	Experiment title:	Experiment number:
	E-field induced alignment of organically modified clay-based electrorheological fluids	**01-02-924**
Beamline: **BM01A**	Date of experiment: from: **24 Nov 2010** to: **27 Nov 2010**	Date of report: **Sept 2013**
Shifts: **9**	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 different nano-layered silicate clays. Firstly, we have compared the dynamics and final arrangement of synthetic clays that were organically modified clay minerals with their non-modified counerpatrs. The modified clay particles disperse well in non-polar liquids, such as silicone oil, and do not aggregate (as was the case in our previous studies using unmodified clays). Therefore we were able to obtain better organized final chain structures when compared to the non-modified clay dispersions. Secondly, we have investigated differences between two natural clay minerals that have similar chemical composition but important structural layer stacking differences, including shapes.

The particle orientation and structuring was of primary interest in this study. Since each particle is a stacked clay system, the investigatigation of a Bragg peak diffraction rings allowed to determine the degree of anisotropy in the system in presence of the E-field. In addition, we investigated electric-field-induced alignment of these particles as a function of temperature in a paraffin-wax system, i.e. during metling and crystalization of the paraffin-wax.

Majority of the questions we had raised before the experiment, have been answered and results can be found in three publications (see the last paragraph). The sample preparation, an experimental set-up and the results are summarized below.

RESEARCH SUMMARY:

We used synthetic fluorohectorite clay purchased from Corning Inc. The 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. This clay mineral was chemically modified using cationic surfactant, CTAB, that changes the surface properties of clay particles and make them hydrophobic preventing formation of large clay aggregates when dispersed in non-polar media, such as oils or oligomers. In the first part of the experiment we used silicone oil Dow Corning 200/100 Fluid, whereas in the second part was used paraffin-wax from Sigma-Aldrich (ASTM D 127), as a suspending liquid. The clay powder and the silicone oil were mixed making up electrorheological fluids, that responses to application of external electric fields.

The wide angle x-ray scattering experiment (WAXS) was carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The beamline BM01A was equipped with a two-dimensional image detector. The sample to detector distance was calibrated using a standard LaB_6 sample that enabled detection of scattering in a q-range of approx. 0.2 – 2 $Å^{-1}$.

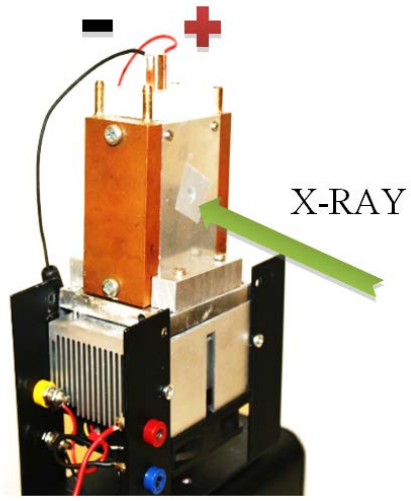

Fig..1. Experimental setup for studying dynamic alignment of clay particles during melting and crystallization of clay/paraffin-wax composites

The experimental setup is shown in figure 1. The custom-made heating cell consisted of an electrically insulating acrylic glass in the form of a cubic cuvette, with two electrodes separated by a gap of 1 mm, which was mounted inside the copper housing. Temperature was controlled via both Peltier element and water bath. DC Electric fields upto 0.75 kV/mm were used. The electrical system contained a current limiting resistor to eliminate any risk related to high voltage. Temperature between RT and 150 was used.

Prior to the application of the electric field, the clay particles were randomly dispersed into the non-polar medium. The formation of chain-like structures aligning parallel to the E-field was observed after its application. Dynamic changes in the clay orientational order can be observed from two-dimensional WAXS patterns. Figure 2 shows radially integrated WAXS patterns from 001 Bragg diffraction from the layered silicate sheets within clay particles. The azimuthal plots show clear anisotropy in the system, i.e clay particles aligned along the electric field direction.

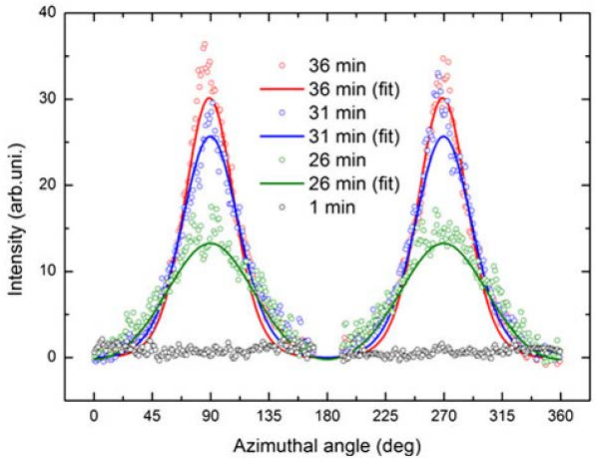

Fig..2. Azimuthal plots of the first Bragg peak amplitude (001) measured at different times during paraffin melting

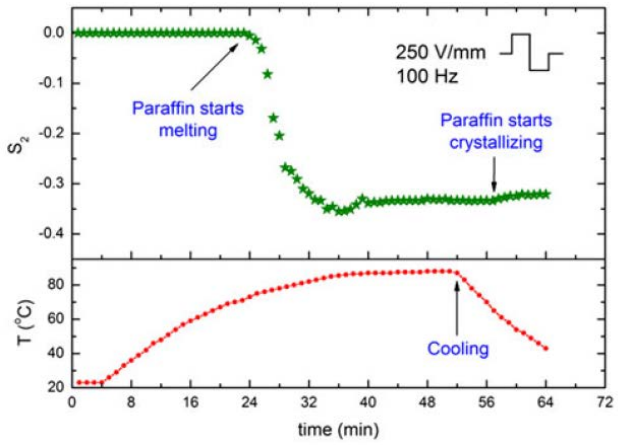

Fig..3. Development of the anisotropy in the system expressed by the nematic order parameter S_2

The degree of this anisotropy can be quantified and expressed as the nematic order parameter S_2. The development of the anisotropy during the paraffin melting is shown in Figure 3.

We also studied the self-assembly from kaolinite and halloysite clay particles. We found that the overall alignment in E-field of the polarized kaolinite particles was significantly better compared to that of polarized halloysite particles, and that was mainly a result of the different kinds of aggregates each type of particles

formed, although similar columnar final structures were made out of these aggregates in the presence of an external E-field.

Future prospect to this work:

In all previous studies we intentionally prepared samples using similar sample concentration, since there is a strong dependency of particle concentration on the final particle arrangement. However, this dependency has not been described yet, and this is interesting from both from the point of view of applications and in terms of fundamental properties. Recently we observed (using optical microscopy) that electrophoretic effects play important role in final arrangement of clay particles and we anticipate that it influences the particle jamming which is related mainly to the clay concentration.

In a future, we wish to study both (i) the influence of the following parameters: clay particle concentration, size and polydispersity on their final arrangement in electric-field-assembled structures, and (ii) dynamical changes of alignments when electrophoretic forces start stimulating re-arrangements.

PUBLICATIONS:

Applied Clay Science **77-78**, 1-9, (2013).

Electric-field-induced structuring and rheological properties of kaolinite and halloysite

Abstract: Electric-field-induced structuring of kaolinite and halloysite particles was studied in respect to their electrorheological (ER) response in silicone oil and in paraffin dispersions. The structural and morphological properties of both clay minerals were studied by XRD, FTIR, SEM, TEM and TGA techniques. The dipolar arrangement induced under application of an electric field was investigated by 2D-WAXS and optical microscopy techniques. The ER response of the samples was measured by both the shear rate controlled method and bifurcation tests. Kaolinite particle dispersions were found to have an improved ER response relative to dispersions of halloysite particles. Finally, the electric currents of these ER fluids were measured and the results revealed differences in the current-magnitude between halloysite- and kaolinite-based silicone oil dispersions..

Journal of Materials Research **28**, 1349-1355, (2013).

Electric field nematic alignment of fluorohectorite clay particles in oligomeric matrices

Abstract. We study the behavior of fluorohectorite synthetic clay particles dispersed in paraffin wax. We report wide-angle x-ray scattering related to electric-field-induced alignment of the embedded clay particles. The development of anisotropic arrangement of the particles is measured during melting and crystallization of the composites. The degree of anisotropy is quantified by fitting azimuthal changes of the clay diffraction peak intensity to the Maier-Saupe function. This parametric function is then used to extract both the full width at half maximum (FWHM) and the amplitude of the anisotropic scattering and eventually to estimate a nematic order parameter for this system. Finally, the time evolution of the one-to-zero and zero-to-one water layer transition in
paraffin embedded fluorohectorite clay galleries is presented, and we demonstrate that such particles can be used as "meso-detectors" for monitoring the local water content in bulk carrier matrices, such as paraffin wax.

European Physical Journal E **35**, 9, (2012).

Dipolar structuring of organically modified fluorohectorite clay particles

Abstract. This report focuses on both the characterization of organically modified fluorohectorite (Fh) clay particles and their electric-field–induced alignment when suspended in a non-polar liquid (silicone oil). Thermal decomposition temperatures of the surfactant molecules adsorbed on the clay surfaces and those being intercalated between clay crystalline layers were measured by thermal gravimetric analysis (TGA). Zeta potential measurements confirmed the successful modification of the clay surfaces. Optical microscopy observations showed that the sedimentation of modified particles was much slower compared to that of the non-modified system. It was shown that organic modification has a significant effect on colloidal stability of the system, preventing particles from forming large aggregates when suspended in a non-polar liquid. There are also signs of a slight increase in overall alignment of the clay particles when exposed to in an electric field, with the nematic order parameter (S2) being higher for the organically modified particles, compared to that of the non-modified counterparts. This behaviour is mainly a result of the formation of smaller and more uniform aggregates, in contrast to the large aggregate structures formed by non-modified clay particles.