Butterfly Light Scattering Pattern and Rheology of a Sheared Thixotropic Clay Gel

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The behavior of a thixotropic clay gel under shear flow is studied by combining a static light scattering technique and rheometric measurements. In the rest state, the gel structure is composed of micrometer-sized aggregates associated as a fractal mass. Under steady shear, a butterfly-type light scattering pattern is observed. This can be related to a contraction and a stretching of the micrometer-sized aggregates, perpendicularly to the shear direction. The influence of the shear rate on the disaggregation process is also studied and correlated to rheometric measurements. [S0031-9007(97)04678-4]

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Knowledge of the flow-induced structure in thixotropic colloidal suspensions is of crucial importance in understanding the complex rheological behavior observed in these materials. Indeed, species dispersed through the matrix of these systems form aggregates under the effect of attractive and repulsive forces. This can produce a continuous aggregated structure throughout the available volume of the sample. These materials may then have yield stresses and/or viscoelastic properties that are dependent upon both time and shear rate. To understand these strongly nonlinear types of behavior, the aggregation processes under shear flow can be studied either by means of theoretical and numerical models [1–4], or radiation scattering measurements [5,6]. A combination of scattering techniques and rheometric measurements is of vital interest in the experimental study of such materials.

This article reports on the experimental study of a model material, namely, a synthetic clay of the hectorite type, Laponite. This consists of disk-shaped particles, 30 nm in diameter and 2 nm thick [7]. In an aqueous medium at low ionic strength $[\mathrm{NaCl}] < 5 \times 10^{-3}$ mol/l and with a $p\mathrm{H} = 9.5$, this clay forms a transparent thixotropic gel [8].

Contrary to what is commonly accepted concerning these clay suspensions, study of the structure at rest [9,10] showed that it is the large length scales (of the order of one micrometer) that govern their macroscopic behavior.

The aim of this article is to examine the influence of shear flow on structural changes in these thixotropic suspensions at large length scales, and to link these with their macroscopic properties. The effect of shear rate intensity will also be studied.

To do this, rheometric bulk measurements were combined with static light scattering in the suspensions under shear flow. The results are compared with Potanin's theoretical results on disaggregation under shear [2].

The Laponite XLG suspensions were prepared under high shear in a solution of distilled water and NaCl (10^{-3} mol/l) at a temperature of 20 °C. A transparent thixotropic gel at a pH of 9.5 is obtained in a clay concentration domain extending from 0.9×10^{-2} to 5×10^{-2} g/ml, which corresponds to a volume fraction ϕ_v of 0.35 to 2% [9].

Rheometric measurements were carried out on a controlled speed rheometer (Weissenberg-Carrimed). Two types of configuration were studied: first, a plate-plate arrangement with quart disks of radius 20 mm, of roughness about 0.05 μm, and gap width 0.4 mm, and second, a cone-plate arrangement (angle 4°21, radius 24.5 mm) for which the surface of the apparatus was covered with glass paper of 200 μm roughness. In a previous article [8], it was shown that instabilities occur in flowing thixotropic and yield stress fluids. By monitoring the kinematic field, it was possible to determine the volume fraction and shear rate domains for which correct deformation occurs throughout the entire bulk of the sample. For all the suspensions studied in this article, the stresses are higher than the yield stress of the material, and the flow regimes correspond to homogeneous macroscopic deformations of the sample, without interface effects such as wall slip.

The laser scattering facility used for this study was the same as previously [9]. A specific tight shear cell was built for the experiment reported hereafter. The sample, which has a fixed thickness $e_0 = 0.4$ mm, is sheared between two parallel quartz disks, one of which is turned at an angular rotation speed ω around the axis Ox (Fig. 1). The laser beam is directed along Ox, perpendicular to the disks held in the plane Oyx, at a point along the horizontal axis Oz, situated at a distance R_c from the axis of rotation Ox. The velocity $\mathbf{V} = -v\mathbf{y}$, is collinear to the axis Oy. The intensity of scattering due to the sample is measured by the 2D detector along the plane Oyz. Consequently, the plane of observation corresponds to the plane (v, z). The local shear rate $\dot{\gamma} = R_c\omega/e_0$ at a given radius R_c is therefore in the plane Oxy. The scattering intensity $I(\theta, \psi)$ is recorded throughout the test by means of the camera and video system. θ is the scattering angle, and ψ is the azimuthal angle required to track the shape anisotropy in the scattering pattern. The scattering vector $\mathbf{Q}$ has a modulus defined by $Q = (4\pi n/\lambda)\sin(\theta/2)$ which extends from 2×10^{-5} to 4×10^{-4} Å^{-1} (n is the refractive index of the suspending

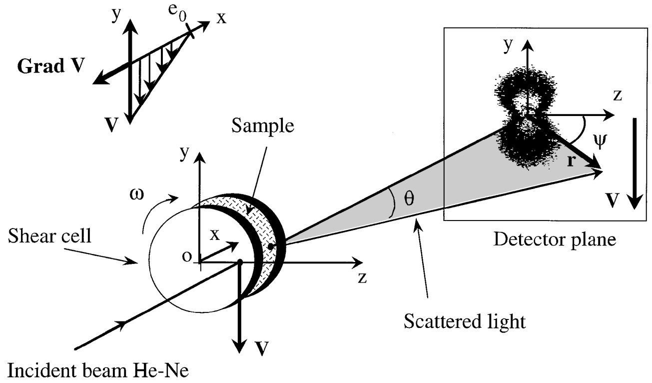


FIG. 1. SLS under shear. Plane-plane shear cell and coordinate system for the optical setup.

medium, λ the radiation wavelength). All the patterns were taken with the same exposure time of $1/2000$ s.

At rest, the structure was studied by combining scattering measurements for various types of radiation x-rays, neutrons, and light) [9,10]. The network that is set up as the suspension swells to form a thixotropic gel is due to the formation of micrometer-sized aggregates consisting of a dense pile of subunits measuring a few tens of nanometers. The micrometer-sized aggregates, which combine in a fractal mass with a fractal dimension D, form the continuous three-dimensional isotropic structure that gives the gel its texture. The gelation time, denoted t_p, corresponds to a slow aggregation process (taking several weeks), the kinetics of which are heavily dependent on the particle volume fraction. In a volume fraction domain close to the sol-gel transition ($0.35\% \leq \phi_v \leq 0.56\%$), the micrometer-sized aggregates form bundles ($D = 1 \pm 0.05$), giving the gels a fibrous texture [Fig. 2(a)] and then the aggregation process stabilizes after about 100 days. In a high volume fraction domain ($1.20\% \leq \phi_v \leq 2\%$), the structure is more heterogeneous, with zones of dense and less dense particle concentrations ($D = 1.8 \pm 0.01$), and then the gelation stabilization time is about 200 days. Between these two volume fraction domains, there is a transition zone (with the fractal dimension rising from 1 to 1.8), corresponding to an entanglement of the micrometer-sized aggregate fibers to produce an increasingly dense structure. It has been demonstrated that the fractal dimension of the structure and hence the particle density in the aggregates governs the changes in yield stress with volume fraction [9,10].

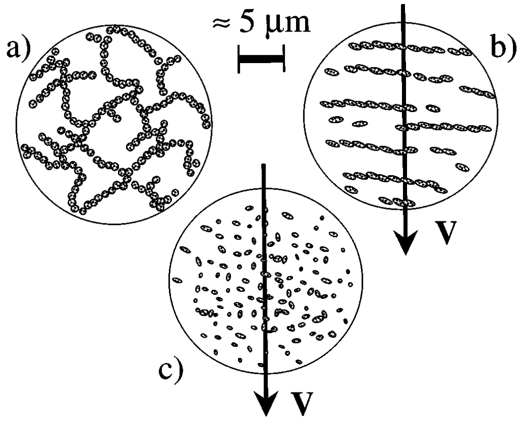
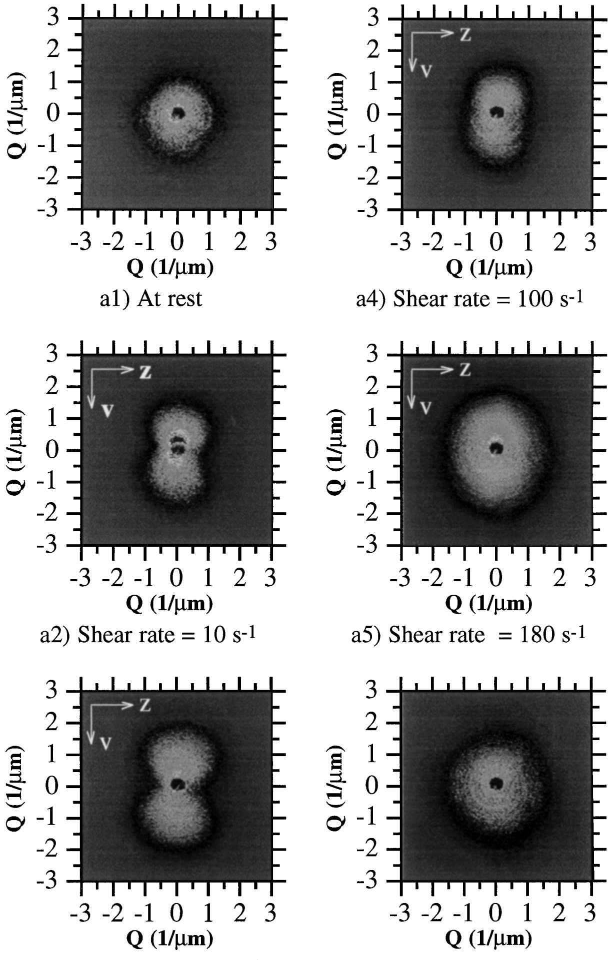


FIG. 2. Structure of Laponite (a) at rest (case $D = 1$) (b) under shear below the critical shear rate, and (c) under shear beyond the critical shear rate.

Under steady shear, gels belonging to the volume fraction domain for which the fractal dimension of the fibrous structures is of the order of 1 ± 0.05 produce extremely anisotropic scattering patterns. A butterflylike scattering pattern can be seen at shear rates of 10 and 40 s^{-1} [Figs. 3(a2) and 3(a3)].

A butterflylike scattering pattern of this kind has already been observed on silica-silicone composites [11,12] or on semidilute entangled polymers [13] and also on semidilute aqueous solution of wormlike micelles [14,15]. But here, the structure of Laponite gels at rest is composed of bundles of micrometer-sized aggregates that give a



a1) At rest

a4) Shear rate = 100 s^{-1}

a2) Shear rate = 10 s^{-1}

a5) Shear rate = 180 s^{-1}

a3) Shear rate = 40 s^{-1}

a6) at rest after shear

FIG. 3. SLS of suspension of Laponite under shear at $\phi_v = 0.56\%$, [NaCl] = 10^{-3} mol/l, pH = 9.5, t_p = 150 days.

fractal dimension $D = 1$ and not $D = 1.8$ as in silica-silicone composites. This form of scattering pattern is attributed to fluctuations in the particle or aggregate concentrations in the direction of flow, while no heterogeneity is detected perpendicular to the flow. This implies that the scattering intensity increases parallel to the direction of flow, while a dark streak appears perpendicular to it [6]. The scattering intensity $I(\theta, \psi)$ can be written as the following Fourier transformation of the spatial correlation function of concentration fluctuations in density of particles:

$$I(\theta, \psi) = A \int d\mathbf{r} \langle \delta_c(\mathbf{r}) \delta_c(0) \rangle e^{i\mathbf{Q}\cdot\mathbf{r}} = \frac{A}{c} S[\mathbf{Q}(\theta, \psi)],$$

where $S[\mathbf{Q}(\theta, \psi)]$ is the structure factor, and $\delta_c(\mathbf{r})$, is the fluctuation in clay particle concentration at the position $\mathbf{r}(\theta, \psi)$. DeGroot *et al.* [12] suggested that shear makes the largest flocs contract in the direction of flow by rolling themselves up and turning their main axis perpendicular to the velocity, thus forming a rollerlike structure. According to them, this deformation and stretching of the aggregates causes the development of a butterflylike scattering pattern.

The present authors tried to link the rheometric behavior of the samples to these structural observations obtained by light scattering. The stress value of the steady regime corresponds to a certain state of destructuring of the aggregate network. Depending on the shear rate applied, it is possible to observe various states of the structure in steady regime (Fig. 3). With an increasing shear rate, the dark streak perpendicular to the direction of shearing decreases until it is completely filled by the scattering intensity in the direction of flow [Fig. 3(a4)]. Above a critical shear rate, the butterflylike scattering pattern is replaced by an anisotropic scattering pattern with no extinction of the scattering intensity perpendicular to the direction of flow [Fig. 3(a5)]. When shearing is stopped after the high rate of 180 s^{-1}, the scattering pattern remains slightly anisotropic [Fig. 3(a6)]. The return to an isotropic scattering pattern characteristic of rest [Fig. 3(a1)] occurs over large length scales (several hours), corresponding to the time taken by the sample to recover its macroscopic properties after heavy shearing [8]. This demonstrates the thixotropic character of this colloidal suspension, and, in particular, the reversible character of the aggregation process.

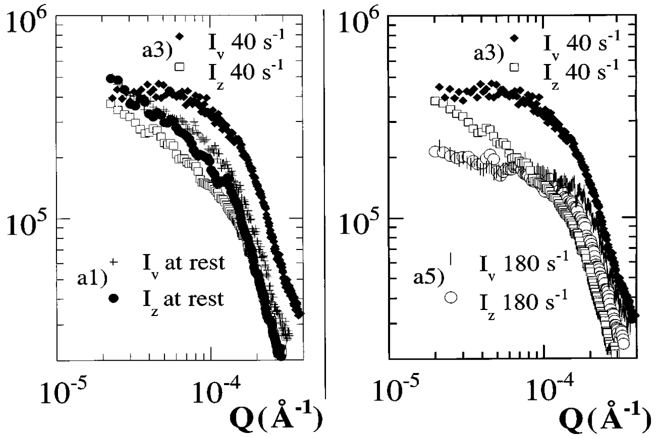


FIG. 4. Intensity distributions along the velocity direction (I_v) and normal to it (I_z). $\phi_v = 0.56\%$, [NaCl] $= 10^{-3}$ mol/l, pH = 9.5, $t_p = 150$ days.

Figure 4 shows the scattering intensity I_v parallel to the velocity direction and I_z perpendicular to it. I_v and I_z are obtained by integration of patterns on a strip of $Q = 0.53\ \mu\mathrm{m}^{-1}$ wide, centered to the beam stop. At rest, the scattering is directionally independent, characteristic of scattering from homogeneous isotropic dispersion. At increasing shear rate and below the critical shear rate, scattering is enhanced along the velocity direction, and the scattering intensity normal to it is reduced. At 40 s^{-1}, I_v/I_z increases from about 2 to 5 for the Q domain extending from 6×10^{-5} to 3×10^{-4} Å^{-1}. Above the critical shear rate, at 180 s^{-1}, the scattering again becomes isotropic, and both the intensities I_v and I_z weaken on the Q domain extending from 2×10^{-5} to 10^{-4} Å^{-1}. This decrease in intensity at length scales of about one to five micrometers seems to show that the breakdown of the gel is mainly attributed to an alteration of fractal structure, at the highest length scales probed in the gel.

On the steady regime flow curve (Fig. 5) this change in structure at increasing shear rate is characterized by an increase in stress (a decrease in the viscosity of the suspension). Close to the critical shear rate, which here is about 130 s^{-1}, there is a change in the slope of the stress versus shear rate curve. Beyond the critical shear rate, stress rises faster with shear rate, corresponding to the disappearance of the butterflylike scattering pattern, and the reduction of the scattering intensity.

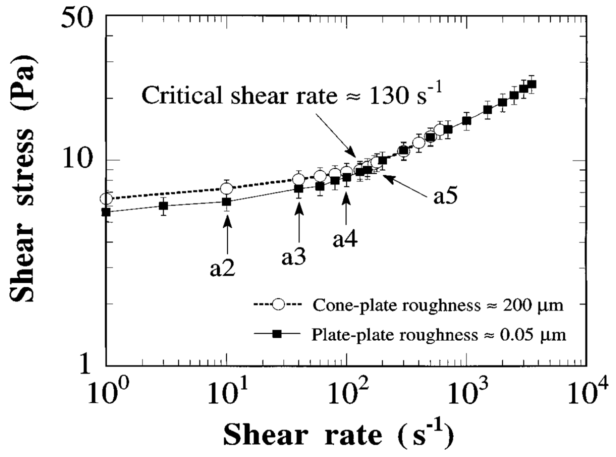


FIG. 5. Shear stress level in steady regime, as a function of shear rate. $\phi_v = 0.56\%$, [NaCl] $= 10^{-3}$ mol/l, pH = 9.5, $t_p = 150$ days. The labels (a*i*) correspond to the scattering patterns (a1)–(a5) on Fig. 3.

It is interesting to recall the results of the work carried out on the structure of Laponite suspensions under shear, using small-angle neutron scattering techniques [7]. At these small length scales (from 1 to 100 nm) on Laponite suspensions subjected to high shear, no particle alignment was noted when shear was applied. This corroborates the conclusion that it is indeed at large length scales that the effect of shear on the structure is preponderant.

In the light of these results, a possible interpretation may be proposed for the change in structure of Laponite suspensions under shear. This is as follows. At low shear rates, under the effect of hydrodynamic forces, the micrometer-sized aggregates contract and roll up on themselves. They form more concentrated rollers than in the remainder of the suspension. These rollers are aligned in a direction perpendicular to the flow [Fig. 2(b)]. Beyond a critical shear rate, no further contraction is possible, and the roller-shaped aggregates are then broken up into pieces [Fig. 2(c)]. The size of the suspended aggregates then decreases as the shear rate increases. The scattering pattern becomes increasingly isotropic and less and less intense. This suggests that the suspension consists of objects of ever decreasing size at the length scale observed. Such an interpretation is consistent with theoretical studies performed on the disaggregation process during flow [2–4]. This theoretical study also proposes the existence of a critical shear rate, beyond which any additional contraction of the aggregate is impossible. The destructuring process corresponds then to a fall in the number of particles per aggregate at a constant fractal dimension, and the breakup can be attributed to mechanical stresses.

In conclusion, this study reveals the main mechanisms involved in the disaggregation of flowing thixotropic suspensions of Laponite, thanks to a combination of light scattering and rheometric measurements. For the first time, a butterflylike scattering pattern has been observed in a thixotropic suspension of clay for which the structure at rest has a fractal dimension $D = 1$. Furthermore, this study shows that it is indeed the length scale of the order of one micrometer that governs the highly non-Newtonian behavior found in these clay suspensions. In addition, the disaggregation process that occurs in Laponite suspensions during flow validates the theoretical study carried out [1–4] and demonstrates the existence of a critical shear rate.

Lastly, this article recalls the crucial advantages of combining physical techniques for investigating the structure of materials and rheometric measurements, with a view to understanding the complex rheological behavior of this type of thixotropic colloidal suspension.

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