An experimental study of the time dependency of organoclay suspensions

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Résumé :

Dans ce travail, la dépendance temporelle des suspensions d'argile organiquement modifiée a été étudiée expérimentalement. Des mélanges d'hectorite modifiée et du gasoil ont été préparé à différentes concentrations massiques. Un ensemble de trois expériences a été utilisé pour caractériser la thixotropie des suspensions. Les résultats ont démontré que les suspensions ont un comportement non-Newtonien qui dépend du temps. Les rhéogrammes ont montrés que les suspensions sont rhéopectiques à des concentrations supérieures à 4%. Les courbes d'écoulement ont été modélisé par le modèle d'Herschel-Bulkley. Les courbes des vitesses de cisaillement à l'équilibre à des cisaillements constants ont été tracés et comparés aux courbes d'écoulements. Les courbes de la vitesse de cisaillement et de la viscosité en fonction du temps, après un changement soudain du cisaillement, ont illustré la dépendance au temps des suspensions d'argile modifiée. Ces résultats seront utilisés pour décrire l'évolution cinématique des suspensions étudiées.

Abstract:

In this work the time dependency of organically modified clay suspensions was experimentally studied. Mixtures of a modified hectorite and gasoil were prepared at different concentrations. Three experimental sets were used to characterize the thixotropic behavior of the suspensions. It has been shown that modified hectorite suspensions exhibit a time-dependent non-Newtonian behavior. Hysteresis loop measurements showed that suspensions exhibit an anti-thixotropic behavior at loadings greater than 4%. The Herschel-Bulkley model was used to fit the loading flow curves. Equilibrium shear rates at constant shear stresses were plotted and compared to the flow curves. A good matching of the Herschel-Bulkley model parameters, applied on both the equilibrium and the flow curves, was found. Plots of the shear rate viscosity as a function of time, after a sudden change (diminishing / increasing) of the shear stress from an initial value (Build-up / Break-down), have illustrated the time dependency of the modified hectorite suspensions after reaching a reference intern structure state. These results will be used to describe the kinetics evolution of the suspensions.

Keywords: Thixotropy; Organoclay; Microstructure; Time

1 Introduction

Modified clays or organoclays are usually made using smectite clays, in particular, sodium montmorillonite and hectorite because of their high cation exchange capacity [1]. In this modification process, cations present in the interlayer space (Na+, K+, …) are replaced by organic cations such as quaternary ammoniums [2]. Organoclays are widely used as viscosifiers in paints, cosmetics, greases, oil-based drilling fluids and more recently in nanocomposites where organoclays, called in this case nanoclays, with a size inferior to 0.5 µm are mixed with polymers to make highly temperature resistant materials.

The swelling of modified clays in organic media has been largely studied by several authors [2], [3]. It has been shown that many parameters can influence the processes of organoclay swelling and gelling like: nature of dispersing media, nature of clay and organic modifier [4], [5]. It has also been shown that the presence of a polar activator in the solving media can be of a major influence on the swelling of organoclays [6].

Rheology and structural behavior of smectite suspensions have been largely discussed by several authors as a function of the concentration in clay, PH of the suspension and the influence of adding different polymers to the clay suspension [7], [8], [9], [10]. Nevertheless, only few authors discussed the rheology of organoclays [11], [12], [13], [14], [15], [16]. One of the most detailed works on organoclay suspensions rheology was reported by Zhong and Wang [13] who discussed the yield behavior of exfoliated modified clay suspensions at different concentrations.

2 Materials and methods

2.1 Materials

The clay used for the experiments is an organically modified hectorite clay manufactured by Elementis Specialties, UK. Hectorite is a member of the smectite clay family and thus can swell and exfoliate in water. The unit cell formula for the hectorite is Na0.74 [Mg5.33 Li0.60] (Si7.98 Al0.02) O20F2.69(OH)1.31. It belongs to the phyllosilicate 2:1 family and are formed by and octahedral layer sandwiched between two tetrahedral layers [17], [1]. The hectorite platelets are more or less uniform and elongated in shape as they crystalize along a preferred axis. This hectorite is modified by replacing its interlayer cations by a quaternary ammonium salt cation. Modification of clay surfaces has taken a lot of intention recently looking at its major role in manufacturing organoclays, used along with polymers to make nanocomposites. The quaternary ammonium cation used to fabricate the organoclay studied in this work is a dimethyldialkyl quaternary ammonium cation.

2.2 Preparation of the organoclay suspensions

Clay suspensions with mass concentrations of 3, 5 and 8 wt% were studied. Dispersion medium is gasoil. Given that the preparation protocol has a big influence on the reproducibility of results, an identical procedure was used to prepare all the suspensions. Organoclay powder was first dispersed in gasoil and homogenized under a constant magnetic agitation of 500 tr/min for 24h. The prepared suspensions were then left at rest for 24h at 20°C and stirred at 250 tr/min for 1h prior to each experiment.

2.3 Experimental procedures

A controlled stress rheometer was used to perform all the measurements (AR2000, TA Instruments) equipped with a cone-and-plate geometry (diameter: 60 mm; angle: 2°). Temperature was controlled using a Peltier system and all measurements were conducted at a constant temperature of 20.0±0.1 °C. Given that concentration has a big influence on the thixotropy of the dispersion [8], all the measurements were conducted in an oil saturated environment to prevent the evaporation of the dispersion medium. The plate of the rheometer geometry was covered by a rough surface (sand paper) with a roughness of 30,2 μm to prevent wall slipping.

3 Results and discussion

3.1 Hysteresis loops

In order to obtain reproducible data, all suspensions should be at the same structural state at the beginning of the experiments. For that, a constant high preshear was conducted for 10 minutes to all suspensions in order to reach a total destruction of the internal structure. Then, suspensions where left at rest for 60 minutes to allow them find ,to a certain degree, their initial structure [9]. A continuous ramp of 60 minutes was then applied, followed by a constant plateau at the highest shear stress for 60 minutes before reversing the ramp to measure the downward flow curve. Shear rate-shear stress curves of modified hectorite at different concentrations (5, 6 and 8 wt%) are represented in Fig.1. These tests have showed that hectorite suspensions in gasoil are overall rheopectic with a significant time dependency at high organoclay loadings (8%). Hysteresis loops show that the behavior of organoclay suspensions is dependent on shear rate. Regarding the upward flow curve of the rheogram, four different regions and an overall two regimes can be identified. Each region corresponds to a different state of structure of the suspension: (i) The first region represents a plateau where shear rate increases continuously at a quasi-constant shear stress, this behavior could be explained by the internal rearrangement of particles induced by the change in shear rate [9], [18], in this case, thus it is deforming, the sample does not flow. (ii) the second regime represents a quasi-Newtonian plateau with a slop of -1 at very low shear rates. In their work on oil-based drilling fluids, Herzhaft et al [19] have shown that this quasi-Newtonian behavior is due to the high level of elasticity of the fluid at low shear rates. At rest, the fluid develops a solid-like structure which makes it move as a single bloc at low shear rates. (iii) the third behavior of the curve is a plateau at a quasi-constant shear stress. This region represents a transition separating between the quasi-Newtonian and the shear-thinning regimes. (iv) in the high shear rate region, a small variation of the shear stress conducts to a drastic rise of the shear rate. This shows that the suspension started to flow after the transition zone and that the elasticity of the material is diminishing. The behavior of the modified hectorite suspension in this regime is shear thinning and can be mathematically modelled using a simple power law model [9].

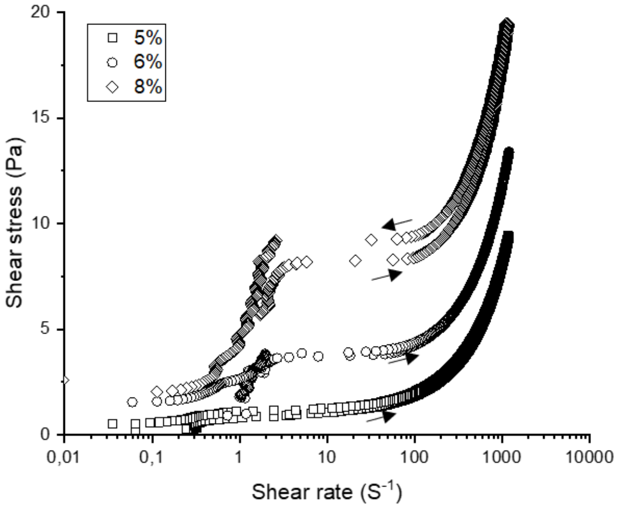

Fig. 1. Flow curves of modified hectorite suspension (5%, 6% and 8%)

3.2 Steady state measurements:

Although hysteresis loops can give a general idea about the time dependency characteristics of the material, the analysis of their results still difficult because of the simultaneous change of two variables during the experiment: shear stress and time. That is why cyclic shearing measurements were only used to qualitatively describe the behavior of the organoclay suspensions. For a more precise description of the behavior of the material, one variable should be fixed.

3.2.1 Reconstruction of flow curves:

In a first part, shear stress was fixed, and shear rate and viscosity changes were recorded as a function of time. Different shear stresses were chosen for each concentration at different structural states using the hysteresis loop curves. After attending the equilibrium, the values of shear rate and viscosity were plotted as a function of shear stress. The same conditioning protocol as for hysteresis loop measurements was applied followed by a 45 minutes step for each shear stress. The same fluid sample was used for all shear stresses in each concentration in order to avoid having experimental errors from changing samples.

As it is illustrated in Fig.2., time dependency characteristics increase with organoclay loadings. For the 5% concentration, a good matching between the upward flow curve and the steady state measurements which indicates either the absence of any time dependency, which is unlikely to be the case due to the time dependency of this suspension that will be discussed in section (3.2.2), or reaching the steady state at each point of the curve. For the 6% and 8% concentrations in the other hand, yield stress is higher in the flow curves than in the steady state curves (see Table 1), this is due to the short time given to the suspension to rearrange its internal structure and reach yield in the case of flow curves. Starting from a rest structure, time dependent materials may flow at lower shear stresses if given the sufficient amount of time [20].

Concentration	**n**		**K** [Pa sn]		**τ_c** [Pa]	
	Break down	**Equilibrium**	**Break down**	**Equilibrium**	**Break down**	**Equilibrium**
5%	0,90 ± 0,01	0,98 ± 0,01	0,01 ± 0,00	0,01 ± 0,00	0,81 ± 0,02	0,62 ± 0,01
6%	0,86 ± 0,01	0,77 ± 0,14	0,02 ± 0,00	0,04 ± 0,04	2,73 ± 0,04	0,78 ± 0,02
8%	1,01 ± 0,02	1,03 ± 0,31	0,01 ± 0,00	0,01 ± 0,01	6,95 ± 0,06	7,00 ± 1,86

Table 1. Rheological parameters of the Herschel-Bulkley model for the Break down and equilibrium flow measurements.

3.2.2 Break-down and Build-up curves:

In a second part, the reaction of the material towards fixed stresses at a reference stage of structure was investigated (unlike the first part where the experiments started from an unknown structure). In this part, and for clarity purposes, only the curves of a 5 wt% suspension are presented, curves presenting the behavior of other concentrations will be the object of a future paper. A sudden decrease (for build-up experiences) or increase (for break-down experiences) of shear stress was applied on a 5 wt% sample that had been sheared until equilibrium at 2 Pa and 8 Pa for break-down and build-up experiences, respectively. A fresh sample was loaded for each shear stress in order to start all the experiments from the same structural state. Evolution of shear rate and viscosity as a function of time was recorded (Fig. 3.).

As it is illustrated in (Fig. 3.), and in both break-down and build-up experiments, organoclay suspensions exhibit a time dependent behavior where the intrinsic structure of the sample changes under a constant shear stress. After a sudden increase of shear stress (see Fig. 3: (a) and (b)), shear rate increases gradually until reaching the equilibrium value after 10 seconds of shear. Viscosity, in the other hand, shows an instantaneous decrease that reflects the viscoelastic relaxation followed by a gradual decrease until reaching the equilibrium value.

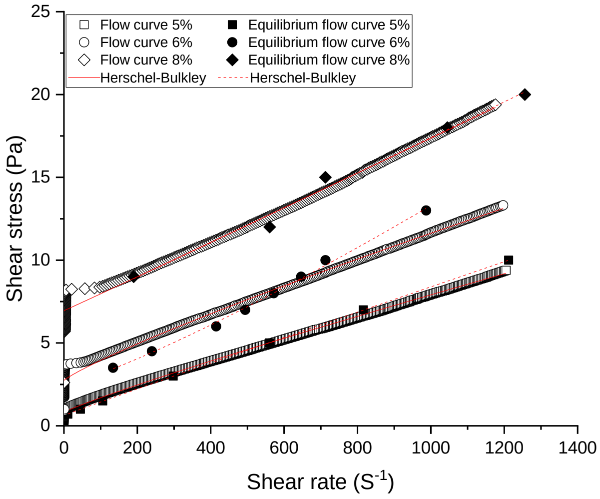

Fig. 2. Loading and equilibrium flow curves of 5%, 6% and 8% modified hectorite in gasoil suspensions fitted using the Herschel-Bulkley model.

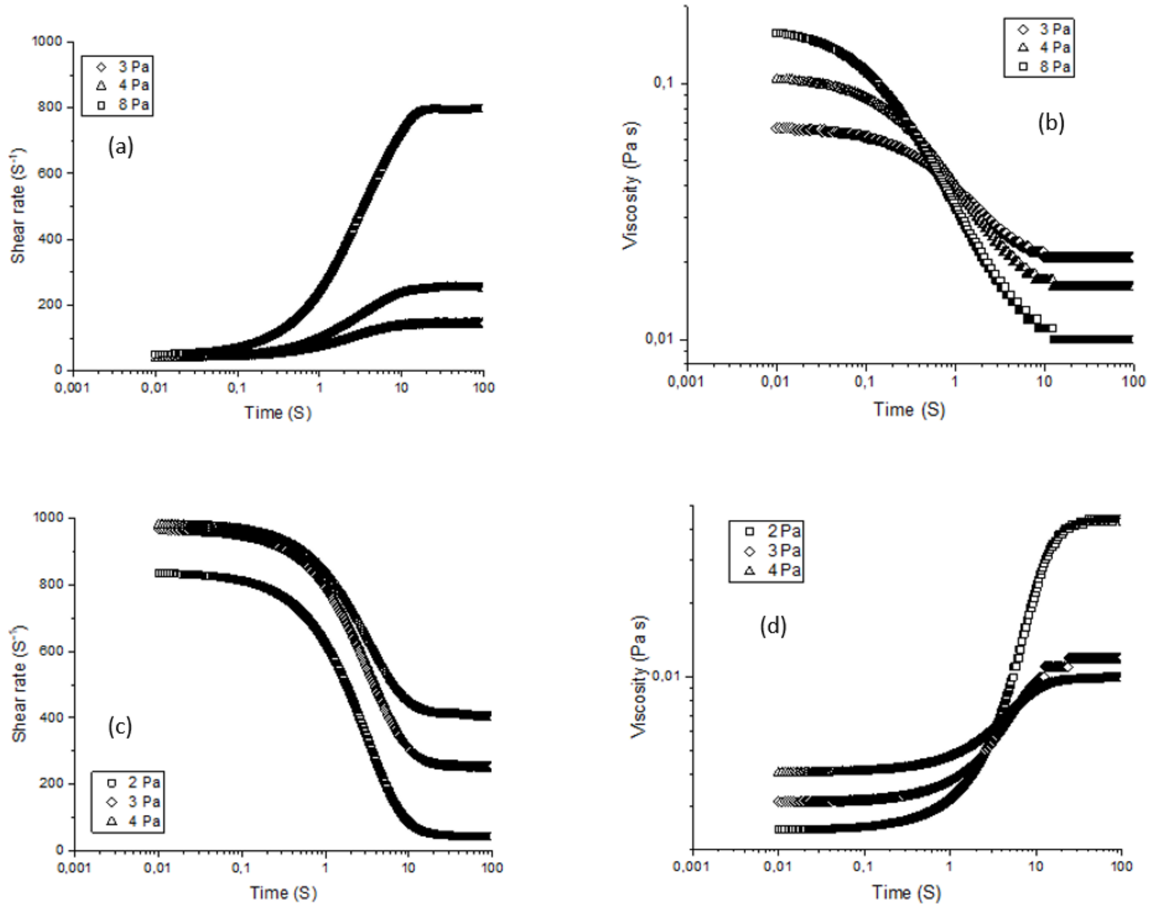

Fig. 3. Build-up and break-down of a 5 wt% organoclay suspension: (a) shear rate as a function of time of a break-down from an initial shear stress of 2 Pa, (b): Viscosity as a function of time of a break-down from an initial shear stress of 2 Pa, (c): shear rate as a function of time of a build-up from an initial shear stress of 8 Pa, (d): viscosity as a function of time of a build-up from an initial shear stress of 8 Pa.

As all stress steps, in this case, were applied on a fully structured fluid (2 Pa is a value belonging to the yield stress region), the gradual decrease of viscosity can be than explained by the destruction of the interne structure of the sample with time. After applying a stress higher than yield stress, the applied force becomes higher than the hydrogen bonds connecting clay platelets which leads to the destruction of the 3D structure of the organoclay platelets and thus the decrease of viscosity[15]. In the case of build-up experiments (curves (c) and (d) of Fig. 3.), all experiments begun from a totally broken intern structure (8 Pa corresponds to a shear rate of 825 s^{-1}). A sudden decrease of shear rate was observed after a step down of shear stress to 2 Pa. This sudden decrease, which was not observed for the rest of shear stresses, can be explained by the tendency of the clay platelets to form a solid-like structure at stresses belonging to the yield region. After that a gradual decrease of shear rate was registered until equilibrium. Regarding the viscosity curves, the same instantaneous viscoelastic relaxation, as in the break-down experiments, was observed, followed by a gradual increase until equilibrium (about 10 s of restructuration). This increase of the viscosity is due to the restructuration of the fluid at lower shear stresses and thus lower destruction forces. After lowering shear stress from 8 Pa to 2 Pa, a higher slope of the viscosity curve, compared to the 3 Pa and the 4 Pa stress step downs, was noticed. This is mainly due to higher capacity of restructuration of organoclay intern network at stresses near to the yield stress. At the yield region, the organoclay has the tendency to form a 3 D structure because of the interactions between clay platelets and the surfactants used in the modification process.

4 Conclusion

The rheological behavior of modified hectorite suspensions was investigated. Particularly, the relation between the structure of the organoclay and the time dependency of its suspensions was also studied. According to the results of this work, some conclusions can be drawn:

- Organoclay suspensions exhibit a time dependent behavior. Among the several parameters controlling the flow behavior of the suspensions are: the organoclay weight fraction, nature of the clay and the surfactant used to manufacture the organoclay as well as the nature of the dispersing media, the conditioning steps proceeded before the measurements, the resting time under the geometry, the structural state at the beginning of the experiment and the applied shear stress ramp.
- Modified hectorite clay used in this study dispersed in gasoil exhibits a non-Newtonian behavior which was modeled using the Herschel-Bulkley equation. The yield stress was found to be increasing with the loadings in organoclay while both the consistency and the flow index remained constant. The same model was used to correlate equilibrium curves.
- It has been shown that organoclay suspensions used in this work are time dependent. Cyclic shearing experiments showed that the time dependency characteristics are more present in concentrated suspensions. Break-down and build-up experiments illustrated the destruction and the formation of the intrinsic structure starting from a totally formed and broken structure, respectively.

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