Dynamic Column Formation in Na-FLHC Clay Particles: 
Wide Angle X-ray Scattering and Rheological Studies

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Abstract. The dynamic chain and column formation of 5wt.% clay particles suspended in silicone oil has been studied using synchrotron Wide Angle X-Ray Scattering (WAXS) technique and rheometry. The anisotropic arrangement of particles described by the global order parameter S has been investigated. The WAXS data have also allowed distinguishing between the chain and column formation processes by comparison of the change of WAXS angular plots maxima with the current density growth in function of time. The saturation time t_s (after which there was no change in the system observed) was estimated. In addition, the rheological properties of the ERF have been measured including the static yield stress.

1. Introduction
Electrorheological fluids (ERFs) are liquids that solidify, or become very viscous, under an electric field. The transition from liquid into a solid-like state indicates that there is an inner ordering of the ER-constituents, which leads to a change in the rheological properties. Application of an electric field induces polarization of the suspended dielectric particles and a chain-like structure can be formed along the electric field direction [1-3]. Recently, the Giant Electrorheological (GER) fluid was discovered and it differs from the conventional ER fluids by exceeding the theoretical upper bound [4,5] of the yield stress, reaching 250 kPa at 5 kV/mm [6,7]. That discovery opens new horizons in the field of ER systems and inspires rheologists for working on further developments of such systems. In order to predict the response and behavior of ERFs under an applied electric field, it is important to gain an understandable knowledge of the physical mechanism of the chain and column formation and its dynamics. In the present study, synthetic clay particles Na-fluorohectorite (Na-FLHC) suspended in insulating, non-polar silicone oil form with time chain-like structures when subjected to an external electric field. The time needed to create columns of aggregated particles varies as the electric field (0.35, 0.5 and 0.75 kV/mm) increases. Wide Angle X-Ray Scattering (WAXS) diffraction patterns reveal changes of the direction of the dipolar moment induced in clay particles when the electric field is applied. The anisotropic arrangement of particles forming the chain can be described by the global order parameter S. The detail description of the system geometry, fitting procedure and calculations of S parameter can be found in the report of Meheust Y, et al. [8]. In-depth analysis of the system measured can be obtained using rheometry. The shear stress $\tau$ as a function of a shear rate $\gamma$ can reveal the type of ER fluid and in case of samples of this study the shear stress is represented by the Bingham plastic rheological model [9,10]

2. Sample preparation and characterization methods
The synthetic Na-FLHC clay was purchased from Corning Inc. (New York) in a form of powder. According to supplier, its chemical formula is given as $\text{Na}_0.6(\text{Mg}_{2.4}\text{Li}_{0.6})\text{Si}_4\text{O}_{10}\text{F}_2$ per unit cell, where Na is an interlayer exchangeable cation. A silicone oil Dow Corning 200/100 Fluid (dielectric constant of 2.5, viscosity of 100 mPa·s and specific density of 0.973 g/cm³ at 25°C) was used as a suspending liquid as a relatively non-polar and non-conductive medium, with a DC conductivity of the order of magnitude of $10^{-12}$ S/m. The preparation of the ER fluid was undertaken by the following procedure. Clay powder was crushed with a pestle and mortar, and then dried in vacuum oven for 12h at 90°C. At
the same time the silicone oil was heated at 110°C for 12h. After that, the clay powder and silicone oil were mixed in glass tubes and vigorously hand-shaken for ~2min, then placed in an ultrasonic bath for 1h and again vigorously shaken for 1h in an orbital shaker. The clay concentration was assumed to be ~5 wt.% and it sedimented rather slow, however for rheological data collection the sample needed to be pre-shaken each time before measurement.

The wide angle x-ray scattering experiment (WAXS) was carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The X-ray beam with wavelength of 0.72Å and 0.3x0.3mm² beam size at sample was used. On the beamline BM01A a two-dimensional MAR 345 image plate detector with diameter of 345mm and a read-out time of around 40s was installed. The WAXS experiment was performed at RT for sample at rest (no liquid flow through a custom-made scattering cell). Electric fields from 0.35 to 0.75kV/mm have been chosen as a result of the following observations: for the electric filed above 0.75kV/mm the chain and column formations are too fast to be distinguished; electric fields below 0.35kV/mm however are too week for particles to form any chains.

The rheological properties of the clay suspensions were measured at RT, under DC electric fields using a Physica MCR300 rheometer.

3. Results and discussion

Normally, the Na-FLHC particles are randomly dispersed into the silicone oil (fig.1a). Microscopy images of the sample experiencing an electric field for different time are shown in fig.1b, 1c. The formation of column-like structures aligning parallel to the field is clearly observed. Many of thin chains are formed first (~1-20µm) and they attract each other resulting in creation of thicker (~50-200µm) columns. After the time t₁ (which will be called here the saturation time) no major changes in the system are noticeable. Figure 1d is obtained prior to the application of an electric field and isotropic pattern can be observed, since particles are distributed randomly with not specified orientation. The two-dimensional WAXS patterns in figures 1e and 1f are becoming gradually more intensive in time, and the dependence of intensity for azimuthal angle φ is pronounced. This change of the 1st Bragg peak intensity in time is plotted as function of the azimuthal angle φ and presented in figures 2a and 2b for different electric (DC) fields.
There are three possible events which can influence these WAXS pattern changes while time passes by: either clay platelets are being more orientated along the electric field or/and clay particles are forming chains or/and chains are coarsening into column-like structures in a range of the X-ray beam. These three situations can occur in different time range or they may overlap in time. By looking at figures 2 and also taking into account the calculations of S parameter (tab.1) one can conclude that the intensity does not changes due to particle orientation and it is rather dependent on the dynamic chain or/and column formation. The mean orientation distribution hardly changes and S oscillates around 0.63, 0.65 and 0.60 under applied fields of 0.35 kV/mm, 0.50 kV/mm and 0.75 kV/mm, respectively.

| Time  | 0.35 kV/mm | 0.50 kV/mm | 0.75 kV/mm |
|-------|------------|------------|------------|
| 15s   | 0.63       | 0.62       | 0.53       |
| 1min  | 0.61       | 0.62       | 0.64       |
| 1min45s | 0.62     | 0.64       | 0.65       |
| 2min30s | 0.62      | 0.64       | 0.58       |
| 3min15s | 0.67      | 0.68       | 0.60       |
| 6min  | 0.67       | 0.68       | 0.60       |
| Avr.  | 0.65       | 0.67       | 0.60       |

Table 1. Calculated order parameters for Na-FLHC clay suspension under an electric fields of 0.35, 0.50 and 0.75 kV/mm.

The current density increases when chains are being formed. However, it does not change while chains coarsen into the column. Therefore by comparison between the current density growth and the change of WAXS angular plots maxima versus time (fig.3), both chain and column formation processes can be distinguished. This information might be of importance when one needs a self-assembly from particles to lead into the single chain formation rather than aggregated column creation. For 0.75 kV/mm and 0.50 kV/mm electric fields the current density curves overlap with WAXS data indicating the chain formation is followed by rapid column aggregation. However, for the lowest electric field current density increases faster than the WAXS records for the same field pointing out that the column formation occurs slower comparing to higher electric fields. That follows the thermal theory of coarsening [11,12], which describe the collision time of two chains as follows: \[ t_c \sim \rho^{3/2} \cdot k_B T^{-1/2} \cdot E^{-1} \], where \( \rho \) is a distance between two chains. Thus, when the electric field \( E \) increases (more rapid chain formation entails both the decrease of distances between chains and the increase of current resulting in the temperature \( T \) rise) the coarsening occurs more rapidly. For the different field strength, the intensity for azimuthal angle and integrated q values becomes saturated at the different time \( t \), which was estimated as: ~195s, ~150s and ~60s for electric fields of 0.35kV, 0.50kV and 0.75kV, respectively. One can see that the data and its fitted curves in fig. 2b are left- or right-shifted. This is due to the movement of a columnar structure that can be tilted in respect to the reference orientation while being formed.

Fig.4 shows the yield stress \( \tau_y \) of different clay particle concentration \( \Theta \) as a function of electric field \( E \). The power law with exponent \( \alpha \) of 1.57, 1.77, 1.67 and 1.64 was used to fit the results for the samples with 5, 10, 20 and 40 wt.% of clay particles, respectively. The exponent \( \alpha \) is commonly found in the range between 1 and 2 [13]. The yield stress for the sample with 5wt.% of clay particle was estimated as 16 Pa at 1kV/mm. whereas the yield stress of 102 Pa was measured for the sample with 40wt.% of clay particles. As one can see the yield stress \( \tau_y \) and what follows the apparent viscosity \( \eta \) of the ER suspension is largely dependent on the particle concentration \( \Theta \) and the
relationship is nearly linear. Similar results have been found by many researchers [9] and the fibrillation model was used to derive that dependence. However simple and very limited, the fibrillation model can be also suggested here as the mechanism of the ER effect. In this model particles can be polarized and aligned as a dipole along the direction of the electric field. The interaction between the polarized particulates would be increased, resulting in the obvious ER effect. The particle could bear some net charge, arising from the non-uniform polarization or ionic adsorption, thus electrophoresis could contribute to the particle motion. This particle migration was observed using optical microscope and also confirmed by the experiment described below. Steady shear stress for a DC electric field was compared with a low-frequency (50Hz) periodic AC field of the same RMS voltage values. The results are shown in the inset of figure 4. The shear stress is higher when the AC power supply is used. This is due to the fact that electrically induced particle migration is minimized.

4. Conclusion

The dynamic chain and column formation of 5wt.% clay ER suspension has been studied by means of WAXS technique and rheometry. It was shown that the mean orientation distribution hardly changes in time (15sec – 6min) and the order parameter oscillates around 0.63, 0.65 and 0.60 under applied fields of 0.35 kV/mm, 0.50 kV/mm and 0.75 kV/mm, respectively. The WAXS experiments have also allowed distinguishing between the chain and column formation processes by comparison of the change of WAXS angular plots maxima with the current density growth versus time. For the lowest electric field (0.35 kV/mm) there was clear evidence that coarsening of chains into the thicker columns occurs much slower comparing to the samples at higher fields, where column formation takes place immediately after chains are being formed. The saturation time $t_s$ (after which there was no change in the system observed) was estimated as: ~195s, ~150s and ~60s for electric fields of 0.35kV, 0.50kV and 0.75kV, respectively. The formation of chains and columns is more rapid when an applied voltage is higher. Steady shear stress for a DC electric field was compared with a low-frequency periodic field and a slight increase in the shear stress was observed due to the minimization of particle migration. In addition, the most important electrorheological properties have been measured which included both the electric field and also particle concentration dependent yield stress tests.

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