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ESRF

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The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	Experiment title: **Dynamics of electrorheological chain formation in synthetic nano-layered silicates**	Experiment number: **01-02-796**
Beamline: **BM01A**	Date of experiment: from: **5 Dec 2007** to: **7 Dec 2007**	Date of report: **March 2010**
Shifts: **6**	Local contact(s): Dr. Dmitry Chernyshov	*Received at ESRF:*

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Report:

The main focus of the reasearch was put on electric field induced structuring from nano-layered silicate clays. The basic particles forming the chains in this case are made of X-fluorohectorite ($X\text{-}Mg_{3-x}Li_xSi_4O_{10}F_2$), a synthetic swelling clay. Here X is an interchangeable cation, for example Na^+. These clay particles were suspended in non-conductive and non-polar silicone oil making up a rheological fluid (ERF). ERFs are complex fluids that solidify, or become very viscous, when submitted to an applied electric field. The transition from a liquid to a solid-like state indicates that an internal ordering of the ER-constituents has appeared, leading to dramatic changes in the rheological properties. Application of an electric field induces polarization of the suspended dielectric particles. They consequently orient in the field and aggregate, which results in the formation of a chain-like structure parallel to the electric field direction.

The particle orientation and aggragation was of primary interest in this study. Since each particle is a stacked clay system with water intercalated, the investigatigation of a Bragg peak diffraction rings allows to determine the degree of anisotropy in the system in presence of the E-field.

There are several interesting aspects to study for such a system, among them the dynamics of individual particle polarisability, the dynamics of chain formation, and the dynamics of chain bundling. Another interesting aspect is the chain structure both during formation, during destruction and under stable conditions. Other important questions, like macroscopic strength of the chain system as well as of individual chains, may be answered by macroscopic rheological studies. Some of these questions have been answered and results can be found in two publications (see the last paragraph) and the sample preparation, an experimental set-up and the results are summarized below.

RESEARCH SUMMARY:

Synthetic fluorohectorite clay was purchased from Corning Inc. (New York) in the form of powder, and cation exchanged into sodium fluorohectorite (Na-Fh) in our lab. Its final chemical formula is given as $Na_{0.6}(Mg_{2.4}Li_{0.6})Si_4O_{10}F_2$ per half 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/cm^3 at 25°C) was used as a suspending liquid, providing a relatively non-polar and non-conductive medium. The clay powder and the silicone oil were mixed making up ERFs with following concentrations 1, 5, 10, 20 and 40 wt.%, respectively.

The wide angle x-ray scattering experiment (WAXS) was carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. An x-ray beam with a wavelength of 0.72 Å and a 0.3x0.3 mm^2 beam size at the sample was used. The beamline BM01A is equipped with a two-dimensional MAR345 image plate detector with diameter of 345 mm. The sample to detector distance was set to 350 mm and calibrated using a standard LaB_6 sample, resulting in a maximum diffraction angle 2θ of about 26° that enabled detection of scattering in a q-range of approx. 0.2 – 2 Å^{-1}.

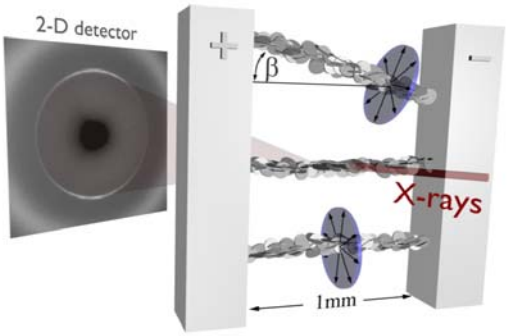

Fig..1. Experimental geometry for the WAXS measurements. Particles are forming chains along the E-field.

The experimental geometry is shown in figure 1. The custom-made sample cell consisted of an electrically insulating acrylic glass in the form of a cubic cuvette, where the top part can be opened for inserting two identical 1x1x50 mm thick copper electrodes separated by a gap of 1 mm. Electric fields from 0.35 to 0.75 kV/mm were chosen as a result of the following observations: for electric fields above 0.75 kV/mm the chain and column formations are too fast to be followed experimentally, and electric fields below 0.35 kV/mm are too weak for particles to form any chains.

Prior to the application of the electric field, the Na-Fh particles are randomly dispersed into the silicone oil. The formation of chain-like structures aligning parallel to the E-field is observed after its application. Many thin chains are formed first (with thickness in the range 1 to 50 μm) and they subsequently attract each other resulting in thicker (in the range 50 to 200 μm) columns. After a time t_s (the saturation time), no major changes in the system are noticeable by optical microscopy.

Dynamic changes in the clay orientational order can be observed from two-dimensional WAXS patterns. Figure 2 shows WAXS patterns from a suspension, without (a) and with (b) an E-field of 750 V/mm applied. The inner diffraction ring lies at 0.51 Å^{-1} and is attributed to the (001) Bragg diffraction from the layered silicate sheets within clay particles. Typically, the distance d_{001} is close to 12 Å when one layer of water is intercalated between silicate sheets [10]. The outer peak at 0.83 Å^{-1} is due to the silicone oil, i.e. the maximum in its radial distribution function. The 1st Bragg peak intensity changes in time after the electric field has been applied. This change can be better appreciated when the intensity of the (001) Bragg diffraction peak is plotted as a function of the azimuthal angle φ as shown in figure 3..

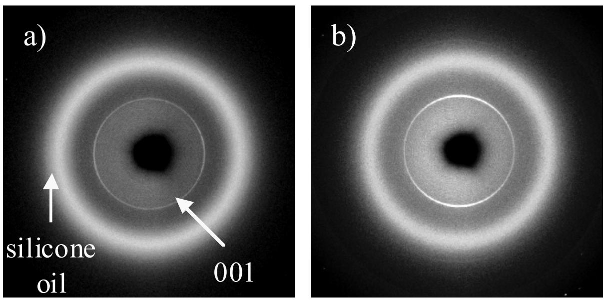

Fig. 2. WAXS patterns of clay particles without (a) and with (b) E-field applied.

Table 1 shows values of the order parameter calculated for different E-fields. There seems to be no evidence of E-field dependence, nor time dependence on the order parameter *S*, for the E-field range (350 - 750 V/mm) and time scale (15 s – 6 min) addressed in this study. One can conclude that the clay aggregates rotate and align along the E-field much faster (probably in ms time scale) than chains (seconds) and columns (seconds/minutes) are formed.

The amplitude of the WAXS azimuthal profiles is a measure of the average particle orientation in the scattering volume, but it also scales with the number of particles existing within this volume. Since we find that the order parameter is nearly constant with time, the amplitude change seen in Fig. 3 is a demonstration of how the number of particles contributing to the scattering increases in time. This observation is a sign of the progressing chain and bundle formation inside

the scattering volume, where (1) already formed chains are attracted to each other and/or (2) particles being still in motion (electrophoresis) finally attach to an existing chain. Both effects can increase the lateral dimensions of chains. The two processes, namely particle orientation and chain formation, may affect each other to some extent, but the particle orientation is the initial step and is largely finished when the chain formation takes over, as illustrated by the order parameter values along with the data in Fig. 3.

Table 1. Calculated values of the anti-nematic order parameters *S* under different E-field strengths.

E-field	S_{an} (average)
350 V/mm	**0.63 ± 0.01**
500 V/mm	**0.64 ± 0.02**
750 V/mm	**0.60 ± 0.05**

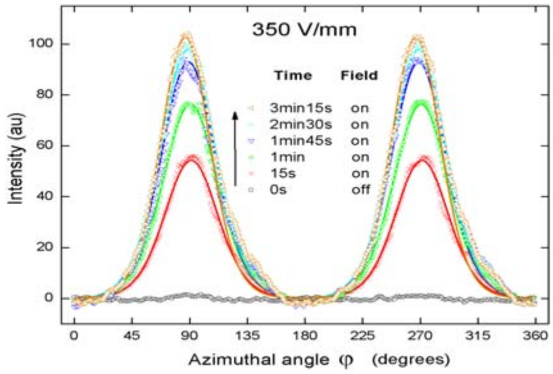

Fig. 3. Azimuthal plots of the changes with time of the 1st Bragg peak amplitude under an E-field of 350 V/mm.

Apart from the data provided for WAXS diffraction patterns, other results were obtained by measurements of a leak current density of ERF was measured for different electric field strengths and clay particle concentrations. It was found that the leak current density depends on electric field and clay concentration as follows: $J \sim \Phi^{0.74} E^{2.12}$.The dielectric constant was derived from the measured capacitance.

In addition, the most important rheological properties of our ER fluid have been measured, which includes the dependence of the yield stress both on the electric field and on the particle concentration . It was observed the following scaling behaviour: $\tau_y \sim \Phi^{0.87} E^{1.66}$.

Future prospect to this work:

Extend the study of <u>organically modified</u> clay particles. Since now the modified clay particles are well dispersed in the oil, and do not aggregate (as was the case in the study described above using unmodified clays), we expect both "cleaner" final chain structures and also "cleaner" dynamics during the clay structuring.

PUBLICATIONS:

J. Phys.: Condens. Matter 2010 (in press)

Electric Field Induced Structuring in Clay-Oil Suspensions: New Insights from WAXS, SEM, Leak Current, Dielectric Permittivity, and Rheometry

Abstract: The electric field induced structuring from clay-oil suspensions has been studied by means of wide angle X-ray scattering, rheometry, scanning electron microscopy, as well as leak current density and dielectric constant measurements. The clay particles' orientation distribution was inferred from the azimuthal changes of the clay diffraction peak intensity. The angular width of that distribution was quantified through an orientational order parameter. Chain and column formation processes were distinguished by comparison of the time evolution of the diffraction peak amplitude with that of the current density. Leak current density was measured for different electric field strengths E and clay particle concentrations Φ. The following scaling relation was found: $J \sim \Phi^{0.74} E^{2.12}$. In addition, the dependence of the yield stress on the electric field and on the particle concentration was measured and shown to scale as : $\tau_y \sim \Phi^{0.87} E^{1.66}$.

J. Phys.: Conference Series 149 (2009) 012026

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

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.