Influence of an adsorbing polymer on the aging dynamics of Laponite clay suspensions

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Clay–polymer dispersions in aqueous solutions are of great interest due to their industrial applications and intriguing physical properties. Aqueous solutions of bare Laponite particles age spontaneously, from an ergodic to a non-ergodic state, in a time varying from hours to months depending on Laponite concentration. When a polymer species, such as polyethylene oxide (PEO), is added to the solution, it weakly adsorbs on clay particle surfaces modifying the effective interaction potential between Laponite particles. A dynamic light-scattering study was performed to investigate the effect of polymer on the aging dynamics of the system by varying the polymer concentration at a fixed polymer molecular weight ($M_w = 200{,}000$ g/mol). The results show that arresting phenomena between clay particles are hindered when PEO is added and, thus, a slowing of the aging dynamics with increasing PEO concentration is observed. A possible mechanism is progressive coverage of the clay surface by polymers, which grow with increasing PEO concentration.

Keywords: colloids; Laponite; polyethylene oxide; aging; gel/glass

1. Introduction

Clay–polymers complexes are of technological interest due to their application in a wide range of industrial formulations, such as rheological modifiers or stabilizers. The interaction between clay and polymers is especially interesting due to the fact that polymers can be used as fine-tuners of the interaction potential between colloidal particles; thus, improving our understanding of the mechanism and origin of structural arrested states, such as gel and glass [1,2].

Laponite is a synthetic hectorite clay that, when dispersed in water, originates a charged colloidal suspension of discs with a strongly negative charge on the face and a weakly positive/negative charge on the rim [3]. The competition between attractive and repulsive interactions causes aqueous dispersions of Laponite to display non-trivial behavior up to very low clay concentrations [4–11]. In fact, clay dispersions spontaneously age from an initial liquid-like state to a final arrested solid-like structure, which is gel- or glass-like, depending on Laponite concentration [7]. The fundamental physics of the interaction

between clay particles, the mechanism of gel/glass formation and the role of the attractive/repulsive interactions remain a subject of debate and need to be better understood [4–11].

A simple method of clarifying the role of attractive and repulsive terms in the interaction potential of Laponite systems is to modify the relative contribution of the two terms and study its effect on the aging phenomenon and the final arrested states. The addition of a water-soluble adsorbing polymer, such as polyethylene oxide (PEO), affects the kinetic behavior of Laponite dispersions [12–16]. A small-angle neutron-scattering study of this type of system has shown that PEO adsorbs around Laponite particles [17]. By fixing the molecular weight and increasing PEO concentration, the effective coverage surface of the clay discs increases, leading to steric stabilization of the colloidal dispersion. Steric hindrance, due to excluded-volume interactions between polymers, acts against the formation of an arrested state. Therefore, the arresting process becomes progressively hindered with increasing PEO concentration and, in limiting cases, could be completely avoided.

A dynamic light-scattering study on the arresting kinetics of Laponite/PEO mixtures at fixed clay and polymer concentrations, but with varying molar mass of PEO, was performed by Nelson et al. [13]. It was found that the addition of polymer decreased the rate of aggregation due to steric stabilization via polymer adsorption. However, the effect was not quantified in relation to the amounts of polymer added and no other systematic studies are reported in the literature. Nelson et al. [13] added salt to the solution resulting in a decrease in the characteristic screening length of the repulsive part of the potential.

In this paper, we report a dynamic light-scattering study on the influence of PEO addition at a fixed molecular weight ($M_w = 200,000$ g/mol) on the kinetics of arrested state formation in the Laponite system. A slowing of the characteristic aging dynamics of the Laponite systems was observed, clearly dependent on PEO concentration. However, the formation of a final arrested state is never avoided, even at the highest polymer concentration investigated.

2. Experimental details

Laponite RD (Laporte Industries, London, UK) with a density of 2570 kg/m³ was used as-received. Each crystal was composed of ~1500 unit cells with the empirical chemical formula $Na_{0.7}^+[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$. The clay powder is composed of single crystals with a three-layer structure: the central layer is made up of magnesium and lithium atoms bonded with oxygen and OH groups to form an octahedral structure. This layer is sandwiched within two tetrahedral structures of silicon with sodium atoms, exposed on the surface of the platelets [3]. When this type of chemical architecture is dispersed in water, it releases Na ions from the surface due to an ionization phenomenon, leading to a net negative charge of several hundred elementary charges. On the other hand, due to a protonation phenomenon of the OH groups on the plate rim, a weakly positive charge can occur. Therefore, in water, Laponite clay forms a colloidal dispersion of charged disc-like particles with a diameter of 25 nm and a thickness of 1 nm with both attractive and repulsive interactions. Polyethylene oxide (PEO) with a molecular weight of $M_w = 200,000$ g/mol was supplied from Sigma-Aldrich (St. Louis, MO, USA) and used as-received. The general chemical formula of PEO is $-[CH_2CH_2O]_n-$, which is a linear

chain obtained by polymerization of ethylene oxide. Using the empirical relation $\ell = M_{\mathrm{w}}^{0.57}/18.4$ reported in [18,19], the characteristic linear length of the chosen polymer was estimated as $\ell \approx 57$ nm, comparable with the dimensions of a Laponite disc.

A PEO stock solution at $C_{\mathrm{PEO}} = 1\%$ was prepared by adding a weighed quantity of polymer to 18-MΩ high-purity deionized water and stirring the dispersion at room temperature for several hours. The stock solution was then diluted with deionized water to obtain PEO solution at two different weight percentages ($C_{\mathrm{PEO}} = 0.4$ and 0.5%). Laponite/ PEO samples were prepared by dispersing the desired percentage of Laponite powder at a fixed concentration of $C_{\mathrm{w}} = 2.0\%$ in weight in this solution. Laponite/PEO dispersions were then stirred vigorously for 30 min. The start of aging (or waiting) time ($t_{\mathrm{w}} = 0$) is defined as the time when the stirring process ends.

Dynamic light-scattering (DLS) measurements were performed using an ALV-5000 logarithmic correlator in combination with a standard optical setup based on an He–Ne ($\lambda = 632.8$ nm) 10-mW laser. The intensity correlation function was directly obtained as

$$g_2(q, t) = \frac{\langle I(q, t)I(q, 0)\rangle}{\langle I(q, 0)\rangle^2},\tag{1}$$

where q is the modulus of the scattering wavevector, defined as $q = 4\pi n/\lambda \sin(\theta/2)$ with $\theta = 90°$ in this experiment. The dynamic structure factor $f(q, t)$ can be directly obtained by inverting the Siegert relation:

$$f(q, t) = \sqrt{\frac{g_2(q, t) - 1}{b}},\tag{2}$$

where b represents the coherence factor. All measurements were performed at room temperature.

3. Results and discussion

Dynamic light-scattering measurements at a fixed Laponite concentration ($C_{\mathrm{W}} = 2.0\%$) for two different PEO concentrations ($C_{\mathrm{PEO}} = 0.4$ and 0.5%) of fixed molecular weight $M_{\mathrm{w}} = 200,000$ g/mol added to the dispersion were performed at several waiting times to clarify the effect of the polymer on aging dynamics. As an example, correlation functions at increasing waiting times t_{w} for a neat Laponite sample and the $C_{\mathrm{w}} = 2.0\%$, $C_{\mathrm{PEO}} = 0.4\%$ sample are shown in Figure 1.

It is evident that both systems undergo aging (i.e. the characteristic dynamic properties of the sample change with waiting time) reflecting the structural rearrangement inside the sample during the transition from an ergodic to an arrested non-ergodic state. In particular, the dynamics becomes progressively slower with increasing waiting time t_{w}.

The correlation functions (Figure 1) decay following a two-step behavior: two different relaxation processes, a fast and a slow one, are present in the system at two different time-scales in all the investigated samples, with and without added polymer. Therefore, adding a polymer species to Laponite dispersions do not greatly modify the characteristic shape of the autocorrelation functions. For this reason, we can utilize the same quantitative analysis
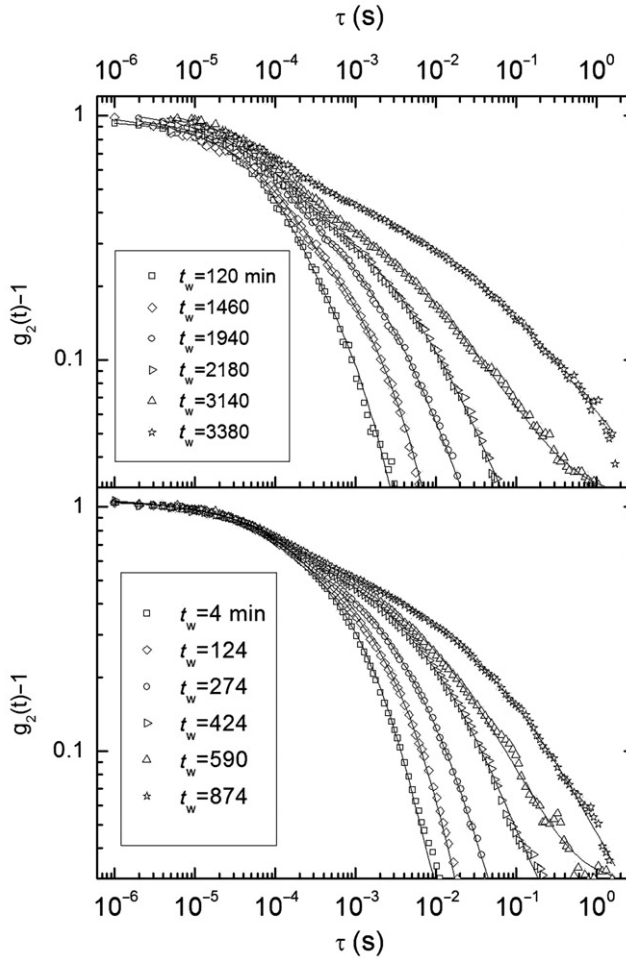
Figure 1. Waiting time evolution of autocorrelation functions for neat Laponite sample at $C_w = 2.0\%$ (top panel) and a $C_w = 2.0\%$, $C_{PEO} = 0.4\%$ Laponite–PEO dispersion sample (bottom panel). Solid lines represent fits obtained through Equation (3).

previously used for neat Laponite samples [5,6], and the $g_2(t)$–1 behavior is fitted using a sum of simple and stretched exponential functions [5,20]:

$$g_2(q, t) - 1 = b\left(a \cdot e^{-(t/\tau_1)} + (1-a)e^{-(t/\tau_2)^\beta}\right)^2, \quad (3)$$

where b represents the coherence factor and a, τ_1, τ_2 and β are shape-fitting parameters.

As an example, the dynamic structure factor $f(q, t)$ (open circles) for the sample of $C_w = 2.0\%/C_{PEO} = 0.4\%$ at $t_w = 3.00 \times 10^4$ s, with the fit (full line) and two contributions (dotted and dashed lines), are shown in Figure 2. The goodness of the fit is evident; moreover, one can easily identify how the two different terms in Equation (3) contribute to the fit. The first decay, describing the fast dynamics (τ_1) on a short time-scale, is related to
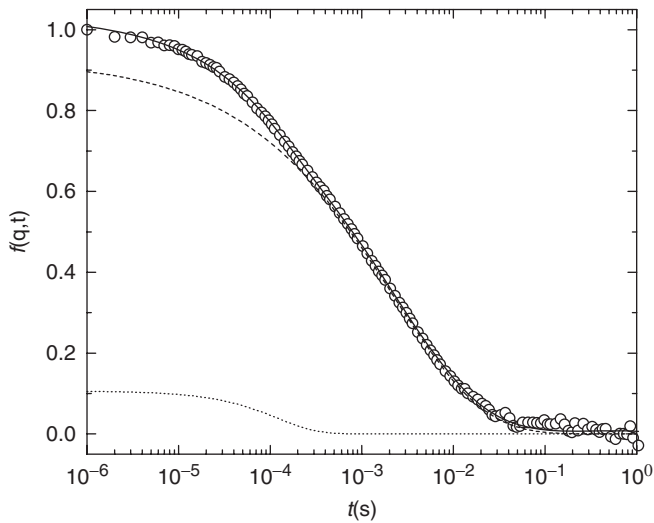
Figure 2. Dynamic structure factor $f(q, t)$ (Equation (2)) (open circles) for the sample at $C_w = 2.0\%$ and $C_{PEO} = 0.4\%$ at waiting time $t_w = 3.00 \times 10^4$ s and the corresponding fit with Equation (3) (full line) with simple exponential (dotted line) and stretched exponential (dashed line) contributions.

a vibrational diffusive mode of the single particle inside the cage of its neighbor and is well described by the single exponential curve (dotted line of Figure 2). On the other hand, slow dynamics on a longer time-scale, which is manifestly non-Debye, is described by a stretched exponential function (τ_2 and β) and is shown in Figure 2 (dashed line). This second decay is related to structural rearrangements and displays the complexity of the system. The fits for different waiting times are shown in Figure 1 as solid lines superimposed onto the data (symbols).

The dependence of the time correlation functions on waiting time t_w yields quantitative information on the influence of added PEO on Laponite dispersions. We define a useful quantity, which takes into account both slow dynamic parameters, i.e. relaxation time (τ_2) and stretching parameter (β), the mean relaxation time [5]:

$$\tau_m = \frac{\tau_2}{\beta} \Gamma\left(\frac{1}{\beta}\right). \tag{4}$$

The waiting time behavior of τ_m, for samples at a fixed Laponite concentration ($C_w = 2.0\%$) and different PEO concentrations ($C_{PEO} = 0\%$, i.e. neat Laponite, filled circles; $C_{PEO} = 0.4\%$, open squares; $C_{PEO} = 0.5\%$, open triangles), are shown in Figure 3.

As observed in our previous studies on neat Laponite dispersions, all samples show a characteristic exponential growth of mean relaxation time τ_m, which reflects the progressive slowing down of the dynamics. At a certain waiting time, designated t_w^∞, a divergence appears [5]. At this time, the raw autocorrelation spectra has undergone a crossover from a complete to an incomplete decay. This behavior is an indication of ergodicity breaking – a sign of transition towards an arrested state [5,21,22]. Therefore, this critical waiting-time value is a good estimate (in excess) of the time the system needs to undergo complete transition from a liquid-like ergodic state to a solid-like non-ergodic arrested state. It has been observed that t_w^∞ depends on Laponite concentration; i.e. the
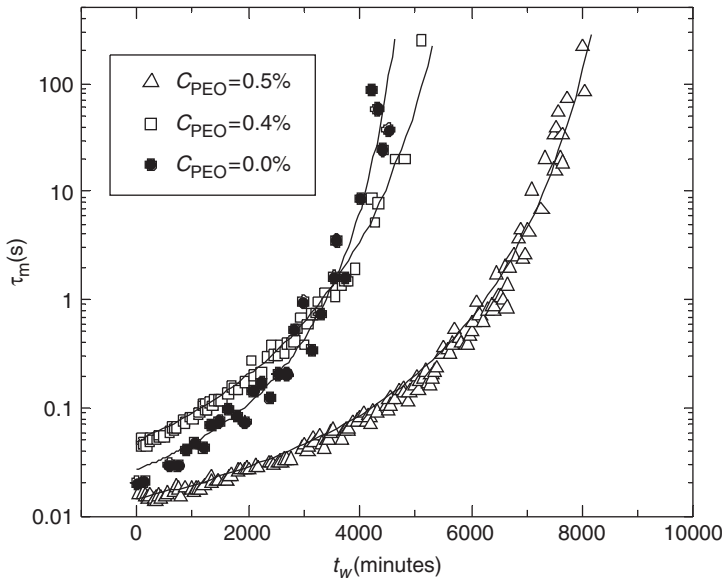
Figure 3. Waiting time evolution of τ_m for samples with fixed Laponite concentration ($C_w = 2.0\%$) without added PEO (full circles) and for two different PEO concentrations ($C_{PEO} = 0.4\%$, open squares; $C_{PEO} = 0.5\%$, open triangles). The more PEO added to the dispersion, the more the dynamics of the system toward an arrested state are slowed down. Solid lines are fits obtained through Equation (5).

higher the clay concentration, the less time needed by the system to age and complete the ergodic to non-ergodic transition [5,8]. Moreover, at fixed Laponite concentration, the addition of salt to Laponite dispersions causes an abrupt decrease in the value at which divergence of the τ_m appears [6]. In the following, we will discuss what happens to this value when increasing quantities of PEO are added. We can obtain the t_w^∞ parameter for each investigated sample by fitting the waiting-time behavior of mean relaxation time with a phenomenological law [5]:

$$\tau_m = \tau_0 \exp\left[\frac{B}{1 - (t_w/t_w^\infty)}\right], \tag{5}$$

where B, τ_0 and t_w^∞ are fit parameters. The fitting curve obtained via Equation (5) are shown in Figure 3 as solid lines and well describe the samples with added PEO. Figure 4 shows that t_w^∞ increases with increasing PEO concentration.

In detail, samples with $C_{PEO} = 0.4$ and 0.5% needed ~1.3× and ~1.8×, respectively, the time needed by neat Laponite sample (at the same clay concentration) to age to the final arrested state. This is due to the presence of the adsorbing polymer, i.e. the more PEO added to the dispersion, the more efficient the coverage of the clay surface and, thus, the barrier against aggregation. Consequently, the kinetic towards the arrested state slows down. Nevertheless, complete suppression of aggregation at the studied PEO concentrations was not observed. Moreover, due to the length of the polymer ($M_w = 200,000\,\text{g/mol}$, $\ell \approx 57\,\text{nm}$), which is comparable to the distance between two Laponite particles, a bridging phenomenon cannot be ruled out and may be present in the system. In this study, the exact
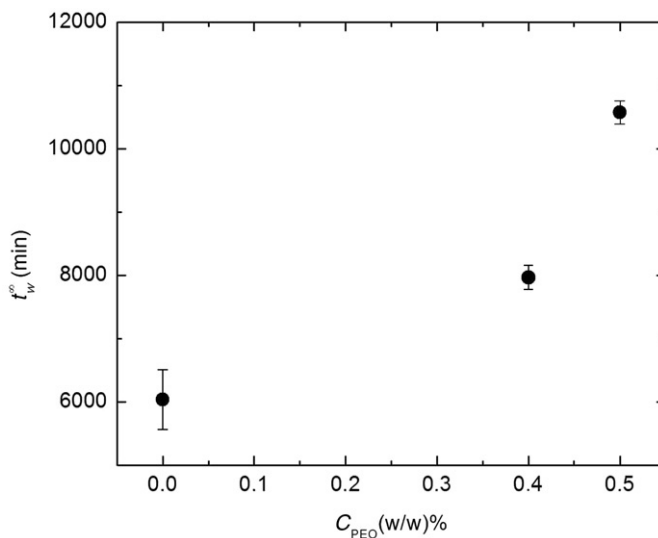
Figure 4. Values of t_w^∞ for samples with Laponite concentration $C_w = 2.0\%$ at different PEO concentrations. Increasing of PEO concentration causes an increase in critical waiting time: arrest becomes progressively hindered and, therefore, the gelation kinetics are slowed down.

contribution of the bridging phenomenon to the slowing of the dynamics cannot be estimated, but we can obtain useful data from the fast relaxation time τ_1.

This time is related to vibrational motion and the dimensions of single particle inside a cage of neighbors. The behavior of τ_1 is shown in Figure 5, which increases at increasing waiting time for all samples investigated. Fitting this behavior with a single exponential function, yields a value of the τ_1 parameter at waiting time $t_w = 0$, designated τ_1^0. This value is an indication of the dimensions of the particular 'objects' in the dispersion. We also define a dimensionless time constant $\tau^* = \tau_1^0/\tau_0$, where $\tau_0 = 76\,\mu s$ is the decay time measured for bare Laponite particles in solution at $t_w = 0$. The values of τ_1^0 for $C_{PEO} = 0.4$ and 0.5% samples are 79 and 74 μs, respectively. Thus, the dimensionless quantity $\tau^* \approx 1$, indicating that the dynamics are indistinguishable from that of bare Laponite in solution. Since the polymer adsorbs on the face of the discs rather than on the edges [13], there is no increase in the longest dimension and there is no change in the translational diffusion coefficient. Therefore, the decay time for bare Laponite particles and Laponite particles with adsorbed polymer are the same, and $\tau^* \approx 1$. These arguments suggest that, at least for these polymer concentrations, bridging between particles is improbable.

Figure 5 shows a clear dependence of τ_1 on polymer concentration, in agreement with the observation for mean relaxation time τ_m (Figure 3).

Figure 6 shows the waiting time behavior of the stretching parameter β for all samples investigated ($C_{PEO} = 0\%$, i.e. neat Laponite sample, filled circles; $C_{PEO} = 0.4\%$, open squares; $C_{PEO} = 0.5\%$, open triangles). For all samples, the value of the stretching parameter decreases with time from ~0.7 to ~0.2. This quantifies the behavior of the raw photon correlation spectra shown in Figure 1, where it is evident that the curves become progressively stretched with increasing waiting times. In this case, the dependence on polymer concentration is clear and consistent with the behavior found for mean relaxation time τ_m and fast relaxation time τ_1.
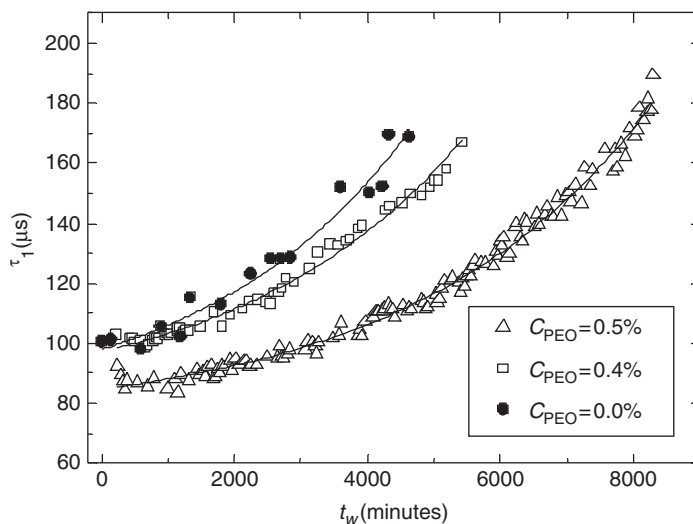
Figure 5. Waiting time evolution of τ_1 for samples with fixed Laponite concentration ($C_w = 2.0\%$) for a neat Laponite sample (full circles) and for two different PEO concentrations ($C_{PEO} = 0.4\%$, open squares; $C_{PEO} = 0.5\%$, open triangles). The solid lines represent fits with a simple exponential function.
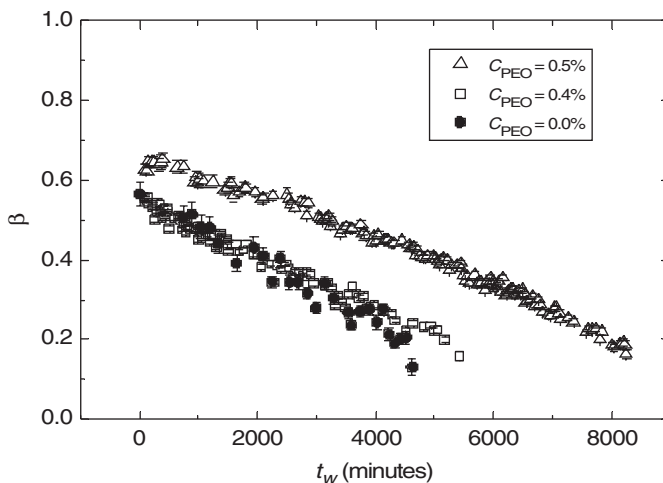

Figure 6. Waiting time evolution of the stretching parameter β for samples with a fixed Laponite concentration ($C_w = 2.0\%$) for neat Laponite sample (full circles) and for two different PEO concentrations ($C_{PEO} = 0.4\%$, open squares; $C_{PEO} = 0.5\%$, open triangles).

4. Conclusions

Dynamic light-scattering measurements have been performed on aqueous Laponite samples with various polyethylene oxide concentration added to the dispersion (at a fixed molecular weight of $M_w = 200,000$ g/mol). We have shown that addition of PEO modifies

the gelation kinetics with respect to pure Laponite samples. Because the shape of raw autocorrelation functions do not show drastic changes, we can apply the same fit analysis introduced previously for Laponite clay in water [5,7] and with the addition of NaCl [6]. Binding between Laponite particles is inhibited by the addition of this polymeric species, which adsorbs on the clay surface. This leads to a slowing down in the formation of the Laponite final arrested state. We have also shown a clear dependence of this phenomenon on PEO concentration. This is in agreement with the suggestion that increasing PEO concentration corresponds to growth in the coverage surface of Laponite discs by the adsorbed polymer and an increase in the repulsive term due to steric hindrance, which progressively hinders dynamical arrest. An extensive study to improve our understanding of the dependence of aging on PEO and molar mass of PEO is ongoing.

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