

DIPOLAR ORDERING OF CLAY PARTICLES IN VARIOUS CARRIER FLUIDS

ORDENAMIENTO DIPOLAR DE PARTÍCULAS DE ARCILLA EN DIVERSOS FLUIDOS

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We investigate here examples of complexity in composite materials. The objective of the paper is to show that clay particles can be aligned in different hosting media, such as: silicone oil, paraffin-wax, polystyrene and ambient air. The use of an electric field is an easily controllable, non-intrusive manner of inducing such an alignment. Depending on the medium used, a large span in time constants for the orientation and reorganization has been observed. Furthermore, the reorientation may be frozen into the material, thus permanently changing its properties.

Se investigan ejemplos de complejidad en materiales compuestos. El objetivo de este artículo es demostrar que se pueden alinear partículas de arcilla en diferentes medios como aceite de silicona, parafina-cera, poliestireno, y aire. El uso de un campo eléctrico resulta una vía fácilmente controlable y no-intrusiva de inducir el alineamiento. Se observa un amplio rango de constantes de tiempo para la orientación y la reorganización en dependencia del medio utilizado. Aún más, la reorientación puede congelarse en el material, de tal suerte que sus propiedades cambian permanentemente.

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INTRODUCTION

Application of an external electric field to a suspension of dielectric clay particles induces polarization of the particles. They will consequently re-orient and aggregate, and this results in the formation of a columnar structure parallel to the electric field direction. The clay particles polarize along their silica sheets, i.e. their stacking direction will be normal to the direction of polarization [1]. The mechanism of the polarization in clays is still under discussion, although one hypothesis is that the intercalated ions and water molecules, which are movable, could play a central role in particle electrical polarization. The resulting induced dipole is attached structurally to the clay particle, and this causes clay particles to reorient and interact, as suggested in [1]. However, recent measurements performed by us indicate that the contribution from the outer surface charges may be dominant, and the particle alignment is then determined by its shape, i.e. so that the longest axis of a single clay particle (or aggregate of particles) will be parallel to the direction of E -field lines [2].

The clay polarization is a rapid process ($< \mu s$) that is followed by a particle re-orientation with a rotation time proportional to the carrier fluid viscosity and inversely proportional to: firstly the difference in the dielectric constants between particle and medium; and secondly the electric field squared (see also [3]). The time scale for particle rotation is in the range of 10^{-3} to 10^1 s, for E -field between 50 and 2000 V/mm and viscosity of

carrier fluid such as silicone oil between 100 and 500 mPa·s [2]. If the particle concentration is high enough, and a minimum critical E -field is applied, chain formation occurs via a particle dipole-dipole interaction [4].

The phenomena described above may be utilized in many different ways and just a few examples are: (i) Electro-rheological fluids (clay particles in silicone oil) in which the so-called liquid-to-solid reversible transition occurs via the application of an external E -field. Such a transition is manifested by changes of ER properties, namely: viscosity, yield stress, storage and loss moduli, etc. [5, 6, 7]. Some examples of application of ER fluids are: fast acting hydraulic valves or clutches [8]. (ii) Nanocomposites (clay particles in polymers), since the aspect ratio of the clay platelets and the interfacial contact area between the clay and matrix are high, the incorporation of small amounts of such inorganic filler into a polymer medium can significantly improve the properties of the resulting polymer/clay nanocomposites. Such nanocomposites can attain a high degree of stiffness and strength [9]. Furthermore, the presence of the dispersed phase results in additional properties, such as flame retardancy or enhanced barrier properties (e.g. gas permeability), when compared to either component [10, 11]. In many situations it is not only the *presence* of the well-dispersed filler but also its *orientational* ordering that may improve certain physical and

chemical properties. The electric-field-induced alignment of clay particles can thus be used to obtain and control a range of the desired material properties.

The above examples have clearly an application-oriented character. However, the focus of our studies is on better understanding of basic physics of such complex systems. Apart from already mentioned hosting media, we also here report for the first time structuring from clays in atmospheric air. The common denominator, for all studied systems, is the clay particle alignment in the presence of an E -field.

SAMPLES

Two types of clay particles, namely laponite (Lp) and fluorohectorite (Fh) are used in the present investigations. The synthetic Lp clay was purchased from Laponite Inc. and the synthetic Fh clay was purchased from Corning Inc. They both belong to the smectite family of clay minerals. Smectites are 2:1 phyllosilicates that possess a net negative charge on the surface of each crystalline layer. Counter ions are located between these lamellar sheets to balance for that charge. Exchangeable cations such as Na^+ , Li^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} or Fe^{2+} are common. The chemical formulas are: $\text{Na}_{0.7}[(\text{Mg}_{5.5}\text{Li}_{0.3})\text{Si}_8\text{O}_{20}(\text{OH})_4]^{0.7-}$ for Lp clay and $\text{Na}_{1.2}[(\text{Mg}_{4.8}\text{Li}_{1.2})\text{F}_4\text{Si}_8\text{O}_{20}]^{1.2-}$ for Fh clay, respectively. They are silicates where a fraction of Mg^{2+} ions is substituted by Li^+ in trioctahedral sites resulting in a negative structural charge [12]. Fluorohectorite has been reported from X-ray data to retain a stacked structure of lamellar particles composed of between 20 and 100 unit layers when dispersed in water, whereas laponite is known to exfoliate into single unit layers in aqueous suspensions [13]. The individual Lp clay particle resembles a disc of average diameter around 30 nm, whereas the size of Fh clay can be as large as several μm .

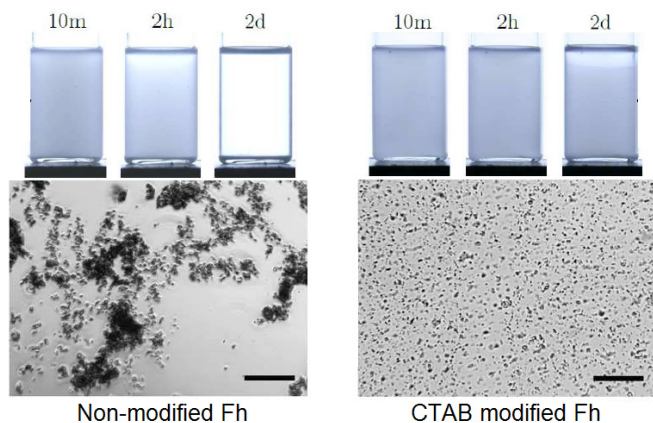


Figure 1: Microscope images of non-modified Fh (left) and organically modified CTAB-Fh (right) clay particles suspended in silicone oil. The length of the bar corresponds to 200 μm . The pictures of the glass vials with samples (top) illustrate the sedimentation dynamics. Adopted from [16].

Clays, in their natural forms, are hydrophilic, or depending on the context they may be referred to as organophobic. When suspended in a non-polar medium, such as silicone oil or polymeric matrix, they tend to form large agglomerates and

consequently sediment (see Figure 1). Addition of surfactants is commonly used to prevent particle agglomeration, which then slows down particle sedimentation, or if the particles are small enough (i.e. magnetic particles in ferrofluids), ensures that they are held in suspension by Brownian motions [14]. Another reason for modifying clays is the ease of uniform dispersion in an apolar polymer matrix. To promote compatibility between the inorganic filler and apolar polymers, it is necessary to chemically modify the inorganic clays by intercalation of organophilic cations, which expand the interlamellar space of the clay, decreasing the interaction among the silicate sheets, and facilitating the diffusion and accommodation of polymeric chains [15].

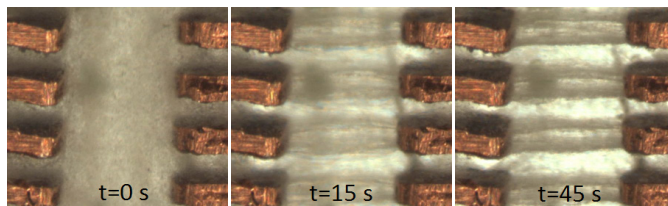


Figure 2: Optical microscopy images of clay/oil suspension without E -field applied (left) and a field of 1000 V/mm (middle and right).

RESULTS

Clays in silicone oil. The preparation of the ER fluid was undertaken by the following procedure. Na-Fh clay powder was crushed with a pestle and mortar, weighed and placed in an oven for 12 h at 110 $^{\circ}\text{C}$. The silicone oil was heated at the same conditions. Subsequently, the clay powder and silicone oil were mixed in glass tubes and sealed. The solutions were then vigorously hand-shaken for 2 min and placed in an ultrasonic bath for 1 h. Before each measurement the samples were hand-shaken again. The clay concentration was approximately 5 wt.%.

Firstly, optical observations were conducted. For that purpose the ER fluid was placed between two electrodes with pre-defined shapes as shown in Figure 2. The gap between the electrodes is roughly 1 mm and the electric field is applied horizontally.

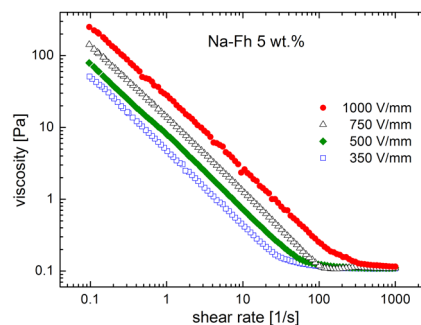


Figure 3: Flow curves for 5 wt.% clay particles suspended in silicone oil. Different electric field strengths are used, influencing the shear viscosity.

When no E -field is applied, the Fh particles are randomly dispersed into the silicone oil, as shown in Figure 2 (left). Microscopy images of the sample under a DC electric field of 1000 V/mm taken at different times, 15 s and 45 s are shown

in Figure 2 (middle and right). The formation of column-like structures aligning parallel to the field is clearly observed. Several thin chains are formed first, and these subsequently attract each other resulting in the creation of thicker columns. After a certain time (here several minutes) no major changes in the system are noticeable.

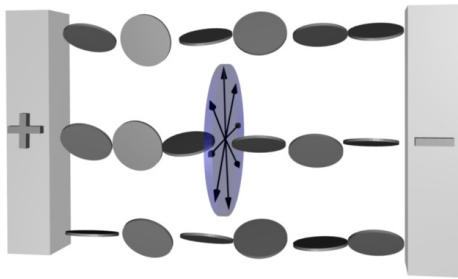


Figure 4: The sketch of the clay alignment in so-called anti-nematic configuration (see text for details).

Imagine now shearing the ER fluid perpendicular to the E -field direction. If the E -field is not present, the shear viscosity of such a sample (silicone oil and only 5 wt.% of clay) is close that of pure silicone oil. However, once the electric field is applied, so that the particles are oriented against the flow, the shear viscosity of a fluid containing clay particles is expected to increase. As the curves in Figure 3 show, this is also what is seen experimentally.

Clays in paraffin-wax. The particular type of paraffin-wax used here has its melting point around 65 °C and was chosen for two major reasons: (i) optimal melting and crystallization temperatures, providing both easy composite preparation and appropriate stiffness of the composite when in solid form at room temperature; (ii) a relatively non-polar and non-conductive material that can be used as an electrorheological carrier fluid when in the melted state. Fluorohectorite particles (~5 wt.%) were dispersed in the melted paraffin and then poured into a custom-made mould with two electrodes. The electric field strength of 500 V/mm was applied and kept for a few minutes until the paraffin crystallized and cooled down to room temperature. The solid composite was then investigated using wide-angle X-ray scattering.

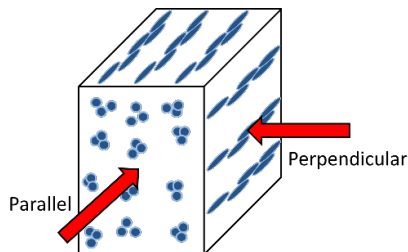


Figure 5: Simple sketch of what the X-ray beam probes in the sample.

When a 2-D X-ray pattern (like those shown in Figure 6) is integrated along the radial direction with a narrow q -range (2θ -angle) around the Bragg ring, one obtains a 1-D azimuthal plot which is then fitted using a parametric function. The fitting allows extracting parameters that are further used to calculate the nematic order parameter (S_2) (for details see [17]). This parameter ranges from $-1/2$ to 1, where 1 indicates perfectly

oriented particles in the nematic configuration, 0 means no orientational order, and finally $-1/2$ indicates perfectly oriented particles in the anti-nematic configuration [6, 17, 18]. It is expected that the clay particles align in the anti-nematic geometry and the validity of such assumption is tested below.

Several 2-D X-ray images were taken from the same sample at different polar angles, with the rotation axis parallel to the reference direction, which is here the direction of the E -field. The nematic order parameter was calculated for four sample positions and the results are presented in Table 1.

Sample rotation	0	30	60	90	Avg
Order parameter	-0.37 ± 0.01	-0.35 ± 0.01	-0.37 ± 0.02	-0.36 ± 0.01	-0.36 ± 0.01

We observe that the nematic order parameters do not differ significantly from each other indicating that there is no preferential orientation along the polar angle. The arrowed disc shown in Figure 4 represents the plane perpendicular to the E -field direction, and that is in fact the average particle stacking direction. The black arrows indicate that clay normals are oriented without any preferred polar direction.

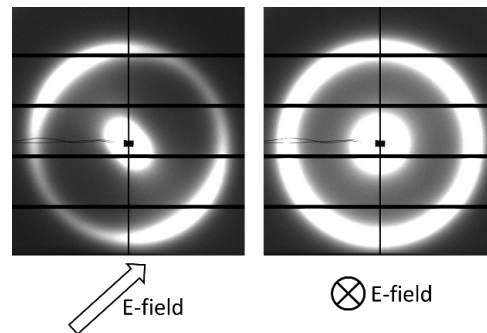


Figure 6: SAXS-patterns from PS/CTAB-Fh with permanently aligned clay chains. Remark: the sample is tilted 45 degrees in the x - y plane.

Clays in polystyrene. When aligning clay particles in liquid media the alignment may be lost after a while when the electric field is turned off. An approach to freeze the chain structure was tested by solidifying the matrix while the electric field was applied. The matrix, styrene monomer, polymerizes to give solid polystyrene polymer (PS). A 1 wt.% sample of organically modified CTAB-Fh (see [16] for details) was dispersed in styrene monomer and a small quantity of a radical initiator, benzoyl peroxide, was added. The clay/monomer suspension was filled in square shaped glass capillaries, which were sealed with a flame torch. The capillaries were then immersed in an 80 °C silicone oil bath, and placed between two plate electrodes. The electric field over the electrodes was set to 830 V/mm, and the samples were left to polymerize for 7 days. The resulting PS-clay composites were investigated with small angle X-ray scattering (SAXS) at the Dubble beam line at ESRF in Grenoble, France. The samples were probed with the X-ray beam perpendicular and parallel to the direction of clay chains

(see Figure 5). The main ring comes from the characteristic spacing between clay crystalline sheets, and $d_{001} \sim 4 \text{ nm}$. A pronounced anisotropy of the d_{001} peak is seen in Figure 6 (left) due to clay alignment, i.e. on average, particles orient with their stacking direction perpendicular to the E -field lines. When probed along the chains the pattern looks isotropic, as shown in Figure 6 (right), since there is no preferential orientation of clay particles along the polar angle (see also [18, 19]).

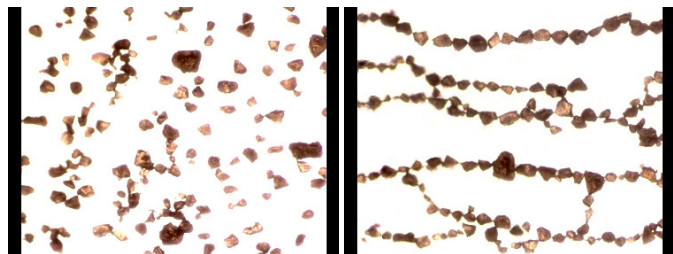


Figure 7: Laponite particle aggregates between two electrodes without E -field applied (left) and with an AC E -field of 500 V/mm (right). The images have been edited to enhance the contrast.

Clays in air. As the final example, we show laponite clay alignment in atmospheric air. Laponite clay powder stored in our laboratory at $\sim 23 \text{ }^\circ\text{C}$ and RH in range between 10 and 30 % was used. Such particles normally form aggregates and their sizes can span a few orders of magnitudes reaching a few mm . In the present work the size of the aggregates were between 10 and $100 \mu\text{m}$. Figure 7 shows clay particle aggregates between two electrodes with no E -field applied (left) and with an AC E -field of 500 V/mm (right). The electrodes were kept horizontally and images were taken from above. Clay particles lied on a thin glass substrate, and when the electric field was applied the set-up was gently tapped, lowering the friction as the particles were momentarily suspended in air.

As can be seen, most of the clay particle aggregates align with their longest axis along the E -field direction. However, there are several particles disobeying that rule, and these making bridges between individual chains allowing for charge transport. It is possible that the dominant part of the clay polarization occurs only on the clay aggregate surface, not the bulk, i.e. in the clay galleries. However, it is difficult (if not impossible) to draw a firm conclusion on this point, since we deal here with large aggregates. Therefore our future work will be focused on reducing the complexity of the system by working with *single* clay particles, such as vermiculite.



Figure 8: High concentration of laponite particle aggregates between two electrodes with an AC E -field of 500 V/mm applied. Several particle aggregates (red-color-marked) were not able to re-orient fully with their longest axis along the E -field lines due to jamming. This will effectively lower the value of the nematic order parameter.

In Figure 8 we also present structuring from particles in air, but this time the clay concentration is significantly higher. A possible jamming transition may occur where many particles have very little freedom to re-orient (see red-coloured particles). This is an ongoing study and more results are expected in the near future.

CONCLUSION

We have provided examples of recent results from our work on manipulation and orientation of asymmetric particles in external fields. Clay particles are ideal for this purpose due to their inherent large anisotropy and correspondingly high degree of polarizability. When placed in an apolar medium and subjected to an electric field, the particles will orient and organize within a time frame that depends principally on factors such as E -field strength and viscosity of the surrounding medium. We have shown how these effects may be induced in various media, with a large span in viscosity, from silicone oil, via polymer matrices to solidified wax, and even air. The clay particles may form chains that span the entire sample volume, thus changing the macroscopic properties of the material. Most notably, there will generally be a large change in the overall rheological behavior, and materials of this kind are therefore highly interesting for applications where the mechanical and structural properties should be manipulated via an electric field.

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