surface, resulting in a steric stabilizing layer around the particles, as illustrated schematically in Fig. 2(c). In this case, a single PEO macromolecule adsorbs on a single laponite disc on average. For a laponite concentration of 0.75 wt.%, and a polymer concentration of 0.25 wt.% (near the phase boundary), the molar ratio of polymer to disc is 0.9:1. This indicates that there is enough polymer to completely cover the discs at concentrations of polymer above the phase boundary, consistent with the picture proposed in Fig. 2(c).

The configurations of PEO–laponite complexes depicted in Fig. 2 are for solutions at rest; upon application of shear, the situation changes dramatically. When the laponite surfaces are not fully saturated by PEO, the effect of shear is to lower the coverage of some surfaces by breaking the bonds between the polymer and the clay [6]. At the same time, new bonds are formed between the polymer and clay particles belonging to other

aggregates. As the size of these new aggregates grows, it becomes even easier to stretch them out by shear. One way of characterizing this is by means of the Peclet number of the aggregates, $Pe = \dot{\gamma}a^2/D$ where $\dot{\gamma}$ is the shear rate, a is the aggregate size and D is the aggregate diffusion coefficient. The Peclet number characterizes the ratio of shear to diffusion, and is a measure of the importance of the shear rate compared with the relaxation rate due to diffusion. As the Peclet number increases, the effect of the shear rate becomes greater, and since $Pe \sim a^3$, it increases rapidly with the aggregate size. Eventually, these large aggregates span the entire sample, forming the ‘shake-gel.’ Since the adsorption energy of PEO on laponite is a few $k_B T$, thermal fluctuations are sufficient to cause the shake-gels to relax and revert back to their original fluid state. As the polymer concentration increases, the laponite particles become completely saturated with PEO, and the polymer segments on the surface of the laponite repel each other. Then, no reasonable level of shear is able to cause bridging of the particles by the PEO because of the stabilization due to the polymer coating; thus, for high PEO concentrations, the liquid phase persists, as shown in the phase diagram in Fig. 1. Therefore, the phase boundary between a shake-gel and a liquid defines the limit of complete coverage of the laponite surfaces by the adsorbed PEO for a fixed laponite concentration. Since the phase boundary is linear in shape, we obtain a value of the saturation coverage from the slope of the line, which is 0.455 mg m^{-2} . We are unaware of any measurements of this saturation value for laponite–PEO mixtures; however, by comparison, from adsorption isotherms for silica–PEO mixtures, the saturation value is 1.0 mg m^{-2} for PEO with $M_w = 2\,000\,000 \text{ g mol}^{-1}$ [15,16]. This is in reasonable agreement with the value for laponite, particularly considering the difference in particle shapes and molecular weights of the PEO.

The nature of the shear that causes gelation is not simple. The shaking rate used is about 200 rpm, and in the geometry of the cell, this corresponds to a linear shear rate of $\dot{\gamma} \approx 20 \text{ s}^{-1}$. This is not a large shear; indeed if a similar shear rate is applied in a controlled geometry in a rheometer,

no gelation is observed. This suggests that extensional flow is important in the aggregate growth. The flow pattern in the shaken sample comprises recirculating eddies which change their size and orientations rapidly in time, so the shear rate is spatially non-uniform. A fluid parcel is rapidly accelerated and decelerated. We also generate instantaneous stagnation points, so there will be local regions of large extension. A complete understanding of the nature of the flow that causes gelation requires additional experiments; however, since the behavior observed with shaking is reproducible, we use this to induce gelation for our studies.

3.2. Static light scattering measurements

The physical picture described in the previous section to explain the shake-gel behavior relies on the assumption that PEO adsorbs on laponite. To test the validity of this assumption, we perform static light scattering measurements on the unshaken laponite–PEO mixtures and compare to scattering from solutions of laponite and PEO. The measurements are performed at several angles, ranging from $\theta = 15$ to 150° ; however, there is little variation with angle, except for a slight increase at the lowest angle. This behavior is reasonable since we are probing length scales large compared with those typical of the laponite–PEO aggregates. Therefore, we focus on the scattering at 90° . We find that the mixture scatters more than the sum of the individual components, which is an indication of adsorption [12,13]. As a simple estimate of the effect of the adsorption, we assume that a single PEO adsorbs on each laponite particle. The scattering intensity from each coated particle is the coherent sum of the scattering from the individual laponite particle and PEO polymer; therefore, the scattered fields add, rather than the intensities. The scattering intensity per laponite particle is $I_{\text{LAP}}/N_{\text{LAP}}$, where I_{LAP} is the measured scattering intensity from the pure laponite solution, and N_{LAP} is the number concentration of laponite particles. Similarly, the scattering intensity per PEO polymer is $I_{\text{PEO}}/N_{\text{PEO}}$, where I_{PEO} is the measured scattering intensity from the pure polymer solution, and N_{PEO} the number concen-

tration of PEO polymers. To parameterize the adsorption, we define a normalized scattering intensity:

$$\tilde{I} = \frac{N_{\text{PEO}}(\sqrt{I_{\text{LAP}}/N_{\text{LAP}}} + \sqrt{I_{\text{PEO}}/N_{\text{PEO}}})^2}{I_{\text{MIX}}} \quad (1)$$

where I_{MIX} is the scattering intensity from the laponite–PEO mixture. This expression implicitly assumes that only a single polymer adsorbs per laponite particle, and that the concentration of each is sufficiently low that there is no interaction between the particles. We plot the variation of \tilde{I} as a function of PEO concentration in Fig. 3 using a fixed laponite concentration of 1.25 wt.%. When the laponite coverage is saturated, we expect $\tilde{I} = 1$. By contrast, for PEO concentrations below saturation, there is less than one laponite particle per polymer, and we expect $\tilde{I} < 1$; by contrast, for PEO concentrations above saturation, there are fewer laponite particles, and an excess of PEO polymers, and we expect $\tilde{I} > 1$. As seen in the Fig. 3, $\tilde{I} = 1$ at a PEO concentration of about 0.5 wt.%, which is in good agreement with the saturation value determined from the phase behavior.

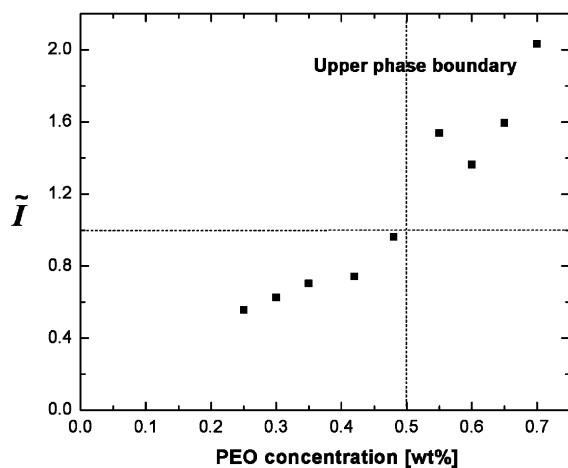


Fig. 3. The reduced intensity \tilde{I} as a function of polymer concentration, for fixed laponite concentration of 1.25 wt.%. We define the phase transition when $\tilde{I} = 1$, found to be $C = 0.5$ wt.%, in reasonable agreement with the observed macroscopic upper phase boundary.

3.3. Dynamic light scattering measurements

Dynamic light scattering gives additional information about the configuration of the adsorbed polymer on the laponite [15,16] prior to the formation of the shake-gel. We again fix the concentration of laponite at 1.25 wt.%, and vary the concentration of polymer. We measure the decay time of the normalized field–field autocorrelation function, g_1 at a scattering angle of $\theta = 90^\circ$; a separate set of measurements confirms that there is no anomalous dependence on scattering angle, other than that expected for single particle diffusion [17]. We find a nearly exponential decay of g_1 indicating a reasonably monodisperse distribution of scatterers. This allows us to characterize the scatterers with their characteristic decay time τ , the larger the scatterers, the more slowly they diffuse, and the larger is their decay time. Thus, we define a dimensionless time constant $\tilde{\tau} = \tau/\tau_0$, where $\tau_0 = 0.24$ ms, the decay time measured for the bare laponite particles in solution. This decay time is consistent with the diffusion time of individual laponite discs that are 25 nm in diameter. Surprisingly, as shown in Fig. 4, at low PEO concentrations, $\tilde{\tau}$ is greater than one; moreover $\tilde{\tau}$ decreases with increasing PEO concentration, reaching $\tilde{\tau} \approx 1$ when the concentration of

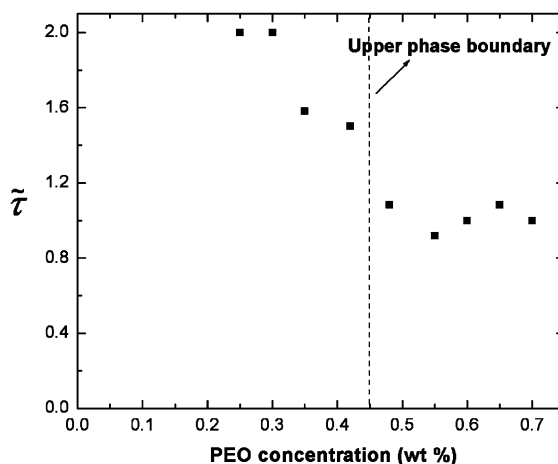


Fig. 4. The dimensionless time scale $\tilde{\tau}$ as a function of PEO concentration, for a fixed laponite concentration of 1.25 wt.%. The upper phase boundary at $C = 0.45$ wt.% is consistent with a change in $\tilde{\tau}$ from 2 to 1.

PEO reaches about 0.45 wt.%, the saturation value. At the highest polymer concentrations, the dynamics are indistinguishable from that of bare laponite in solution and $\tilde{\tau} = 1$. These data are, in fact, consistent with our physical picture. At low PEO concentrations, the polymer bridges several laponite discs, and so $\tilde{\tau} = 2$, reflecting the larger particles. As the concentration of polymer is increased, the polymer completely coats the laponite disc. However, the polymer used has a radius of gyration $R_g = 32$ nm, which is comparable to the diameter of the laponite discs. Since the polymer adsorbs on the face of the discs rather than the edges, there is no increase in the longest dimension of the discs, and there is no change in the translational diffusion coefficient, so that the decay time for the fully saturated laponite particles is the same as for the bare laponite particles, and $\tilde{\tau} = 1$. The transition occurs at a PEO concentration of approximately 0.5 wt.%, in good agreement with the value observed in the phase diagram.

3.4. Relaxation times of shake-gels

The mechanism for the formation of shake-gels involves formation of new bonds between PEO and laponite, creating larger aggregates. The energies of the new bonds formed are of order a few $k_B T$, and thermal fluctuations are enough to cause the polymer to revert to its stable configuration prior to the application of shear. The equilibrium polymer concentrations we use are near the overlap concentration, $C^* \approx 0.36$ wt.%, the polymer disentanglement time plays no significant role in the relaxation process; instead, the time scale of relaxation must depend solely on the number of new bonds that have been created due to shear. As the polymer concentration increases, the laponite surfaces approach complete coverage, and fewer new bonds are created by shear. This implies that the relaxation time must decrease with increasing polymer concentration. This is supported by the results shown in Fig. 5, where the relaxation times, t_r , of the shake-gels are plotted as a function of polymer concentration, at a fixed laponite concentration (1.25 wt.%). The time scales vary over nearly four orders of magnitude, for a very small change in polymer concentration.

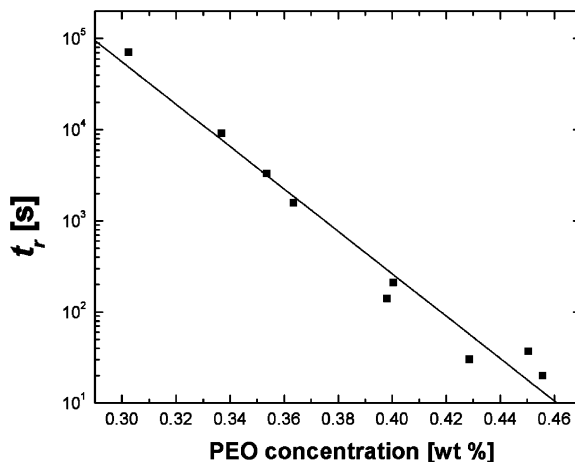


Fig. 5. Relaxation times of 1.25 wt.% laponite shake-gels as a function of PEO concentration. The relaxation time scales vary over nearly four orders of magnitude, for a very small change in PEO concentration.

Furthermore, for polymer concentrations near the transition in the phase diagram, for 0.45 wt.%, the time scale for relaxation was only a few seconds. An intriguing observation is that the time scales for the relaxation appear to be exponential in polymer concentration, suggestive of an activated process.

Further refinement of the physical picture presented here requires quantitative knowledge of the polymer adsorption and details of the polymer conformation before and during shear. Techniques such as neutron scattering [12,13] may be useful for this, especially in the unsaturated regime where the laponite surfaces have low polymer density and shake-gel behavior is observed. Theoretical approaches that look at structure and entropy of polymer chains in the presence of colloidal particles [18] may also aid in the understanding of the relaxation times.

4. Conclusions

A shear-induced transition from fluid to solid is observed in mixtures of clay and polymer, for certain concentrations of laponite and PEO. The phase behavior as a function of both laponite and PEO concentration is determined by visual ob-

servation. The PEO adsorbs on the laponite particles; when the adsorption is not fully saturated, the PEO can bridge laponite particles, causing aggregates to be formed. Application of strong shear can desorb some bonds of the PEO, and readsorb them onto other laponite particles, causing the aggregates to grow substantially, and a gel to form. These shake-gels can be rigid enough to support their own weight. As the PEO coverage increases, each laponite particle becomes saturated, and shake-gels no longer form. The adsorption behavior of the PEO on the laponite is measured with both static and dynamic light scattering, and confirms the coverage assumed in our picture of the phase behavior. The behavior observed for the laponite–PEO mixtures is consistent with that observed for silica–PEO mixtures, although the shake-gels formed with laponite are more rigid than those reported with silica. The mechanism of shear-induced gelation in colloid–polymer mixtures is qualitatively different from that observed in shear-thickening polymer solutions such as ionomers or telechelic polymers. In the case of colloid–polymer mixtures, the polymer conformation is not substantially altered under shear, unlike the ionomer case, where the polymer stretches considerably. Although the bond energies are very different, the resulting gel is quite strong in both the limiting cases.

A complete understanding of this flow-induced gelation will require characterization of several aspects of the macroscopic and microscopic behavior of the system. Our results demonstrate the contribution of surface saturation to the behavior of flow-induced gelation, providing a tool to relate quantitative characterization of polymer adsorption to macroscopic behavior. These results also provide a method to predict the range of concentrations for observation of the transition, allowing for the design of rheological experiments to

effectively measure the macroscopic behavior and gel properties.

Acknowledgements

We thank Southern Clay Products for the clay particles used in this paper. We also thank G. McKinley, T.A. Witten, T. Kohl, D. Pozzo, S.-Y. Tee and S. Pautot for stimulating discussions. This work was supported by the NSF (DMR-9971432).

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