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Temperature dependence of aging kinetics of hectorite clay suspensions

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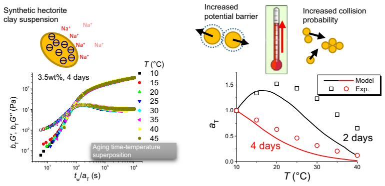
GRAPHICAL ABSTRACT



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ABSTRACT

The aging of salt-free hectorite suspensions with different concentrations (c_L = 2.9, 3.2 and 3.5 wt%) stored for 2 days or 4 days was studied by rheology at different temperatures. The evolution of storage and loss moduli G' and G'' during aging followed aging time–temperature superposition. The temperature dependence of the shift factor a_T, which reflected the aging kinetics, was interpreted by the reaction-limited colloidal aggregation (RLCA) mechanism with counterion condensation in calculating the double-layer interaction of the charged clay particles. Temperature dependence of the plateau modulus and yield stress of the suspension aged for 800 s was modeled with the soft glassy rheology (SGR) theory. The estimated noise temperature x indicated that the sample aged at higher temperature corresponded to a deeper quench in the nonergodic state. Under larger amplitude of oscillatory shear, the suspension exhibited a strain rate-frequency superposition (SRFS). The shearing eliminated the effects of aging and heating.

1. Introduction

Aging behavior is ubiquitous among systems with very slow dynamics that are far from equilibrium [1,2]. The dynamics of these systems is so slow that it cannot completely relax within the experimental time window t. Instead, the dynamics continuously slows down with the waiting-time t_w, *i.e.*, the time elapses since the quench of the system. The system relaxation time τ grows at a similar rate with t_w as $\tau \sim t_w^{-\mu}$ and μ is close to 1. This means that the observer can hardly wait for the system to be fully equilibrated.

Aging and slow dynamics have been experimentally observed in soft glassy materials, such as gels [3], emulsions [4], microgels [5], and even biological systems [6], Although the physics and chemistry of these systems differ dramatically among each other, their dynamics shares similar aging process as mentioned above. Specifically, time-aging time superposition are commonly observed from these systems, where the measured relaxation function at different waiting-times t_w can be scaled into a master curve if the time axis is reduced to t/τ [7].

One of the popular theoretical interpretations of the aging phenomenon is the trap model [8]. In this model, the system is described as a particle evolving on a complex energy landscape with broad distribution of trap depths. The trap model is adopted into the soft glassy rheology (SGR) model [9,10] to account for the linear and nonlinear rheology and the aging effect of complex fluids. However, the exact relationship between the model parameters with the material elements in the real space is still unsolved [11]. Other models for aging and slow dynamic behavior of glassy materials include the extension of mode-coupling theory (MCT)

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[12], the non-equilibrium self-consistent generalized Langevin equation (NE-SCGLE) theory [13], and the generalized fluctuation–dissipation relationship [14]. Despite these successful efforts, a full understanding of the microscopic mechanism that governs the common aging behavior remains a significant challenge.

Among many model systems used for experimental study of aging dynamics, the synthetic hectorite clay suspension is one of the most investigated [15], which is consist of charged disc-like nanoparticles suspended in water. Depending on the clay concentration and ionic strength, the clay suspension can age into several phases, such as fractal gels, [16] repulsive (Wigner) glasses [17], and attractive glasses [18]. Besides time-aging time superposition [19], the clay suspension exhibits some other scaling relationships during aging, which can be categorized into two classes. The first one is the time-X superposition with X being temperature [20] or adsorbed polymer concentration [21]. The change in these conditions uniformly shifts the relaxation to longer or shorter time without changing the spectrum. The second class is the aging time-X superposition, X being temperature [22,23], salt concentration [24], or the concentration of adsorbed polymer [25]. These superposition phenomena indicate that the aging kinetics of the suspension follows a universal route. Changes in condition X shift the system to earlier or later stage (younger or older age) on the kinetic route. The synergy of the two classes of scaling properties has recently been shown for a hectorite-poly(ethylene glycol) system [21], suggesting the existence of a correlation between the dynamics and kinetics beneath the apparent aging phenomena. It is now wondered what microscopic mechanism governs the phenomenological universality.

In the present paper, we will show that the aging kinetics of the hectorite suspension at different temperatures can be understood by the interparticle interaction within the theory of reaction-limited colloidal aggregation (RLCA), and the effect of temperature on the slow dynamics of the aged suspension can be modeled by the soft glassy rheology (SGR) model after mapping the model parameter with experimental results.

2. Experimental section

2.1. Sample preparation

Synthetic hectorite clay of gel-forming grade LAPONITE®XLG (Rockwood Ltd.) was used after dried overnight against anhydrate $CaCl_2$ in vacuum at room temperature. Aqueous suspension of clay concentration c_L was prepared by slowly mixing the dried clay with deionized water (18.2 MΩ cm) under stirring for 15 min and then ultrasonic homogenization for another 15 min until a transparent suspension was obtained. Suspensions of $c_L = 2.9$, 3.2, and 3.5 wt% prepared in this way were stored for 2 days before conductivity, *p*H, and rheology measurements, which were denoted as L2.9-2d, L3.2-2d, and L3.5-2d, respectively. Another sample of the 3.5 wt% suspension stored for 4 days before measurements was denoted as L3.5-4d. All samples were sealed in vials with parafilm during the storage.

2.2. Conductivity and pH measurements

Suspension conductivity was measured using a conductivity meter (DDS-307, Shanghai REX Instrument Factory) with a platinum black electrode (DJS-1c). The *p*H value of suspensions was detected using a PHB-3 *p*H tester (Shanghai Sanxin Instrumentation, Inc.). Samples were sealed with parafilm during measurements to avoid CO_2 dissolution.

2.3. Rheology measurements

Rheology measurements were carried out on a stress-controlled rheometer (AR-G2, TA Instruments) using a cone-and-plate fixture with diameter of 40 mm and cone angle of 1°. A thin layer of silicon oil was laid on the rim of the fixture to prevent water evaporation and CO_2 dissolution. Before every measurement, the sample was pre-sheared at a shear rate of 3000 s^{-1} for 100 s to achieve a reproducible initial state. Then, the aging of the clay suspension was immediately monitored by applying a sinusoidal strain $\gamma(t) = \gamma_0 \sin\omega t$ with a constant strain amplitude $\gamma_0 = 0.5\%$ and frequency $\omega = 6.28$ rad/s. The storage and loss moduli G' and G'' were recorded as a function of the evolution time t_w. The start of the aging ($t_w = 0$) was defined as the end of the pre-shearing procedure. The dynamic frequency sweep, dynamic strain sweep, and steady state viscosity measurement were performed on samples after the same pre-shearing and a delay time of 800 s. The delay allowed the sample to reach a repeatable gelled state for the measurements.

3. Results and discussion

3.1. Aging time–temperature superposition

Fig. 1a shows the evolution of the storage and loss moduli G' and G'' during aging of the sample L3.5-4d at different temperatures. During the rheology measurement, this sample exhibits a fluid-to-solid transition as indicated by the transition from $G' < G''$ to $G'' < G'$. The crossover $G' = G''$ appears at earlier time (smaller t_w) as the temperature increases, meaning that the sample ages faster at higher temperature.

When the curves in Fig. 1a are shifted to superimpose the crossover of $G' = G''$, all the curves collapse into a master curve as depicted in Fig. 1b. The curve of $T_{ref} = 10$ °C is taken as the reference. The horizontal shift factor a_T is defined as $t_c(T)/t_c(10\,°C)$, where t_c is the time at which $G' = G''$. a_T decreases with increasing temperature as shown in the inset of Fig. 1b, indicating that the rate of aging increases with increasing temperature. The vertical shift factor b_T varies slightly around 1, meaning that the vertical shift is negligible for optimizing the superposition.

The samples L2.9-2d, L3.2-2d and L3.5-2d stored for 2 days exhibit the same superposition as that of L3.5-4d. The horizontal shift factor is plotted in Fig. 2. Unlike the case of L3.5-4d, a_T of the samples stored for 2 days shows a maximum in the range of temperatures studied.

Upon dispersed in pure water, the sodium cation Na^+ between the layers of the clay is released into water, leaving the corresponding number of negative charges on the surface of the clay particle. Without addition of NaOH, there should be a small amount of positive charges on the edge of the particles due to the protonation of OH groups, resulting in the *p*H of the suspension usually higher than 7 [15]. Fig. 3 depicts that, for sample L3.5-4d, *p*H generally lies above 9.5 and decreases with increasing temperature. The ion product constant of water increases from 0.292×10^{-14} at 10 °C to 4.195×10^{-14} at 45 °C. Consequently, the OH^- concentration is very low around 10^{-5} to 10^{-4} M and also increases accompanying this temperature increase. The number of rim charges per clay particle estimated from $[OH^-]$ is around $1e \sim 3e$, where e is the elementary charge. The results of the other samples are similar with the number of rim charges not higher than $10e$ (data not shown here).

The suspension conductivity σ_c was measured for L2.9-2d, L3.2-2d, L3.4-2d and L3.5-4d as a function of temperature and demonstrated in Fig. 4a. For all the samples, the conductivity increases with increasing temperature. The conductivity is contributed by