



Rheology of Colloidal Clay Gels and their Mixtures

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Abstract

We studied the use of Laponite EP, an organically surface coated laponite, as an alternative of xanthan in product formulation. Its combination with bentonite in agrochemical formulation showed similar rheological behaviour as the commonly used xanthan - bentonite combination. Laponite EP and bentonite display some synergism: analogous rheological properties could not be achieved using each clay alone or using a non-coated laponite RD - bentonite blend. The microstructure suggested two networks cooperating. The results highlighted the effect of the coating on the rheology of the clay and the product. Although the surface coating did not impact the surface charge of the clay, it may have prevented the adsorption of other components on its surface. The rheological behaviour of the gel Laponite EP - bentonite under diverse conditions was modelled using a mixture design approach. We varied the amount of salt (MgCl_2) and surfactant (Tween 20) in the solution as well as the pH (from 4 to 9). We focused on modelling the storage modulus G' , the loss modulus G'' and the critical stress σ_c . The models obtained underlined some complex interactions with antagonistic effects between the components.

The ageing of attapulgite, bentonite gels and their mixture was examined using rheology (oscillatory and creep tests) and microscopy (HPF Cryo-SEM and X-Ray tomography). The rheological results showed that the gels became stronger and more viscous with time. For bentonite, this could be explained by the rearrangement of the platelets over time and an increase in their connections. Regarding attapulgite, the strengthening of the gel was delayed compared to the other gels due to a change in the long range structure of the network getting more large pores. The rheological trend followed by the clay blend is similar to the one found for bentonite which determines its rheology. However, the evolution of the microstructure formed by the platelets in the mixture differs. The pore size distribution of the blend was analogous to the one found for attapulgite. Microscopic images suggested the formation of two networks interacting. Akin to bentonite, the long range structure of the gel did not show any drastic change with time. Therefore, the time effect on the rheology of the composite may have been due to stronger interactions between the needles and the platelets at a short range.

Declaration

This thesis is submitted for the degree of Doctor of Philosophy in Physical and Theoretical Chemistry at the University of Oxford. No part of this thesis has been accepted or is currently being submitted for any degree, diploma, certificate or other qualification in this University or elsewhere. This thesis is wholly my own work, except where indicated.

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Chapter 1

General introduction

1.1 Context of the project

Seven billion was the estimated global population reached in October 2011. With a growth rate over 60 million people per year, the global population should reach 9.7 billion people in 2050 [1]. Such increase of population has direct consequences on agriculture which therefore, needs to produce enough food to feed people and livestock, and to produce energy. In addition, food diet has gradually changed in high income countries involving more calories and more diverse food [2]. Increasing food production can be achieved by increasing the amount of land cultivated and/or by increasing the yield of the existing farms [3]. However, the first option presents large negative environmental and social impacts. It is also hard to achieve since agriculture already occupies 50% of the habitable land. In addition, a growing population will also lead to a decrease in the size of the farms due to the cities' expansion or the increase of rural population [4]. The second option also has an environmental impact, though to a lesser extent, and is therefore preferable. There are different techniques already used by farmers to improve their productivity: the use of hybrid crops, pesticides and fertilizers. Genetic manipulation is also used since the Green Revolution, in 1950-1960, to create crops with improved yield or resistance towards pesticides [5,6].

Pesticides are traditionally used to control pests responsible for damaging cultivation and decreasing food production. There is more and more interest in using sustainable pest control system, mainly for the growing organic agriculture. Organic and sustainable practices were

developed to prevent infestation of crops: such as the Integrated Pest Management (IPM) used before the introduction of synthetic pesticides in the early 1940s [7]. One strategy of IPM is to enhance natural competitors to prevent the development of pests [8]. For example, Carabid beetles could be used due to their predatory diet [9]. Diversifying plant growth also helps to improve pest adversaries by providing the food they need. However, since the 1940s, synthetic pesticides comprising herbicides, insecticides and fungicides were chemically produced. The property of a pesticide depends on the active ingredient (AI) present in the formulation. For instance, AzoxystrobinTM is the active ingredient developed by Syngenta used in the commercially available fungicide called Amistar[®] [10]. An example of herbicide is the product called Callisto[®], containing the active ingredient MesotrioneTM. When the active ingredient is a solid, the final product can have different forms such as a suspension concentrate (SC), an emulsifiable concentrate (EC) or an oil dispersion (OD) [11,12].

1.2 Stability of suspension concentrates

A suspension concentrate is the main type of pesticide formulation and constitutes a dispersion of solid particles, the AI, in a continuous fluid. To ensure good efficacy of the dispersion, it was demonstrated that 90% wt. of the active ingredient has to feature a size below 10 μ m [13]. Consequently, SCs are colloidal dispersions and are prone to destabilisation due to sedimentation or creaming, and particles aggregation or coalescence.

Sedimentation or creaming are due to gravity. When gravity overcomes the Brownian motion of the particles, a separation appears between the dispersed phase (the particles) and the continuous one. If the particles are denser than the surrounding liquid, they sediment to the bottom. Such effect is referred to as sedimentation. However, if the particles are less dense than the fluid matrix, the particles go to the top. This process is called creaming.

Particles aggregation or coalescence are due to the following properties: some attractive interactions between the particles and the polydispersity of particles' size and charge [14]. Aggregation refers to the process by which particles cluster together whereas coalescence implies the fusion of two particles or droplets. Such phenomena appear when the attraction between particles is high due to Van der Waals forces. It can also be triggered by the addition of a third component causing depletion. This leads to heterogenous repartition of the components in the system. Aggregation or coalescence can be prevented by generating repulsion between the parti-

cles. To do so, dispersants can be added to the formulation of SC to increase the stability of the particles. They are also used to guarantee a good wettability, i.e. to favour the hydration of the particles [15, 16]. Reducing the polydispersity of the system also hinders particles aggregation. In fact, large particles can act as seed for agglomeration. This is particularly true for emulsion where small particles can merge with larger particles in the case of Ostwald ripening.

To assess the long-term stability of a suspension concentrate, accelerated storage tests, using centrifugal force or temperature, and rheological tests are used [17]. Rheology is defined as the science of flow and deformation of material [18]. It is used broadly in industry as a measurement technique in product formulation. In fact, in addition to giving an idea of product stability, it also allows the assessment of its texture or mouth feel, which is very important in the food industry for instance.

1.3 The use of thickener or gelling agents in product formulation

To prevent, or slow down, creaming or sedimentation, thickeners and gelling agents are employed to increase the viscosity of the dispersion [19]. Gelling agents form a gel through various formation processes leading to gels having various structure and different rheological properties. Thus, it is difficult to define the notion of gel accurately. However, gels feature some characteristics such as the development of a long range structure capable of resisting a deformation. [20, 21]. Therefore, gels display both characteristics of solids and liquids. Such a fluid is qualified as viscoelastic. There exists a large variety of thickening and gelling agents, among them are hydrocolloids and clays [19]. Hydrocolloids consist of long chain polymers, polysaccharides and proteins, capable of increasing the viscosity or forming a gel when in water [22, 23]. In lots of cases, a synergy between different thickening agents is seen and therefore used in industrial applications. The combination of xanthan and guar gums, used in the food industry, is a good example of synergy modifying rheological properties [24]. Xanthan-bentonite also displays valuable interactions characterised by an increase in the consistency of a solution and a more shear thinning behaviour [25]. This former combination is used frequently in the formulation of agrochemical products.

1.3.1 Xanthan used as thickening agent

Xanthan is a negatively charged polysaccharide, synthesised by *Xanthomonas campestris*. It has a high molecular weight and is used as thickening agent to give a particular rheological property to a formulation even at low concentration. When alone in solution, xanthan chains form intra- and inter-molecular non-covalent interactions leading to a very entangled network [26]. This network increases the viscosity of the solution at rest which slows down sedimentation and creaming. Upon application of shear, the xanthan chains dissociate and align with the flow decreasing therefore the viscosity of the solution. This behaviour is called shear thinning [22,27]. These rheological properties still stand at high temperature and high salinity. That is why xanthan is used in many applications, such as paints, food, cosmetics, pharmaceuticals and so on, despite its high price compared to other thickening agents. When used in combination with other particles, xanthan may cause depletion interaction [28–30]. In some cases, this process leads to a metastable state with two continuous phases formed, resulting in a gel. In other cases, it has been observed that the depletion interaction caused by xanthan leads to a quick creaming of the emulsion droplets [31]. It has also been reported that aggregation of spheres can occur in xanthan solution due to the decrease in viscosity in the trail of the initial falling particle [32]. The effect of xanthan on stabilizing a solution depends on the physico-chemical properties of the other components. For instance, some active ingredients are used as soluble salt in agrochemical formulation leading to a change in ionic strength and pH of the solution. In this case, xanthan may not be efficient in stabilizing the dispersion. In addition, since xanthan is a polysaccharide, it may get spoiled by microorganisms over time. This affects the rheology and shelf life of a commercial product. Hence, industries are seeking alternatives to it.

1.3.2 Clay used as gelling agent

A variety of clays are also used in product formulation. They have the advantages of being safe, cheap, and present in large amounts. Some of them have been used for medical applications since prehistory [33], and they are also used as thickeners for lots of applications [34]. It is important to distinguish clay from clay minerals, although the term clay is often used as clay mineral, which will be the case in this thesis. Guggenheim and Martin defined clay as “a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate

water contents and will harden with dried or fired” [35]. Nevertheless, this definition may have some limitations. In fact, defining clay as a ”naturally occurring product” would automatically prevent any synthetic material of being called as such, which is not the case for Laponite. In the same article, they also define and discuss clay mineral as: “phyllosilicate minerals and to minerals which impart plasticity to clay...”.

The main clay minerals used belong to the groups of smectite, palygorskite, kaolinite and talc. They are characterised by the following properties [34]: a layered structure with one of the dimension being on a nanometer scale; anisotropy of the layers or the particle; different types of surfaces; the easy coating of a face; plasticity and hardening. Plasticity refers to the property of a material which can be deformed and retain the shape of the deformation while hardening consist in strengthening a medium. They are subject to isomorphous substitution giving rise to a negatively charged surface [36]. Isomorphous substitution also leads to the presence of exchangeable cation, rendering the clay surface hydrophilic [37]. One of their faces is also charged due to broken bonds of the crystal structure. The charge depends on the pH of the environment and the type of metal ion [37]. If the pH is below the point of zero charge, i.e. isoelectric point, the surface is positively charged. If otherwise, the surface has negative charges. The presence of charges and their distribution gives rise to the development of electrostatic interaction and the formation of an electrical double layer [38], both implied in the gel formation. However, as stated previously, gels are naturally metastable and therefore evolve with time. Such evolution, called ageing, affects their rheological properties and is usually irreversible [39]. This can be a limitation of their use in product formulation as it impacts the product shelf life.

This work focuses on bentonite, attapulgite and Laponite clays. Bentonite is a naturally occurring clay mainly composed of sodium montmorillonite, as represented in figure 1.1a. The latter one is a planar phyllosilicate belonging to the smectite group [34]. It has a platelet shape of micrometer length. In dry powder, clay minerals are stacked together forming bigger particles. When in contact with water, the clay minerals experience swelling which corresponds to the separation of the clay layers after filling the interlayer space with up to 4 layers of water molecules [40–42]. This is possible due to the presence of cations in the interlayer space and the higher attraction of the exchangeable cation for water than for the clay surface. During swelling the clay minerals are pushed further apart, until delamination. This leads to smaller particles containing less unit layers. In the case of bentonite, the interlayer cation is sodium, leading to

the chemical formula: $\text{Na}_{0.33}[(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{O}(\text{OH}))_2(\text{SiO}_2)_4]$ [36].

Attapulgite, also called palygorskite, is also a naturally occurring clay of chemical formula: $(\text{H}_2\text{O})_4(\text{OH})_2\text{Mg}_5\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$ [43]. Its clay mineral is represented in figure 1.1b. It has a needle shape of micrometer length. Unlike bentonite, it is a non-swelling clay due to its ribbon structure formed by the discontinuity of the octahedral layer and the continuity of the tetrahedral one. Its rheological properties are also less sensitive to salt than bentonite [44], thus its application as a gelling agent in salt-based products.

Laponite™ is a synthetic clay, developed by Laporte Industrie Ltd [45], made of smectite similar to hectorite, see figure 1.1c. The chemical formula is: $\text{Na}_{0.7}^+[(\text{SiO}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$ [46]. It is composed of nanometer disks. Similar to bentonite, it is also capable of swelling. As synthetic clay, it is usually pure and consequently used as a model system in many research.

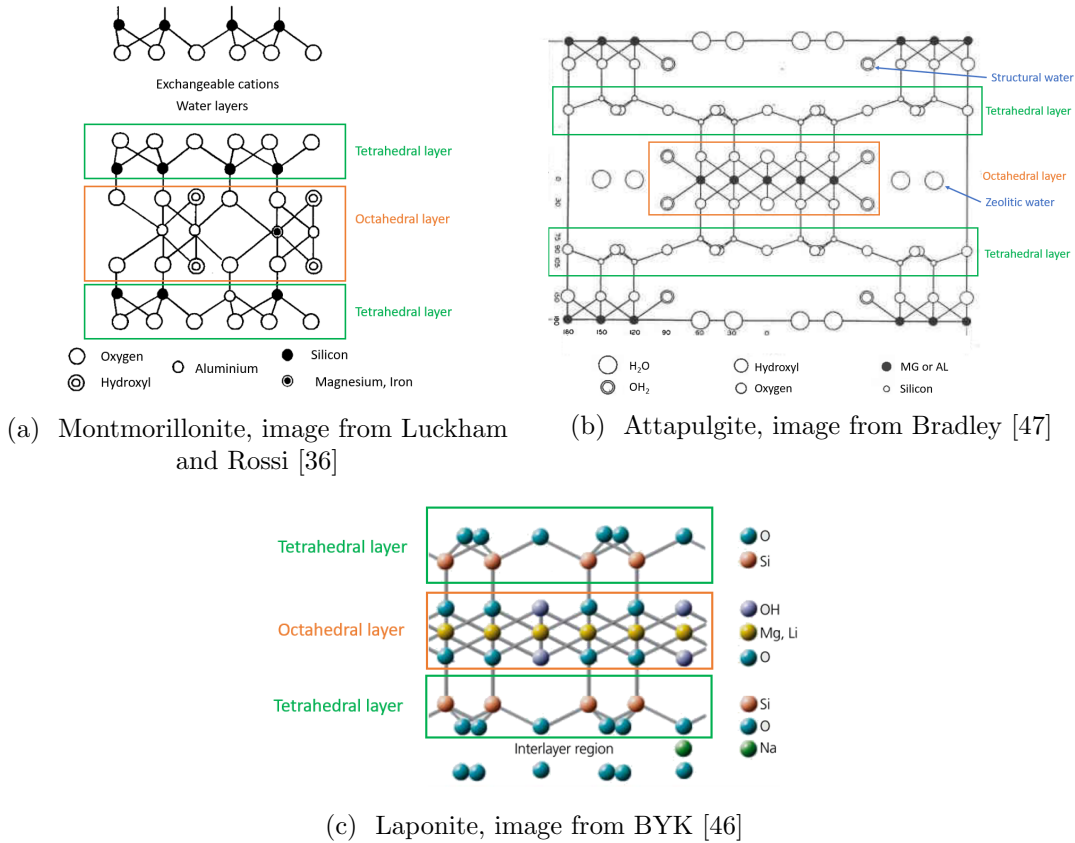


Figure 1.1: Scheme of the structure of the clay minerals

Another interesting property of clays is the possibility of coating their surface due to their large specific surface area and cation exchange capacity. This can be done through cation exchange, adsorption of molecules on their surface, or grafting [48]. Coating changes the clays surface properties and their rheology. Hence, clays that are hydrophilic can become hydrophobic

and can be used to stabilize oil-based systems. An example is the hydrophobic coated bentonite called Bentone™.

1.4 Scope of the thesis

The objectives of this project were twofold:

The first goal was to find an inorganic compound, a clay, that can be used as a replacement for xanthan in product formulation while maintaining the rheological properties of the product.

The second aim was to study the ageing of clay gels on their rheological properties and their structure.

This thesis is set up as follows:

In the next chapter, we present the theoretical background and the methodology applied using rheology and microscopy. We also describe other analytical techniques used in this project to characterise a compound.

In Chapter 3, we investigate the use of Laponite EP, an organically coated Laponite, as a replacement for xanthan and compare it to its non-coated analogue. Laponite EP was also used in product formulation in combination with bentonite and the rheology of the resulting interaction was studied. Finally, we tried to characterise the coating of Laponite EP that gives the compound such particular rheology.

In chapter 4, we focused on the combination of Laponite EP - bentonite gel. We modelled and predicted some of its rheological characteristics in various chemical environments using response surface methodology. We varied the amount of salt, i.e. the ionic strength, the amount of surfactant and the pH.

In chapter 5, we determined the effect of ageing on the rheology of attapulgite and bentonite clay gels and their mixture. We used oscillatory and creep tests. Some results could be fitted with a Leong model allowing the determination of some characteristic time of ageing.

In chapter 6, we studied the ageing effect on the microstructure of the same gels as in chapter 5, using High Pressure Freezing (HPF) Cryo-SEM and X-Ray tomography. We presented different models of the structural ageing of bentonite and attapulgite and discussed them in light of published work.

Finally, we summarised the key findings of this work in the general conclusion and completed the overall picture of the ageing of three clay gels.

Chapter 2

Theoretical background and Experimental methods

We present the theoretical background regarding rheology, imaging and characterisation techniques. Firstly, this chapter presents the main rheological tests performed in this project as well as the model equations associated with them to characterise the different fluids. Secondly, the principles of imaging techniques are explained followed by the challenge that constitutes the sample preparation. Finally, techniques allowing the determination of the chemical composition of a molecule is explained followed by techniques on surface and thermal characterisation.

2.1 Introduction

Nowadays, due to the research performed to enhance existing characterisation techniques or to develop new ones, scientists have a great variety of techniques at their disposal, which can be used to increase their understanding of their material of interest. Our project focuses on the use of clay to form a colloidal network gel for the purpose of being used as thickener for agrochemical product. Therefore, the knowledge of how such a material behaves under flow or how it deforms when submitted to a constraint is necessary and can be achieved by the use of rheology. The rheological properties of a material are the result of its structure, i.e. how the particles interact. Therefore, it is relevant to determine how the single units of clay interact to build a structure. This can be achieved using microscopy techniques. Furthermore, the

arrangement of the clay units happens at their interface, and thus, depends on their surface. Therefore, quantifying some physical characteristics of the surface of the clay is useful to explain a change of rheological behavior or organization. A measurement which gives information of the surface charge of a particle is called zeta potential measurement. It is possible to modify a surface characteristics, such as its hydrophobicity/hydrophylicity or its electrostatic charge for instance, by coating it with organic compounds. The nature of such compound can be investigated via analytic techniques giving information on the elemental composition of a molecule, its functional groups if any and its thermal properties as well.

In this chapter, we present first the theoretical background and method of the main techniques used in this project starting with rheology in section 2.2. Second, section 2.3 explains the imaging techniques used. The final section 2.4 presents the tools used to characterise our clay system.

2.2 Rheology

Rheology is commonly defined as the science of flow and deformation of materials applied to characterise very diverse materials such as concrete, food product or biofilm for instance, [18]. Nowadays, due to the development of high-performance rheometers, rheology comprises a variety of tests that focus on different characteristics of the material like its properties at rest or under flow.

2.2.1 Characterisation of a material at equilibrium: a link to their microstructure

A material can be classified as a pure liquid or a pure solid. The behavior of a pure liquid is governed by Newton's law (equation 2.1) and is modeled by a dashpot representing the loss of energy due to viscous force. Pure solids are determined by Hooke's equation (2.2) and are represented by a spring.

$$\sigma = \eta \times \dot{\gamma}, \quad (2.1)$$

$$\sigma = G \times \gamma, \quad (2.2)$$

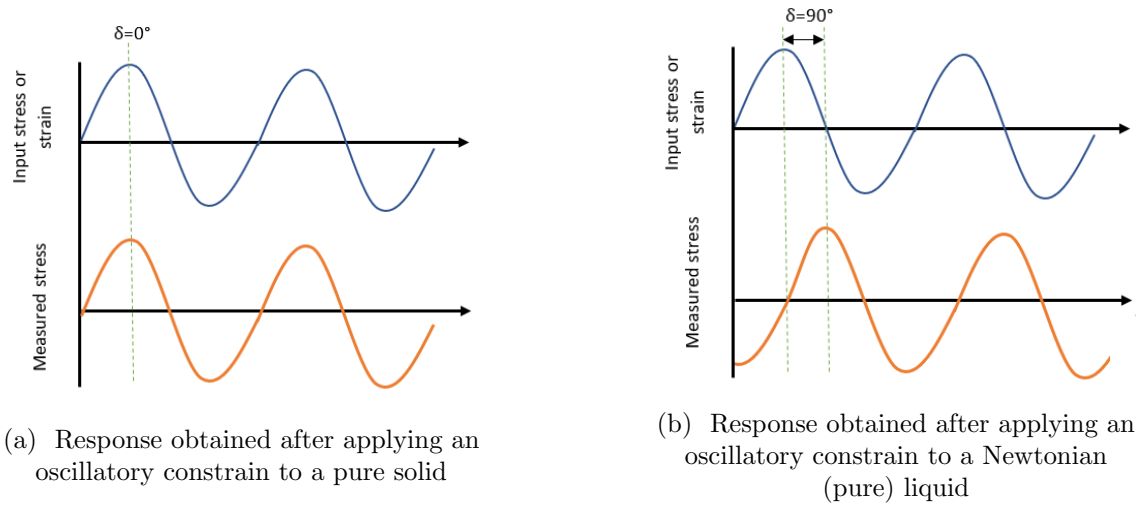


Figure 2.1: Representation of the different responses obtained from oscillatory measurements according to the nature of the fluid. A viscoelastic fluid would have a phase shift between 0° and 90°

where σ is the stress (Pa), γ the strain, $\dot{\gamma}$ the strain rate (s^{-1}), η the viscosity (Pa.s) and G the modulus (Pa).

However, most substances display characteristics of both liquid and solid and are represented by dashpots and springs (see figure 2.2a). They are called viscoelastic fluids. Different tests exist to characterise such fluids, such as oscillatory measurements (see figure 2.1) or creep test as described in the following sections.

Oscillatory measurement

An oscillatory measurement consists of applying an oscillatory constraint to a material. For such a test, either the strain or the stress applied to the sample varies at a constant frequency or the frequency of oscillation changes at a constant deformation or stress. The response is the resulting stress due to the fluid which allows the determination of its complex modulus (G^*). G^* features a real part called the storage modulus (G') corresponding to the storage of energy by the fluid, and thus, accounting for its solid-like behavior. The imaginary part, the loss modulus (G''), corresponds to the loss of energy due to viscous forces, therefore representing the liquid part of the fluid. The response of a pure liquid to an oscillation results in an oscillation shifted by 90° to the input wave, hence it is in phase with its derivative (the strain rate), see figure 2.1b. However, the output wave of a pure solid is in phase with the input one, hence with the deformation, see figure 2.1a. For a viscoelastic fluid, like the gels studied here, the oscillatory

stress response following an oscillatory deformation will be shifted between 0° and 90° .

Performing a strain or stress oscillatory test on a viscoelastic fluid shows a region for small enough deformation, for which the resulting stress seems to be independent of the input constraint and consequently stays constant. This region is called the linear viscoelastic range (LVR).

The gels studied here comply with some rheological definition of a gel with G' larger than G'' in the LVR, thus displaying a solid-like behavior up to the critical strain or stress (σ_c or γ_c), when the structure of the gel starts being impacted by the input force. The values of G' and G'' in the LVR reveal how strong the gel is. Furthermore, G' is constant at low frequency of the oscillations which also implies that within this frequency range, the critical stress stays constant.

Clay based gels undergo ageing: their rheology changes with time. Such changes can be fitted using a Leong model as described by equation 2.3, [49]. This was established based on the Smoluchowski theory using second order kinetics to predict the bond formation [50].

$$G'(t) = G'_\infty \times (1 - (1 - (\frac{G'_0}{G'_\infty})^{\frac{3}{2}})/(1 + K_r t))^{\frac{2}{3}}, \quad (2.3)$$

where G'_∞ represents G' at an infinite time, G'_0 the initial storage modulus and $1/K_r$ is the Leong time constant. This model fits the results observed for bentonite particularly well and can also be applied to fit the evolution of the yield stress with time [51]. However, it has some limitations at short time since it uses a second order kinetic model. It is also limited at long time, with discrepancies between the experimental values and the predicted ones since the limiting G' used in the model is reached at $t \rightarrow \infty$ which is experimentally impossible to obtain.

Time oscillatory test

Time oscillatory test consists of submitting the gels to oscillations having a constant strain or stress and frequency. It gives the evolution of G^* , G' and G'' with time and is used, in this work, to check that the gel has reached equilibrium before undergoing any additional test. In fact, clay based gels need time to reach equilibrium due to interactions that has to be established between the single units to form a network. Such equilibration requires hours to days depending on the type of clay. For non-swelling clays, attapulgite for instance, only a few hours is necessary whereas swelling clays like bentonite need at least a day. In addition, the use of time sweep test

between rheological tests allows to ensure that the gel is in the same state before starting the next procedure.

Creep test

A creep test consists of applying a constant stress to a material during a certain time and measuring the strain, see figure 2.2b. From it, the compliance function J (Pa^{-1}) is defined as shown by equation 2.4 and represented in figure 2.2b:

$$J(t) = \frac{\gamma}{\sigma_0}, \quad (2.4)$$

where γ corresponds to the strain measured and σ_0 to the applied stress.

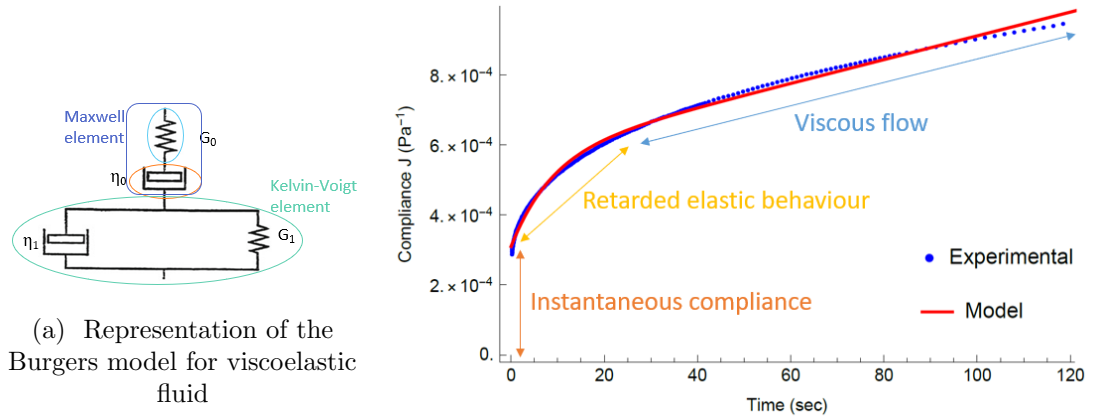


Figure 2.2: Conceptual representation of some viscoelastic fluid and their response to a creep test

Viscoelastic systems can be modelled by a succession of dashpots and springs according to different configurations [18, 52] like the Maxwell model (spring in series with a dashpot) and the Voigt element (spring in parallel with a dashpot). More complex models exist such as the Burgers model, figure 2.2a, comprising of a Maxwell model in series with a Kelvin-Voigt element. Such a representation allows the determination of a model for $J(t)$ as shown by equation 2.5, [53]:

$$J(t) = J_0 + J_1 * (1 - e^{-\frac{t}{\tau_\epsilon}}) + \frac{t}{\eta_0} \quad \text{with} \quad \tau_\epsilon = \frac{\eta_1}{G_1}, \quad (2.5)$$

where J_0 , the instantaneous compliance, models the behavior of the Maxwell spring responsible for the instantaneous response observed at the beginning of the compliance curve (see figure 2.2b). J_1 , the retarded compliance, considers the spring involved in the Kelvin-Voigt element and τ_e represents the retardation time of the Kelvin-Voigt element. This second term accounts for the second part of the compliance curve introducing some irreversible loss of energy due to the dashpot of the Kelvin-Voigt model but still featuring some recoverable energy. G_0 , G_1 , η_0 and η_1 are the modulus or the viscosity associated with the spring or dashpot of the Maxwell and the Kelvin-Voigt elements respectively as shown by figure 2.2a. The last term of the equation 2.5 accounts for irreversible loss of energy due to viscous forces as represented by the dashpot of the Maxwell element. The use of such a model allows to link the compliance to the modulus of the different parts according to the following equation 2.6:

$$J_0 = \frac{1}{G_0}, \quad J_1 = \frac{1}{G_1}, \quad (2.6)$$

However, it doesn't allow the conversion from $J(t)$ to $G(t)$ which can be performed using the Hopkins-Hamming method.

It is therefore possible to determine the parameters, G_0 , G_1 , η_0 and η_1 that are characteristic of a gel. With ageing, we expect these parameters to vary. The Leong model as described in section 2.2.1 can also be used to model their evolution with time.

2.2.2 Characterisation of a flow

Flow properties can be assessed experimentally by performing a flow ramp consisting in measuring the stress resulting of a linear or logarithmic increase or decrease in the shear rate within a specified range. Such experiment allows to characterise the flow using the viscosity and the yield stress, which we will focus on here.

The viscosity expresses the loss of energy due to friction force exerted by one layer of fluid on another one during flow. As already stated in section 2.2.1, a pure liquid is represented by Eq 2.1, and has a viscosity which is independent of the time and shear rate. However, for a viscoelastic fluid, the viscosity can increase with the shear rate (shear thickening fluid) or decrease (shear thinning fluid). Here, we focus only on shear thinning properties facilitating the flow due to the alignment of particles in its direction.

The second characteristic is the yield stress corresponding to the amount of stress that needs to be applied to trigger a flow. A yield stress fluid should not move until it is exposed to a minimal value.

The viscosity and yield stress are important parameters to tailor the formulation of an industrial product. Some thresholds of viscosity at certain shear rates are defined and allow the assessment of a formulation for commercialisation. Yield stress is of particular interest as it resists the sedimentation of an active ingredient, for instance pesticides or pigments, as long as it is high enough. However, the higher the yield stress, the more pressure you need to apply to the system to handle it.

Different equations have been developed to model the flow behavior of fluids [54]. Among them, particular attention will be drawn to the power law Casson model as described by equation 2.7 applied to a yield stress fluid.

$$\sigma^{\frac{1}{2}} = K_0 + K_C(\dot{\gamma})^{\frac{1}{2}}, \quad (2.7)$$

where σ is the stress, $\dot{\gamma}$ the shear rate, K_0 the intercept of the curve with the y-axis from which the Casson yield stress σ_{0C} can be calculated as $\sigma_{0C} = (K_0)^2$. The Casson viscosity is determined by $\eta_C = (K_C)^2$

Such a model is very useful for industries to determine the yield stress of a fluid in a quick and standardised manner. However, the yield stress is a very controversial notion of which the existence is still subject of debate and which can vary according to the experimental method used [55,56]. Hence, determining the yield stress using such a model does not necessarily correspond to its real value but allows to make some distinctions between fluids.

2.2.3 Methodology used for rheology experiment

The measurement of such properties is performed by a rheometer, AR-G2 stress controlled from TA Instruments in this case, allowing us to apply a stress or a strain on the sample through the use of a geometry. The geometry contains the sample during the measurement and creates different types of flow. It comprises a fixed part to which the sample must adhere and a moving

part (rotor) via which the force is applied. One of the most common geometries is the concentric cylinder, see figure 2.3 [18], which can be used with different rotors: DIN rotor or the vane rotor as shown in figure 2.4. The former one is used in industry for the measurement of weak gels as a standardised method. The latter one is particularly suitable for highly viscous gels that need to undergo a minimal disturbance when setting up the experiment.

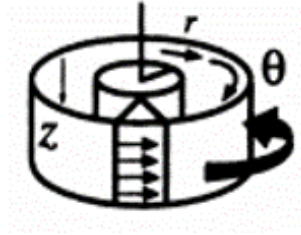


Figure 2.3: Concentric cylinder geometry and Taylor flow associated [18]

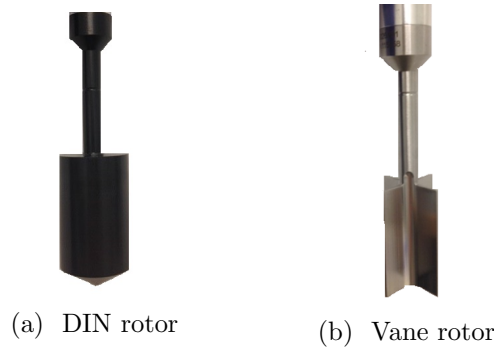


Figure 2.4: Different rotors used in this work

2.3 Imaging techniques

2.3.1 Theory of the techniques

We used a variety of imaging techniques. The first one is Scanning Electron Microscopy (SEM). SEM projects an electron beam on the surface of a sample, from which two main types of signals are emitted and captured by different detectors as depicted by figure 2.5. The first type are secondary electrons corresponding to superficial electrons that were ejected from the sample after being excited by the input beam. The second type are the backscattered electrons (BSE). These are electrons coming from the beam and leaving the sample after undergoing scattering or deflection [57]. Hence, they come from deeper into the surface than the secondary electrons. Such technique allows to image a surface when applying a narrow electron beam.

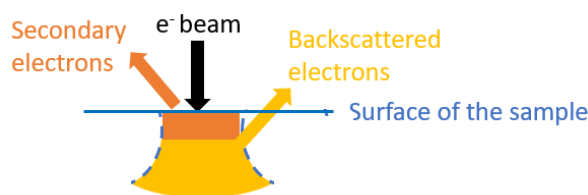


Figure 2.5: Schema representing the two types of electrons resulting from the surface of a sample after being excited by an electron beam

The second technique is X-Ray tomography. X-Rays are electromagnetic radiations with a wavelength ranging between $\sim 10^{-15}$ to 10^{-12} m, typically generated by acceleration then deceleration of high energy electrons, or by electrons relaxing to an inner atomic orbital [58]. They can be generated in different ways: the first way is by using a thermionic cathode producing electrons, which are then accelerated using an electric field. These electron beams hit an anode which slows down the electrons generating therefore X-Rays. The second way of producing X-Rays uses an electron gun to generate electrons which are then accelerated through a linear accelerator and a booster ring. When the path of the electrons is changed using a magnet, they decelerate and generate a very bright light directed towards a beam. Afterwards, a series of slits and mirrors are used to orientate the beam and select the correct frequency for the experimental station called beamline where experiments are performed.

2.3.2 Method used for X-Ray imaging

We first tried to image our gels using a X-Ray laboratory device from Zeiss, which allows to resolve structure as thin as $0.7\mu\text{m}$ with a maximum power of 30kV. However, none of the microstructure of our gels could be seen. Therefore, we used a more powerful X-Ray flux such as the one generated at the Diamond Light Source synchrotron. We used the Diamond Manchester Imaging Branchline (I13-2) beamline, capable of performing tomography at an energy as low as 8keV. The I13-2 beamline also has a Multilayer Monochromator (MLM) allowing the selection of a single wavelength called monochromatic light. For such installation in figure 2.6, the X-Ray beam remains fixed and parallel while the sample rotates around its vertical axis and the detector catching the X-Rays that were transmitted through the sample is located behind it. Therefore, this beamline can perform X-Ray tomography to see the microstructure of samples since the X-Ray adsorbed by a sample depend on its composition. Tomography allows the visualisation of 3D structures (tomogram) due to the rotation of the sample allowing to image all parts of

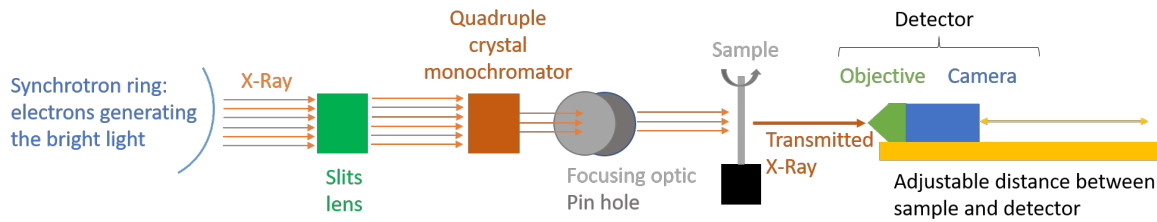


Figure 2.6: Schema of the I13-2 beamline at Diamond Light source

it, and after the assembling of all 2D radiographs [59]. From these radiographs, an algorithm reconstructs the 3D structure.

2.3.3 Method of sample preparation

A key step when imaging samples using Cryo-SEM is the sample preparation. The gels studied in this project contain lots of water, up to 90% wt., which plays an important role in building the structure of the gel by hydrating the clay units through hydrogen bonding or osmotic pressure [60,61]. Hence, it is important to prepare the sample in a way that preserve the water content and the interactions between the single units of the clay and the clay and the water. To do so, different sample preparation methods exist [62,63] among which a particular attention will be drawn to nitrogen plunge and high pressure freezing (HPF).

A nitrogen plunge consists of immersing a small amount of sample (milliliters) contained in a well into liquid nitrogen to freeze it very quickly. High pressure freezing is performed by sandwiching micro-litres of sample between two carriers as depicted in figure 2.7. Afterwards, the sample is frozen very quickly by increasing the pressure.

Both techniques have their advantages and drawbacks. A N_2 plunge allows the deposition of more sample into the well. Such a sample may retain its original structure more easily than with HPF. Samples are also more quickly prepared and transferred into the Cryo-SEM device. However, the drawback of this technique stems in the freezing rate, which may not be fast enough, leading to the formation of ice crystals impacting the structure of the sample [63]. Therefore, the N_2 plunge usually used for clay imaging, may lead to the formation of a honeycomb structure. The aforesaid structure features broad cells having thick walls, due to aggregation of clay particles, and enclosing water pores. Deirieh et al. found different structure of the same soil when plunged into different liquids each having different temperatures and consequently freezing rates [64]. Holzer et al. also criticised this technique on bentonite [62].

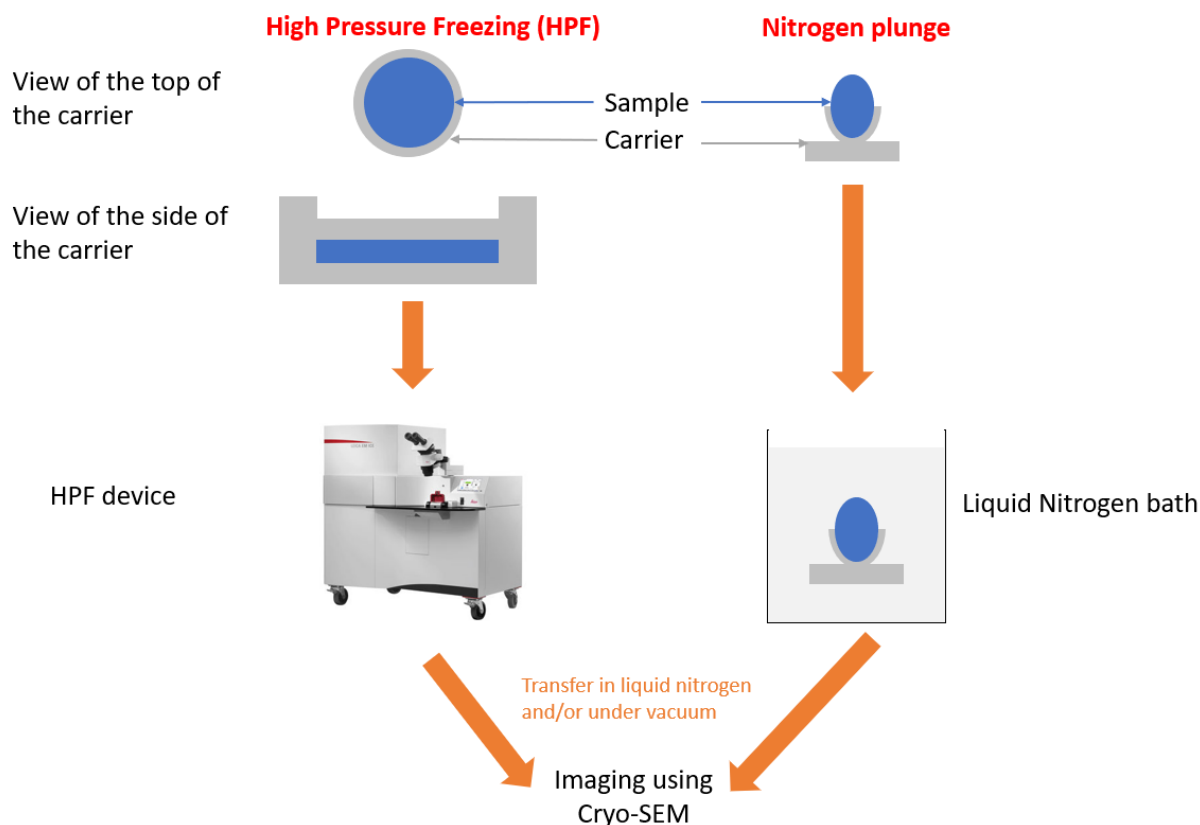


Figure 2.7: Simplified representation of high pressure freezing (HPF) versus N_2 plunge followed by Cryo-SEM imaging

Due to the very high freezing rate, high pressure freezing prevents the formation of ice crystals allowing the sample to retain its structure. Nevertheless, this technique requires the deposition of a very small and precise amount of fluid, usually pipetted, impacting the structure of the gel. The amount of sample is key since too much or too little sample will result in slowing down the freezing, leading to the formation of ice crystals at the interface between the sample and the top carrier. In addition, with the sample being trapped between two carriers, the top one exerts some pressure on it, which may also impact the structure of the gel.

In the case of a gel, the ideal method could be X-Ray tomography as this is a non-destructive technique which does not require any specific sample preparation. A sample contained in a capillary of 1mm internal diameter can be imaged. Nevertheless, the bigger the sample, the lower the power, which may give rise to water bubbling, making the structure move and rendering any image reconstruction impossible. This effect can be reduced by using a filter in the path of the beamline or by using a monochromator. However, when using a monochro-

mator (allowing the use of a single wavelength) the X-Ray source must be stable, otherwise a blurred image will be generated [59]. Transmission X-Rays have already been used by Zbik et al. to image different clays [65,66]. However, a lack of resolution prevents a reliable interpretation of the structure at a nanometer scale.

2.4 Characterisation techniques

2.4.1 Method used to determine the chemical composition of a molecule

One clay used in this project is a Laponite coated by an organic material. Such clay features rheological properties differing from the original Laponite as will be explained in Chapter 3. No detail related to this organic material could be found through its manufacturer BYK. Therefore, we tried to chemically characterise it through the use of IR and NMR.

Fourier Transform-Infra Red (FT-IR) spectroscopy uses radiations at wavelength beyond the spectrum of the visible light. All molecules vibrate and rotate according to its chemical composition and type of bond. Hence, molecules will adsorb photons from IR corresponding to their energy levels. It is therefore possible to obtain an absorption spectrum characteristic of a molecule when submitted to a range of IR wavelength. According to the wavelength of the absorbed peak, the nature of the chemical bonds like Si-OH, Mg-OH can be determined.

We also used solid state Cross Polarization Magic-Angle-Spinning (CPMAS) ^{13}C NMR. This technique relies on the electromagnetic properties of the nuclei of the molecules. NMR is a technique sensitive to the chemical environment of the nucleus: the nature of the neighbouring atoms or the type of bond. Once excited, the system will relax to its equilibrium at a characteristic frequency based on its environment.

2.4.2 Surface characterisation of clay

Theory of zeta potential

The single units of a clay interact with one another to form a network through different forces, such as electrostatic interactions which depends on their surface charge. When in suspension in water, an electrical double layer will form at the surface of a single unit as shown in figure 2.8.

This double layer comprises a first layer very close to the clay, called the Stern layer, enriched in counter ions (attracted by the charge at the surface of the clay) and depleted in ions of similar charge as the surface of the clay [36]. The concentration of these counter ions decreases as the distance from the clay increases. This forms the second diffuse layer within which there is a boundary where on the inner side, ions move with the particles whereas if they are outside of it, they do not move. This boundary is called the plane of shear. The potential of this plane is called the zeta potential and is supposed to be equal to the potential of the Stern layer. Hence, the zeta potential brings information regarding the charge of a surface of a particle, which depends on the pH of the suspension and can be influenced by coating. A negative zeta potential is found for particles with negatively charged surface and vice versa for positive zeta potential. This measurement sheds some light on whether or not the coating of laponite EP influences the surface charge of laponite. Furthermore, a suspension with $|z| > 30mV$ should be stable.

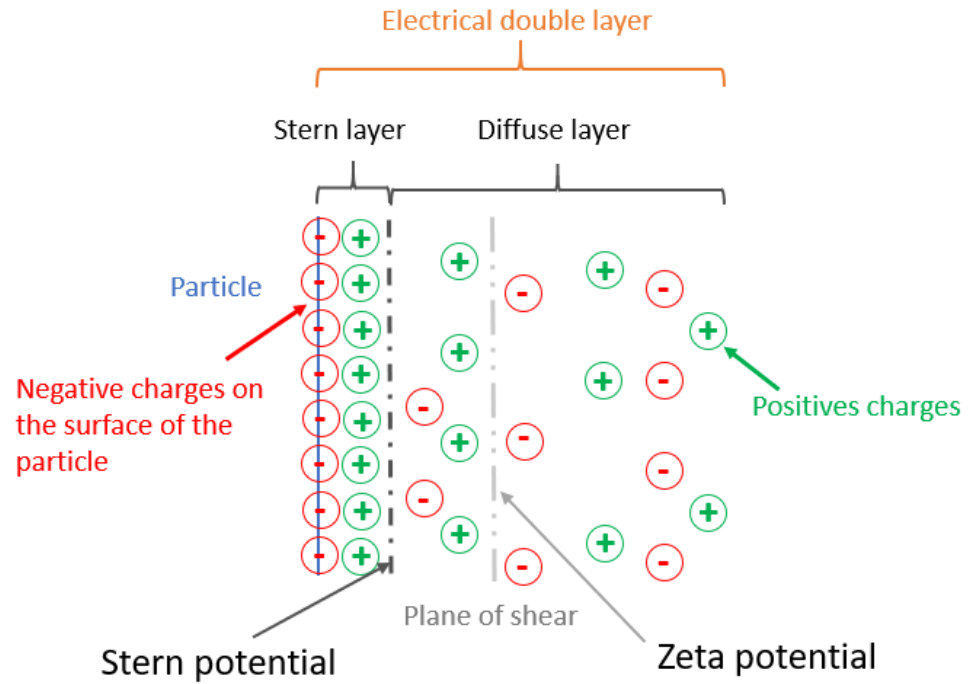


Figure 2.8: Representation of the electrical double layer formed around a single unit of clay with a negatively charged surface

Method employed

We used a zetasizer to determine the zeta potential of suspensions of clays in water. This technology uses an electric field which triggers the motion of the charged particles. The zeta

potential is related to the velocity of the particle also called the electrophoretic mobility, see equation 2.8. The velocity of a particle is measured by laser doppler velocimetry.

$$z = \frac{3 \times U_E \times \eta}{2 \times \epsilon \times f(\kappa a)}, \quad (2.8)$$

where z is the zeta potential, U_E the electrophoretic mobility, ϵ the dielectric constant, η the viscosity and $f(\kappa a)$ the Henry's function which value is around 1.5 in our study.

2.4.3 Thermal characterisation

We used Thermogravimetric Analysis (TGA) complementary to Differential Scanning Calorimetry (DSC) to characterise the behavior of clay or gel when increasing the temperature. With TGA the temperature of the sample is increased while recording its mass. It is a powerful technique to determine the temperature at which evaporation or final decomposition occurs. DSC allows the determination of the heat flow of a component according to equation 2.9. It consists in increasing or decreasing the temperature applied to a sample at a certain rate while comparing its heat flow to a control sample.

$$\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(T, t), \quad (2.9)$$

where $\frac{dQ}{dt}$ is the heat flow in W/g, C_p the heat capacity in J/K and $f(T, t)$ the kinetic function of the heat flow.

Consequently, it gives the nature of the thermal reaction, i.e. endothermic or exothermic. Among endothermic events we can quote evaporation, glass transition, melting and so on. Exothermic reactions can be crystallisation, oxidation and so on.

Chapter 3

Rheological study of different clays as a replacement for Xanthan

We investigated the use of Laponite EP, a laponite whose surface was coated with an organic compound, as a replacement of xanthan for the formulation of agrochemical products containing anionic surfactants. The study revealed that the combination Laponite EP-bentonite led to similar rheological properties as the currently used xanthan-bentonite mix, i.e. the storage modulus G' , the critical strain γ_c , the Casson yield stress σ_c and the Casson viscosity η_c were similar. Such similarity could not be achieved by using Laponite EP or bentonite on their own because of some synergy between the two clays. Such interacting effect may be due to the existence of two interconnected networks as revealed by imaging techniques. The mixture of the non-coated Laponite RD with bentonite was not as successful as the Laponite EP-bentonite blend highlighting the effect of the coating. Such coating did not impact the zeta potential of the clay. It did not affect the structure of the laponite disk either as it was applied only on its surface. The presence of the non-ionic surfactant Tween 20 with Laponite EP or RD showed that the coating may hinder the adsorption of the surfactant by the clay.

3.1 Introduction

Commercial products for various applications are made of an active ingredient (AI), imparting its main functionality, dispersed in an oil or, in our case, an aqueous based matrix. The formulation

of such a colloidal dispersion is challenging for industries aiming at delivering products that meet consumers' expectations. Colloidal dispersions are not stable systems but face creaming or sedimentation (in this work) leading to a phase separation between the AI and the rest of the media. The use of a thickener or gelling agent is therefore needed to stabilise the system over time modifying its rheological properties, for instance by creating a gel. In the case of the gels studied here, G' (the storage modulus) must be above G'' (the loss modulus) and the dispersion has to display shear thinning properties, i.e. its viscosity decreases when the shear rate increases.

A common thickener used in industry is xanthan, an anionic polysaccharide synthesised by the bacteria *Xanthomonas campestris*. When in presence of other particles, xanthan is known to form a gel by depletion interaction leading to a phase enriched in polymer and a phase poor in polymer. If in arrested state, these two continuous phases create a particulate gel stabilising the system [28]. Xanthan is also known to display synergistic effect with other thickening or gelling agents like clays [25], thus the application of such a combination for industrial product formulation. However, the use of xanthan features the following drawbacks: 1) as polysaccharide it undergoes bacterial degradation shortening the product shelf-life, 2) it can fail to form a gel depending on the properties of other chemicals entering in a product formulation such as the AI. Therefore, it is of interest to find an alternative thickener that is safe and could potentially be used to formulate several products. However, the rheological properties of the final products must be maintained as well as their shelf-life.

Inorganic materials displaying shear thinning properties, such as bentonite, kaolin, attapulgite, Laponite, are potential candidates for the replacement of xanthan [67]. Nevertheless, clays display different rheological behavior to xanthan when at rest. Under certain conditions, they are known to form a "house of card" structure forming a network, spanning the whole sample and leading to the formation of a gel [68–70]. However, this model has been extensively questioned [71] and another explanation was given by Norrish [60] where interactions between clay platelets are made through repulsive forces between the electrical double layers. More recently, Jonsson et al. found that an overlapping coin configuration of the laponite disk is the most energetically favourable [72]. Our work focuses on the use of Laponite, a nanometer size disk-shape synthetic clay, of which the rheological properties can be modified by surface coating, such that the resulting Laponite matches different environmental conditions. Here, we focus on Laponite EP, an organically coated Laponite manufactured by BYK. Similarly to the interac-

tions displayed by a mixture of clay-xanthan, clays can also be mixed with other polymers or other clays having different shape or size [73–78].

In this chapter, we show how Laponite EP can be used in the formulation of a model agrochemical product replacing xanthan while keeping the same rheological properties of the final product. Such an agrochemical product is called suspension concentrate (SC). We mixed Laponite EP with bentonite and assessed the effect of such interaction on the rheology of SCs. The cooperation between the two clays was investigated microscopically by using High Pressure Freezing (HPF) Cryo-SEM. Additional tests regarding the shelf life were also performed to assess the long term stability of such SCs. Additionally, we attempted to define the nature of the organic coating and the property it affects which resulted in a different rheological response compared to uncoated laponite.

The first section of this chapter (section 3.2) presents the materials and methods used in this study. The second part lays out the results obtained (section 3.3) which are discussed in section 3.4. A conclusion (section 3.5) presents the main findings of this work.

3.2 Materials and Methods

3.2.1 Materials and methodology used to screen new compounds

We used Laponite RD and Laponite EP from BYK. Laponite RD corresponds to a raw Laponite of chemical formula: $\text{Na}_{0.7}^+[(\text{SiO}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$ whereas Laponite EP is an organically coated Laponite chosen for its capability of still forming a gel in aqueous system with high amount of salt or extreme pH. Bentonite was purchased from Wilfrid Smith and corresponds to Bentopharm B20. Xanthan (Rhodopol 23) was bought from Solvay and propylene glycol from Sigma-Aldrich. A millbase provided by Syngenta containing the pesticides Azoxystrobin (here the AI) and anionic surfactant was used for the formulation of suspension concentrates (SCs).

The methodology used to compare the rheological properties of the clays themselves, or any formulation thereof, was the following:

- 1) The rheological parameters of gels made of Laponite EP 2% or xanthan 2% in water were experimentally determined. They were all prepared by adding a suitable weight of clay into water. Then the dispersion was high sheared, using the high shear mixer Ultra-turrax digital

T25 from IKA with the S 25 N-18G impeller, until the thickener was homogeneously dispersed, i.e. no macroscopic aggregate could be seen and the flow of the gel was homogeneous when pouring. The gels formed using Laponite EP or xanthan were centrifugated at 1000 rpm for 5 mins for the Laponite EP gel to remove air bubbles. The rheological results obtained for Laponite EP 2% wt. were compared to the ones obtained for a 2% xanthan gel.

2) Afterwards, gels containing the millbase, a thickening agent and propylen glycol were made. Such a mixture is referred to as suspension concentrates (SCs). The procedure to prepare such gels was as follows: Water was added first followed by the millbase to get to a final concentration of 200g/L of active ingredient (AI). Secondly xanthan 2% or Laponite EP 2% or Laponite RD 5% gel was added followed by the addition of Bentopharm 10%. The amount of thickener added was tailored so the final product meet rheological targets detailed in section 3.2.2. Thirdly, propylene glycol was added to a concentration of 120g/L. The SCs were stirred afterwards with a magnetic stirrer until complete homogenisation. Each SCs was rheologically characterised and compared to the control sample containing 2g/L of xanthan and 25g/L of Bentopharm.

A formulation work was performed thereafter by adjusting the concentration of Laponite EP and Bentopharm to get a rheological behavior of the SC as close as the one obtained for a commercial product. The validation of SCs was also performed by carrying out a shelf-life study (see part 3.2.3) and the results were compared against referenced values determined by Syngenta.

3.2.2 Description of the rheological tests

The rheological procedure performed to determine the rheological properties of clay gels or SCs was established by Syngenta and reproduced at the University of Oxford using a stress controlled rheometer AR-G2 from TA Instruments with a 60mm diameter parallel plate or a concentric cylinder with a DIN rotor. This test includes the following steps all performed at 25°C:

- 1) Conditioning step including a pre-shear at 100 s^{-1} for 60s followed by an equilibration for 20 minutes. This step is performed to homogenize the fluid and remove all its history, allowing a good reproducibility of the results,
- 2) Strain amplitude oscillation from $\gamma = 10^{-4}$ to $\gamma = 10$ with 3 conditioning cycles and 2 sampling cycles,
- 3) Conditioning with a pre-shear at 600 s^{-1} for 60s followed by a rest for 10 minutes,
- 4) Flow ramp up and down from 0 to 600 s^{-1} ,

Syngenta has defined some rheological requirements based on the results of this test. From the amplitude sweep, it has been defined that a suitable SC must comply with the following:

- G' being between 20 and 50 Pa,
- $\gamma_{critic} \approx 0.01$,
- $G'/G'' \approx 3$.

The flow ramp was fitted using a Casson model (see equation 2.7 in part 2.2.2) from the 7th point to avoid taking noise or any potential wall slip into account. Syngenta's requirements are: $\sigma_C \in [2 - 4]$ Pa, $\eta_C < 70$ Pa.s, $\eta_{10s^{-1}} < 700$ mPa.s and $\eta_{20s^{-1}} < 420$ mPa.s.

3.2.3 Procedure to study the suspension concentrate shelf life

Two tests set up by Syngenta were performed on fresh SCs and SCs kept for 4 weeks at 40 °C to assess their stability over time. The first test was a pourability test consisting in weighing an empty 25mL cylinder ($W1$), then pouring the gel inside and recording the new weight ($W2$). The weight of the sample was given by $W3 = W2 - W1$. Then the gel in the cylinder rested for 30 minutes at room temperature. Afterwards, the cylinder was emptied and the weight of the empty cylinder was measured again ($W4$). The weight of the SC residue was given by $W5 = W4 - W1$ and the percentage residue by $W5/W3 * 100$. SCs passed the test if their pourability before ageing is below 9%.

The second test was a dilution test carried out by adding 1mL of SC into a cylinder filled with 100mL of water. The cylinder was then inverted until complete dispersion of the residues. The spontaneity of the dispersion and the number of inversions were recorded. Qualitative criteria to assess dispersion were as follows: Good (A) - the SC was almost completely dispersed when poured into water, Fair (B) - more than 50% of the SC was dispersed and less than 50% of the SC was not dispersed, Poor (C) - Dispersion was less than 50%.

The rheology of the SCs was also assessed after storage with the same rheological test as described in part 3.2.2

3.2.4 Microstructure of Laponite EP and Bentopharm gel

The microstructure of the gels formed by Laponite EP 2% and Laponite EP 5g/L + Bentopharm 20g/L was assessed by high pressure freezing (HPF) the samples followed by Cryo-SEM to image the gels (see details in part 2.3). The HPF device was an EM ICE from Leica and the Cryo-SEM a Hitachi SU8220. Once the samples were high pressure frozen, they were kept under liquid nitrogen until imaging. The sublimation was performed under vacuum at -93°C for 10mins followed by a sputtering at 5.0mA for 15secs repeated twice. The samples were imaged afterwards using the backscattered electrode at different powers.

3.2.5 Chemical and thermal characterisation of Laponite EP compared to Laponite RD

We used solid state Cross Polarization Magic-Angle-Spinning (CPMAS) ^{13}C NMR (see part 2.4.1) on the Laponite EP powder obtained from BYK. This technique was employed to determine the nature of the component used to coat Laponite EP. Fourier Transform-Infra Red (FT-IR) spectroscopy (see part 2.4.1) was performed on Laponite EP and Laponite RD powder as this technique is sensitive to any chemical groups present in a molecule. A difference between Laponite RD and Laponite EP should appear on the spectra due to the organic coating of the latter one. A third analysis coupling thermogravimetric analysis to gas chromatography and mass spectroscopy (TGA-GC-MS) was also performed by Syngenta on both Laponite powders to detect their elemental composition and the proportion of the chemical elements.

We performed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (see part 2.4.3) tests on Laponite EP and Laponite RD powders to investigate the nature of bonding between the organic compound and Laponite that makes Laponite EP. TGA experiments were performed using a Mettler Toledo TGA system, from room temperature up to 1000°C at a rate of $10^{\circ}\text{C}/\text{min}$ while the mass of the sample was recorded. The DSC tests were performed using a DSC Q20 from TA Instruments. We used an aluminium pan with a pin hole in the lid and included an equilibration at -40°C or 40°C followed by a ramp up to 400°C at a rate of $10^{\circ}\text{C}/\text{min}$. Afterwards, a cool down step was performed to -40°C or 40°C at the same rate. Then, the first heating step was repeated. All tests were performed under nitrogen.

3.2.6 Surface characterisation of Laponite and mixes of Laponite and Tween 20

Solutions of Laponite RD 0.5% and Laponite EP 0.1% were used for Zeta potential measurements, using a NanoZ Zetasizer from Malvern Instrument with a U cell (see part 2.4.2), to determine whether the coating of Laponite EP has any impact on the surface charge of the clay compared to Laponite RD. Moreover, to learn if the Laponite EP coating influences the interaction between Laponite and the non-ionic surfactant Tween 20, from Sigma (cmc=60mg/L), zeta potential measurements were also performed on Laponite EP/RD 0.25g/L + Tween 20 0.05% or 0.5% and Laponite EP/RD 5g/L + Tween 20 1%. The tests comprised an equilibration at 25°C for 2 minutes to avoid any convective flow which could affect the results, followed by 3 measurements.

3.3 Results

3.3.1 Rheology

Firstly, we compared the rheological behavior of Laponite EP 2% wt. gel to the one of xanthan 2% wt. (see figure 11 in the Appendix). Although the stress obtained during the flow ramp for Laponite EP was below the xanthan one, both curves were parallel showing similar flowing behaviour at high shear rate. Laponite EP 2% and Rhodopol 2% networks show similar values for G' and G'' at low strain. However, the critical strain γ_c for Laponite EP is much lower than for the polysaccharide, which is due to the different nature of the interactions taking place in each sample.

Secondly, to confirm the use of Laponite EP or RD as gelling agent, we characterised the rheological behavior of SCs made using such inorganic compounds as alternative to xanthan. The strain oscillation and flow ramp test performed on Laponite EP or RD 5g/L + Bentopharm 20g/L (see figure 3.1) show that the sample containing Laponite EP features a similar rheological behaviour for both the strain oscillation test and the flow ramp as the reference sample containing xanthan. In fact, the formulation with Laponite EP displays a $G' = 31.7\text{Pa}$, a γ_c between 1.0 and 1.6%, a Casson yield stress of $\sigma_c = 3.43\text{ Pa}$ and a $\eta_c = 10.97\text{mPa.s}$. Such values comply

with rheological requirements for agrochemical products. Regarding the use of Laponite RD in SC formulation, although the stress modulus G' on the linear viscoelastic range is similar to the one obtained for the reference sample (27.0Pa), the critical strain γ_c is higher than the target of 1%, $\gamma_c=2.56\%$, and the curve shows a steeper slope at higher strain characteristic of brittle material. Furthermore, the Casson yield stress is too low ($\sigma_c = 0.98$ Pa) to prevent the sedimentation of the AI. Hence, Laponite RD cannot be used for the formulation of SC.

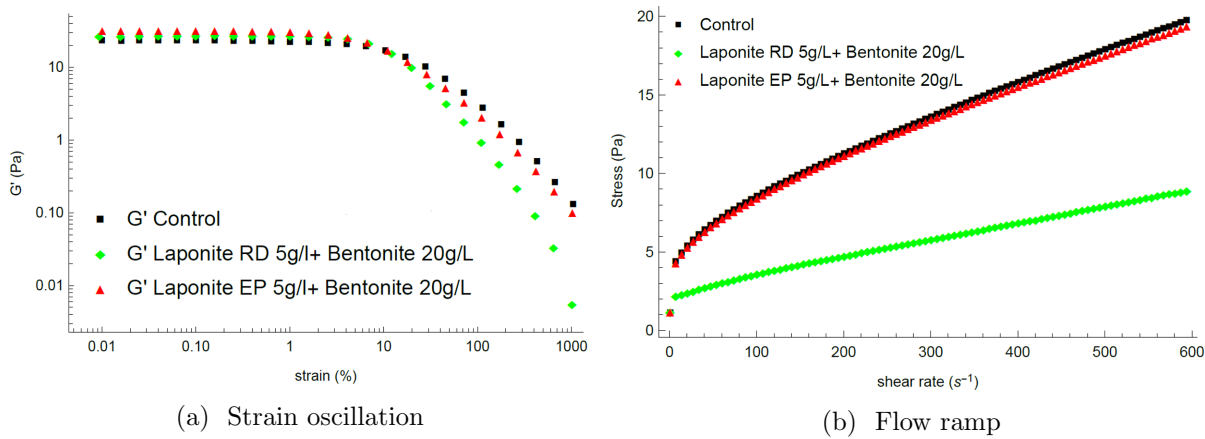


Figure 3.1: Comparison of the rheological behaviour of Laponite EP or RD 5g/L + Bentonite (Bentopharm) 20 g/L to the control sample xanthan 2g/L + Bentopharm 25g/L

As shown by figure 3.1, Laponite EP seems to be able to replace xanthan for the formulation of SC. Although the graphs represented on figure 3.1 were performed using one data curve, the whole experiment was repeated several times both at the University of Oxford and at Syngenta by different people. All results obtained show a good reproducibility of the experiments. Nonetheless, the right formulation of Laponite EP and/or Bentopharm needs to be determined. The rheological results of different combination of thickeners, in figure 3.2, reveals a synergistic effect between Laponite EP and Bentopharm (bentonite). Bentopharm 20g/L or Laponite EP 5g/L on their own render gels that are not strong enough to prevent the sedimentation of the AI ($\sigma_C < 2$ Pa, $G' < 20$ Pa for both gels); their curves are below the control one for the flow ramp and the strain oscillation. Increasing the amount of bentopharm to 40g/L only increases σ_C from 0.28 Pa (at 20g/L) to 2.74g/L compared to 3.5 Pa obtained when adding 5g/L of Laponite EP. Interestingly, such a gel is very strong at rest with $G'=113.2$ Pa and therefore cannot be used for the formulation of SCs. The opposite behavior is found when doubling the amount of Laponite EP; such a gel features $\sigma_C=4$ Pa, but $G'=16.5$ Pa only. Hence, doubling the concentration of Laponite EP leads to a gel which is not strong enough at rest but would resist a flow. Only the synergistic interaction between Laponite EP and Bentopharm gives a suitable behaviour at rest

and during a flow as shown in figure 3.2.

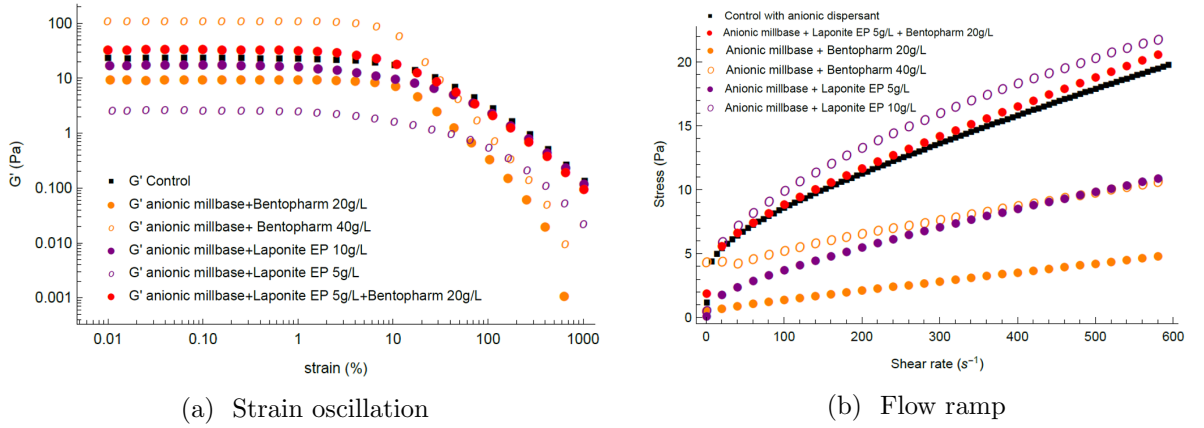


Figure 3.2: Comparison of the rheological behaviour of SCs containing different proportion of thickeners. Note that the curves here correspond to a single measurement consistent with other data (obtained at Syngenta) and macroscopic results.

The storage study of formulations containing Laponite EP and Bentopharm(15 or 20 g/L) (figure 3.3) shows that they are stable after 4 weeks of storage at 40°C. All samples display a storage modulus G' , critical strain γ_c , a Casson yield stress σ_c and a Casson viscosity η_C complying with the rheological targets for agrochemical products (see section 3.2.2).

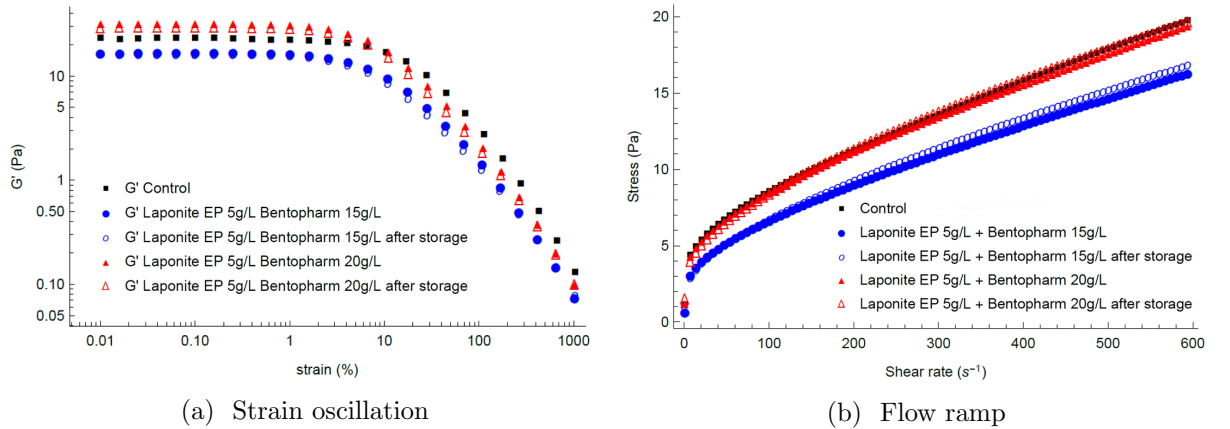


Figure 3.3: Shelf life study of SCs containing Laponite EP 5g/L and Bentopharm compared to the control sample. Note that this experiment was performed on only one sample and it is consistent with a macroscopic assessment of the formulation and the pourability test.

3.3.2 Shelf life study of suspension concentrates containing Laponite EP

Table 3.1 shows that most formulations feature an acceptable pourability and dilution. Although the pourability for the formulation containing bentonite 20g/L is slightly above the 9% threshold, it displays a good dilution grade and number of inversion (number of times we turn

it upside down). In line with the results obtained from the rheological test after storage, we notice only a slight increase of the pourability and no effect on the dilution. Therefore, these two formulations are considered stable with time and can be considered for the formulation of commercial products.

Table 3.1: Pourability and dilution obtained for different formulations containing Laponite EP and Bentopharm (bentonite)

Sample	Pourability (%)	Dilution	
		Grade	Number of inversions
Laponite EP 5g/L + Bentonite 15g/L	6.6	B (Fair)	2
Laponite EP 5g/L + Bentonite 15g/L after storage	7.18	A (Good)	2
Laponite EP 5g/L + Bentonite 20g/L	9.4	A (Good)	2
Laponite EP 5g/L + Bentonite 20g/L after storage	9.99	A (Good)	2

For the following of the project, we will focus on the formulation Laponite EP 5g/L + Bentopharm 20g/L as the rheology of this SCs is comparable to the one of the commercial product (see figure 3.3).

3.3.3 Microstructure of Laponite EP - Bentopharm gel

Laponite EP 2% is a very concentrated gel with areas where the clay forms blocks of materials. These parts are separated by areas where the clay units are more delaminated and feature small pores as revealed by figure 12 in the Appendix. Such heterogeneities in the gel may be due to its preparation: a non-homogeneous shear mixing can lead to more concentrated areas. In figure 12b in the Appendix, Laponite EP displays 2 different structures: the first one has a micrometer size and forms a network spanning the sample. This structure, where the clay disks form cells enclosing water, is similar to the one found on Laponite by Du et al. [79], and is connected to the second structure. This second structure is a thinner, filament-type structure. Both structures formed by Laponite EP are probably made of disks overlapping at their edge-face point of interaction. Additional, superposed sheets of the same structure may be the reason of the micrometer structure seen [79]. The filament-like structures are also in the Laponite EP - bentonite gel, in addition to the bigger bentonite platelets, see figure 3.4b. Hence, the gel formed by the clay mix may feature two connected networks, one constituted of bentonite and one of Laponite EP as displayed in figure 3.4c. As shown in figure 3.4a, the blend clay gel displays a very dense network made of fine sub-units. Note that even at 10kV, it is still possible to see heterogeneities in the gel with areas of filament-like structure of Laponite EP, which could again

be due to the initial preparation of both Laponite EP and Bentopharm.

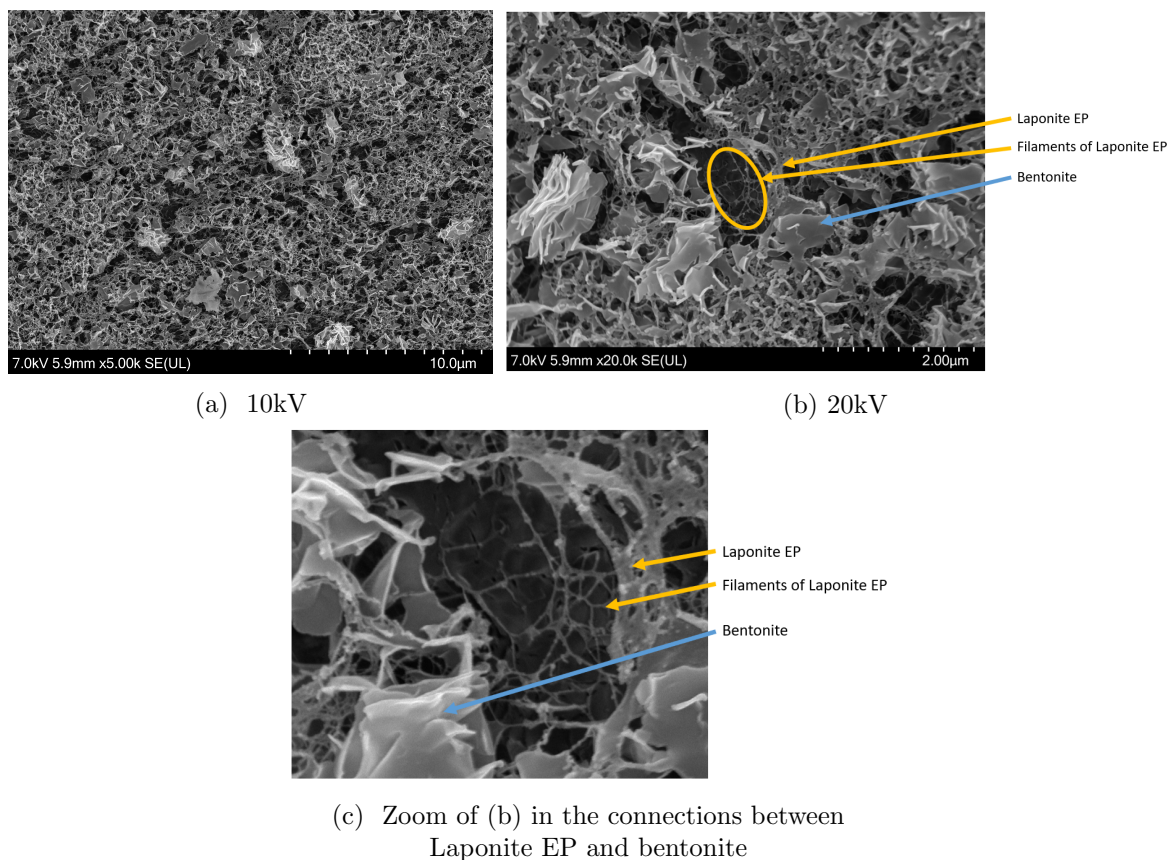


Figure 3.4: Microstructure of a Laponite EP 5g/L + Bentopharm 20g/L gel revealed by HPF Cryo-SEM

3.3.4 Chemical and thermal characterisation of Laponite EP

In the previous sections, we successfully replaced xanthan by a mixture of Laponite EP-bentonite. We also saw the microstructure of the network formed by such a blend. In this section, we focus on characterising chemically and thermally Laponite EP compared to the raw Laponite RD. Results from the TGA-GC-MS analysis shows that Laponite RD contains approximately 90% of hectorite clay and 10% of water whereas Laponite EP is composed of 75% hectorite clay, 15% organic material and 10% water. Table 3.2 reveals the organic elemental composition of Laponite EP which features a higher amount of carbon and hydrogen than Laponite RD due to its organic coating. Furthermore, according to the relative amount of carbon and hydrogen, the component used for the coating could be some carbonyl group such as acetone or acetate. However, it is surprising to find any nitrogen associated with such compounds although an external source of contamination cannot be ruled out.

Table 3.2: Results of the TGA-GC-MS performed on Laponite EP and Laponite RD powders

	Laponite EP	Laponite RD
C	11.4	0.48
H	3.13	1.92
N	0.25	0

The NMR spectrum obtained on Laponite EP (graph 3.5a) shows a carboxyl function at 174.54 ppm, [80]. The attribution of the second peak at 102.36 ppm to a chemical function is not clear and may correspond to unsaturated carbon-carbon ($-C=C-$) or nitrile function ($-C \equiv N$) which could explain the amount of nitrogen found for Laponite EP by TGA-GC-MS. The very intense peak at 73.72 ppm corresponds to saturated carbon ($-CH_2-$). Such intensity may suggest that the coating contains lots of ethyl group as in surfactant for instance. The two peaks at 21.3 and 25 ppm account for the presence of methyl ($-CH_3$) in the molecule [81].

FT-IR spectra found for Laponite EP and Laponite RD (figure 3.5b) are very similar. The peaks at 3417.1 cm^{-1} and 1635.36 cm^{-1} correspond to water physically adsorbed on the clay [82,83] and the peak shoulder found at 3655 cm^{-1} corresponds to the overlapping vibration of Si-OH and Mg-OH. The peak at 972 cm^{-1} may be attributed to Si-O stretch [84], and the peak at 661.2 cm^{-1} may be due to hydroxide vibration of Mg_3OH [85]. The spectra of Laponite EP and RD may feature some difference between 1200 and 1400 cm^{-1} with small peaks appearing for Laponite EP. However, this zone is not clear and could either be a peculiarity of Laponite EP or these are only peaks due to the hydration of the clay.

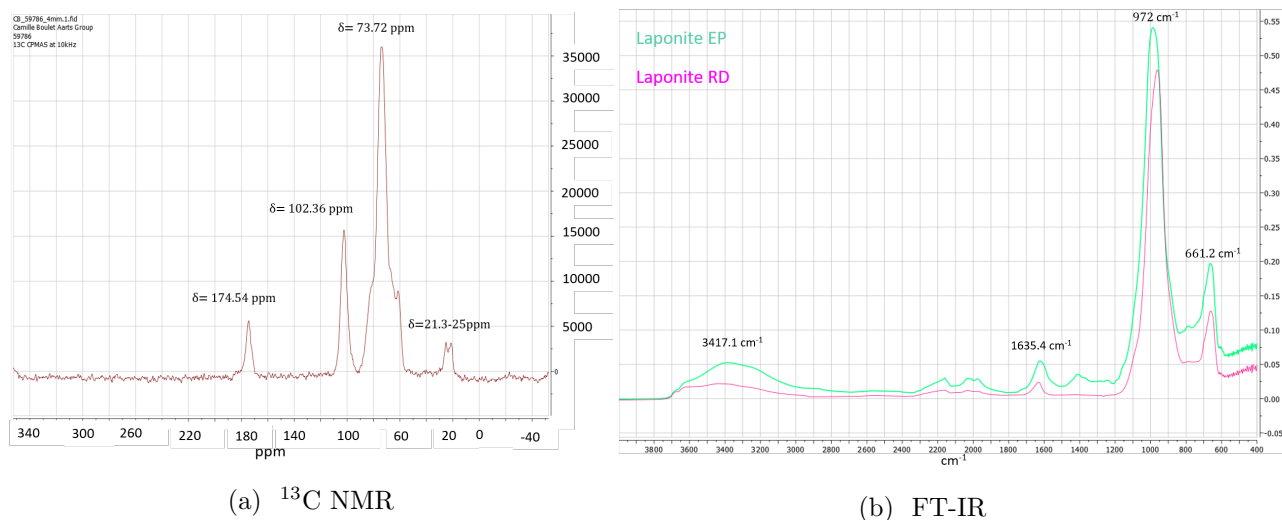


Figure 3.5: Chemical characterisation of Laponite EP compared to the non-coated Laponite RD

TGA results (figure 3.6a) show two mass losses for Laponite RD. The first one is caused by evaporation of water being weakly bounded to the clay as shown by the endothermic peak between 50°C and 150°C on the DSC heat flow curve (figure 3.6b) [84,86,87]. Afterwards, the mass gradually decreases due to the slower evaporation of water that is more tightly bound to the clay. The second mass loss around 700°C could be caused by a dehydroxylation followed by a recrystallization of the clay [86,88]. The TGA curve for Laponite EP is alike except for an additional loss of mass event around 300°C corresponding to an exothermic reaction as shown by DSC (peak at 293.86°C in figure 3.6b). Such an exothermic event may be due to the decomposition of the organic material, although any oxidation of it could be ruled out as the experiment was performed under nitrogen.

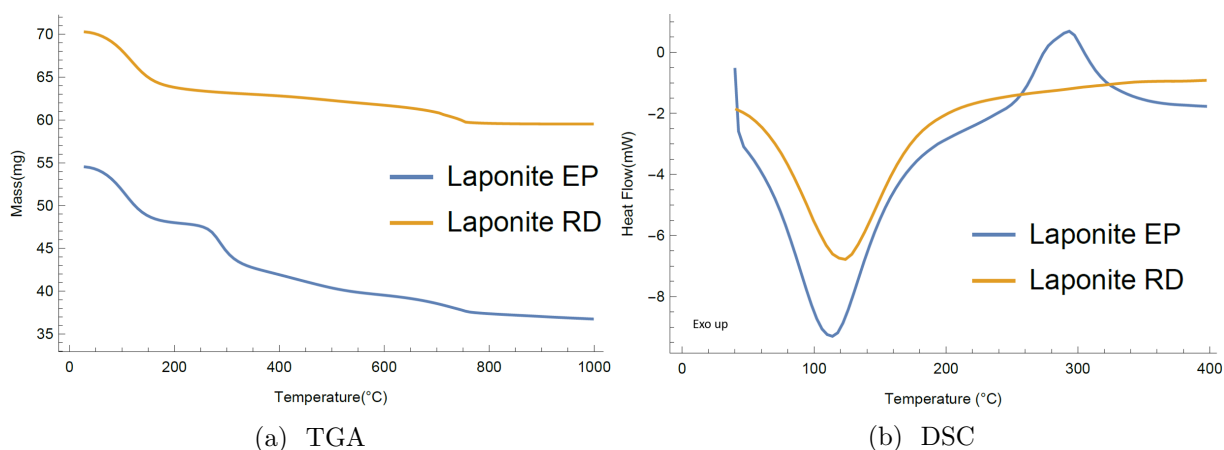


Figure 3.6: Thermal characterisation of Laponite EP compared to the non-coated Laponite RD. Each experiment was performed only once and showed consistent results.

3.3.5 Surface characterisation results

Zeta potential measurements performed on Laponite EP 0.1% and Laponite RD 0.5% (table 3.3) did not reveal any difference in the surface charge of Laponite EP and Laponite RD with both negative zeta potentials accounting for negatively charged surfaces. The addition of Tween 20 led to an increase in the zeta potential of both Laponite EP and RD, in line with the work performed by Yalçın et al. on bentonite with anionic surfactant [89]. Laponite RD with Tween was found to have a less negative zeta potential than Laponite EP with Tween meaning that for the same amount of Tween 20, there were more negative charges on the surface of Laponite EP than Laponite RD. Furthermore, all zeta potentials of Laponite EP and Tween were below -30 mV implying that such suspensions were stable. This was not the case with Laponite RD for

which the zeta potential dropped very close to -30 mV with the addition of Tween resulting in a dispersion that can easily aggregate. Such phenomenon could not be observed for the sample directly tested. However, experiments containing a more concentrated mixture of Laponite RD and bentonite with Tween 20 aggregated very quickly after mixing the components, revealing the instability of such a dispersion.

Table 3.3: Zeta potential of Laponite EP, Laponite RD and their mixture with Tween 20. Note that the results presented below correspond to the average of 3 measurements plus or minus the confidence interval (calculated with a Student law).

Sample	Zeta Potential (mV)	pH
Laponite RD 0.5%	-56.1±1.0	10.3
Laponite EP 0.1%	-53.4±3.5	9.0
Laponite EP 0.25g/L + Tween 0.05%	-48.1±4.4	8.6
Laponite RD 0.25g/L + Tween 0.05%	-39.9±4.9	9.1
Laponite EP 0.25g/L + Tween 0.5%	-34.1±2.1	7.7
Laponite RD 0.25g/L + Tween 0.5%	-25.0±6.7	8.2
Laponite EP 5g/L + Tween 1%	-45.8±1.4	8.3
Laponite RD 5g/L + Tween 1%	-29.8±3.3	10.2

3.4 Discussion

The rheological behavior of Laponite EP 2% and xanthan 2% at rest differs at high strain due to the nature of the different materials and the physical interactions between particles. Xanthan is well known to induce a gel by depletion interaction when in presence of other particles [23,90,91]. When alone in solution, xanthan chains form non-covalent bonds between them or within a chain [26]. Regarding clays, repulsive and attractive electrostatic forces between the laponite disks in pure solution drives their interactions, leading to the formation of an overlapping coin or a house of card structure [72,92]. Despite such differences, the mixture of Laponite EP - bentonite leads to the same rheological behavior as xanthan-bentonite in suspension concentrates. We note that the suspension also consists of crystals of pesticides and anionic surfactants in addition to the coating of Laponite EP, which also contributes to similar rheology.

Furthermore, a “synergistic” effect between Laponite EP and bentonite was observed in SC. Such repercussions between clays of different shapes have already been reported in the literature showing a strengthening of the structure [75,78]. Such interactions can be explained microscopically by the formation of two highly connected network as revealed by HPF Cryo-

SEM images (see figure 3.4). The connection between the two clays may be responsible for the strengthening of the gel in line with Pujala et al. [75]. Furthermore, the difference of size between the two clays (Laponite EP disks are nanometer size whereas bentonite platelets are micrometer size) and the difference of isoelectric point of the edges of the clays may lower the repulsion and promote edge-face attraction. In fact, the isoelectric point (point of zero charge) for the edges of Laponite was reported between pH 10-11 [93]. Therefore, in a Laponite EP - bentonite mixture of pH 9 (<10), the edges of Laponite are positively charged, thus creating attraction between the clay units [94]. This could result in an increase in the number of connections between the two clays compared to each clay alone. The same interactions can still stand in the SCs studied here since the pH is between 8 and 8.5. The higher the number of connections between the sub-units, the stronger the gel at rest and the higher the yield stress. However, this size difference may also favour friction between particles when increasing the shear rate, which explains the higher shear stress found [67].

The coating of Laponite EP also impacts the rheology of the suspension concentrate as compared to the use of Laponite RD for which no yield stress could be found. In addition, a steeper decrease of G' at high strain appears with Laponite RD despite similar rheological behavior within the LVR. Again, this could be due to the brittle rheological behavior of inorganic material that may be dampened to some extent by the coating of Laponite EP. Such coating could be some acetate according to the elemental composition analysis and NMR spectra, or some surfactant which could explain the intense peak found for $-\text{CH}_2-$. Surprisingly, the negative zeta potential of Laponite EP was the same as the one for Laponite RD. This means, firstly, that the coating does not impact the surface charge so any rheological difference between Laponite EP and Laponite RD is unlikely to be due to a change in electrostatics force; and secondly, the molecule used for the coating is negatively charged which again points to acetate. If a surfactant provided the coating of Laponite EP it would have to be anionic. However, some studies revealed that anionic surfactants do not adsorb a lot on the surface of laponite, ruling out such compound as potential coating [95]. Another argument in favour of acetate stands in the lowest pH found when using Laponite EP compared to Laponite RD (see Table 3.3). Additionally, the similarity between the TGA curves of Laponite RD and Laponite EP might suggest that the coating only affects the surface of the clay and not its structure, in contradiction to what Guimarães et al. or González et al. reported. Both authors studied chemically modified surface laponite and noticed an increase of the dehydroxylation temperature of the modified laponite compared to

the raw one [88,96]. Guimarães et al. attributed such effects to a change in structure due to the grafting whereas for González et al. the coating offered a protection of the clay against heat effect by decreasing the heat transmission. Moreover, the DSC curve obtained for Laponite EP in figure 3.6b shows a single broad peak corresponding of the decomposition of the organic material which can be an argument for the use of a small molecule as coating since a bigger molecule would likely show more than one decomposition peak [95].

Furthermore, the presence of dispersant/surfactant in the formulation and its nature (anionic or non-ionic) have a different impact on the gel when Laponite EP or RD is used because of the coating. Non-ionic surfactants can bind to the surface of Laponite RD through hydrogen bonds between their polar head group and either the hydroxyl group of the clay or a water molecule linked to the exchangeable cation [36,95,97,98]; this is less clear for anionic surfactants. Some authors reported a nil adsorption of anionic surfactant in the clay interlayer and only little adsorption on their surface [95,98] whereas other studies showed an adsorption on the edges of bentonite platelets [99]. The zeta potential measurements performed on Laponite EP or RD + Tween 20 decreased as the amount of Tween increased due to the screening of the charges by the non-ionic surfactant [89,98]. We found a lower zeta potential for samples containing Laponite RD compared to Laponite EP upon addition of Tween which could be explained by a smaller adsorption of Tween on Laponite EP compared to RD. This could be the result of the coating which would hinder the adsorption of Tween on the surface of the clay. However, the coating of Laponite may not be applied on its whole surface giving some free areas available for Tween to interact, causing the decrease of zeta potential for Laponite EP with Tween.

3.5 Conclusion

We report the use of Laponite EP, an organically surface coated laponite, in combination with bentonite as an alternative of xanthan for agrochemical product formulation. We managed to obtain similar rheological behavior of suspension concentrates (SCs) with anionic dispersants using Laponite EP-bentonite thickeners as the currently used xanthan-bentonite mix. At rest, both SCs feature a storage modulus G' between 20 and 50Pa and a critical strain γ_C around 1%. The flowing properties revealed a similar Casson yield stress (σ_c) between 2 and 4Pa and an infinite Casson viscosity (η_c) below 70mPa.s. Furthermore, the results of the shelf-life study

with the combination Laponite EP-bentonite conclusively showed good stability of the dispersion with time.

We found a synergistic effect between Laponite EP and bentonite allowing the SCs to fulfill industrial rheological requirements which could not be met by the use of only one clay. Images obtained using High Pressure Freezing (HPF) Cryo-SEM may reveal the existence of two interconnected networks which may explain the cooperation between the clays. The strengthening of the network at rest may be due to the increased number of interactions allowed by the difference in size and charge between Laponite EP and bentonite. Such differences may also be responsible for the increase in shear stress at higher shear rate of the SC.

Such rheological properties could not be reached when using a similar combination of Laponite RD-bentonite meaning that the coating of Laponite EP plays a key role in the rheology of the final formulation. Nevertheless, Laponite EP and Laponite RD showed similar negative zeta potentials implying firstly that the organic compound is negatively charged and secondly that it does not impact the surface charge of the disks. The electrostatic interactions may stay the same in such case. TGA and DSC analysis revealed that the coating concerned only the surface of the clay and did not impact its structure. The coating may hinder the adsorption of Tween 20 (non-ionic surfactant) by the clay giving possibilities to different formulations. The surface coating may correspond to acetate according to chemical analysis.

Additional information on the use of Laponite EP-bentonite as a replacement of xanthan for agrochemical product formulation can be found in a patent [100] presenting the results of the studies performed using non-ionic dispersant millbase or other active ingredients. However, further work is required to define how the surface coating of Laponite EP changes its behavior when in contact with non-ionic surfactant as well as to quantify its interaction with bentonite alone or in SCs.

Acknowledgments

We would like to thank Martin Grossel, an emeritus fellow at the University of Southampton and emeritus student in Christ Church College, University of Oxford, for his precious help in the chemical characterisation of Laponite EP. We also would like to thank Dr. Errin Johnson at the Sir William Dunn School of pathology for performing the high-pressure freezing sample preparation. We also acknowledge Jean-Yves Mugnier at Syngenta who carried out the Cryo-

SEM imaging and whose help for setting the imaging experiment has been very important.

Chapter 4

Mixture design applied to the rheology of clay gel mixtures

We used mixture design to predict rheological parameters, namely the storage and loss modulus G' and G'' and the critical stress σ_c , of mixtures of Laponite EP and bentonite clay. Laponite EP is an organically coated laponite displaying unusual rheological behaviour compared to its unmodified form. We examined the effect of salt (magnesium chloride) and of surfactant (Tween 20) varying the pH between 4 and 9. We found reliable complex models with significant higher order terms showing that the rheological behaviour of the gels was not a function of each single compound, but instead the result of multiple interactions. Such interactions had an antagonistic effect on G' and G'' . Stronger gels were found at low concentrations of magnesium chloride and Tween 20. The gel stability in response to stress increased with the amount of Tween 20, but decreased with magnesium chloride. Such distinct behaviour may be the result of interactions between the platelet charges and the different components, as well as salting-in versus salting out effects. We identified the conditions for which the values of G' were suitable for agrochemical products. The method presented here is a quick and reliable approach to formulate products with targeted rheological properties.

4.1 Introduction

The stability of colloidal particles remains a key challenge for many industries, such as agro-chemical, cosmetic, food industries and so on. Colloids can aggregate, sediment or cream, which may adversely affect the product's properties and ultimately the consumer's experience. Several features can be tailored to deal with such effects; these include the interactions between the colloidal particles, their buoyancy, or the rheological properties of the suspension, which is the topic of this work. We will focus on the visco-elastic properties, of a particle gel; which in this case also stops or slows down sedimentation. The formation of a particle network also hinders the separation into macroscopic phases. A good example of colloidal system is pesticide that are sold under the form of a suspension concentrate. Such a suspension features particles of active ingredients, of about a micrometer in size, dispersed into water in our case. Other ingredients, such as dispersants, thickeners, are added to stabilise the system over time.

In this study, we focus on gels that have the following properties: the storage modulus G' (corresponding to the energy stored by the fluid) has to be larger than the loss modulus G'' (corresponding to the energy lost due to viscous forces) and G' needs to be fairly constant as a function of the oscillation frequency. Furthermore, there may be other rheological requirements to satisfy the consumer, e.g. a shear thinning suspension will facilitate the flow upon application of a strain or stress to a product. Such rheological properties are important for pesticides formulation for the following reasons: to guarantee a homogeneous spread of the active ingredient throughout the product, i.e. avoid phase separation; to insure a good pourability, so that the product can be easily poured into a water tank by the farmer before spraying in the field.

A wide range of materials may be used to form a gel. Among them, inorganic compounds such as clays, are used in industry as *thickeners*. They have the benefit of being safe, cheap and abundant. In this work, we focus on mixtures of bentonite and Laponite EP clays. Laponite EP is a clay developed by BYK. The surface coating of the Laponite has a strong effect on the rheological properties of the clay itself, and the clay maintains its thickening properties at high ionic strengths or in the presence of surfactants [100]. This is also true when used in combination with other components in product formulation. In particular, when mixed with another clay, synergistic effects give additional control over the rheological properties of the suspension, which forms the basis of the current study.

Rheological properties of clays also vary according to their environment. Salt, surfactants, polymers, and the acidity all influence the suspension's rheological response [101–103]. Usually, studies are performed by varying only one parameter at a time. Nevertheless, when formulating a product, a potential large number of components is being used and the rheological properties of the final product are a complex function of the proportion of each component as well as their interactions. Such a response cannot be probed by varying only one parameter at a time. Response Surface Methodology (RSM) allows to determine the effect each component has on the rheological behaviour of the suspension, as well as its interaction with other components or parameters, by varying multiple parameters simultaneously. This methodology has attracted considerable interest in recent years for its use in formulation and process optimization, but also in more academic research [104–106].

In this study, we aim to determine and subsequently predict the effect of varying the ionic strength (using magnesium chloride), the surfactant concentration (Tween 20) and the pH, on the rheological properties of a gel consisting of a mixture of bentonite 20g/L and Laponite EP 5g/L, by means of RSM. These concentrations were found to meet rheological requirements for agrochemical products in presence of pesticides. Therefore, we did not vary the amount of thickener used but rather the concentration of other components. This is to mimic different pesticide formulations. Magnesium chloride was chosen since it has a high ionic strength and it is highly hygroscopic. It can also model some active ingredients made from salt for herbicide application. Tween 20 was selected as it is used to improve the efficacy of herbicides and the wettability of the particles. We study the following rheological parameters: the storage modulus G' , the loss modulus G'' , and the critical stress σ_c corresponding to the end of the linear viscoelastic range (LVR).

This chapter is organized as follows: firstly, we will review the theoretical background on the use of response surface methodology (section 4.2); secondly comes the materials and methods part in section 4.3; thirdly, the results (section 4.4) will be presented and will examine the models obtained for each rheological parameter leading to their discussion in section 4.5. Section 4.6 will provide the conclusion.

4.2 Response surface methodology

4.2.1 Theoretical background of RSM

Response surface methodology is an approach including statistical experimental design (DoE), regression modelling and optimisation method. It allows the identification and fitting of an appropriate response surface model. The response surface is the surface defined by the regression model associating the input variable, experimental factors and/or components, to a response. It provides powerful tools saving industry time and money to quantify behaviour and interactions [107–109]. Unlike traditional methods, in which one parameter is varied at a time, response surface methodology (RSM) involves simultaneously varying different parameters. Contrary to the classical method, RSM enables to probe interactions between variables influencing the behavior of the system. Here, we will briefly introduce the theory behind it.

We assume that the response Y is a function of the input variables ξ_i according to: [108]

$$Y = f(\xi_1, \xi_2, \dots, \xi_k) + \epsilon, \quad (4.1)$$

where f is a polynomial function of the input parameters ξ_i and ϵ the error or residue between the true response Y and the one given by f . The error accounts for experimental noise. The function is then determined using different experimental designs depending on the aim of the study or the complexity of the interactions between the input variables. A general model for a polynomial function of degree 1 can be written as:

$$Y = b_0 + \sum_i b_i x_i + \epsilon, \quad (4.2)$$

where b_0 is the mean of the responses, b_i the coefficients of the model and x_i the input variables. The model described by equation 4.2 can feature higher order terms to take curvature of the response into account. The higher the degree of the polynomial the more interactions between components take place in the system driving the response away from linearity.

In RSM, variables are independent factors, of which the coefficients represent the slope of the response: a positive coefficient implies an increase in the response, whereas a negative coefficient implies a decrease in the response, as a function of a particular variable. If coefficients

of second degree or higher are significant, they capture the curvature of the model showing either synergistic or antagonistic effects. Note that the effect of each variable cannot be interpreted separately if higher order terms are significant. In that case, the focus is only on the interactions between the input variables.

RSM requires that input parameters over the applied range have a significant impact on the response, which requires an initial study to define such relevant parameters. This may be based on results from literature, industrial constraints, or previously performed experiments.

The coefficients are determined by choosing a design that gives the experimental conditions at which tests must be performed depending on the aims of the project and the complexity of the model. The simplest design, called screening design, used in the preliminary phase, is to screen for the dominant variables; typically one wants to reduce the number of variables to around 2-4. More advanced designs typically used in literature are the Box-Behnken or central composite designs [110,111]. After collecting responses from each experiment, a polynomial model is fitted to the data and the coefficients are determined using the least squares method.

4.2.2 RSM in practice

Once the input variables have been found, the range for each variable needs to be determined, which is based on the required response. For applications such as process improvement, the methodology of steepest ascent/descent may be used to find a new range for each variable leading to the maximisation/minimisation of the response [108]. Irrespective of the type of model, response surface methodology will need the experiments to be run in random order at different set values, called levels, within the range of each variable. The range spanned by all variables sets the experimental domain. Models differ by the location of the experimental points (varying therefore the shape of the experimental domain), the number of levels required for each variable, and the number of experiments required.

The range of each variable needs to be coded, i.e. vary between -1 and 1 and centered around 0 to be able to compare effects; this is done as follows:

$$x = (X - \frac{X_{high} + X_{low}}{2}) / (\frac{X_{high} - X_{low}}{2}), \quad (4.3)$$

where x is the reduced variable, based on the experimental X which varies between X_{low} and X_{high} .

4.2.3 The case of mixture designs

As stated previously, RSM is used to model and/or predict a response based on independent factors. However for many applications, in e.g. food science, chemistry or product formulation, a response will depend on components (ingredients and reagents for example) called mixture variables which are expressed in mol/mass ratio. Such a system features a dependency relationship between the mixture variables, since the sum of their proportions is equal to 1: this is called mixture design. Additionally, mixture variables can be constrained by an upper or lower threshold depending on the system or industrial feasibility. In addition to mixture compounds, independent external factors, called process variables, such as temperature or pH may also influence the response.

A model for mixture design is shown by equation 4.4 for a polynomial of degree 1, [112,113]:

$$Y = \sum_i a_i^* x_i + \epsilon, \quad (4.4)$$

where $a_i^* = b_0 + b_i$.

In a mixture model, mixture variables are not coded as they range between 0 and 1. However, when using process factors combined with mixture components, the process factors need to be coded following equation 4.3.

The mixture design model (equation 4.4), although similar to equation 4.2, does not include a constant term as it would lead to an overparameterised model. Overparameterised models lead to a non-unique solution for the same response. Furthermore, coefficients of the first order terms, also called linear blending terms, represent the response when only one component is applied at 100%. It is possible to estimate coefficients for higher order terms (up to the 4th-5th order) although they are often not significant and may correspond to noise. If a process variable is included in the model, coefficients in front of the interaction between a mixture component and the process factor show the influence of the process variable on the blending behaviour.

The model used in this study is described by equation 4.5 where:

- the first term corresponds to the linear blending term,
- the second term is the second order binary blending term,
- the third term is the third order binary blending term which models more complex binary blending behavior,
- the fourth term is the fourth order ternary term,
- the fifth term of the model represents the effect of the pH on the blending behavior [113,114].

$$Y = \sum_{i=1}^3 \beta_i X_i + \sum_{i=1, i \neq j}^3 \beta_{ij} X_i X_j + \sum_{i=1, i \neq j}^3 \delta_{ij} X_i X_j (X_i - X_j) + \sum_{i=1, i \neq j \neq k}^3 \beta_{ijk} X_i^2 X_j X_k + \sum_{i=1}^3 \beta_{pH,i} X_i pH + \epsilon. \quad (4.5)$$

Here, X_i , X_j , X_k refers to the concentration of MgCl_2 , Tween or water respectively, and β_{ijk} and δ_{ij} are the coefficients.

The goal of this study is to probe the rheological response of clay gels in order to predict them. This is done by using an I-optimal design to generate the experimental conditions in the experimental matrix [107]. Such an I-optimal design is the most appropriate design for such a study since it aims at minimizing the average prediction variance. It allows more experimental conditions to be taken within the experimental model thereby improving the prediction.

4.2.4 Model validation

Several criteria are used to define a model and assess its quality. Firstly, coefficients of the model have to be significant i.e. different to 0, as indicated by a p.value below 0.05 (for a risk α set at 5%). The quality of the model has to be evaluated before and after removing coefficients using the other parameters. Terms with non-significant coefficients that did not contribute to a better quality of the model are removed, unless they improve the model, or if a higher order interaction including the variable is significant.

Secondly, models are compared using the root mean square error RMSE, the Akaike Information Criterion value AICc and the Bayesian Information Criterion value BIC [115]. The root mean square error indicates to what extent the experimental response cannot be explained by

the model. The AICc and the BIC are linked to the likelihood function that has to be maximised when determining the parameters β_i (equation 4.5). Specifically, the BIC enables not to overfit a model. Hence, lower RMSE, AICc and BIC indicate a better model [116].

Thirdly, the lack of fit is performed to determine if the model is adequate. It compares the variance of the experimental error determined using repetition of experiments, to the variance of the residues using an F test. If there is a lack of fit (i.e. $p\text{-value} < 0.05$), the model should be changed.

Fourthly, the predictive capability of the model are appraised using the prediction error sum of squares PRESS and used in the calculation of R^2_{press} . PRESS is a cross validation procedure [113]. Models with higher R^2_{press} should be selected.

Lastly, models can be validated by performing additional experiments with random conditions within the experimental domain but preferentially not too close to the points used to establish the model [114]. The experimental results are compared with the predicted ones. The closer the values, the better the model. Moreover, the higher the number of validating points, the more robust the validation is. Checking the model's accuracy is done by fitting a linear function to the curve of the experimental response versus the predicted response. Such a linear fit for a good model has a slope of 1 and an intercept of 0.

4.3 Materials and Methods

4.3.1 Material used and preparation of the gels

Laponite EP, a Laponite (chemical formula: $\text{Na}_{0.7}^+[(\text{SiO}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$) coated with organic compounds and manufactured by BYK was used in this study. The bentonite used is Bentopharm B20 (chemical composition $\text{Na}_{0.33}[(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{O}(\text{OH}))_2(\text{SiO}_2)_4]$) provided by Wilfrid Smith. Pre-gels of Laponite EP and Bentopharm were made using the powder directly received from the manufacturer without any further purification. They contained 2% Laponite EP or 10% Bentopharm B20 in water and were made using an IKA Ultra Turrax digital t25 high shear mixer. The shear rate was increased gradually while adding bentonite so as to keep a vortex. Since the rheological properties of a bentonite or Laponite EP pre-gel vary with time due to swelling, chemical and physical restructuring, and ageing [117]; we decided to prepare the

pre-gels a few weeks before performing this study to keep their rheological properties constant during the duration of the whole study (two weeks). Magnesium chloride anhydrous >99% was bought from Sigma-Aldrich and used as salt. Tween 20 was bought from Fisher Scientific and was used as surfactant. Two stock solutions were made to adjust the pH: 1M acetic acid and 0.5M sodium hydroxide NaOH. Each gel was prepared as follow: 1) addition of a small amount of water 2) addition of Laponite EP 2% gel, 3) addition of bentonite 10% gel. When required: 4) addition of Tween 20 and 5) addition of MgCl_2 . The amount of Laponite EP and Bentopharm added corresponded to a final concentration of 5g/L and 20g/L respectively. This is to obtain our reference thickening system. Tween 20 and MgCl_2 were added to reach the final desired concentration, as shown by table 2 in the Appendix. Then the high shear mixer was used to homogenise the gel. The initial pH was measured using a Five Easy plus pH meter from Mettler Toledo and adjusted afterwards. The natural pH of a bare Laponite EP 5g/L + Bentonite 20g/L mixture is around 9.

4.3.2 Determination of the variables and the experimental domain used for RSM

In this study, we focused on the prediction of the storage modulus G' , the loss modulus G'' and the critical stress σ_c of a Laponite EP-bentonite network at rest when varying environmental conditions. We identified the ionic strength, the amount of surfactant and the pH as key parameters. The ionic strength and surfactant concentration were adjusted by varying the amount of MgCl_2 and Tween 20 (non-ionic surfactant) respectively.

The amount of Laponite EP and bentonite was kept at a concentration of 5g/L and 20g/L, so the mixture design used 3 components (MgCl_2 , Tween 20 and water) and a process factor (the pH). The sum of the mass fraction of the 3 mixture components omitting Laponite EP and bentonite was recalculated so that their sum was equal to 1. Some constraints on the concentration of MgCl_2 and Tween 20 were set such that the rheological responses stays similar to those of commercial products. Therefore, the maximum amount of surfactant and salt were set at 20% and 5% respectively corresponding to an ionic strength of 1.7g/L. The pH was varied from 4 to 9. The water content could vary between 65% to 100% wt. The model considered was defined in part 4.2.3 (equation 4.5) to account for complex interactions between the mixture components and between the mixture components and the process factor.

We used JMP, SAS software version 16.0 to generate the experimental matrix shown in table 2 in the Appendix and also in figure 4.1, to establish and analyse the models. Nineteen experimental conditions spread over the domain, were carried out. Five of them were repeated to be able to calculate the pure error and consequently the lack of fit of the model. Each testing condition was performed at a certain pH (4, 6.5, 9) as shown by the respective coded values -1, 0, 1 in table 2 in the Appendix.

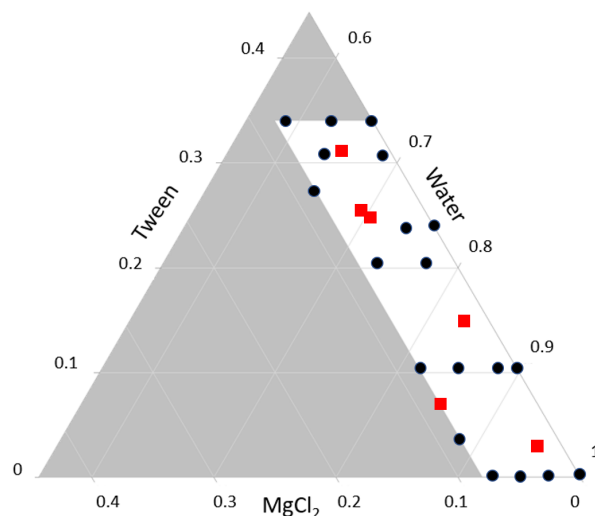


Figure 4.1: Location of testing conditions (black dots) and validating points (red squares) within the experimental domain. Note that each point is associated to a certain pH as defined by the Matrix Design, figure 2 in the Appendix.

4.3.3 Analysis of the models

To check the models, six additional samples were randomly selected within the experimental domain as shown in figure 4.1 and table 4.1. The experimental values were compared to the ones predicted by the models and a fit of the response versus its prediction was evaluated by focusing on the slope and intercept of that fit as described in part 4.2.4. RMSE, AICc and BIC were also used as indicator of a model quality (see 4.2.4). Each PRESS R^2 was calculated by omitting the mean to be consistent with the model of mixture design described in section 4.2.3.

Table 4.1: Experimental conditions of samples used to check the models.

	MgCl ₂	Tween 20	Water	pH
1	0.05	0.25	0.70	-0.6
2	0.02	0.03	0.95	-0.83
3	0.08	0.07	0.85	-0.6
4	0.05	0.25	0.70	0.6
5	0.04	0.31	0.65	1
6	0.02	0.15	0.83	0.2

Note: pH is given as coded value

4.3.4 Rheological procedure and method to determine rheological responses

Rheological tests were performed with an AR-G2 stress controlled rheometer from TA Instruments with a DIN concentric cylinder. The rheological procedure comprised the following tests: 1) a pre-shear performed for 60s at 600s^{-1} , 2) a time sweep at 1Hz and 0.3Pa for about 1.25 hours to allow gels to reach equilibrium, 3) a stress oscillatory test at 1Hz was used to define the linear viscoelastic range (LVR) corresponding to the range of stresses within which G' and G'' are independent of the input stress. Therefore such stress does not significantly impact the structure of the gel. The oscillation frequency of 1Hz was chosen as it corresponds to the standard frequency used by an agrochemical company. Oscillatory tests at 1Hz are performed industrially to assess the characteristics of a formulation. The stress oscillatory test was stopped right after the end of the LVR to avoid damaging the gel. 4) Another time sweep similar to step 2) was performed for 5 minutes to check that the gel was still in the same equilibrium state.

The chemical stability of the formulations was reached within 1.25 hours after preparation. Their rheological properties still evolve after that time, although more gradually, and depends on the amount of Tween or MgCl₂, or the pH [118]. Therefore, to keep some consistency in the determination of the rheology of the sample, the test were performed on fresh gels, i.e. 1.25 hours after preparation. Furthermore, the oscillatory measurement lasted for a very short time during which rheological evolution of the gels are not significant. The oscillatory test allowed us to measure the storage modulus G' , the loss modulus G'' , and the critical stress σ_c . The latter one corresponds to the stress at which the LVR ends and was determined using the Cumulative Sum (CUSUM) method included in the software JMP. Only the lower CUSUM curve was used as shown by figure 4.2 to probe the negative shift of the curve. The lower CUSUM curve is calculated according to equation 4.6 below:

$$C_i^- = \min(0, (x_i - T) + K + C_{i-1}^-), \quad (4.6)$$

where C_i^- and C_{i-1}^- are the value of the CUSUM curve for point i and $i-1$ respectively. The target T is the mean and K called the reference value, is equal to half the standard deviation (SD). A deviation of the curve appears when the distance between the modulus G and the target is greater than $SD/2$ (see figure 4.2). This method probes the variation of the modulus G consistently between the samples. σ_c was taken as the last point above the lowest limit (red curve on figure 4.2 equals to $5 \times SD$).

G' and G'' are obtained by averaging over all the storage and loss moduli within the LVR. The first point belonging to the LVR corresponds to the first point having a torque above $5\mu\text{N.m}$ (value corresponding to the limit of the instrument).

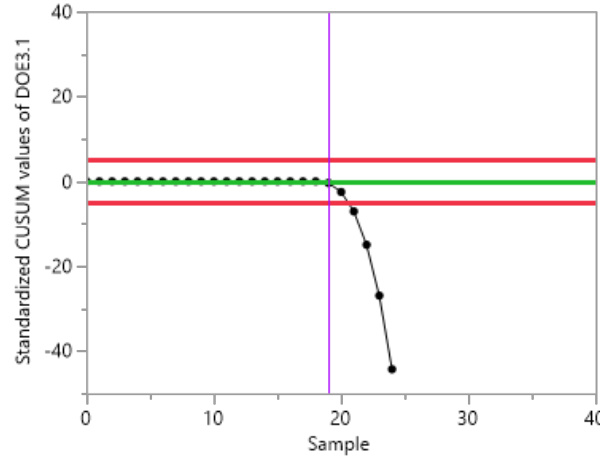


Figure 4.2: CUSUM plot based on G' variation during oscillatory test (at 1Hz)

4.4 Results

4.4.1 Models obtained for G' , G'' , σ_c

Complex models with significant 4th order terms were found for every rheological parameter, see table 3 in the Appendix. This reveals the existence of complex interactions between the components, driving the response away from linearity. The lack of fit and R_{PRESS}^2 used to assess the quality of each model are shown in table 4.2. All coefficients were significant at 5% for the models of G' and G'' . For the critical stress σ_c , non-significant coefficients were kept to

maintain the hierarchy of the model featuring significant higher order term. As shown in table 4.2, no lack of fit was found for any models with all p.value >0.05 . The PRESS R^2 found for G' , G'' and σ_c were 0.92, 0.92 and 0.95 respectively, meaning that 92% or 95% of the potential future values can be predicted. In the following sections, the models will be analysed separately and assessed using validation points as described in part 4.3.3.

Table 4.2: Lack of fit and R^2_{PRESS} obtained for G' , G'' and σ_c after oscillatory tests performed at 1Hz.

Model	G'	G''	critical stress
Lack of fit	0.24	0.21	0.79
R^2_{PRESS}	0.92	0.92	0.95

4.4.2 Analysis of the model obtained for the storage modulus G'

The model found for G' , (table 3 in the Appendix) leads to response surface (contours) plots shown in figure 4.3 at pH 4, 6.5 and 9. The parts of the graphs highlighted by white dots correspond to formulations that comply with industrial requirements, i.e. for agrochemical products, G' typically ranges between 20 and 50Pa. This is to insure that the product will be stable for a long enough time without being too strong to be handled. (private communication Carl Formstone, 2018).

As shown by the plots, the pH has a significant effect on the blending behaviour with a lower pH favouring higher values of G' and hence stronger gels. The isoelectric point of bentonite is around 7 [119], and around 10.5 for raw Laponite [93]. Therefore, at pH 4, both bentonite and Laponite feature positively charged edges. These positive charges can interact attractively with the negative charges present at the surface of the clay particles. Furthermore, the electrical double layer, at such pH and in presence of salt, is contracted. This decreases the repulsion between particles to allow them to get closer to each other [39]. These two phenomena lead to a stronger gel. Mixture components have the strongest effect on G' , causing greater variation in the response. In fact, stronger gels, up to 50Pa were found at low concentrations of $MgCl_2$ and Tween 20. This is due to complex antagonistic effects between the components such as the interaction $MgCl_2$ *Tween or $MgCl_2$ *water for instance. Such antagonistic effects will tend to decrease G' as we increase the concentration of $MgCl_2$ and Tween 20.

The curves of measured G' versus predicted G' , figure 4.4, are used to validate the model.

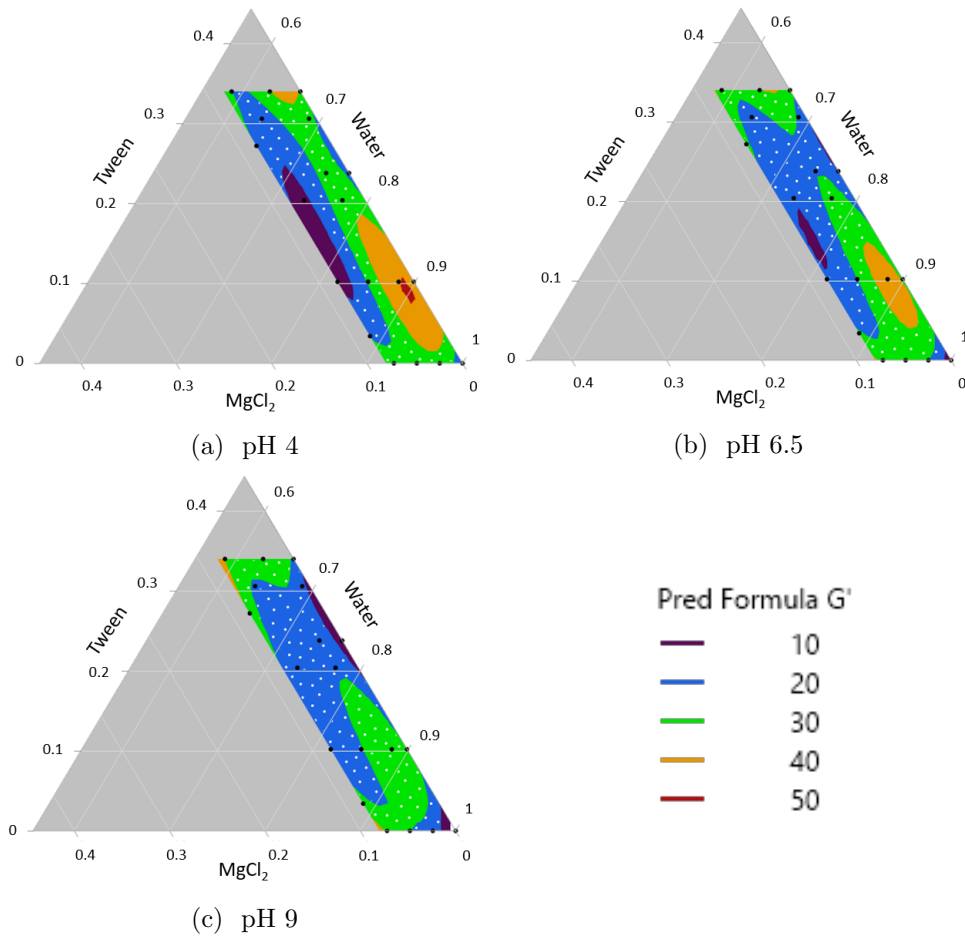


Figure 4.3: G' responses according to levels of MgCl_2 , Tween, water and pH for oscillations performed at 1Hz.

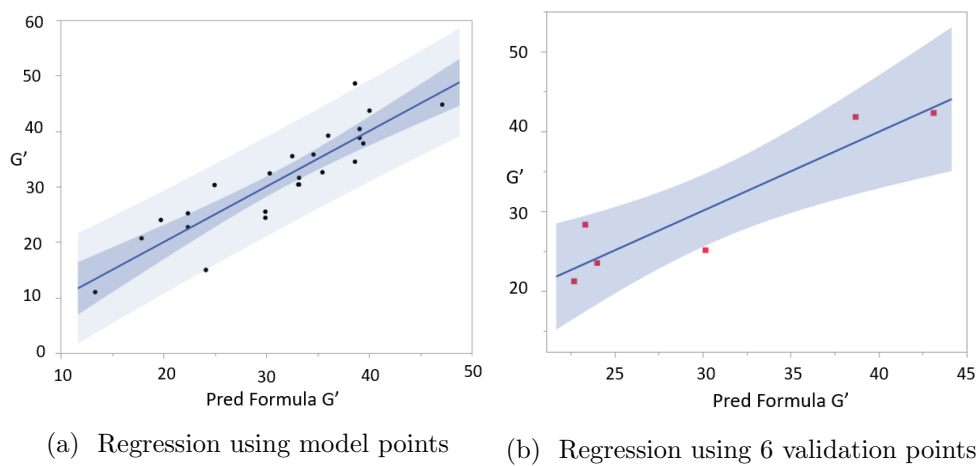


Figure 4.4: Model validation using experimental G' (Y axis) versus predicted G' from the model curve (X axis)

The inner confidence interval is associated to the fit whereas the outer one represents the prediction interval. The fitting of the curve figure 4.4b features a non significant intercept and a

significant slope estimated at 0.99 ± 0.6 . Thus, the model can predict values that are within the experimental domain. However, we also tried to predict the response of points, that were obtained for previous studies, featuring similar experimental conditions. Such approach revealed that an extra point at the edge of the experimental domain (MgCl₂ 0%, Tween 20 0%, pH 4), represented by the black cross in figure 4.4b) was not predicted well by the model. This may be due to additional interactions present at the edges which are not captured by the model. Hence, care must be taken when using the model close to more extreme conditions.

4.4.3 Model analysis for G''

The second parameter of interest is the loss modulus G'' . Its ternary plots at different pH 4, 6.5 and 9 are given in figure 4.5 representing the model described in table 3 in the Appendix. Again the model shows the complexity of the interactions between the constituents causing the curvature. Similarly to G' , the pH has a significant effect on G'' with highest values found at lowest pH. For neutral to alkaline pH, antagonistic effects between the components prevent a rise of G'' at high amount of salt and surfactant, leading to higher values of G'' at low concentration of MgCl₂ and relatively low amount of Tween 20. Nevertheless, at low pH, high values of G'' can also be found at high amount of MgCl₂ irrespective of the amount of Tween 20. Under those conditions, G' decreased; energy loss is promoted while disfavouring the storage of energy.

Fitting the curve of the measured G'' vs predicted G'' shows a significant slope of 1.6 ± 1 and a non significant intercept. The estimate is rather high but associated with a high uncertainty due to the low number of validating points. Hence, the model is capable of predicting G'' reasonably well. However, some limitations of the model may persist perhaps due to the influence of the pH.

4.4.4 Analysis of the model for the critical stress σ_c

Most blends feature a critical stress between 0.3 and 1Pa as shown by figure 4.7 representing the response surface plots for σ_c . This shows the robustness of the formulations, i.e. a slight change in the concentration of MgCl₂ or Tween, or in the pH does not affect the response drastically for most blends. The lowest values for neutral to alkaline pH were found at a high concentration of MgCl₂ and a low concentration of Tween 20. The larger the proportion of Tween 20, the higher

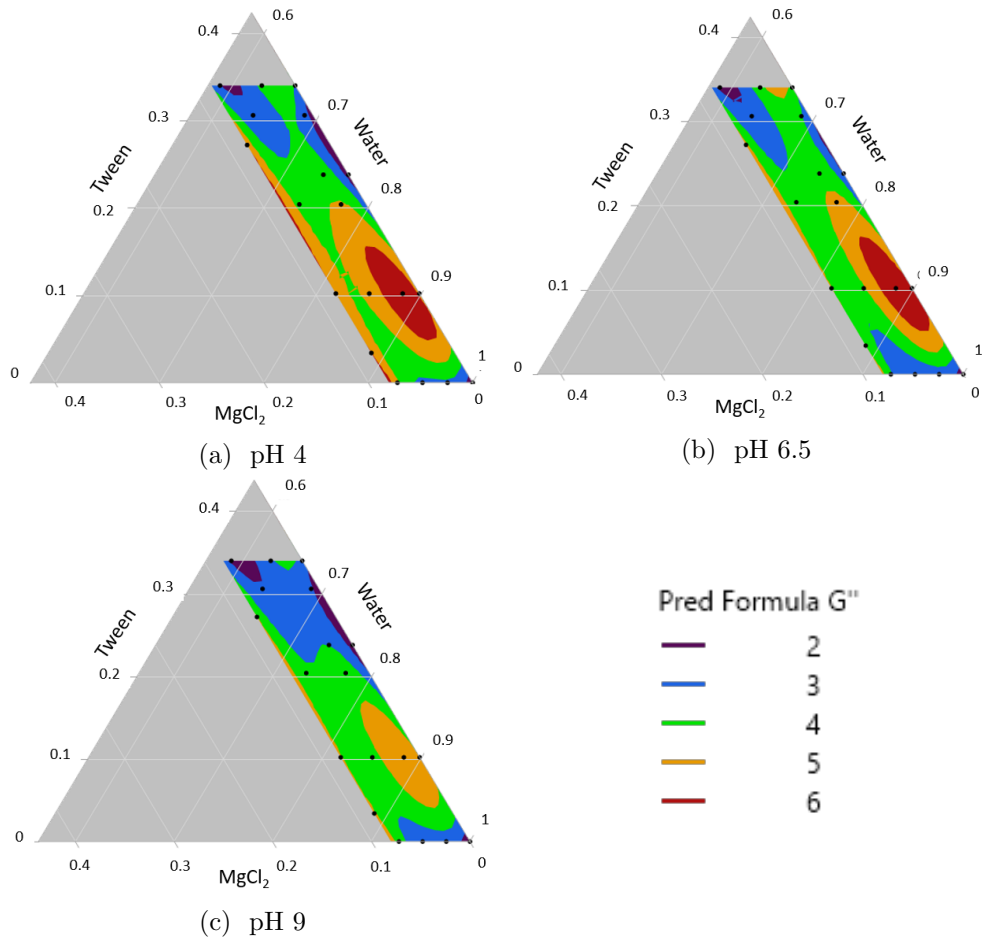


Figure 4.5: G'' responses, obtained at 1Hz, according to levels of $MgCl_2$, Tween, water and pH

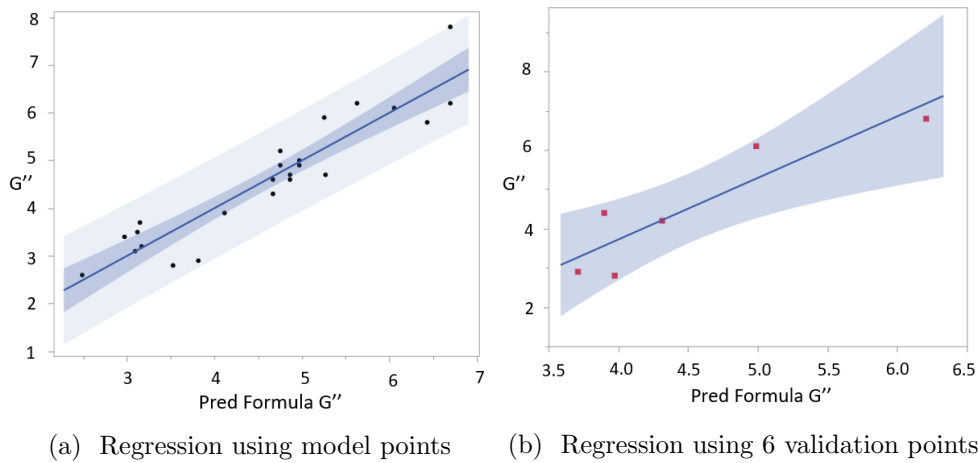


Figure 4.6: Model validation using experimental G'' (Y axis) versus predicted G'' from the model curve (X axis)

σ_c implying that Tween 20 favours the stability of the gel requiring therefore a higher amount of stress for the gel to deform. On the opposite side, $MgCl_2$ seems to lower the critical stress making the gel more sensitive to stress. Although, the pH of the blend has a small impact on

the values of the critical stress, higher values were found at pH 9.

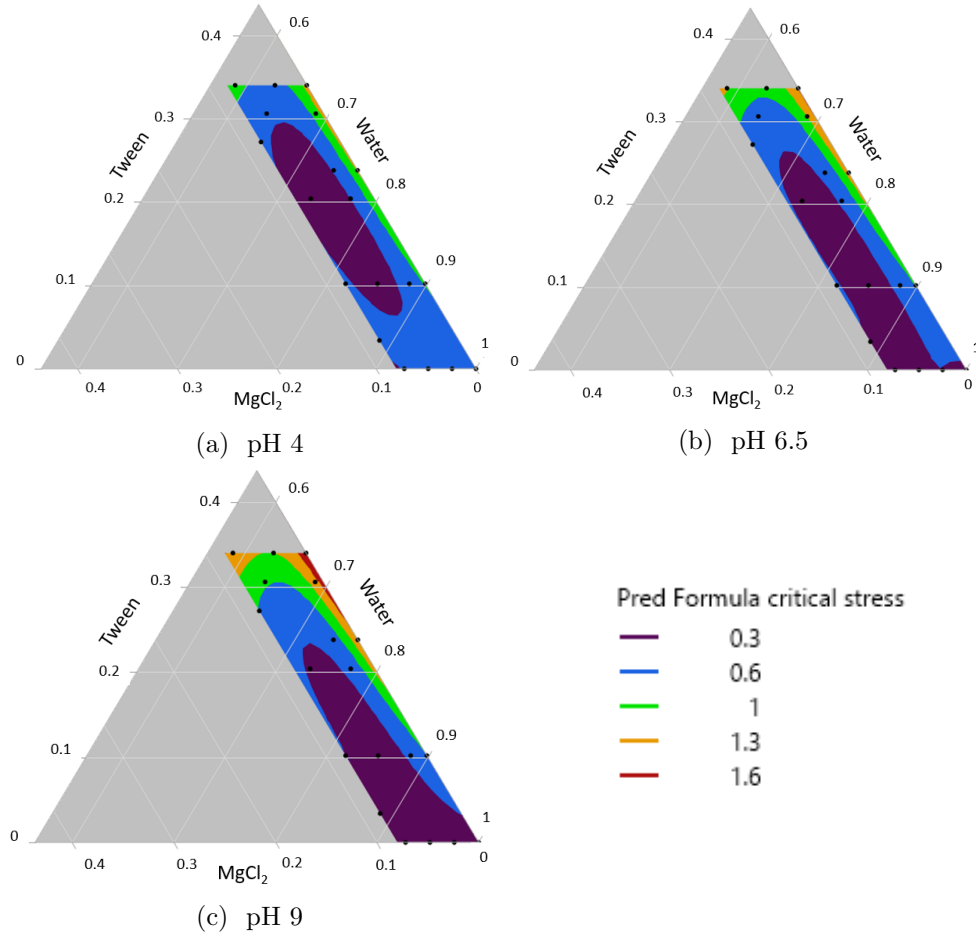


Figure 4.7: σ_c responses, obtained at 1Hz, according to levels of MgCl₂, Tween, water and pH

Figure 4.8 shows the measured σ_c versus predicted σ_c . The critical stress of formulation indicated by the I-optimal design (figure 4.8a) was successfully predicted by the model. However, the linear regression performed on the validating conditions shows a non-significant slope ranging from -1.5 to 0.3, i.e. non-significantly different to 0, and a significant intercept from 0.3 to 1.6. This intercept represents the mean of the response of the validating points. Hence, the model is not capable of accurately predicting the validation samples. This may be caused by the validation points with σ_c falling in a small interval, thus making the values more difficult to differentiate. In fact, different samples among the validating points show a critical stress that are closer to each other than the ones found for some replicates. In other words, the experimental error, i.e. the noise, is higher than the difference of σ_c between the points used for the validation. Under such conditions, the model is not able to differentiate the points. Further samples for the validation are needed to give a wider range of σ_c .

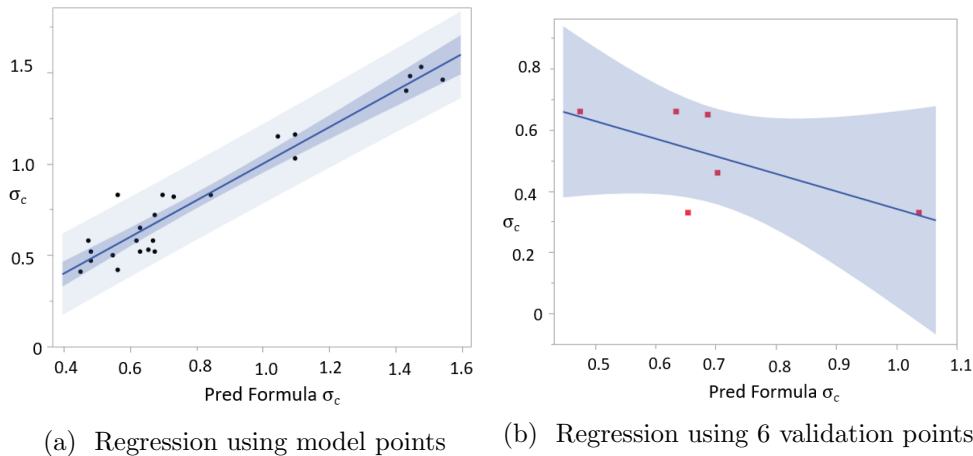


Figure 4.8: Validation of the model using the critical stress versus predicted critical stress curve

4.5 Discussion

As explained in section 4.2, RSM highlights interactions that have a significant impact on the response. For simple models, it can describe the impact such input has on a specific response. It should also be possible to qualify if interactions between different parameters are synergistic or antagonistic. However, for complex models, as is the case here, the response depends on the combination of all terms and the interpretation of each of them becomes more difficult. Surface plots still give an indication of the variation of the response according to the level of the input parameters without analysing the model in detail. They revealed that Tween 20, magnesium chloride, pH and their interactions have an impact on rheological parameters of the gel at rest.

There are few studies in the literature focusing on the mixtures of clays and the subsequent effect on their rheological properties [75–78]. Most often, the clays mixed are of the same size but different shapes. Nonetheless, Pujala et al. [75] mixed montmorillonite and laponite RD at different ratios. They suggested that a homogeneous network was formed when mixing both clays at similar concentration whereas the network is more heterogeneous when one clay predominates. Based on their work, it may be expected that the two clays studied here cooperate to form a single network. This is also consistent with the fact that particles of both clays have similar chemical composition and shape. Furthermore, they feature negatively charged surface due to isomorphous substitution [36], and their edges are either positively charged at pH below their isoelectric points or negatively charged at pH above their isoelectric points, as demonstrated for bentonite [119]. For bentonite, this means pH below or above ≈ 7 and for Laponite below

or above ≈ 10.5 . Consequently, bentonite features positive edges between pH 4-7 and negative edges between pH 7-9. Laponite has positively charged edges in the range of pH used in this study. They are also both swelling clays interacting via edge-edge and edge-face interactions of the platelets [68]. Alternatively, the two clays may form two different networks interacting with each other. In such case, anything affecting one of the networks may impact the other as well, resulting in a change in the whole structure.

The impact of salt alone on bentonite and laponite based gels has been the topic of many studies which will enable us to interpret our results in that light using the response surface plots. We will therefore focus on the effect of salt on our experiments.

The type of salt has an impact on the rheological behaviour of clay. Van Olphen observed that a small addition of NaCl on an initially flocculated bentonite gel lead to a weakening of the structure [92]. This was due to the contraction of the double layer resulting in deflocculation. A further increase in the amount of salt triggered flocculation of the platelets and therefore strengthened the gel.

Rand et al. have noticed the same behaviour as Van Olphen on the addition of NaCl on Na-bentonite [120]. However, they favour the idea of the formation of ribbons due to edge-edge interactions between the platelets. Their study did not prove the existence of edge-face interactions for pH ranging from 4 to 11 with addition of NaCl. For a further discussion, see the review by [36].

Regarding Laponite, studies, mainly performed with NaCl, have shown that the addition of salt increased the rate of aggregation of the disks. This is due to the reduction of the energy barrier due to the screening of the charge of the disks [94, 121]. However, these studies were performed on Laponite RD whereas the present study uses a surface coated Laponite. According to Jonsson et al., Van der Waals forces predominate in a Laponite solution with divalent ions leading to a strong attraction [72].

Effect of magnesium chloride on G'

The ternary plots for G' , figure 4.3, show that at low amount of Tween 20 and acidic to neutral pH, the addition of a small amount of salt leads to a strong gel, whereas the addition of a higher amount of salt results in the weakening of the structure. Similar behaviour was observed by Ö Isik Ece et al. who studied the impact of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ on the viscosity of a 6% bentonite

gel. They reported that at low concentration of MgCl_2 , interactions between the platelets were favoured leading to a stronger structure, whereas as the concentration increased, MgCl_2 weakened the gel. This results from the screening of the positive charges at the edges of the platelets by Cl^- and the exchange of interstitial cation Na^+ with Mg^{2+} [103].

Regarding Laponite gels, a strengthening of the structure reflected by an increase of G' could be expected with increasing MgCl_2 . In fact, Mourchid et al. found that the increase of the concentration of MgCl_2 due to Laponite dissolving over time induced the transition from a solution to a gel [122]. They explained this behaviour by the attractive interactions induced by the divalent salt. However, their study was performed on Laponite RD, whereas we use an organically coated Laponite to which we also added a non-ionic surfactant. The presence of the coating protects Laponite against dissolution at low pH during the duration of the experiment. In fact, the pH at 4 stayed constant during the rheological measurement and up to 24 hours. The coating as well as Tween 20 have an effect on the resulting behaviour of clay upon addition of MgCl_2 due to significant interactions between the mixture components.

Effect of magnesium chloride on G''

G'' roughly follows the same trend as G' upon addition of MgCl_2 i.e. an increase of the storage energy is accompanied by an increase in the loss energy. The loss factor $\tan(\delta)$ may be constant in that region. More interactions between the platelets at low salt, may lead to more friction between the platelets, which leads to an increase in the dissipation of energy. However, at pH 4 and high amount of salt, G'' increases whereas G' displays low values. This lead to an increase of $\tan(\delta)$. We therefore think that in this region, although a gel was still formed, it may be less stable with perhaps different interactions between the platelets promoting energy loss.

Effect of magnesium chloride on σ_c

As previously shown in figure 4.7, Tween 20 somewhat increases σ_c promoting therefore the stability of the gel, whereas the addition of magnesium chloride weakens it to a lesser degree. This may be due to complex interactions between MgCl_2 and Tween 20. According to Morini et al., divalent ions like Mg^{2+} have a salting in effect on polyoxyethylated surfactants due to their interactions with the ether groups [123]. However, Cl^- has a salting out effect hence reducing the hydration of the non-ionic surfactant. They also found that the concentration of salt (NaCl in their study) has an impact on the interaction with Tween 20. This may lead to competition between Tween 20 and the clay for Mg^{2+} and Cl^- . Adding Tween 20 may decrease the amount of magnesium or chlorine screening the charge of the clay, making the structure more stable.

The concentration of Tween 20 (cmc of 60mg/L) also impacts the relaxation time, maybe due to the formation of micelles as well as their shape, as shown by a frequency sweep carried out on a surfactant-based solution by [124].

4.6 Conclusion

The goal of this study was to use response surface methodology to model and predict some rheological properties of a mixed clay gel. Complex models were determined for the storage modulus G' , the loss modulus G'' and the critical stress σ_c revealing multiple interactions between the components of the gel. Models for G' and G'' showed a good agreement between the experimental values and the predicted ones despite some inaccuracies at extreme points of the experimental domain. The model for the critical stress σ_c showed some limitations in predicting the validation points, for which the difference in their σ_c is of the same level as the noise. Therefore, additional validating points yielding to a broader variety of responses may be required.

Overall, we found that G' and G'' were higher at low concentration of Tween and MgCl_2 . σ_c was enhanced by the addition of Tween at neutral or alkaline pH. The pH was found to have a significant impact on all responses and particularly on G'' . Interactions between constituents were found to significantly impact G' and G'' . The components usually display an antagonistic effect resulting in the highest values for G' and G'' at low concentration of Tween or salt. Such interactions can be due to either the screening of the charge at the surface of the clay units or some salting-in and salting-out effect of Mg^{2+} (salting-in), Cl^- or OH^- (salting-out) on Tween 20 or the clay itself. All these properties affect the hydration of the components and their typical separation, impacting rheological properties.

This study has clear industrial relevance: the methodology presented allows to find a targeted formulation for a product, illustrated here for the salt and surfactant concentration, and pH, that lead to the desired rheological properties. Suitable conditions are highlighted by the white dots for G' meeting agrochemical requirements in figure 4.3.

The presented methodology may also have general relevance in the field of rheology to e.g. determine the yield stress. Traditionally, a creep test is used to determine the yield stress of a fluid, but such tests are time-consuming as they need to be repeated at different stress values for

a single sample. The here developed model, capable of predicting the yield stress as a function of sample composition, may be useful.

Lastly, the work presents the richness in behaviour of clay suspensions, and in particular mixtures of inorganic clays, where we have presented rheological insights. A next natural step would be an elucidation of their microscopic structure.

Acknowledgments

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Chapter 5

Effect of ageing on the rheology of clay gels

We characterised the ageing of bentonite 10% wt., attapulgite 10% wt. and their mixture attapulgite 5% and bentonite 5% using rheology. We combined time (60 days) with high temperature (50°C) to accelerate the ageing of the gel at rest. We used an oscillatory test, from which we got the storage modulus G' and the critical stress σ_c , and a creep test to get the compliance $J(t)$. The compliance was fitted with a Burgers model and we focused on the evolution of G_0 , G_1 , η_0 , η_1 corresponding to the spring and dashpot constants of the Maxwell and Kelvin-Voigt element respectively. The results showed that the gels became stronger and more viscous with time with an increase of G' , G_0 , G_1 and η_1 . Surprisingly, the ageing of the mixture of the clay followed the same rheological trend as the pure bentonite gel and the evolution of G' , σ_c , G_0 , G_1 , could successfully be fitted with a Leong model. Some synergistic effect was also to be seen for some parameters, such as G' meaning that the blend led to a stronger gel. Furthermore, these two gels got more stable during the ageing (σ_c increases), and displayed similar values of critical stress, thus the gels were as stable. Attapulgite displayed some peculiarities: G' , G_0 and G_1 increased slowly at the beginning of the ageing and the critical stress stayed constant. Therefore, the ageing of attapulgite was delayed compared to the other two. Furthermore, ageing did not affect the amount of energy needed to disrupt the attapulgite gel as revealed by the evolution of the cohesive energy.

5.1 Introduction

Clay is widely used in many industries for their broad range of properties. They can be used as active ingredient, for instance in cosmetics, or more broadly for their thickening properties. They also have the benefit of being cheap, abundant and safe. They are made of micro-crystalline particles called “clay mineral” [34]. Note that in this study the term clay will be used widely to also refer to the clay mineral, i.e. hydrated phyllosilicates. There exist lots of different clays according to their interlayer structure, their size and so on. In this study, we focus on two naturally occurring clays: attapulgite and bentonite.

Attapulgite, also called palygorskite, chemical formula: $(OH_2)_4(OH_2)Mg_5Si_8O_{20}4H_2O$ [43], consists of 2 tetrahedral sheets enclosing a discontinuous octahedral sheet forming a ribbon. Ribbons are linked to each other by inversion of the tetrahedra [44, 125] and extend in the X-axis forming channels. Such a crystalline organisation and breaking of the structure gives rise to a needle shape with a high aspect ratio: $1\text{ }\mu\text{m}$ length $\times$ $0.01\text{ }\mu\text{m}$ width.

Bentonite, mainly constituted of montmorillonite clay mineral with chemical formula: $Na_{0.33}[(Al_{1.67}, Mg_{0.33})(O(OH))_2(SiO_2)_4]$, is made of two planned layers of tetrahedra enclosing an octahedral layer. It has a form of platelets of about one micrometer in length and nanometer width.

Both clays have a negatively charged surface due to isomorphous substitution, i.e. some atoms are replaced by other atoms of different valence giving rise to a charge deficiency. However, the charge displayed by the edges of the clays is less certain. Edges can be positively or negatively charged depending on the pH of the solution [119, 126]. The point of zero charge is about 7 for bentonite and between 4-4.5 for attapulgite. Therefore, electrostatic interactions between the clay units give rise to the formation of metastable gels spanning the whole sample. The rheological properties of such gels vary at a long time scale. This is referred to as ageing and can lead to phase separation of dispersions. One cause of ageing is gravity. To avoid collapsing, the gel has to be strong enough to stand its own weight, and the weight of additional ingredient in the case of formulation. Hence, ageing naturally takes place in a gel at rest but can be influenced by external conditions impacting the gel structure.

The goal of this study is to rheologically characterise the ageing of attapulgite and bentonite at long time scale in order to better understand the physical phenomenon taking place and their

consequences. Due to the difference in shape and properties of these clays, we are also curious to see how the mixture of both clays will behave with time, will mixing clays slow down or speed up the ageing. In this study, we combine time and temperature to accelerate the ageing process and great care is taken in order to minimize any disruption of the gel while ageing.

This chapter is organised as follows: the materials and methods part (5.2) lays down the experimental methodology used in this study. The results of the study are presented in the next part (section 5.3) and are discussed in the following part (section 5.4). At the end, the conclusion will summarize the main findings of this work.

5.2 Materials and Methods

5.2.1 Materials and methodology used in this study

The bentonite used was bought from Wilfrid Smith and corresponded to Bentopharm B20. The attapulgite used was Attagel 40 from BASF. Three gels corresponding to bentonite 10% wt., attapulgite 10% wt. and their blend attapulgite 5% wt.+ bentonite 5% wt. were prepared by gradually adding the clay powder, as received from the supplier, to DI water while increasing the speed of the high shear mixer. The high shear mixer used was a Silverson L4R with the square hole high shear screen as dispersing tool. Once all the powder was incorporated to the liquid, the gels were allowed to be mixed at high shear for 5 minutes for the single clay gels or 10 minutes for the blend, to ensure their homogeneity. Afterwards, a pre-defined weight of each gel, corresponding to the volume required to perform the rheological tests, was poured into home made single usage flasks. Such flasks were closed by a plastic lid on which grease was applied beforehand, and insulating tape was used to seal the lid to the core of the flask. This was done to prevent evaporation of water during the ageing study performed at 50°C.

The ageing study started once the gels had reached a chemical equilibrium state. To determine when this state was attained, we used a time oscillation experiment carried out on each gel at 25°C to follow the evolution of G' and G'' with time, see the results in section 5.3.1, figure 5.1. A linear regression, starting from the end of the curve, was performed on the data to determine the time at which the curve moves away from linearity. This time corresponds to the time at which the chemical stability was reached, after initial hydration of the platelets

(delamination and exfoliation) and ion motion. It corresponds to the starting time, Day 0, of the ageing study. The results, figure 5.1, show that the stability was reached after 29 hours for bentonite 10%, 21 hours for the mixture and a couple of hours for attapulgite 10%. Therefore, an initial rheological test was performed at that moment and corresponds to the initial state of the gel (Day 0). Afterwards, all the other flasks were stored in the oven at 50°C. Such a temperature was chosen to accelerate the ageing process following similar accelerated storage tests that can be performed for agrochemical products [127]. Rheological measurements were performed on Day 3, 6, 9, 12, 15, 30, 45, 60.

To monitor evaporation during storage, the weight of the system formed by the gel, the flask, the plastic lid and the insulating tape was recorded directly after the gel was poured in the flask and on the day of the rheological measurement. This experiment was repeated a second time on each gel, measuring Day 0, Day 6, Day 15, Day 30 and Day 60, to check that the trend obtained for each rheological parameters during the first ageing study was reproducible.

5.2.2 Design of the single usage flasks

As the goal of this study was to probe the effect of time on the gel, its disruption while loading the rheometer had to be kept to a minimum. Hence, we designed single usage flasks in which the gels were allowed to age and which could be fitted into a Peltier concentric cylinder using an adaptor, see figure 14 in the Appendix, so the gel did not have to be poured from its original container to the rheometer. The flasks had to be made of aluminium to ensure a good heat transfer during the storage and the rheological test at 50°C.

To check that the rheological results obtained on the gel using the flasks were correct, we compared them to the ones obtained using a reference cup from the manufacturer. The tests used for such a comparison comprised a creep test for 5 minutes at 0.5Pa, within the linear viscoelastic range for all gels, and a stress oscillation at 1Hz from 0.01 to 100Pa. The results of both tests for bentonite 10% and attapulgite 10% are presented in figure 15 in the Appendix. We obtained similar curves for the creep and stress oscillation tests for bentonite. Regarding attapulgite, the curves obtained diverged from the reference one either from ~ 50 s for the creep test or ~ 5 Pa for the stress oscillation. A visual assessment of the gel also showed a phase separation between the water and the clay in a freshly made gel once poured into a flask or after performing the tests. This indicated that the clay gel reacted with the aluminium of the

flask. The water may have more affinity for the flask walls than for the attapulgite clay and/or there may be some repulsion between attapulgite and the walls. To overcome this issue, we hard anodized the flasks to prevent any interaction. Such a treatment led to similar curves between the hard anodized flask and the cup from TA for both the creep and the stress oscillation tests, as presented in figure 16 in the Appendix. The gel remains homogeneous without any separation between the water and the clay.

Tailored plastic solvent trap were also made to avoid evaporation of water during the rheological measurement.

5.2.3 Rheological procedure

The rheological tests were performed using a stress-controlled rheometer AR-G2 from TA Instruments using a vane rotor with 4 blades. This geometry is the most suitable for such a study as it allows a minimal disruption of the gel when entering it, it hinders any wall slip between the blades and it is applicable to such strong gels. The rheological procedure comprises the following steps:

- 1) A time oscillatory test for 5 minutes at a stress within the linear viscoelastic range (LVR) to assess the initial equilibrium state of the gel,
- 2) Stress oscillations performed from 0.05 Pa. The test was stopped right after the end of the LVR to ensure that the gel was still in its initial equilibrium state,
- 3) the same time oscillations as in 1) was performed to check that the gel is still at equilibrium,
- 4) a creep test performed for 2 minutes at a stress within the LVR,
- 5) the same time oscillations as in 1) was performed again.

Such a test was performed at 50°C except for the reference one at Day 0, which was performed at 25°C. The critical stress σ_c was determined using a 5% threshold.

A creep test was chosen over other tests such as frequency oscillatory test or stress relaxation for the following reasons [30]: firstly, we used a stress-controlled rheometer; secondly, we focused on the long time behaviour of the gel and finally, it is quick to perform. Since the goal of this study was to determine the impact of time on the gel due to its own physical characteristics, we only apply small constraints to the gels.

5.2.4 Methodology for analysing the creep test

A creep test consists in applying a constant stress while recording the resulting strain over time. The compliance function $J(t)$ defined as shown by equation 2.4 in section 2.2.1 is plotted over time. In this study, the compliance function was fitted with a Burgers model, see section 2.2.1 according to the equation 2.5 [52,53]. From J_0 , J_1 , τ_e it was possible to determine G_0 , G_1 , η_0 , η_1 using equations 2.5 and 2.6 in section 2.2.1.

The evolution of G' , σ_c , G_0 , G_1 , η_0 , η_1 with time were fitted with a Leong model according to the equation 2.3 in section 2.2.1. The parameters G'_∞ , G'_0 and $1/K_r$ of the model were calculated.

5.2.5 Calculation of the cohesive energy

The cohesive energy is defined by equation 5.1 and is commonly calculated using the equation 5.2: [128]

$$E_c = \int_0^{\gamma_c} \sigma d\gamma, \quad (5.1)$$

with E_c the cohesive energy in J/m³, σ the stress and γ the strain. Hence, by replacing σ by $G'\gamma_c$, one obtains the equation 5.2 commonly used:

$$E_c = \frac{1}{2}G'\gamma_c^2, \quad (5.2)$$

with G' the storage modulus and γ_c the critical strain. However, since we performed a stress oscillatory test instead of strain oscillations, the equation 5.1 can be re-written by changing the variable as follows:

Starting from the Hooke's law:

$$\gamma = \frac{\sigma}{G}, \quad (5.3)$$

with G the modulus. Using equation 5.3 to change the variable, and considering G constant within the LVR, one obtains:

$$E_c = \int_0^{\sigma_c} \frac{\sigma}{G} d\sigma, \quad (5.4)$$

resulting in equation 5.5:

$$E_c = \frac{1}{2} \times \frac{\sigma_c^2}{G'}, \quad (5.5)$$

5.3 Results

5.3.1 Determination of the time required for each gel to reach a chemical stability

The time oscillatory test performed on a fresh attapulgite 10% gel, figure 5.1 revealed that the chemical stability was reached a few hours after making the gel. This is due to the fact that attapulgite is a non swelling clay due to its 3D chain structure [43]. Hence, an equilibrium was reached quickly. On the contrary, bentonite 10% has a layer sheet structure with cations located in the interlayer, thus allowing swelling. Therefore, it was expected that bentonite would take much longer to reach equilibrium, see figure 5.1. We also note the similar trend observed for the mixture attapulgite 5% + bentonite 10% to the pure bentonite. Consequently, the clay blend system also took time to reach a fully dispersed state. The linear regression performed on both gels to determine the time needed to reach a chemical stability, figure 5.2, shows that such a state was reached after 29 hours for bentonite 10% and 21 hours for the blend. Such a duration is consistent with the time found by other authors to reach the Surface Chemical Equilibrium (SCE) on bentonite [51, 129, 130].

5.3.2 Effect of the ageing on G' and the critical stress σ_c

The results of the ageing study, in figure 5.3, show a strengthening of all gels, as seen by the increase of G' (figure 5.3a) and an increase of σ_c (figure 5.3b) for bentonite 10% and bentonite 5% + attapulgite 5%. For these two gels, G' and σ_c reaches a plateau from 15 to 30 days of

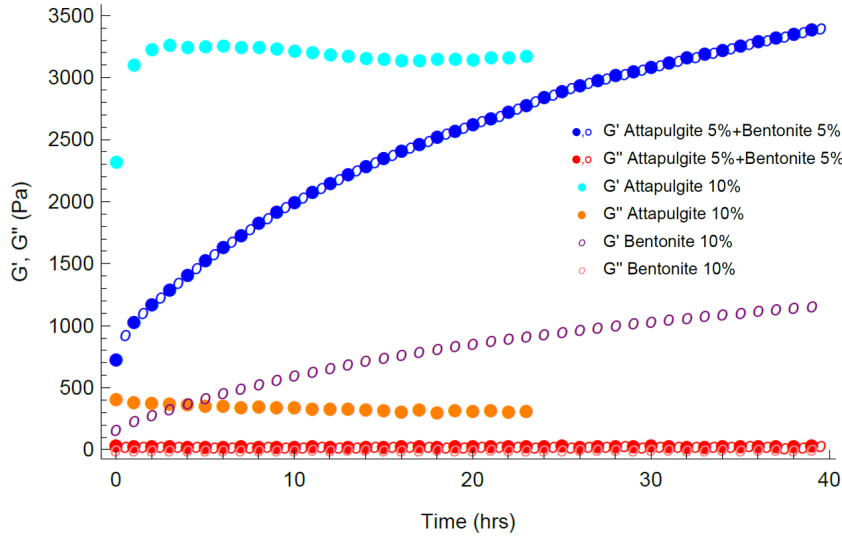


Figure 5.1: Time oscillation performed for each clay gels to check equilibrium

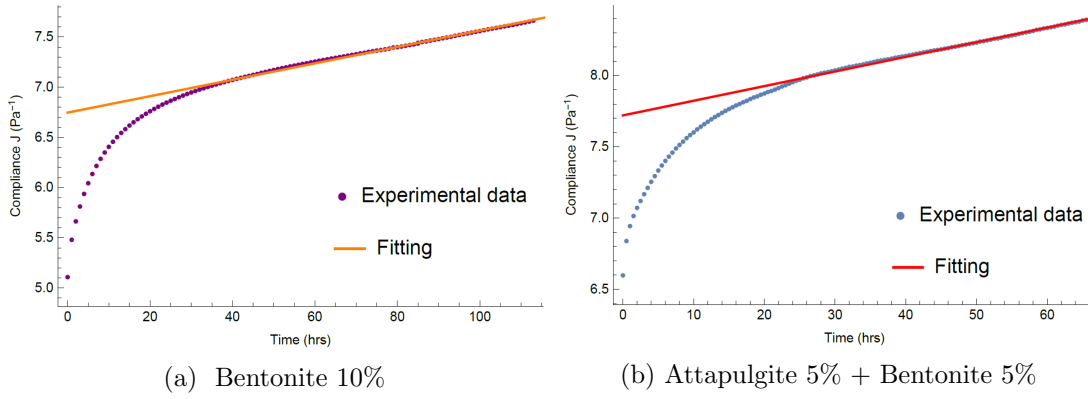


Figure 5.2: Determination of the time required for Bentonite 10% and the mixture to reach stability

ageing. The curves of G' and σ_c of the pure bentonite and the mixture follow a similar trend and could successfully be fitted with a Leong model after removing the experimental points that seem erroneous [49, 51]. The coefficients are reported in tables 5.1 and 5.2. The wrong points (outliers) could be the result of evaporation of water happening during the storage, but more likely, they could be due to some heterogeneity formed during the gel preparation. In fact, it became harder to mix the gel as we increased the amount of clay. Thus, some parts could contain more clay than others impacting the ageing of the gel. Such a model leads to a good fitting of the curves as seen by their R^2 and by the values of G'_0 and σ_c at $t=0$ which are very close to the experimental ones. The same remark can be made for the fitting of the value when $t \rightarrow \infty$. However, it was not possible to fit the results obtained for G' for attapulgit with such a model due to the slow increase of G' at the beginning of the ageing study. Furthermore, σ_c for attapulgit remained constant with time and therefore could not be fitted with a Leong model

either.

Some synergism between the clays are also displayed with higher values of G' found for the mixture than for each pure clay gel. However, such effect does not appear for σ_c for which the value is the same for the mixture as for bentonite.

Although the figure 5.3 represents only the results obtained during the first ageing study, the trend of the curves is reproducible according to the second test.

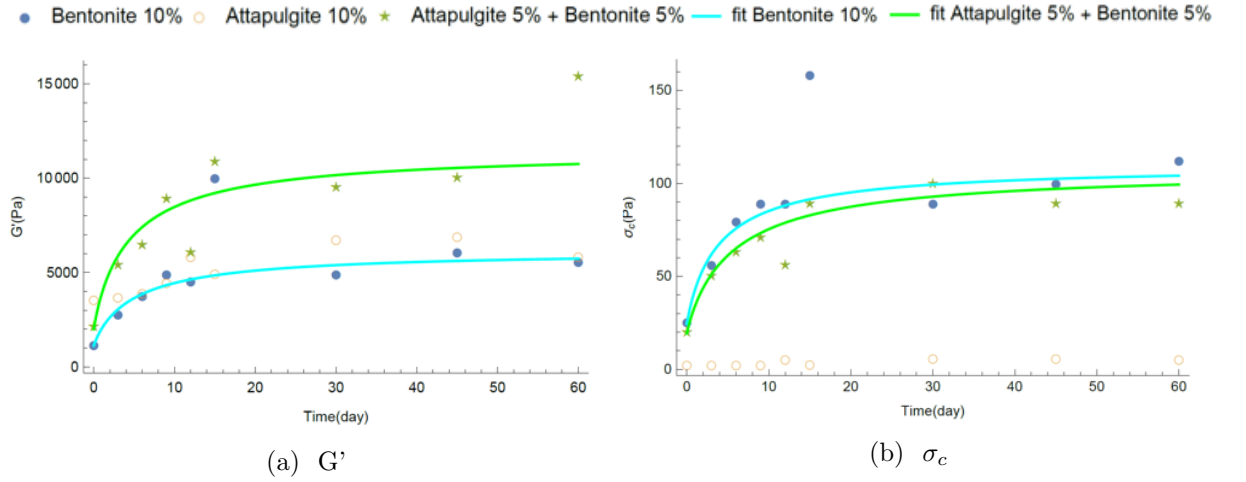


Figure 5.3: Evolution of G' and σ_c during the ageing of Bentonite 10%, Attapulgite 10% and Attapulgite 5% + Bentonite 5%

Table 5.1: Coefficients of the Leong model found for G' for each gel fitted

Samples	G'_0 (Pa)	G'_{inf} (Pa)	$1/Kr$ (day)	R^2
Bentonite 10%	1121	6146	7.2	0.99
Attapulgite 5% + Bentonite 5%	2000	11×10^3	6.4	0.98

Table 5.2: Coefficients of the Leong model found for σ_c each gel fitted

Samples	σ_0 (Pa)	σ_{inf} (Pa)	$1/Kr$ (day)	R^2
Bentonite 10%	25	110	5.4	0.99
Attapulgite 5% + Bentonite 5%	19.3	107.2	8.0	0.99

5.3.3 Effect of the ageing on the cohesive energy

The cohesive energy increases for bentonite and the mixture, as shown in figure 5.4, following the same trend: a rapid increase at the beginning of the ageing followed by a plateau from 15 days. This suggests some rearrangements between the clay units leading to a strengthening of

the gel and followed by a constant state. The cohesive energy for attapulgite stays constant during the 60 days of ageing and is much lower than the one found for the other 2 gels. This could have been predicted since σ_c stayed constant with time and was also lower for attapulgite than for the other gels. The cohesive energy is a measure of the energy that needs to be applied to a system to disrupt it [128]. Therefore, attapulgite needles are less strongly linked to each other than the bentonite platelets and time does not have a significant impact on the cohesive energy.

Furthermore, the mixture of the clay does not lead to a higher cohesive energy than bentonite 10% but rather to very close values. This reveals that interactions between the bentonite platelets and the attapulgite needles take place. Otherwise, we would expect to find much lower values for the mixture containing only 5% of bentonite than for the 10% pure clay gel.

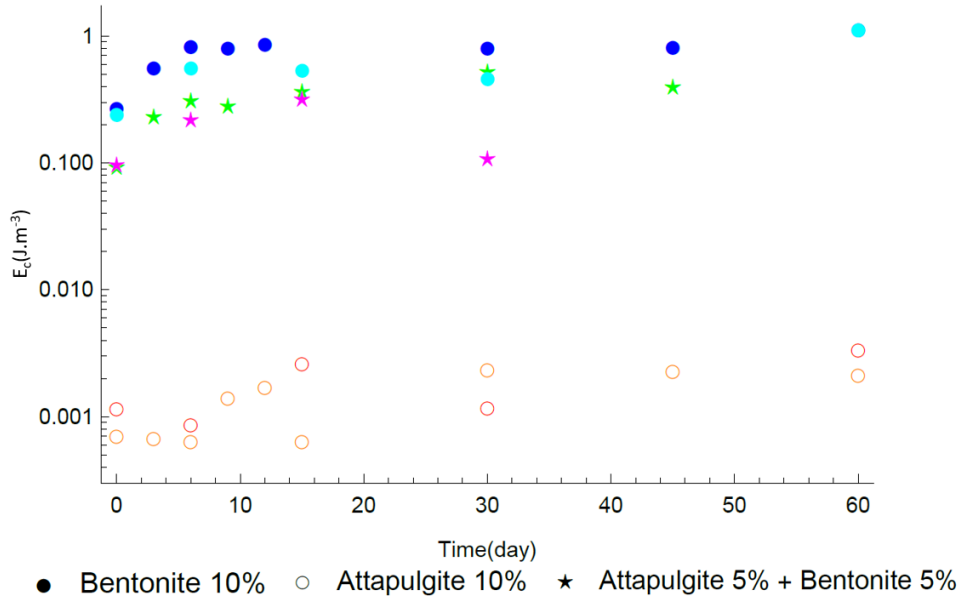


Figure 5.4: Evolution of the cohesive energy during the ageing of Bentonite 10%, Attapulgite 10% and Attapulgite 5% + Bentonite 5%. Points of the same shape but different colors represent the two repetitions.

5.3.4 Effect of the ageing on G_0 and G_1

G_0 and G_1 increase for all gels as shown in figure 5.5 until reaching a plateau from 15 to 30 days of ageing. Again, the curves obtained for bentonite and the mixture follow the same trend and could be fitted with a Leong model, see the coefficients in tables 5.3 and 5.4. The R^2 for the fitting of G_1 for bentonite was only of 0.97. This can be due to the noisy experimental points

found between Day 6 and Day 15 which were higher than the points found at Day 45 and Day 60. The curves for G_0 and G_1 for attapulgite show again a very slow increase at the beginning of the ageing experiment and therefore could still not be fitted with a Leong model.

Surprisingly, some synergism effect can be seen between attapulgite and bentonite for G_0 but not for G_1 , meaning that mixing clays impacts mainly the spring of the Maxwell element rather than the spring of the Kelvin-Voigt element.

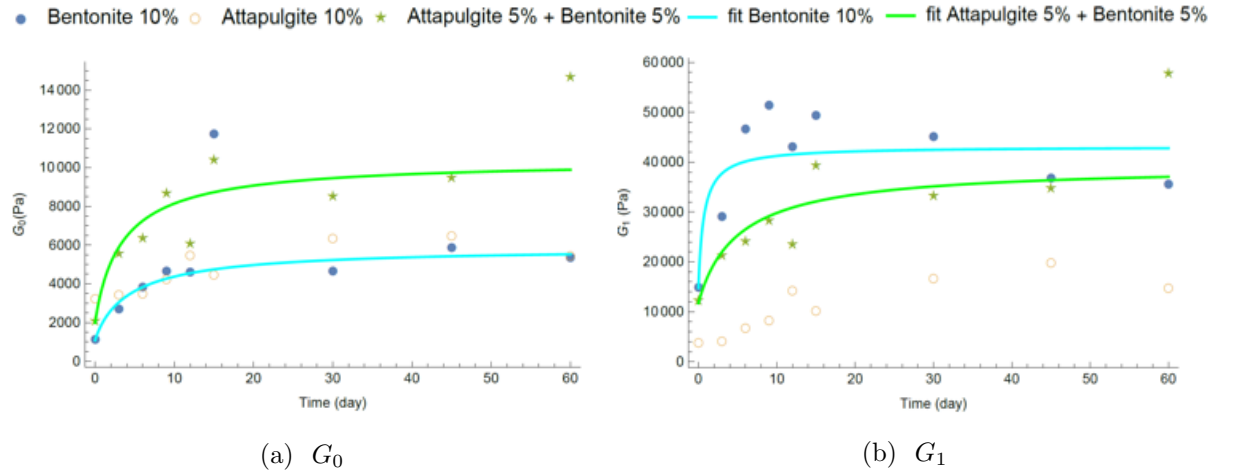


Figure 5.5: Evolution of G_0 and G_1 during the ageing of Bentonite 10%, Attapulgite 10% and Attapulgite 5% + Bentonite 5%

Table 5.3: Coefficients of the Leong model found for G_0 for each gel fitted

Sample	$G_{0,0}$ (Pa)	$G_{0,inf}$ (Pa)	1/Kr (day)	R^2
Bentonite 10%	1091	5878	6.4	0.99
Attapulgite 5% + Bentonite 5%	1989	10^4	5.0	0.99

Table 5.4: Coefficients of the Leong model found for G_1 for each gel fitted

Sample	$G_{1,0}$ (Pa)	$G_{1,inf}$ (Pa)	1/Kr (day)	R^2
Bentonite 10%	15×10^3	43×10^3	0.88	0.97
Attapulgite 5% + Bentonite 5%	12×10^3	39×10^3	6.8	0.99

5.3.5 Effect of the ageing on η_0 and η_1

The values observed for η_0 , figure 5.6a, are about constant throughout the experiment for attapulgite whereas bentonite and the mixture experience a slight increase of η_0 at the beginning of the ageing. On the opposite, the curves for η_1 increase for all gels, as shown in figure 5.6b, and

particularly for attapulgite. Therefore, the effect of time is more pronounced on the dashpot in the Kelvin-Voigt element than in the Maxwell element. The characteristic values for the two dashpots are high, 10^5 to 10^6 Pa.s, revealing the high viscosity of the gels. Such viscosity increases with time as shown by η_1 , which reveals an increase of the friction between the clay units as the gel ages.

No synergistic effect between the clays was found on the viscous behaviour of fresh and aged gels: similar values were obtained for the blend and for bentonite 10% at $t=0$ and during the ageing of the gels. However, the fact that the viscous behaviour for bentonite 10% is about the same as for attapulgite 5% + bentonite 5% still shows the presence of interactions between the two clays. The strength of such interactions is driven by the bentonite platelets rather than the attapulgite needles, maybe due to their shape and/or charge density.

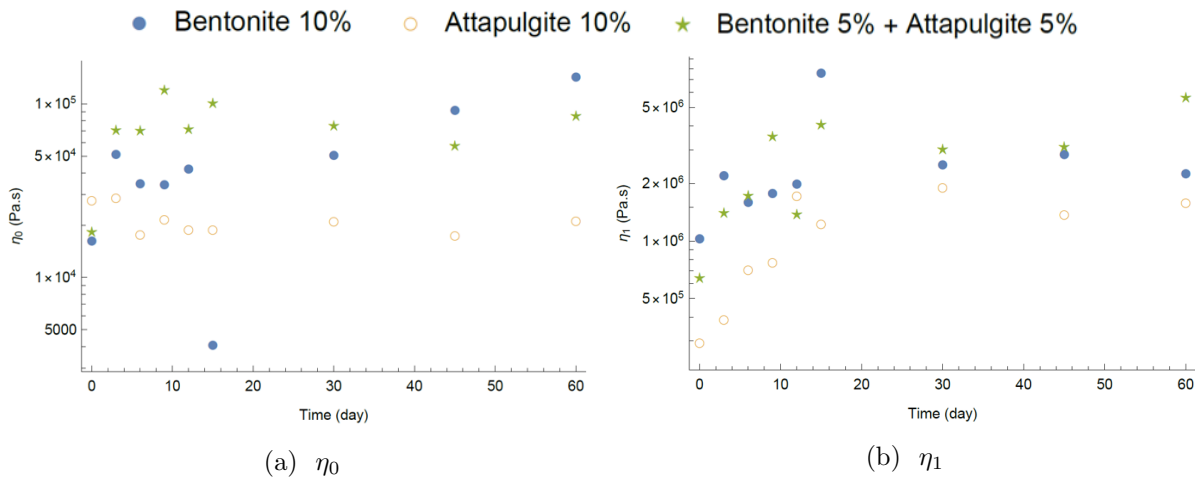


Figure 5.6: Evolution of η_0 and η_1 during the ageing of Bentonite 10%, Attapulgite 10% and Attapulgite 5% + Bentonite 5%

5.4 Discussion

This study revealed an increase of G' , G_0 , G_1 , η_1 during the ageing of all the studied gels. This increase appears early during the ageing for bentonite and the mixture before reaching a plateau. Such effect due to temperature or ageing has already been observed by others, mostly on bentonite [39, 129, 131–133], and less for attapulgite [134]. It is explained by rearrangements of the clay units by Brownian motion of the platelets during ageing driven by the electrical double layer repulsive force [39]. The term rearrangement encloses bond breaking, bond formation as well as orientation, motion of the platelets. This can lead to aggregation with the

occurrence of face-face interactions of the platelets [131,132]. Such interactions are due to the compression of the double layer caused by the motion of the ions in water and accelerated by the high temperature. However, although face-face interactions between bentonite platelets may be promoted by temperature, we think that face-edge or edge-edge interactions (“Y” junctions) persist in aged sample. In fact, we saw that η_1 increased with time meaning that viscous forces within the gels become stronger. This can be explained by at least the following hypothesis: 1) clay units gets closer to each other, 2) the single platelets get various orientation leading to more friction between the platelets. Chang et al. [134], showed that Brownian motion could have two effects on concentrated attapulgite clay (10% volume) in water: a slight increase of temperature would decrease the viscosity of the gel whereas at even higher temperature, the viscosity increases again. According to the same authors, Brownian motion may not have a huge effect in highly concentrated suspension. Nonetheless, the bentonite used here corresponds to a commercial product which is not pure and is likely to contain some electrolyte favoring edge-face interactions [128].

The motion of the platelets or needles is limited by their neighbors and decreases with ageing. This leads to the plateau reached by the gels for G' , G_0 , G_1 , η_1 which corresponds to a state of minimum free energy [39]. We also note that the higher the clay concentration, the less the motion of the particles.

As seen by the results presented previously, attapulgite features a slow increase of G' , G_0 , G_1 at the beginning of the ageing study. Such peculiarity could be the result of different physical phenomena happening between the clay needles. The first part of the curve could still correspond to the initial equilibrium plateau. The second part could be due to the ageing of the clay with molecular rearrangements. Surprisingly, the values obtained for σ_c for this gel barely increased during the 60 days of ageing. Hence, the stability of the structure formed by attapulgite does not evolve with time. Furthermore, although we tried different types of models, see in the Appendix, none of them could successfully fit the curves. Fitting the curve with two Leong models, one at short time and one at longer time, did not give satisfactory results for the first part of the curve either.

For some rheological parameters, synergism between the clays lead to a stronger gel compared to the pure clay gels. The strength of the gel depends on different factors. The first one is the numbers of interactions between the different constituents which in the case of a blend be-

tween bentonite and attapulgite can be between two bentonite platelets, between two attapulgite needles or between a platelet and a needle [78, 135]. The higher the number of connections, the stronger the gel. Additionally, as stated by Chang et al. [129], not all bonds are load bearing but with time and internal restructuring, more and more bonds become load bearing. This hypothesis is conceivable as the gel, mainly at its base, has to overcome gravity. The combination of both physical phenomena can explain the strengthening of the gel: an improved connection, capable of bearing more load, appear between the platelets and the needles and remains over time. The second factor is the electrical double layer which can lead to a stronger structure by repulsion [39]. The difference in shape between the two clays may increase their interaction. Furthermore, although both clays should, in theory, display negatively charged surfaces and edges at alkaline pH, the difference in charge density between the two may also promote their interaction. As a reminder, attapulgite has a low surface charge [126].

A study performed by Neaman et al. [136] revealed that the yield stress of attapulgite suspensions increased upon addition of 40% of montmorillonite or higher. Hence, the proportion of montmorillonite used in the sample influences the rheology of the blend: the more montmorillonite is added to the sample, the more interactions happen between the two clays. As stated by these authors, the proportion of impurities present in the sample also contributes in increasing their rheological characteristics. Another study showed an increase of the viscosity on the mixture when increasing the amount of bentonite [137]. Furthermore, Chemedda et al. [78], investigated the effect of the type of bentonite added to attapulgite. Their study reports that the charge of the bentonite affects the rheology of the mixture: they saw an increase of the yield point at bentonite concentration above 40% only when adding a low charge bentonite.

Such a blend can be relevant in industry as it allows to make a strong gel while decreasing the amount of each clay used. This allows to overcome some challenges faced when preparing pure attapulgite or bentonite gels: for instance when the gels get too strong, it becomes harder to mix and adjuvants are required to decrease the viscosity of the gel.

The experiment reveals that the ageing behaviour of the mixture attapulgite bentonite, in the same proportion, seems to be essentially driven by bentonite. The bentonite network may dominate the whole structure. As shown in the result part 5.3, the curves for the evolution of G' , σ_c , G_0 and G_1 for the pure bentonite and the clay mixture could successfully be fitted with a Leong model. Regarding bentonite 10%, $1/Kr$ found for the different rheological parameters

are similar, between 5.4 to 7.2 days (the results for the fitting of G_1 was not taken into account). These times correspond to the time needed to reach 68% of the plateau value [39]. The value of $1/Kr$ found for bentonite is consistent with the one found by Leong et al. on a 7% SWy-2 gel [39]. However, at such points, the gel still experiences a rapid increase of the rheological properties according to the curves in figure 5.3 and 5.5. The same remark can be made for the blend which features similar characteristic time as bentonite 10%. This emphasises the fact that the rheological properties of the mixture is driven by bentonite and perhaps so is the microstructure of the gel during ageing.

This model has already been used in the literature to model the effect of time on the yield stress or G' for bentonite or laponite [49, 50, 129, 138, 139]. However, some of these authors reported some discrepancies between the model and the experimental points at short and long time [50, 129, 139]. It is due to the second order kinetics used to derive the Leong model and the difficulty to get G' or the yield stress at infinite time. No discrepancy was seen in this study, for which the values of G' , σ_c given by the model when $t \rightarrow 0$ or $t \rightarrow \infty$ are very close to the ones obtained experimentally. This may be due to the way the study is made as we combined an increase of temperature with a long ageing time (60 days), allowing us to determine more accurately G'_∞ and $\sigma_{c,\infty}$, compared to other studies performed only at room temperature for a shorter time.

Furthermore, we saw that the cohesive energy increased throughout the experiment for the pure bentonite and for the blend (section 5.3.3). Hence, during ageing, rearrangement of the microstructure happened, leading to a more stable network. The similarity and proximity of the curves obtained for bentonite and the blend may reveal that a bentonite network could still form in the presence of attapulgite. Nevertheless, some differences between the networks formed by bentonite alone and bentonite in the mixture can also appear. The cohesive energy for attapulgite remained constant. Hence, reorientation of the needles may still take place but it does not improve the stability of the gel. This also highlights that the interaction between the needles differs from the interaction between the platelets which is much stronger. This may again be due to their chemistry or their charge. Electrostatic interactions between attapulgite needles, due to the intrinsic charge of the clays or the formation of the electrical double layer, may not be as strong as they are for bentonite. As shown by Tadros [17], the cohesive energy is a measure of the stability of a dispersion: the lower the cohesive energy, the higher the separation of the constituents. This is consistent with the syneresis (water released at the top of the gel

in our case due to sedimentation of the sample) observed over time for attapulgite but not for bentonite or the mixture. Again, this shows some relevance for industry in using a mixture of clays as it allows a better stability of the resulting network.

5.5 Conclusion

We studied the rheological evolution of bentonite 10% wt., attapulgite 10% wt. and their mixture attapulgite 5% and bentonite 5% during ageing combining time and temperature. To avoid disrupting the gels, we designed inert single usage flasks used for the ageing protocol and to carry out the rheological tests. We performed oscillatory and creep test measurements. From the former test, we focused on G' , σ_c , whereas the compliance obtained from the latter one was fitted with a Burgers model to get G_0 , G_1 , η_0 , η_1 (the spring and dashpot constants of the Maxwell and Kelvin-Voigt elements respectively).

It revealed that bentonite and the mixture become stronger, more stable and more viscous with time, as seen by the increase of G' , σ_c , G_0 , G_1 , η_0 , η_1 . In the case of bentonite, this can be explained by molecular rearrangements bringing the platelets closer to each other and forming new bonds. The interactions between the platelets may be face-to-face but also edge-face forming a “Y” junction. This can be due to the Brownian motion of the particles seeking a lower free energy, but also to the presence of impurities or electrolytes in the commercially available clay powder.

Surprisingly, the rheology of the mixture displays the same trend as the one described by bentonite. Therefore, a bentonite network may dominate the whole structure. For G' and G_0 , a synergism between the clays was seen leading to values that were higher than the ones obtained for the pure clay gels. However, this was not the case for σ_c , G_1 , η_0 , η_1 . Instead, the values obtained for the mixture were about the same as the ones found for bentonite, meaning that the gel is as stable and features similar viscous forces. The effect observed depends on the type and proportion of bentonite added to attapulgite. There is an interaction between the bentonite platelets and the attapulgite needles resulting in a gel with synergistic effect or just equalizing the values obtained with bentonite 10%. The interaction between the units of each clay may be favored by their difference in shape and charge density, although we expect all clay to be in overall negatively charged under the experimental conditions. Such a mixture can be relevant

for industries as it allows to get similar or stronger gel than the pure bentonite or attapulgite while overcoming some challenge of the sample preparation by decreasing the amount of each clay used.

Therefore, both bentonite and the mixture could be fitted with a Leong model for which the parameters found were very close to the ones found experimentally. Both gels feature similar Leong model characteristic time, $1/Kr$. $1/Kr$ was found to appear early in the ageing process, between 5.4 to 7.2 days for bentonite and the composite clay gel. This means that any structural rearrangement leading to the strengthening of the gel happens at the beginning of ageing. However, at this time rheological changes are still happening.

However, attapulgite 10% could not be fitted with a Leong model due to the slow increase of G' , G_0 , G_1 delaying the ageing of the gel. This may be due to rearrangements of the needles taking longer to happen than for bentonite, the needles interact with each other with different mechanism than the bentonite platelets. For such a gel, we observed some syneresis, water released at its top. This is in good agreement with the values found for the cohesive energy which were far below the ones observed for bentonite and the mixture, for which no syneresis was seen.

A further study will consist of using a microscopic approach to characterise the evolution of the microstructure of the clay gels following the same time-temperature combination. The results will be compared to the rheological behaviour described here.

Chapter 6

Ageing effect on the microstructure of clay gel

We determined the impact of ageing on the microstructure of attapulgite 10 % wt., bentonite 10% wt. and their mixture at 5% wt. each. We used high pressure freezing (HPF) Cryo-SEM and X-Ray tomography to image fresh gels and gels aged at 50°C. For all gels, the long range structure displays firstly aggregates made of clay and water spanning the whole sample, and secondly, water between the aggregates forming large pores. The attapulgite fresh gel displays some stacks of needles with different orientations; the aged gel features more single units. The ageing favoured the formation of large pores probably due to Brownian motion experienced by the needles that left the aggregates. The bentonite fresh gel may feature some edge-edge and edge-face interactions in addition to face-face interactions between well defined platelets. However, the platelets were harder to distinguish in the aged gel which also features smaller submicron pores than the fresh gel. However, the long range structure was not significantly affected by the ageing. Mixing the two clays led to the formation of a structure which may be made of two networks cooperating with each other. The short and long range microstructure of the system were not impacted by the ageing. On the short range, no restructuring or swelling of bentonite could be observed, nor a reduction in the pore size. On the long range, the pore size distribution had the same trend as for attapulgite.

6.1 Introduction

Clay has been used by humans since antiquity, for instance for the production of ceramic. Since the years 1930-1940, they have caught more and more interest from academia and industry for their diverse properties [34]. They can be used as a thickener in painting or agrochemical industries, as one of the active ingredients in cosmetics, as adjuvant of drilling fluid and so on [140, 141]. Nowadays, the scientific community explores their use in other fields such as nanotechnology, reaction catalysts, and biology. There exist lots of different clays varying in their chemistry, structure, shape, size and so forth. A well known family of clay mineral is called phyllosilicate and refers to clay with a layered structure [142]. Among them we can quote smectite clays including Na-Montmorillonite, and pyribole including palygorskite [44].

The broad characteristics of clays impart diverse properties to them. Consequently, different clays behave differently under similar conditions or with time. Such characteristics result from their large surface area, the capability of certain clays to swell, their small size and their natural charge giving rise to electrostatic interactions [140, 142]. Among the most studied clays are Bentonite or Na-Montmorillonite, Kaolin, Laponite, Sepiolite and Palygorskite (Attapulgitite).

Lots of scientists have worked on understanding their properties by determining how the clay units interact. To do so, they have used different characterisation or imaging techniques like rheology, Cryo-SEM or TEM, mercury intrusion, X-Ray SANS [62, 64, 65, 143–145]. Different models of clay structure and interaction, such as the so-called house of card structure or the band-like model, have been suggested for bentonite or kaolin clay. However, there is no consensus in the scientific community [60, 92, 146]. Therefore, additional studies using complementary techniques on various types of clays are needed to expand our understanding of clay mineral interactions.

The interactions between the clays, and therefore the properties of the resulting structure, change with time due in part to sedimentation. Such ageing is a burden for industries using clay as a thickener; they see the rheological properties, general aspect and efficacy of their products changing with time. Thus, more and more researches focus on characterising the evolution of the mechanical properties with time [138, 147], as well as determining the change in the microstructure of the system [42, 148]. Clay gel mixtures have also gained more and more interest in recent years since they are common in natural, soil based systems. However, there are

only a few studies available in the literature dealing with clay composites whereas such systems could also be relevant for industries using clays as thickeners.

This study aims at characterising the changes of the structure formed by bentonite, attapulgite clay gels, and their mixture as a function of time. We use a microscopic imaging approach combining High Pressure Freezing (HPF) Cryo-SEM and X-Ray tomography on gels that were aged at 50°C. The former one allows us to resolve the gel down to the clay unit scale, whereas the latter one gives the long range structure of the gel. We also determine the sedimentation profile of such clays using X-Ray attenuation.

This chapter is organised as follows: the materials and methods used are described in the first section (section 6.2). The second section (6.3) lays down the results obtained using the different techniques which are discussed in section 6.4. Finally, the conclusion in part 6.5 summarises the key findings of this work.

6.2 Materials and Methods

6.2.1 Materials used to make the gels

The materials used for this study was the same as the one described in chapter 5, section 5.2.1. Hence, bentonite corresponded to the commercial product Bentopharm B20 from Wilfrid and attapulgite to Attagel 40 from BASF. Note that the clay batches used were the same as in the previous study, Chapter 5. This is important as the naturally occurring clays used were not purified. Thus, they contain impurities and their composition can slightly vary from one batch to another.

The gels, bentonite 10% wt., attapulgite 10% wt. and their mixture attapulgite 5% wt. + bentonite 5% wt. were prepared as described in section 5.2.1. Briefly, clay powder was gradually added to DI water while increasing the shearing rate. After all powder was poured, the shear mixing was kept at high speed for 3 to 5 minutes until complete homogenisation. The high shear mixer used here was an IKA ultra turrax digital t25 with the S 25 N-18G dispersing tool. Afterwards, the same weights of the gels as described in chapter 5, see section 5.2, were poured into the same single usage flasks. The leftovers were poured into a glass jar. All containers were sealed properly. When necessary, we used a lid with grease and insulating tape to prevent

evaporation. The samples were left at room temperature for a few hours for attapulgite 10%, 29 hours for bentonite 10% and 21 hours for attapulgite 5% + bentonite 5% , see sections 5.2.1 and 5.3.1. Afterwards, gels were placed in an oven at 50°C to age.

6.2.2 Method used for the High Pressure Freezing (HPF) Cryo-SEM

The gels were kept for 30 days at 50°C. This was based on the rheological results obtained in chapter 5, see sections 5.3.4, 5.3 and 5.4 showing that the rheological parameters G' , σ_c , G_0 , G_1 and the cohesive energy reached a plateau at that time. Fresh gels containing attapulgite, or bentonite, or bentonite and attapulgite were prepared a few hours, 29 hours and 21 hours, respectively, before performing high pressure freezing. These gels are defined as the reference and were imaged once they reached chemical stability.

High pressure freezing was performed by pipetting or scraping the gels to settle into a 3mm or a 6mm diameter aluminum carrier. Another carrier was placed on top of it as described in chapter 2, section 2.3.3, figure 2.7, forming a cavity of 300µm depths containing the gel. HPF was performed using a Leica EM Ice device. Afterwards, the samples were kept into liquid nitrogen until Cryo-SEM imaging was performed using a Hitachi SU8220. The samples were fractured, sublimated at -93 or -95°C for 3 to 5 minutes depending on the sample, and coated with gold twice at 5mA for 15 seconds. The samples were imaged using either the secondary electrode or the backscattered electrode.

6.2.3 Description of X-Ray tomography

The gels were aged for 53 days and corresponded to the gels imaged using HPF Cryo-SEM. Fresh gels were made to be used as a reference. The gels were placed into glass capillaries of 1mm internal diameter and 1.2mm external diameter. To avoid evaporation of water, a small amount of low viscosity oil was introduced at both ends of a capillary, which was sealed using a microscope cover slip glued at both ends with epoxy glue. For the aged gels, they were poured into capillaries two days before imaging and were put back in the oven to give them enough time to recover a structure. The fresh gels were put into capillaries straight after preparation and were allowed to reach stability at room temperature.

X-Ray tomography was performed at the I13-2 beamline in the Diamond Light Source syn-

chrotron, see section 2.3.2 in chapter 2, using a MultiLayer Monochromator (MLM) to reduce bubbling of the water. The samples were imaged after finding the experimental conditions that rendered the best resolution without affecting the samples. These conditions were the following: energy: 25keV, exposure time: 0.6s, distance sample-objective: 700mm, objective used: $10 \times$ PCO edge 5.5 with a field of view (FOV): 2.1×1.8 mm, pixel size: 0.325 μ m. The 3D reconstruction of the samples was performed after finding their centers of rotation.

The analysis of the reconstruction was performed using the software Avizo following the procedure summarized below:

- A subvolume was extracted from the original set of slices. Note that the dimensions of all subvolumes extracted were the same for all gels.
- A Gaussian filter was applied to reduce the noise in the images. The resulting images displayed a histogram of intensities, from which we read the mean which will be used in the next step.
- The images were binarized using a threshold by criterion. The criterion was set as less than the mean of the histogram of the source image. In other words, the pixels corresponding to the pores are set to 1 and those corresponding to the clay are set to 0.
- Another subvolume was extracted to perform the following steps:
 - The separate object tool was used with a Chamfer-conservative method keeping constant the chamfer distance. A repeatable algorithm mode was used to differentiate the objects. The marker extent value, corresponding to the contrast factor, was selected depending on the gel to keep the resulting image as similar to the initial one as it can be.
 - We applied the Generate Pore Network model (part of the Avizo XPoreNetwork module extension) with the default boundary conditions of 130 000Pa and 100 000Pa as input and output pressure respectively. The fluid viscosity was set at 0.001 Pa.s corresponding to the viscosity of water.

See section 6.5 in the Appendix for the detailed method.

6.2.4 Determination of the sedimentation profile

The sedimentation profile was determined using a LUMiReader X-Ray on three new gels made using the same batch and method as described in section 6.2. However, after preparation, they were transferred into plastic vials suitable with the LUMiReader. Three vials were filled with the same gel for each clay and the mixture, resulting in 9 samples altogether, allowing repeatability

of the ageing experiment. Again, the gels were made sufficiently in advance to have reached chemical stability before performing the first measurement at Day 0. Afterwards, they were kept at 50°C for 60 days. Measurements were performed at day 3, 6, 9, 15, 30, 45 and 60.

6.3 Results

6.3.1 HPF Cryo-SEM imaging

HPF Cryo-SEM imaging of attapulgite 10% gel, presented in figure 6.1, shows that the fresh sample is quite heterogeneous with highly concentrated and poor clay areas, see a highly concentrated area in figure A.1 in the Appendix. This may be due to the sample preparation: pipetting may have disturbed the sample and might have caused such heterogeneities. For fresh samples, most needles form stacks in which all needles are parallel. However, the stacks feature different orientations as can be seen in the micrograph 6.1a.

The old gel is much more homogeneous than the fresh one with a high density of clay spread across the sample as can be seen in figure 6.1c. Stacks of a few number of needles are still to be seen in addition to single needles which also seem to have no particular orientation, see image 6.1d. However, the bundle of needles in the aged sample appeared to be closer to each other than in the fresh sample. Thus, ageing may allow the development of a more compacted structure of the gel, almost nematic-like.

Fresh sample of bentonite 10% gel displays a very dense, rather homogeneous structure (at a scale between 20 and 80µm) with very small pores and no orientation, see in image 6.2a. The absence of long range orientation is a sign that the freezing hasn't impacted the structure of the sample. In fact, a slower freezing would have led to the formation of freezing "line" in addition to crystals. Hence, no honey-comb structure could be seen here in line with previous studies [64]. The bentonite platelets can also be seen and differentiated very clearly, as show by the micrograph 6.2b. It also shows that the platelets have different orientations and therefore edge-face or edge-edge orientations may be seen in the images 6.2c and 6.2b, in addition to face-face interactions. The rectangle in image 6.2c highlights a "Y" junction whereas the circle highlights a junction between the edges of four platelets. We can also see that some platelets are bent with some curved edges, as described by Leong et al. [133]. This may be due to attraction and repulsion with their neighbours [149]. However, some chunks of platelets can be seen on

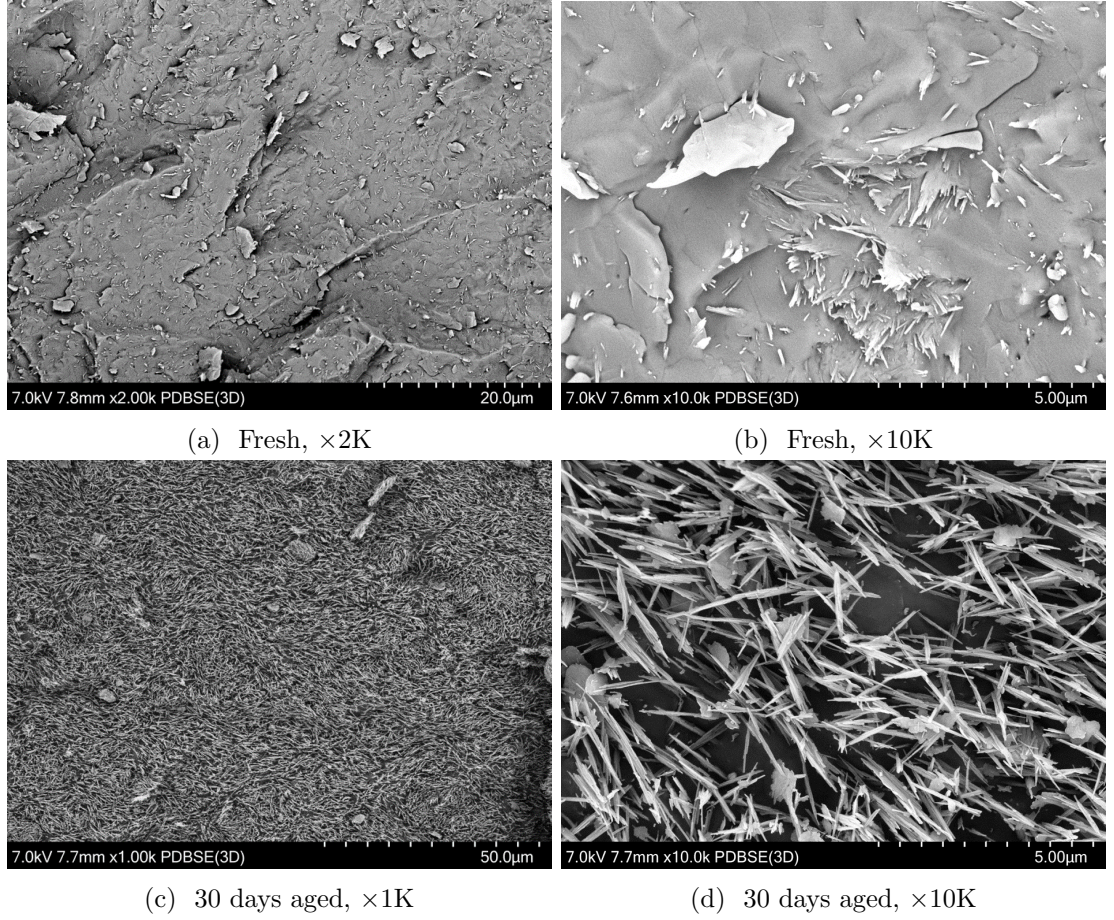


Figure 6.1: HPF Cryo-SEM imaging of Attapulgite 10% wt. at different magnifications

image 6.2b, likely due to the sample preparation: the platelets did not exfoliate.

The structure of the aged sample is also very homogeneous at a scale of $\sim 100\mu m$, as shown by the micrograph 6.2d. No aggregate could be seen, see image A.2 in the Appendix section 6.5. However, it is much more difficult to differentiate the individual platelets. They all seem to be linked to each other forming a single network containing very small pores, see image 6.2e. Therefore, ageing leads mainly to an increase of the connection between the platelets. In addition, ageing results in a decrease in the size of the pores, containing less free water than a fresh gel. This is likely due to the swelling of the non exfoliated platelets seen in the fresh gel at such clay concentration.

HPF Cryo-SEM imaging of the clay composite shows a chaotic structure as seen in figure 6.3. Some areas of the same image display an elongated structure, circled in image 6.3a. This may correspond to some bentonite or attapulgite, which have not fully dispersed. Thus, we can expect some areas of the gel being more concentrated in one clay or the other, possibly due to sample preparation. When increasing the magnification, see micrograph 6.3b, we can

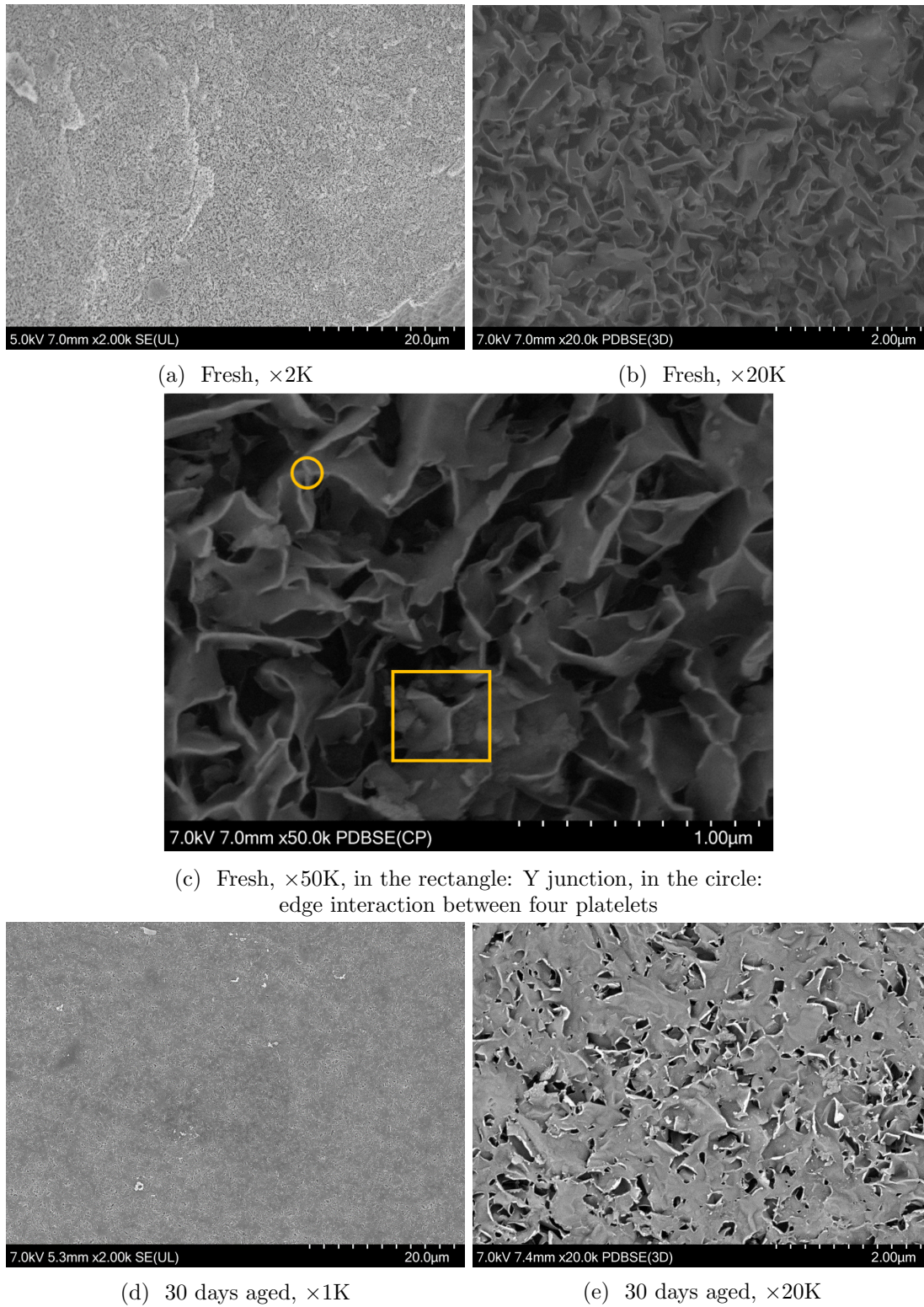


Figure 6.2: HPF Cryo-SEM imaging of Bentonite 10% wt. at different magnifications

differentiate the platelets (circled in figure 6.3c) from the needles (in the rectangle in the same figure). Therefore, we think that each clay may form a separate network which may interact with the other one at some localised contact points. In fact, the distance between the clay

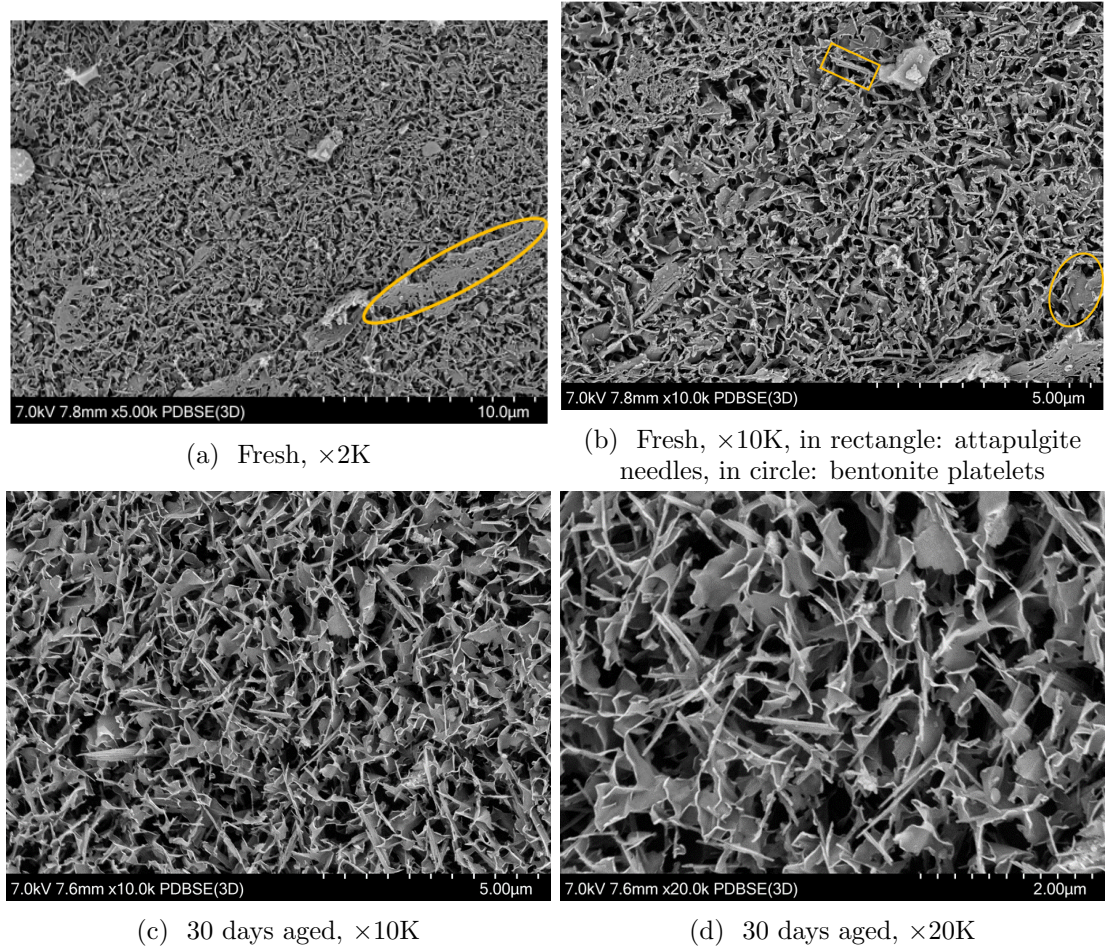


Figure 6.3: HPF Cryo-SEM imaging of Attapulgite 5% + Bentonite 5% wt. at different magnifications

units is so small that they seem to touch each other and both the needles and the platelets are everywhere in the gel. In such a mixture, we can see stacks of needles but also more individual needles than we could observe on the pure attapulgite gel, image 6.1a.

Regarding the aged sample, a homogeneous structure can be seen without any obvious aggregates as shown in the micrograph A.3 in the Appendix. Although, the structure of the aged gel is very similar to the one found for the fresh one, it may be less chaotic, or more organised, than the fresh one due to more connections between the needles and the platelets. Thus, ageing does not seem to significantly impact the pore size of the gel since lots of water could still be found in it. However, comparing images 6.3b and 6.3c, the water channels may be larger for the aged gel than for the fresh one due to this restructuring. Furthermore, in contradiction with the structure of the aged bentonite gel, image 6.2e, the platelets in the aged mixture can still be clearly differentiated.

6.3.2 X-Ray tomography

X-Ray tomography was not able to resolve the structure of the gel down to the individual clay units. However, we can see the structure at a larger scale than with HPF Cryo-SEM as shown by the images A.4 in the Appendix. The 3D reconstructions, showing the clay in dark and the pores in white, display very porous gels in which the clay formed aggregates linked to one another and spanning the whole sample. Such system features large, interconnected pores. It can be qualified as bi-continuous at long range with one phase formed by the clay and the other by the water. Figure A.4 in the Appendix does not show obvious differences between fresh and aged gels: ageing does not significantly impact the long range structure of the gel, i.e. the aggregates, but rather the flocs themselves made of the clay sub-units.

A pore network model was generated using the XPoreNetworkModeling Extension of Avizo allowing us to extract some of the gel characteristics such as: the number of pores, the number of throats (water channels connecting two larger pores), the absolute permeability (capacity of a material to allow water to cross) and the tortuosity (measure the deviation of a pore network from a straight path), as shown by table 6.1. From such analysis, the graphs in figure 6.4 was plotted to compare the pore distribution of fresh and old gels based on the radius of their equivalent sphere. The total number of pores increased significantly with time for attapulgite and decreased slightly for bentonite and the clay mixture. As far as attapulgite is concerned, more large pores (equivalent radius between 5 and 50 μm) are formed during ageing, although the biggest pores are found for the fresh gel, see figure 6.4a.

Regarding bentonite gel, we can see two populations of pores: one which has a size below 1.5 μm and one which has an average size of about 8-10 μm . Taking the model of flocs and aggregates described by Michaels and Boger [148], the first category may corresponds to the pores that are between the flocs and the second correspond to the pores that are between the aggregates. In such a model, a floc corresponds to a particle and the water surrounding it. An aggregate corresponds to a group of flocs.

As far as the clay mixture is concerned, the pore equivalent radius distribution is similar to the attapulgite one with most pores having an equivalent radius between 0 and 2 μm . However, ageing does not seem to affect the pore distribution significantly. Therefore, the pore distribution may be determined by attapulgite whereas the ageing depends on bentonite.

Table 6.1: Properties obtained on the gels from X-Ray tomography from the analysis using Avizo

Sample	Pores	Throats	Absolute permeability (μm^2)	Tortuosity
Attapulgate-Fresh	6.7×10^4	80	9.9×10^{-9}	1.18
Attapulgate-Old	7.9×10^4	742	6.85	1.57
Bentonite-Fresh	12.3×10^4	9.3×10^3	1.50	1.64
Bentonite-Old	11.1×10^4	9.0×10^3	1.17	1.66
Mixture-Fresh	11.5×10^4	1509	5.49	1.66
Mixture-Old	10.7×10^4	1454	6.34	1.61

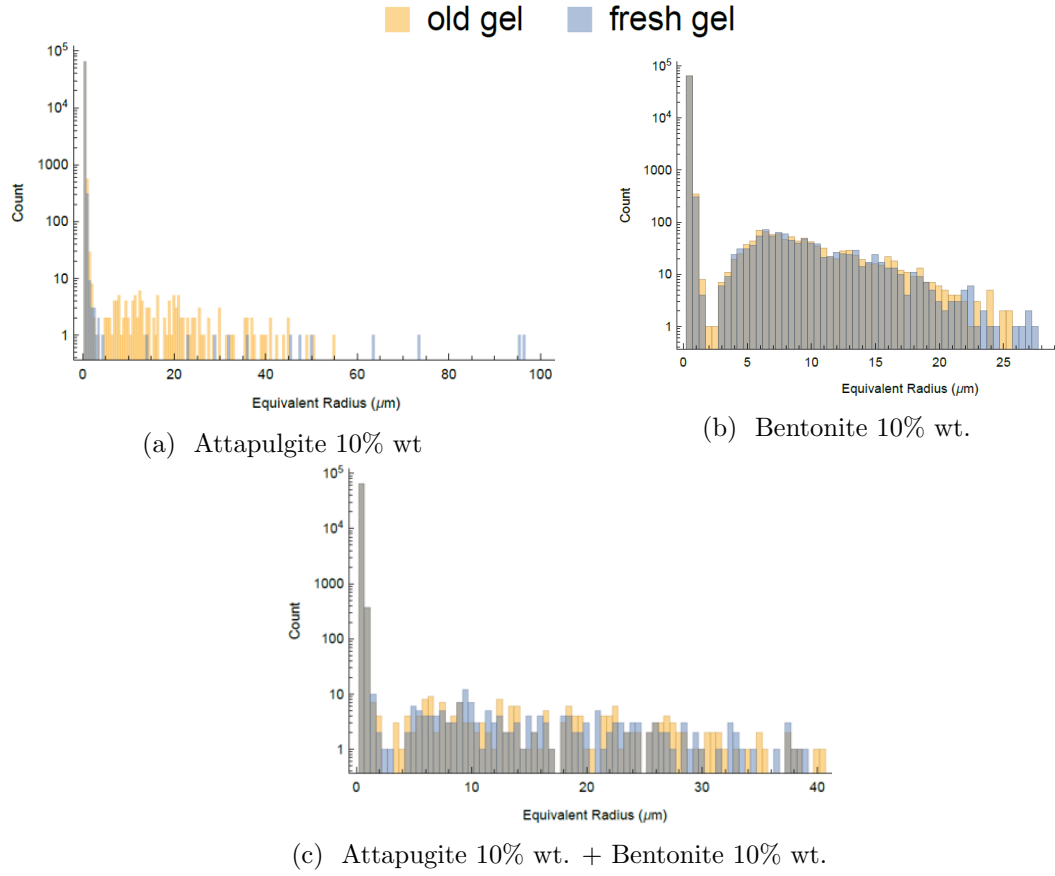


Figure 6.4: Equivalent radius distribution of the pores of fresh and old gels

Note: The grey color results from the superposition of the histograms of the old and fresh gels

The number of throats, absolute permeability and tortuosity increased significantly during ageing for attapulgate whereas they stay roughly constant for the other two gels. Thus, there are more connections between the pores for an aged attapulgate gel than for a fresh one as shown by Figure 6.5a. This can be linked to the increase in number of pores also influencing the tortuosity. In fact, we can expect that if there are more pores, even connected, such a connection would not be straight but would tend to bend around the clay aggregates enclosing the other pores. However, the absolute permeability obtained for a fresh attapulgate gel seems

very low and in slight contradiction with image A.4, in the Appendix, in which we can clearly see the pores. Such a value would make sense only if there exist no connection between the sets of pores. Regarding the tortuosity for bentonite and the mixture, we could have expected a significant decrease for the following reasons: 1) the decrease in the number of pores with ageing and 2) the water flow favouring straighter channels during ageing [148]. Similar imaging experiments at lower and upper places of the gel are needed to clearly determine the effect of sedimentation. The results also show that ageing does not seem to significantly influence the number of connections between the pores for bentonite and the mixture as shown by figures 6.5b and 6.5c. Figure 6.5 also shows that for all gels lots of pores are not connected to one another. These pores may correspond to the smallest ones that we can find between the flocs.

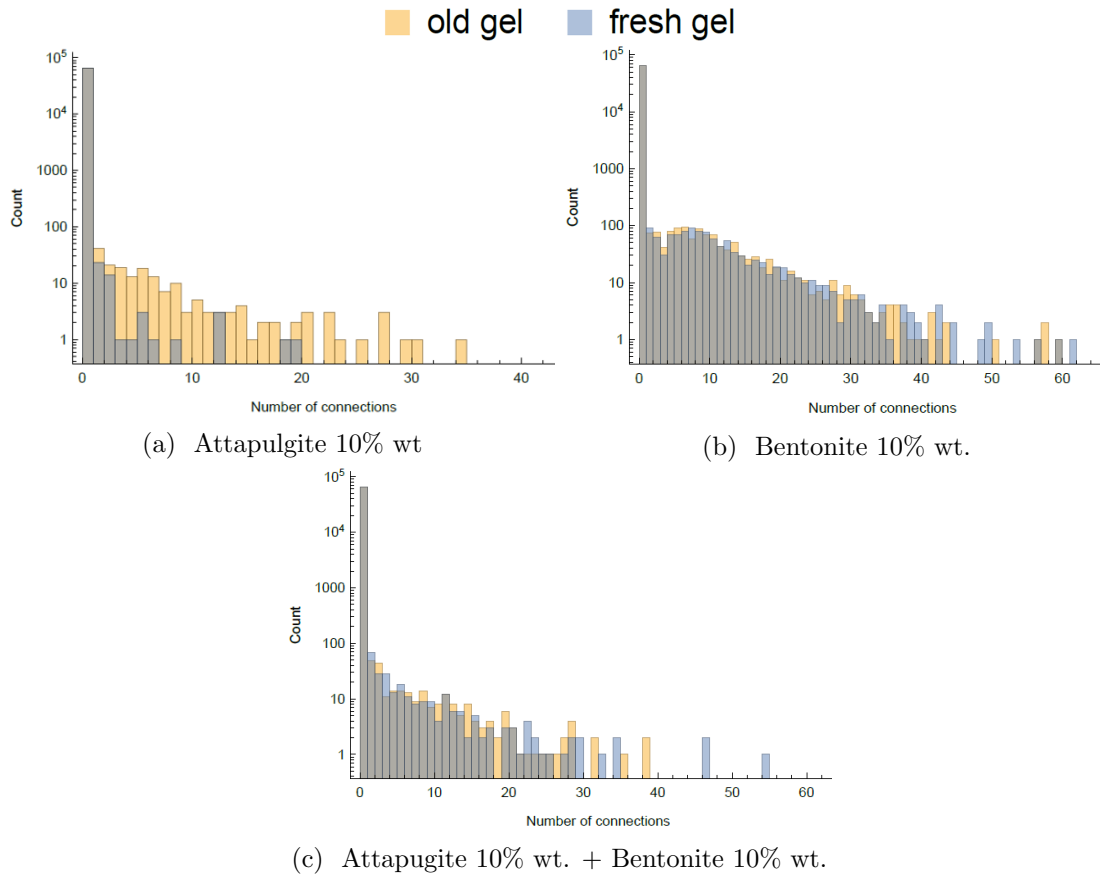
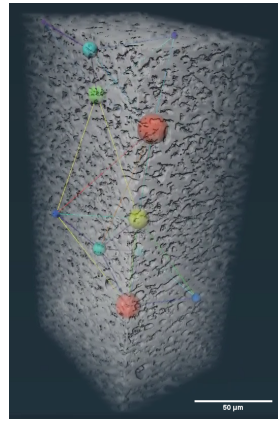
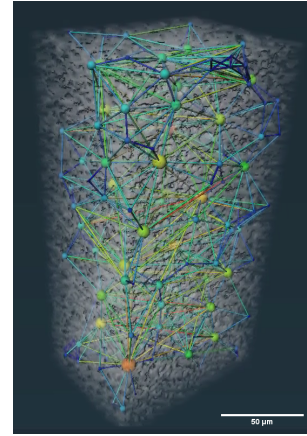


Figure 6.5: Distribution of the number of connection between the pores of fresh and old gels
Note: The grey color results from the superposition of the histograms of the old and fresh gels

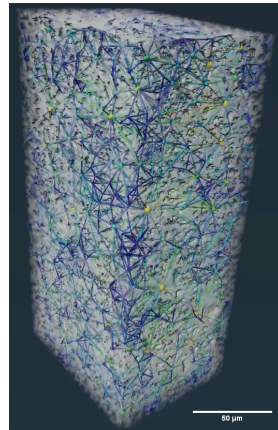
Since we are interested in the long range structure of the gel, we will focus on the pores with volume $>1 \mu\text{m}^3$. Figure 6.6 shows the pore network model with pores that meet this condition. The pore size is indicated by a colour scale (blue: small, red: large). This figure shows that fresh attapulgite gel features a very small number of pores and that ageing leads



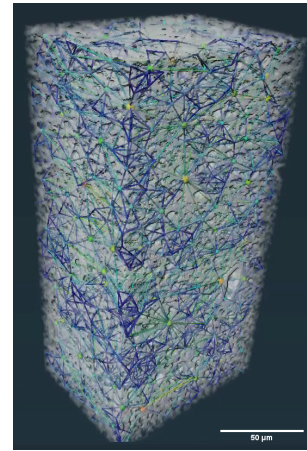
(a) Attapulgite 10% wt. - Fresh



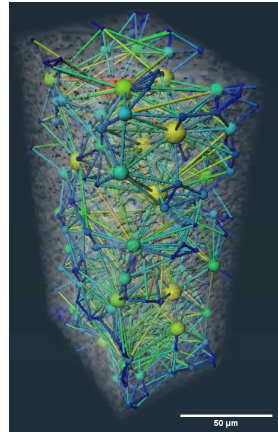
(b) Attapulgite 10% wt. - Old



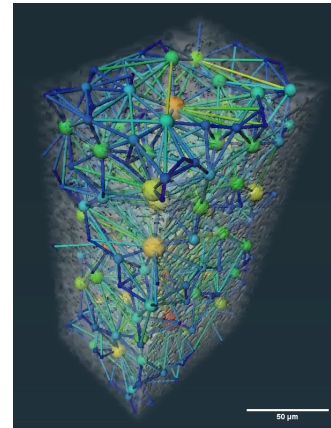
(c) Bentonite 10% wt. - Fresh



(d) Bentonite 10% wt. - Old



(e) Attapulgite 5% wt. + Bentonite 5% - Fresh



(f) Attapulgite 5% wt. + Bentonite 5% - Old

Figure 6.6: Modelisation of the pore network from X-Ray tomography of fresh and old gels for pores with volume $>1\mu\text{m}^3$. Red colours represent big pores and long throats, blue colours represent small pores and short throats. Pores are bright and clays are dark.

to the formation of more large pores homogeneously spread within the sample. However, not much difference seem to appear during the ageing for bentonite and the blend. Although the

bentonite gel may feature more pores with volume $>1 \mu\text{m}^3$ than the clay mixture, the pores are homogeneously spread within the samples for both gels.

6.3.3 Model of the ageing effect on clay based gels from Cryo-SEM and X-Ray tomography

The results obtained during the ageing of attapulgite, see images 6.6a and 6.6b could be explained by reorganisation of the needles during ageing which leads to a more homogeneous spreading of the clay everywhere in the sample. This idea is in line with Brownian motion, increased at 50°C , and repulsive forces between the needles under such experimental conditions. Therefore, we can hypothesise that fresh samples are heterogeneous on the long range with some big pores and some stacks of needles forming agglomerates spanning the whole volume. With time, the stacks would “release” some needles as shown by figure 6.7. These newly free needles interact with each other forming additional aggregates filling the initial pores and building new ones. Therefore, we expect the aged gel having more pores which are bigger on average than the fresh one.

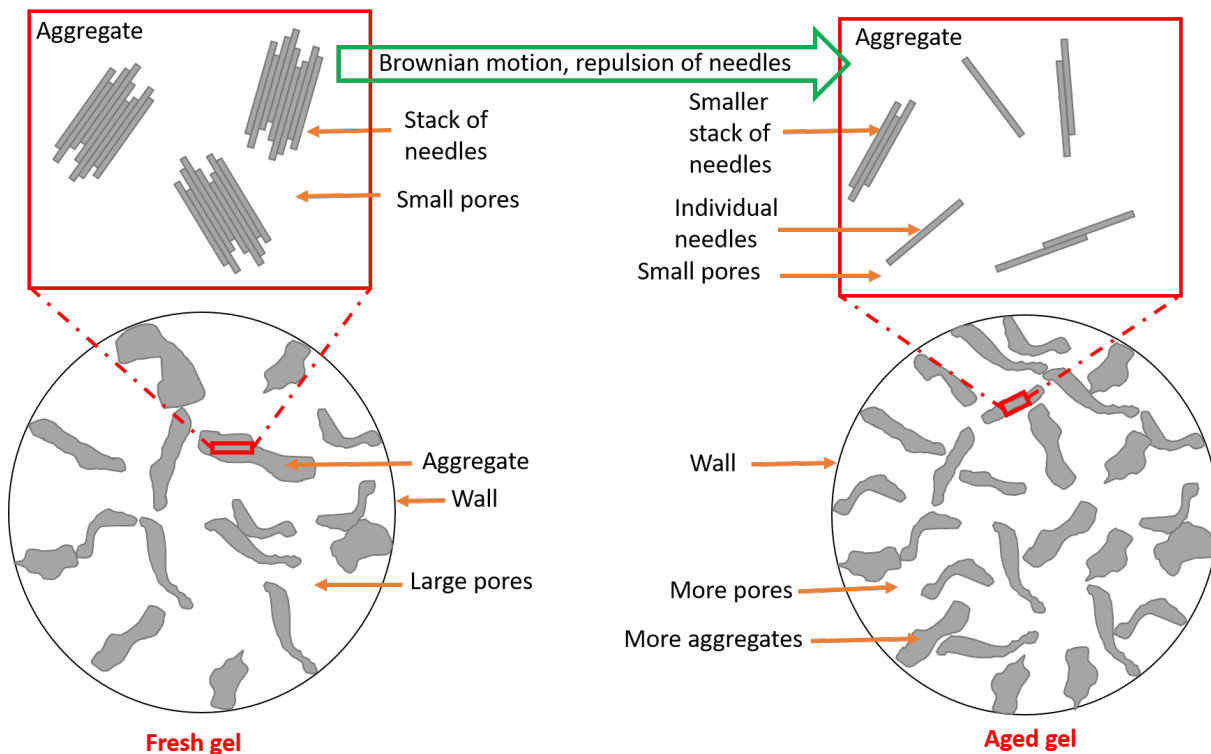


Figure 6.7: Ageing model for Attapulgite 10%

Regarding bentonite, although the effect of ageing on the pore size distribution is not very

clear, see figure 6.4b, ageing may favour the formation of large pores. The same hypothesis as presented above for attapulgite may still hold: Brownian motion of the platelets would disperse them leading to a more homogeneous system. Additional bonds between the platelets may arise through edge-edge or edge-face interactions for instance. However, regarding bentonite, it is important to consider a probable remaining swelling of the platelets at such a high concentration of clay. This would lead to an increase of the volume occupied by one platelet. Therefore, the water contained around the particle would be used for its swelling. Because of the swelling and the increased interaction between the platelets, pores that are inside the flocs will tend to disappear leading to a decrease of the number of the smallest pores as shown in figure 6.8. This is in line with the HPF Cryo-SEM image obtained, see image 6.2e. Note that X-Ray tomography and its subsequent analysis may be inaccurate at that scale.

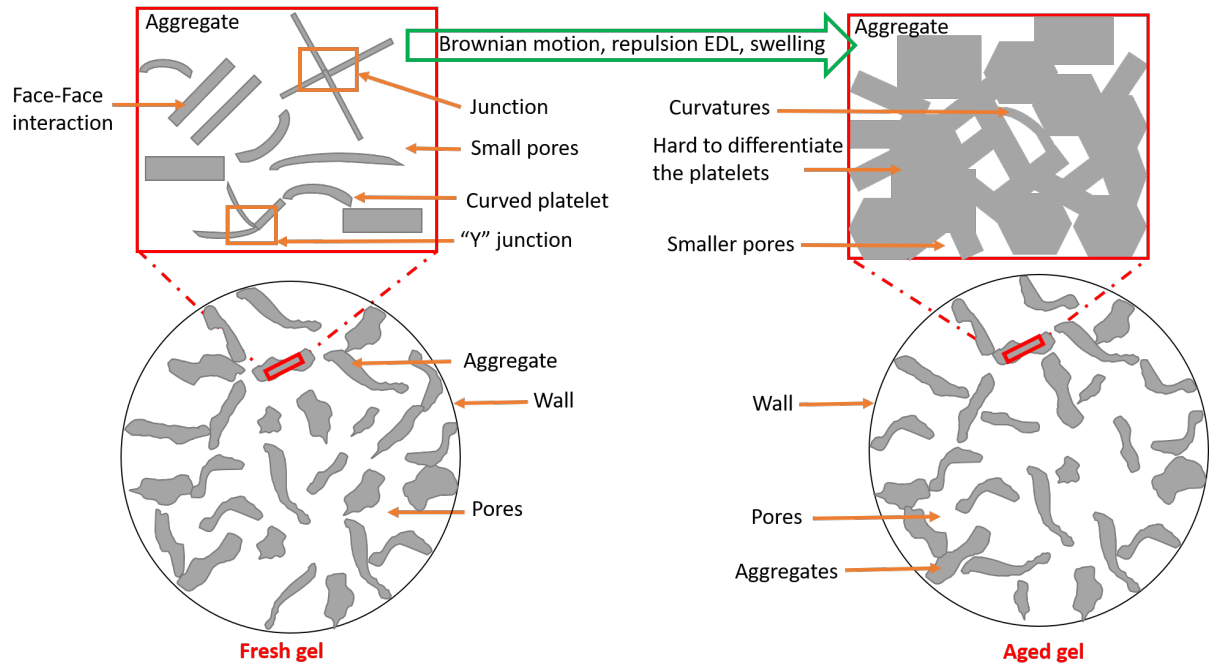


Figure 6.8: Ageing model for Bentonite 10%
(EDL: Electric Double Layer)

Regarding the clay mixture, the results presented in table 6.1 and figure 6.6 does not indicate a clear effect of time on the long range structure of the gel, similarly to bentonite, as shown by figure 6.9. However, figures 6.4 and 6.5 show that the pore size distribution is similar to attapulgite gel imposing the pore characteristics. This is consistent with the HPF Cryo-SEM images obtained, image 6.1d, showing that the bentonite platelets did not experience any microscopic change over time, and secondly, that the structure of the gel stays roughly the same at microscopic lengthscales.

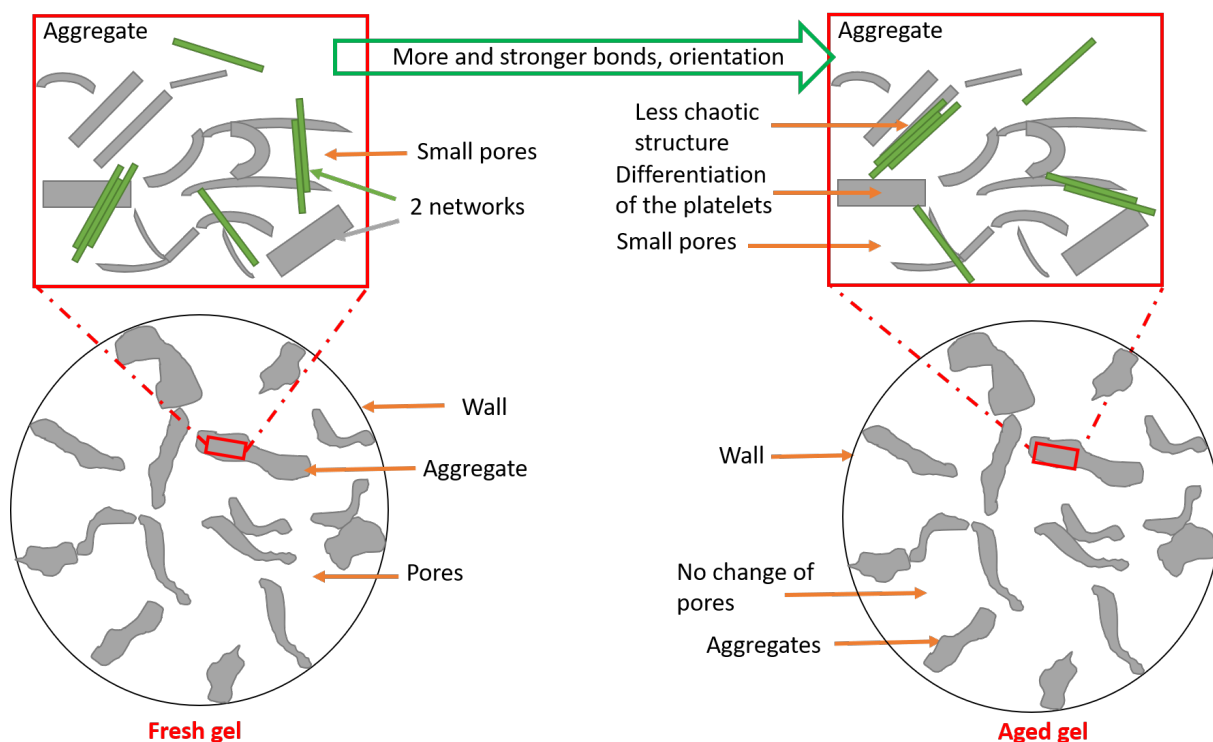


Figure 6.9: Ageing model for Attapulgit 5% and Bentonite 5%

6.3.4 Sedimentation profile

The sedimentation profile obtained during ageing shows that all gels collapse, as seen by the drop of their surface in figure 6.10. However, for bentonite and the mixture we see a homogeneous decrease of the transmission throughout the height of the gel indicating an increase of the concentration of the clay. This is consistent with a shrinkage of the gel. However, for attapulgit, the transmission decreases at the top of the gel but stays constant at its base, see figure 6.10a. This is in contradiction with the consolidation theory developed by Michaels and Bolger [148]. According to these authors, sedimentation happens when the static pressure outweighs the yield stress. In that case, the network starts collapsing at its base, thus increasing the volume fraction and strengthening the gel there. There is also the formation of a constant density layer, which collapses up to a point where the static pressure is equal to the yield stress. This theory was developed for Kaolin which is a non swelling clay with a shape similar to a platelet. We do not necessarily expect bentonite to follow such a theory as it is a swelling clay, but it may be more applicable to attapulgit [30]. In our system, evaporation of water might have happened as well, affecting the top of the gel first as it is closer to the surface.

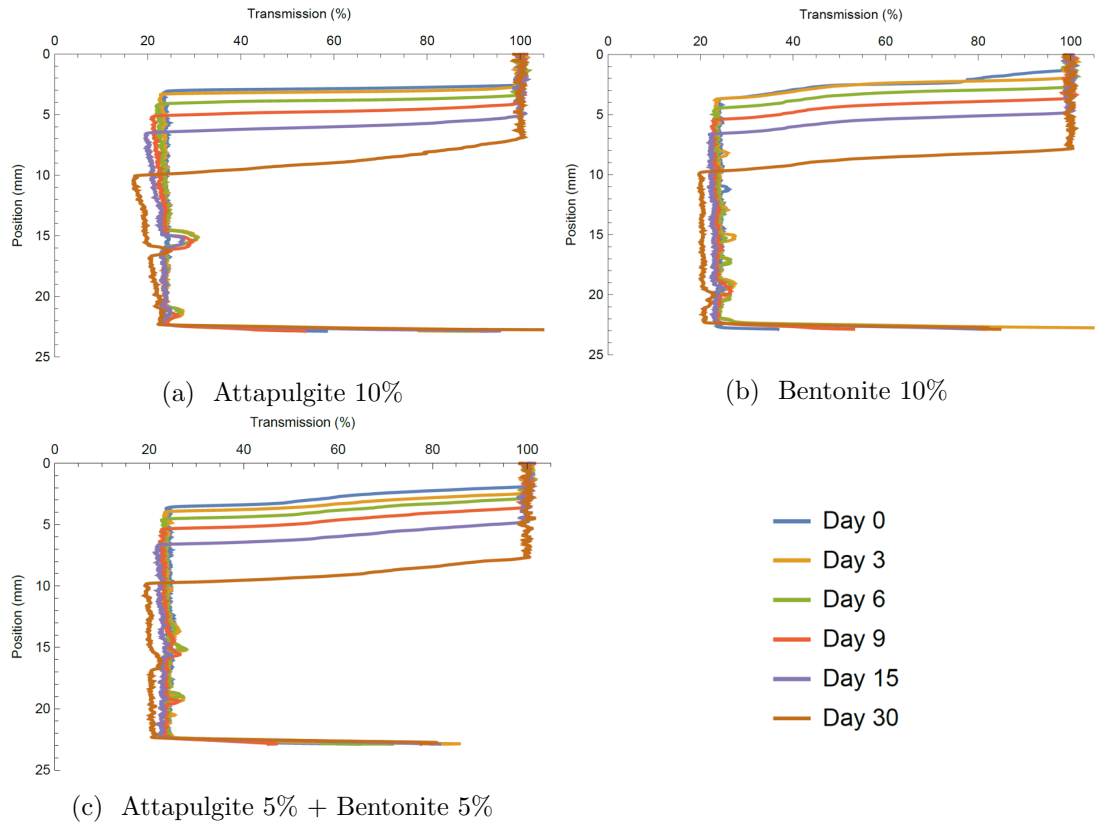


Figure 6.10: Sedimentation profile obtained during ageing of each gel using X-Ray.

6.4 Discussion

We will discuss our findings in the light of the model described by Micheals and Bolger for Kaolin dispersions [148] to explain the long range structure. They define a system made of the clay units and the attached water forming an entity called floc. Such flocs gather to build aggregates. The size of the flocs and aggregates depends on different parameters such as the clay concentration, the gel preparation (the mixing rate for instance) and the collision between them. Since we store the gels at 50°C for longer than a month, the collision rate might be higher in our study than in other work performed at room temperature. Therefore, the aggregates revealed by X-Ray tomography may be larger.

The results obtained from HPF Cryo-SEM on Attapulgit show stacks of needles featuring different orientations. This is in line with previous studies imaging palygorkite at different pH [126, 150]. They attributed the random organisation to the repulsion between the needles featuring negatively charged surfaces at alkaline pH. Note that the pH of the attapulgit used here is 9.8 according to the manufacturer, thus the needles are expected to be negatively charged

(the isoelectric point is at pH about 4-4.5). Furthermore, X-Ray tomography revealed very big pores for attapulgite 10% wt. on fresh and aged gels similarly to what Michaels and Bolger described for flocculated suspension of Kaolin [148].

Regarding bentonite, HPF Cryo-SEM imaging seems to show some edge-edge or edge-face association between the platelets in addition to face-face interactions. Although edge-edge or edge-face interactions are likely to happen, their existence is hard to prove and would require imaging at very high resolution as discussed by Mouzon et al. [63]. In this study, the pH of bentonite was about 9. For such a pH value, Benna et al. stated that the platelets are negatively charged if the pH is above the isoelectric point of 7 [119]. Therefore, they support the idea that the house-of-card structure would not form under such conditions ($\text{pH} > \text{pH}$ of the isoelectric point) if the ionic strength is not very high. However, in this study we can see the formation of bonds with different angles between the platelets forming “cells”, see figure 6.2b, in agreement with the observations made by Leong et al. [133]. This difference can be due to our use of a commercial clay product containing lots of impurities and probably some salt as well. These may have compressed the double layer bringing the clay platelets close to each other and allowing interaction between them. However, the literature is not clear regarding the effect of adding components on a clay gel structure [151].

Furthermore, although the interaction may be repulsive, edge-edge or edge-face interaction may still be possible as the interaction there would be the less repulsive one [146]. This does not exclude the presence of local attractive points as shown by the local contacts (“Y” junction) revealed by HPF Cryo-SEM. Therefore, as stated by others [39], the edge of the platelets is likely to keep some positive charges at pH around 9. The effect of the ageing on the bentonite network at short range is in line with previous findings which could no longer distinguish the individual platelets [42]. However, Leong et al. imaged 2 years aged 6.5% wt SWy-2 gels and could still differentiate the individual platelets [133], despite seeing more interactions between them.

During ageing, the motion of the platelets becomes more and more limited due to the contact with other platelets and the presence of neighbours [133]. Ageing is also accompanied by a decrease in the amount of water between the platelets, as show by figures 6.2e and 6.10b. However, X-Ray tomography did not show any drastic change in the long range microstructure of the network with time. This is in contradiction with what Ye and al., [152] and Delage et al., [42] found on compacted bentonite. They stated that the reorganisation of water during

ageing would increase the pore size within the aggregates but decrease the pore size between them. Such discrepancies may be due to the different ageing conditions impacting the ageing of bentonite [152] as well as the gel composition. In fact, our study was performed on very hydrated gels, 90% of water whereas the amount of water used by Ye and al. for instance was kept below 20%. The same authors have also seen a bimodal pore distribution which we can also clearly see for bentonite. However, the threshold size between the two pore categories is around $1.5\mu\text{m}$ according to graph 6.4b which is much bigger than the one described by Ye et al. [152] which is around 150-200nm. Such differences may be caused by the techniques used: they used mercury intrusion whereas we used X-Ray tomography. As already stated, we could not resolve the nanometer structure of the gel using X-Ray tomography. In addition, since this study focuses mainly on pores with volume $>1\mu\text{m}^3$, we did not try to characterise the pore distribution of the smallest pores. Delage et al. [42] did not show any difference in the pore size distribution between 1 and 30 days of ageing, similar to us. They waited for 90 days to see a difference. However, their samples were allowed to age at room temperature whereas ours were put at 50°C which may have impacted the ageing phenomena by transferring more energy to the system.

The clay mixture may form two networks made of each clay interacting with one another as revealed by the chaotic structure seen from Cryo-SEM. However, each network may differ from the one formed by each clay alone. Cui et al. observed a “cross-overlapping pattern” of the clays [150] that they attributed to “a three dimensional network of sheets and fibers”. The model of flocs and aggregates remains valid according to the X-Ray 3D reconstruction; the flocs are likely to be made of these two clays. We saw that ageing did not have lots of effect on the structure of the gel at short and long range as revealed by X-Ray tomography and HPF Cryo-SEM. Again, this may be caused by the difference in shape and charge between the two clays which also display different structural behaviour over time. For instance, the swelling of bentonite and the increased contact between the platelets, happening with ageing on the pure gel, is hindered by attapulgite. The restructuring of the pores undergone by attapulgite is also prevented by bentonite. It may have a competition between the two clays for the water rendering it less available for gel restructuring. However, although the pores may not be significantly affected with time, it does not mean that the interaction between the two clays does not evolve. The interaction between a needle and a platelet may be favoured over the interaction between platelets or needles.

Some contradictions between this work and already published results may be due to the downside of the techniques used, as recalled in chapter 2, paragraph 2.3.3.

6.5 Conclusion

This work studied the structural evolution and sedimentation profile of bentonite 10%, attapulgite 10% and their composite attapulgite 5% + bentonite 5% during ageing at 50°C using high pressure freezing Cryo-SEM and X-Ray tomography. We established and discussed a model of the ageing of such clays.

For all gels, X-Ray tomography displays a bicontinuous structure made of water contained in large pores and agglomerates made of clay and water spanning the whole samples.

Attapulgite fresh gel was characterised by stacks of needles with diverse orientations whereas the aged gel features more single needles in addition to stacks containing a smaller number of needles. The ageing of the gel is accompanied by an increase in the total number of pores and particularly in big pores. The model supported by this work is that ageing favours the dissociation of the needles in a stack which, after experiencing motion within the gel, are spread into the sample. Such organisation lead to the formation of new aggregates and so new pores between the aggregates.

Bentonite gel features platelets interacting with each other through edge-edge, edge-face and face-face interactions. Platelets are clearly defined in a fresh gel but they are harder to distinguish in an aged gel. This may be due to the increased contact of the platelets and the likely swelling of the remaining non-delaminated platelets. Therefore, at such scale ($\sim 1\mu\text{m}$) ageing decreases the size of the pores inside the agglomerates in contradiction with previous studies. The pore size shows a bimodal distribution with one set of pores between the flocs, inside the aggregates and the other set between the aggregates. The size of the pores between the aggregates was not affected over time. Although, such platelets also move in the gel, this does not significantly impact the long range structure of the gel as shown by X-Ray tomography.

The clay mixture may form two networks cooperating as revealed by the chaotic structure found using HPF Cryo-SEM. The ageing did not significantly impact the structure of the network. Although it seems less disorganised than the fresh sample, it does not display any more swelling or increase connection of bentonite and the pores are also unchanged. Similarly

to bentonite, the long range structure of the gel was not impacted by the ageing. The pore size distribution of the mixture was similar to the one found for attapulgite.

Acknowledgments

We are very grateful to the Diamond light source synchrotron, mainly the I13-2 beamline, Dr. Christoph Rau and Dr. Shashidhara Marathe for allowing to perform the X-Ray tomography experiment on the gels. We also thank Dr. Errin Johnson for high pressure freezing the samples and Jean-Yves Mugnier for imaging them using Cryo-SEM. We are beholden to them for their large contribution in setting up the experiment.

General conclusion

This project had several goals: the first one was to find an inorganic compound that could be used as a thickener to replace xanthan in product formulation. This aim was addressed in chapters 3 and 4. The second objective was to study the ageing of different clay gels using rheology and microscopy. This was the subject of chapters 5 and 6.

Conclusion on the use of Laponite EP in product formulation

In chapter 3, we investigated the use of Laponite EP, an organically coated laponite, to replace xanthan in agrochemical product formulation. Suspension concentrates (SCs) formulated with the combination Laponite EP - bentonite featured similar rheological properties as the mixture xanthan-bentonite. Additional industrial tests, such as pourability and dispersion tests, were also conclusive using this formulation even after an accelerated storage test. The combination of Laponite EP and bentonite displayed some synergy between the two clays since none of the rheological requirement could be met when using each clay alone. HPF Cryo-SEM imaging of the gel showed both Laponite EP and bentonite. Therefore, the resulting structure may be two cooperating networks formed by each clay. The rheology of the SC could not be reproduced using the non-coated Laponite RD with bentonite. This highlights the importance of the coating of Laponite EP on the rheology of the resulting SC. Although the coating did not impact the surface of the platelets, it may have hindered the adsorption of other compounds, like the non-ionic surfactant Tween 20. Even though additional analysis needs to be performed to determine accurately the nature of the organic compound coating Laponite, the experiments performed point towards acetate. After obtaining successful results using the mixture Laponite EP 5g/L - bentonite 20 g/L, we were interested in studying the rheological response of such a blend under

varied environmental conditions.

In chapter 4, we used mixture design to model and predict some rheological parameters of the composite Laponite EP 5g/L - bentonite 20 g/L under different conditions. We varied the amount of salt (MgCl_2), non-ionic surfactant (Tween 20) and the pH (between 4 and 9). We focused on G' , G'' and the critical stress σ_c . Good models could be established for G' and G'' allowing an accurate prediction of these parameters. A suitable model was found for σ_c but the prediction was limited under certain environmental conditions rendering similar responses. The models reveal that the rheology of a sample depends on complex interactions between the salt, the surfactant and the pH. Some antagonistic effects were displayed between the components. Hence, the gel was stronger at low concentration of MgCl_2 and Tween 20 and was stabilised by the addition of Tween 20 between pH 6.5 and 9.

Conclusion on the ageing of clay gels

The rheological study of bentonite 10% wt. gel showed an increase of G' , σ_c , G_0 , G_1 , η_1 and cohesive energy with time suggesting an increase of the interaction between the platelets. This idea is consistent with the evolution of the microstructure of the gel due to ageing, as revealed by HPF Cryo-SEM. A fresh gel displays well defined platelets with face-face, and likely edge-edge and edge-face interactions whereas, on the aged gel, they have merged forming almost a single unit. This merging could be the result of increased contact between the platelets and maybe some remaining swelling. These would have led to a decrease in the amount of free water forming the pores around the platelets. This would have contributed to strengthening the gel. Therefore, the gel becomes more compact with time. The merging between the platelets can generate more frictions and therefore result in an increase of the viscosity parameter η_1 . However, it is hard to define whether or not there are still “Y” junctions between the platelets in the old gel, as hypothesized in chapter 5, since the HPF Cryo-SEM gives 2D images. Furthermore, we saw that the long range structure of the gel did not significantly change with time according to the X-Ray tomography reconstruction. This means that the changes in the mechanical properties of the gel are due to short range rearrangements of the platelets.

As far as attapulgite is concerned, the ageing of the gel showed some delay before G' , G_0 , G_1 started increasing. This delay may be explained by the absence of structural change affecting

the needles themselves during ageing, as shown by Cryo-SEM, but rather by the evolution of the long range structure of the gel, as shown by X-Ray tomography. Therefore, the mechanical strengthening of the gel may be due to long range rearrangement of the needles. Such rearrangement would take longer to happen than short range changes and would lead to an increase in the number of aggregates forming also new pores. The stability of the gel, reflected by σ_c and the cohesive energy, stayed constant. This might be due to the increased number of interactions between the needles, rather than a strengthening of each interaction. This has been demonstrated by HPF Cryo-SEM and X-Ray tomography, showing more interactions between the needles in an aged gel. Some syneresis (water released at the top of the gel) was macroscopically observed and could be caused by the increase in the number of large pores although the gel gets more tortuous with time. However, additional images taken at the top of the gel are needed to ascertain the cause of the syneresis.

Nevertheless, some inconsistencies between the rheological and the microscopical results persist. In fact, the imaging of the gels revealed the formation of aggregates for all clays, and according to Michaels and Bolger [148], the size of aggregates depends on the cohesive forces between the clay units and the flocs. We saw in chapter 5, section 5.3.3 that the cohesive energy for attapulgite is much smaller than the one for the other gels. According to this idea, the size of the aggregates formed by attapulgite would be much smaller than for bentonite and the mixture. However, from a qualitative view of the 3D reconstruction, figure A.4 in the appendix, the size of the aggregates seems to be comparable for all clays. Note that the images were taken at one location of the gel whereas the cohesive energy was determined in the bulk.

The rheological behaviour of the clay mixture was driven by bentonite with rheological parameters following a similar trend with time. However, the microstructure of the gel did not evolve in the same way as bentonite and displayed a disorganised structure. In fact, no swelling or improved connectivity of the platelets could be seen and the size of the small pores stayed the same. Such effects might have been prevented by attapulgite. The microscopic imaging indicated the formation of two networks interacting. Such interaction is supported by the synergistic effect obtained for the clay blend on some mechanical parameters. In fact, if it was not for any interaction between the needles and the platelets, the strength and stability of the gel would be lower than the one observed for the pure clay. Significant lower mechanical values would be obtained when mixing attapulgite and bentonite, either due to the destruction of the gel,

which is in contradiction with our results, or because we use a smaller amount of each clay. In addition, it is hard to conceive that one network formed by the two clays would have such similar rheological properties and cohesive energy as the bentonite network. The structure of the gel displays a similar pore size distribution as attapulgite. Nevertheless, similarly to the bentonite gel, the long range structure of the mixture does not evolve with time. Therefore, a change in the interaction between the networks, either bringing them closer, or with new connections, may be the cause of the mechanical strengthening of the gel and increase in viscosity.

Outcome and future work

This project has provided an alternative ingredient to xanthan for the formulation of agrochemical products. Other industries producing gels, like the paint or cosmetic industry could be interested in the combination Laponite EP - bentonite.

There is a need to explain in more detail why and how the coating of Laponite EP changes its rheological behaviour. Additional surface analyses could be carried out such as atomic force microscopy (AFM) on the pure clays and in presence of Tween 20 for instance. This will measure the adhesion strength between the components. The gelation process of Laponite EP and RD being different, a more thorough analysis using rheology could be performed. Such an experiment would provide some insight into the gelation conditions, such as the concentration or ionic strength required, or the behaviour at different temperature.

Additional experiments using X-Ray tomography could be performed by varying the location of the measurement of the gel and its ageing time. Therefore, we would be able to determine more clearly the effect of ageing on the long range structure and establish a more accurate sedimentation profile. Transmission X-Ray Microscope (TXM) could also be used on a small attapulgite or bentonite gel to try to resolve the clay units. AFM could be employed in the clay mixture in comparison with the pure components to try to determine the strength between the different clay units.

The methodology of mixture design presented here can be used as support for industries concerned about the rheology of their product, and in academia [104]. For the former, it can be used for product development, directly on the final product for optimizing formulations based on rheological criteria. In addition, such modelisation tool based on data analysis is more

and more appreciated by companies as it allows them to get fast and reliable results at a low cost. In academia, such methodology has already been used in food science but not necessarily to predict a rheological response [153]. However, in other fields like chemistry, although the response surface methodology or mixture design approach is known, it is not commonly used and lots of studies keep using the one parameter at a time approach. This traditional method is suitable when the objective is to explain some observed phenomena but not when the objective is to investigate the effect of an environmental variation on a particular property.

This project also considered the use of X-Ray tomography as an imaging technique for clay gel systems. Although X-Ray has already been used in the past, the results were not very conclusive in determining the structure of the clay [65,66]. The experimental conditions need to be improved to get to a higher resolution, but X-Ray tomography already shows the long range microstructure of the gel. Such a technique could be applied to other clays like Laponite EP to see if the coating influences the long range structure of the gel. It could also be used to image commercial products using clay as thickener.

Appendix

Chapter 3

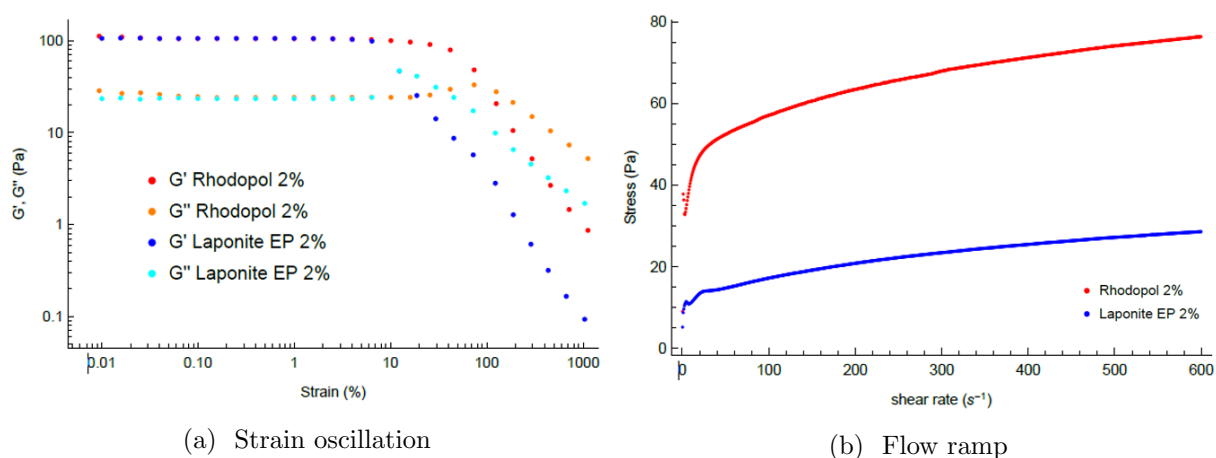


Figure 11: Comparison of the rheological behaviour of Rhodopol 2% wt. and Laponite EP 2% wt.

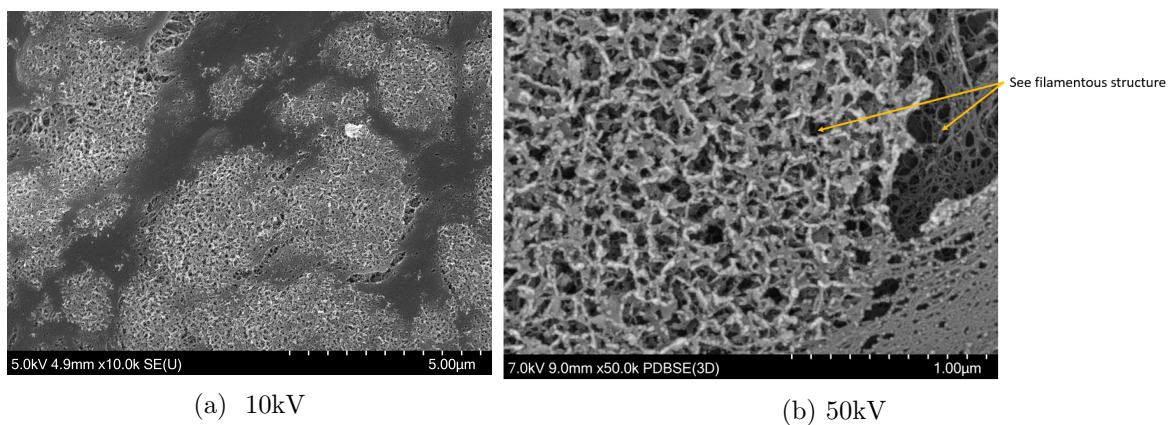


Figure 12: Microstructure of the gel formed by Laponite EP 2% using Cryo-SEM on HPF samples

Chapter 4

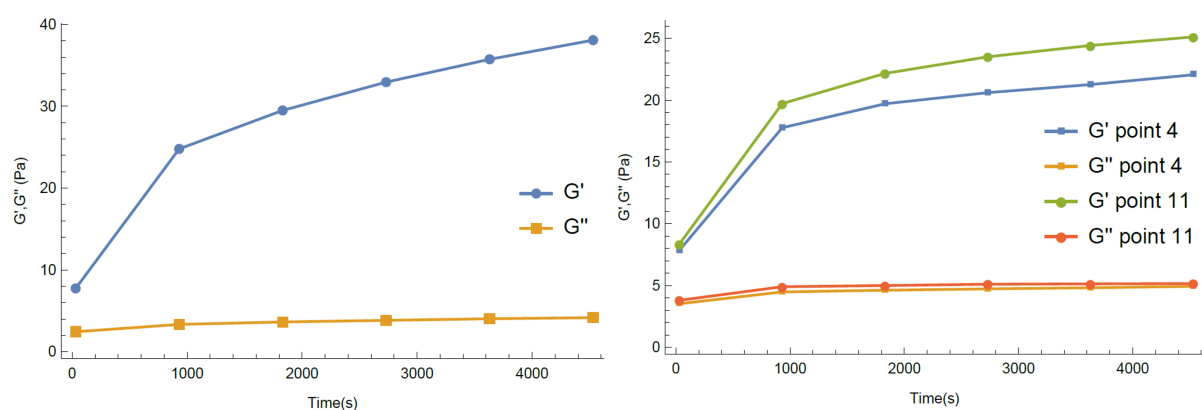
Table 2: Matrix Design

	MgCl ₂	Tween20	Water	pH
1	0.02	0.24	0.74	-1
2	0.00	0.10	0.90	-1
3	0.08	0.27	0.65	0
4	0.06	0.20	0.73	1
5	0.01	0.31	0.69	1
6	0.07	0.34	0.59	1
7	0.02	0.20	0.77	0
8	0.05	0.00	0.95	1
9	0.00	0.24	0.76	0
10	0.02	0.10	0.88	1
11	0.06	0.20	0.73	1
12	0.03	0.34	0.63	0
13	0.08	0.03	0.89	1
14	0.02	0.00	0.98	-1
15	0.08	0.10	0.82	-1
16	0.05	0.10	0.85	0
17	0.00	0.00	1.00	0
18	0.00	0.34	0.66	-1
19	0.02	0.24	0.74	-1
20	0.07	0.00	0.93	-1
21	0.06	0.31	0.64	-1
22	0.02	0.10	0.88	1
23	0.05	0.10	0.85	0
24	0.03	0.34	0.63	0

Table 3: Estimates and p.value obtained for G' , G'' and σ_c

Terms	G'		G''		Critical stress	
	Estimation	p.value	Estimation	p.value	Estimation	p.value
MgCl ₂ (Mixture)	1.9E+05	2.5E-03	3.0E+04	3.0E-04	-55.9	5.1E-01
Tween(Mixture)	4.5E+03	3.0E-04	6.5E+02	<.0001	0.0	1.0E+00
Water(Mixture)	1.3E+01	2.7E-02	2.5E+00	1.7E-03	0.5	6.0E-04
MgCl ₂ *Tween	-2.7E+05	2.4E-03	-4.3E+04	3.0E-04	-1410.7	1.6E-02
MgCl ₂ *Water	-3.0E+05	2.5E-03	-4.6E+04	3.0E-04	60.0	5.2E-01
Tween*Water	-8.1E+03	3.0E-04	-1.2E+03	<.0001	5.6	2.4E-01
MgCl ₂ *Tween*(MgCl ₂ -Tween)	NS	NS	NS		-2508.9	1.7E-02
MgCl ₂ *Water*(MgCl ₂ -Water)	-1.1E+05	2.3E-03	-1.7E+04	4.0E-04	NS	
Tween*Water*(Tween-Water)	-4.2E+03	2.0E-04	-6.1E+02	<.0001	NS	
Tween*pH	NS		-2.5E+00	4.5E-02	0.9	4.9E-03
Water*pH	-8.9E+00	1.5E-02	NS		-0.1	4.3E-02
MgCl ₂ *pH	1.4E+02	2.2E-02	1.4E+01	5.9E-03	NS	
pH*pH	NS		NS		NS	
MgCl ₂ *MgCl ₂ *Tween*Water	NS		NS		9081.0	9.2E-03
MgCl ₂ *Tween*Tween*Water	3.1E+05	2.1E-03	4.9E+04	2.0E-04	NS	
MgCl ₂ *Tween*Water*Water	1.8E+05	2.7E-03	2.9E+04	3.0E-04	1184.5	3.8E-02

Note: NS means non-significant



(a) Laponite 5g/L + Bentopharm 20g/L + $MgCl_2$ 2% + Tween 20 20% at pH 6.5 (point 12) (b) Laponite 5g/L + Bentopharm 20g/L + $MgCl_2$ 4% + Tween 20 12% at pH 9 (point 4 and 11)

Figure 13: Example of time oscillation obtained for different formulations at 1Hz

Chapter 5

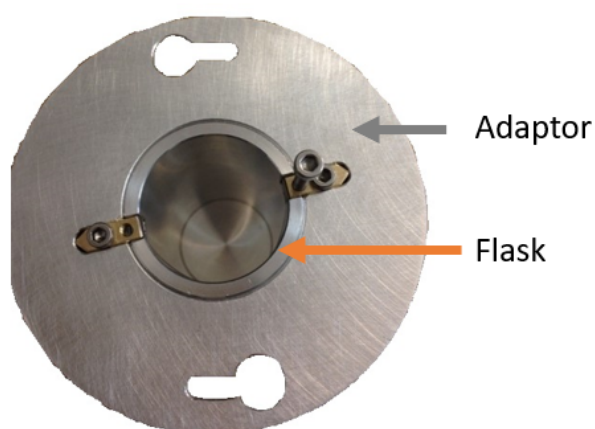


Figure 14: Tailored flask and its adaptor to the Peltier concentric cylinder

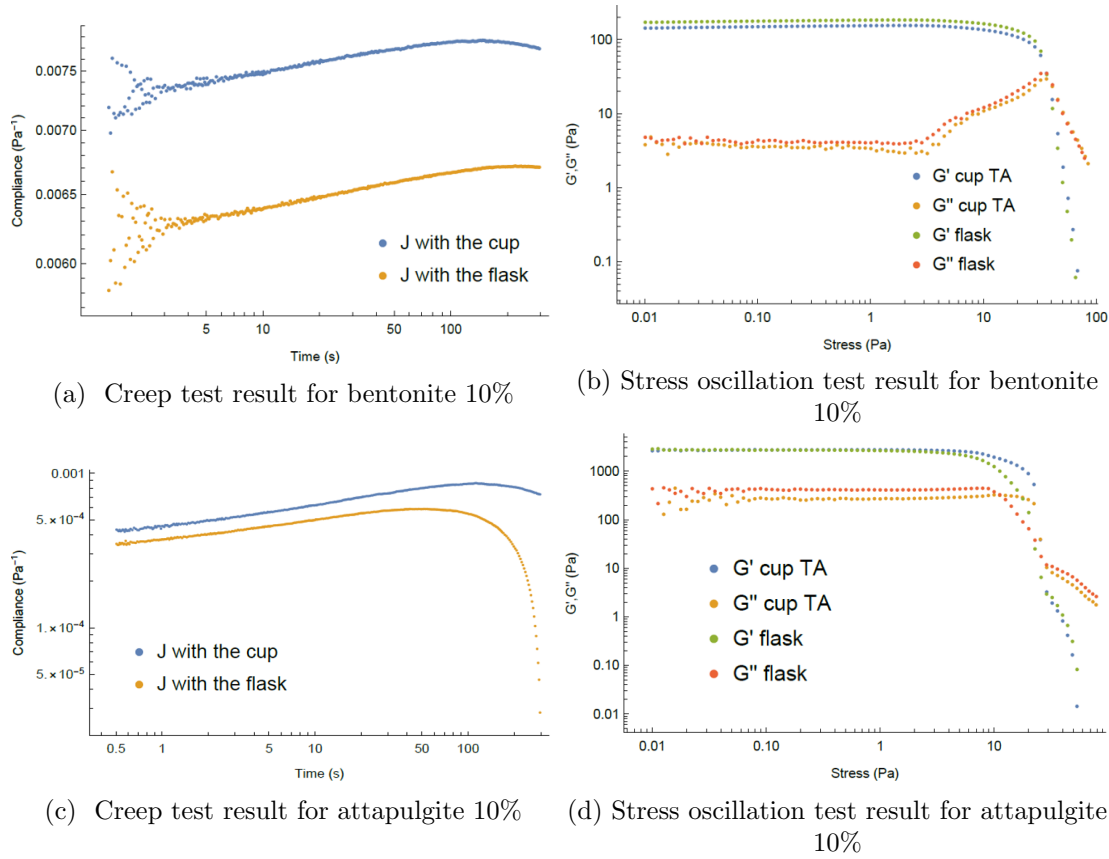


Figure 15: Results of the rheological tests performed on attapulgite 10% and bentonite 10% using the home made flask against a reference one

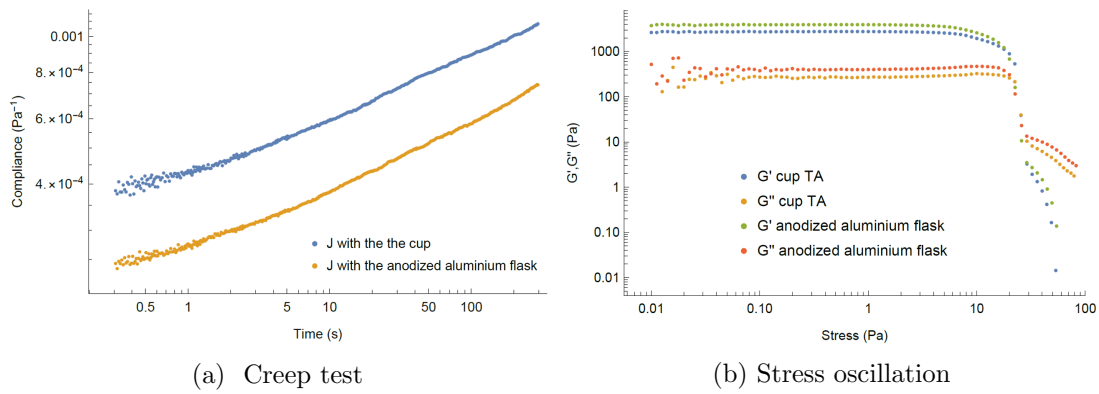


Figure 16: Results of the rheological tests performed on attapulgite 10% after hard anodizing the flasks

Models tried to fit the evolution of G' with time for attapulgite 10%

$$Y = a + b \times \text{Exp}(-t/\tau), \quad (1)$$

$$Y = a \times t^c + b \times (1 - \text{Exp}(-t/\tau)), \quad (2)$$

$$Y = a/(1 + \text{Exp}(b - c \times t)), \quad (3)$$

$$Y = a \times \text{Exp}(\text{Exp}(b - c \times t)), \quad (4)$$

$$Y = a - (a - b) \times \text{Exp}(-k \times t), \quad (5)$$

$$Y = a \times (1 - \text{Exp}(-t/b)), \quad (6)$$

Where a and b correspond to constants for instance G'_0 or G'_∞ . Equation 5 corresponds to the Nguyen-Boger model [138], where $a = G'_\infty$ and $b = G'_0$. Equation 3 and 4 corresponds to the logistic and Gompertz model used for bacterial growth respectively, [154].

Chapter 6

Full description of the analysis of the X-Ray tomography images

X-Ray tomography of the gels gave 2100 slices of dimension $2100 \times 1800 \mu\text{m}$. Such images were used to build a 3D image after reconstruction. Such a 3D volume was analysed using the software Avizo as follows:

- A subvolume of dimensions: $1779 \times 1563 \times 2100$ for all gels was extracted.
- A Gaussian filter was applied to the image to reduce its noise with the following parameters: method: separable, standard deviation: 1, Kernel size factor: 5 for attapulgite, 2 for bentonite and the mixture. The resulting images display an histogram. The mean of the histogram was 78 and 69 for the fresh and old attapulgite, 78 and 71 for the fresh and old bentonite, 68 and 67 for the fresh and old attapulgite + bentonite.
- The images were binarized using a threshold by criterion. The criterion set was less than the mean of the histogram of the source image. Hence, the pixel corresponded to the pores are set to 1 and the one corresponded to the clay are set to 0.
- Another subvolume of size $747 \times 566 \times 1491$ was extracted to perform the following steps:
 - The separate object tool was used using a Chamfer-conservative method. This method keeps the chamfer distance constant, which corresponds to the length of the shortest path between two nearest neighbours. The interpretation was set as 3D, the output type was connected object, the neighborhood 26 and the algorithm mode was repeatable. The marker extent corresponds to the contrast factor. The higher the marker extent, the smaller the number of initial

points that will be used for the watershed. Its value was set to 10 and 7 for the fresh and old attapulgite gels, 4 for the fresh and old bentonite gels and 6 for the fresh and old mixtures.

- We applied the Generate Pore Network model (part of the Avizo XPoreNetwork module extension) with the default boundary conditions of 130 000Pa and 100 000Pa as input and output pressure respectively. The fluid viscosity was set at 0.001 Pa.s corresponding to the viscosity of water.

High pressure freezing Cryo-SEM results

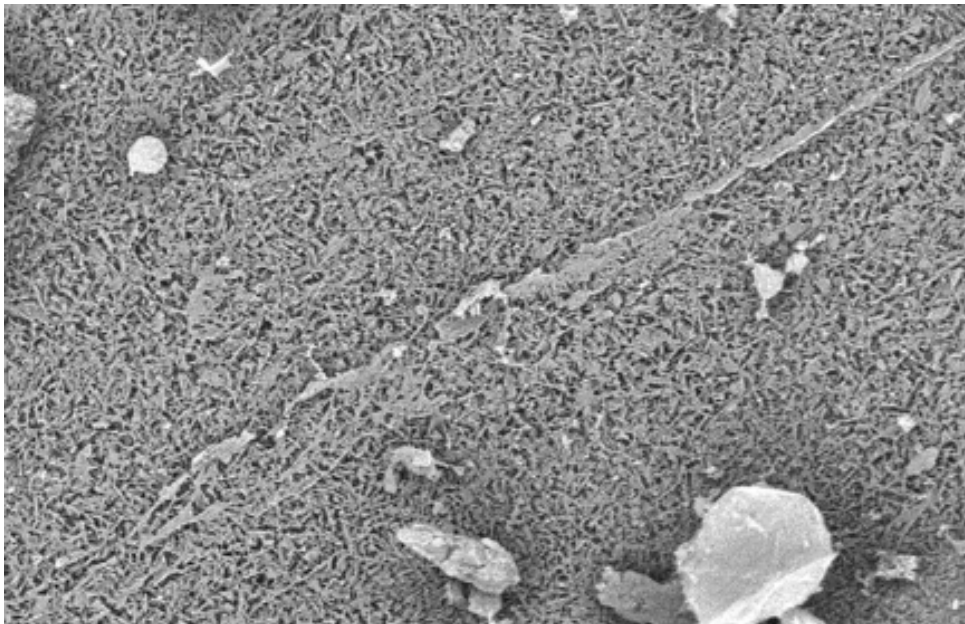


Figure A.1: HPF Cryo-SEM of Attapulgite 10% gel showing an area highly concentrated in needles

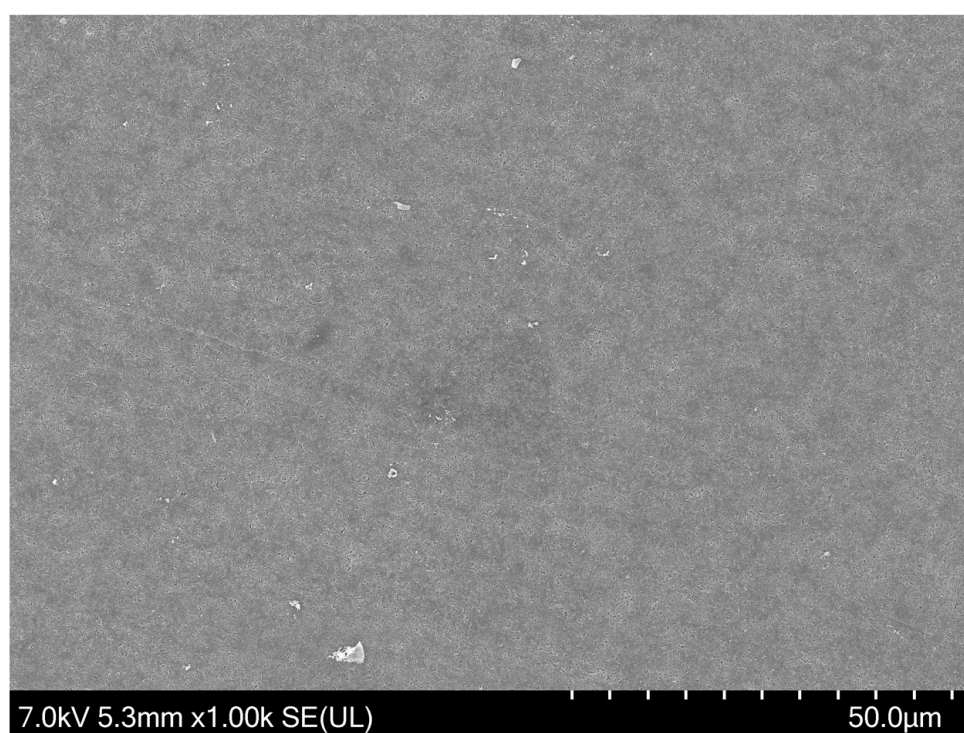


Figure A.2: HPF Cryo-SEM of Bentonite 10% gel showing a homogeneous structure free of aggregates

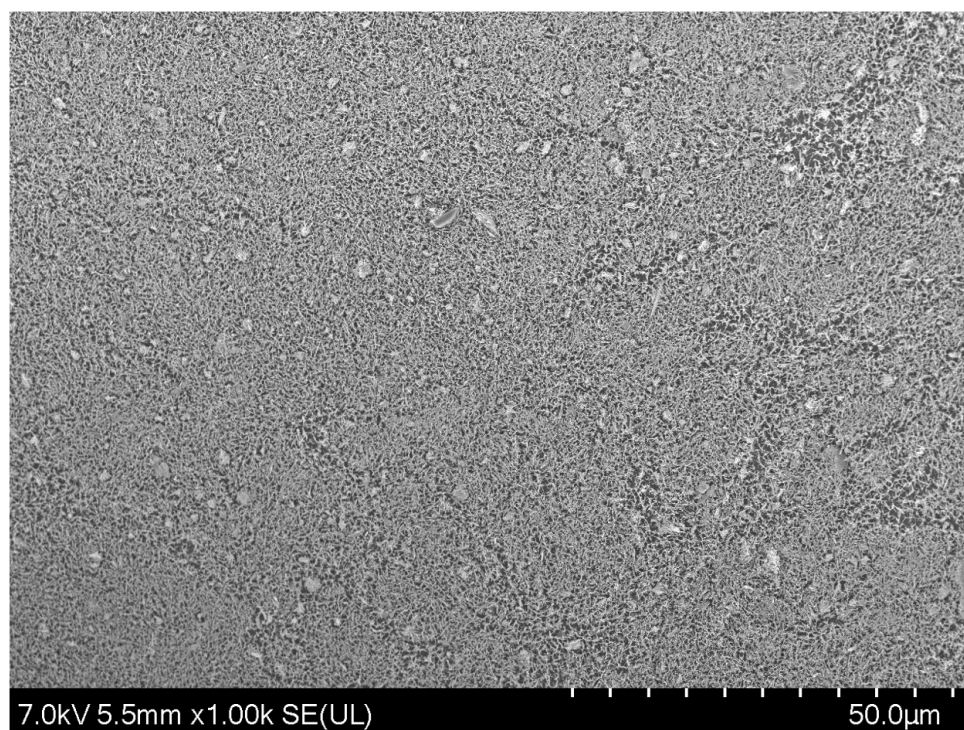
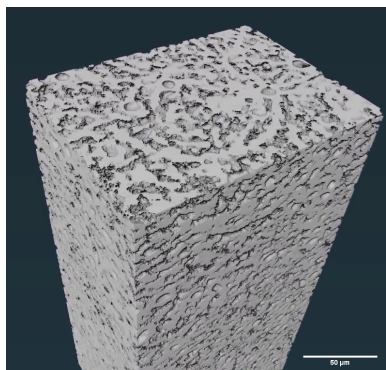
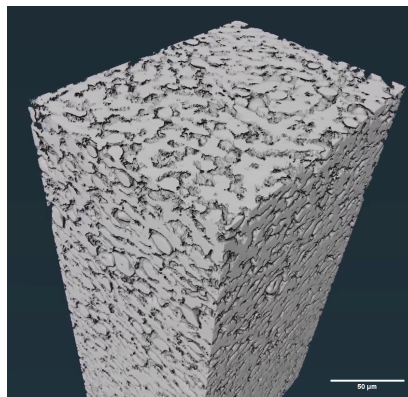


Figure A.3: HPF Cryo-SEM of Attapulgit 5% + Bentonite 5% gel showing the long range structure of the gel

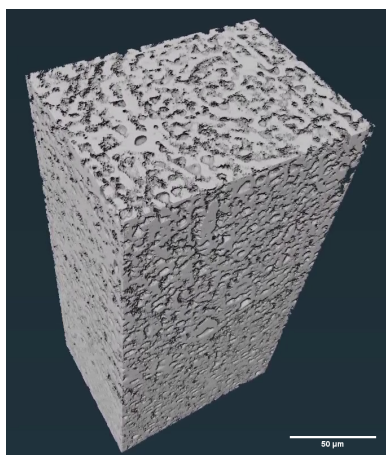
X-Ray tomography analysis



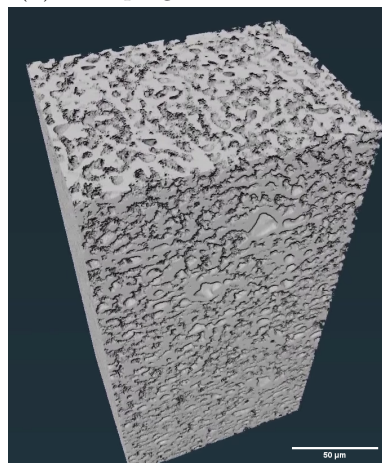
(a) Attapulgite 10% wt. - Fresh



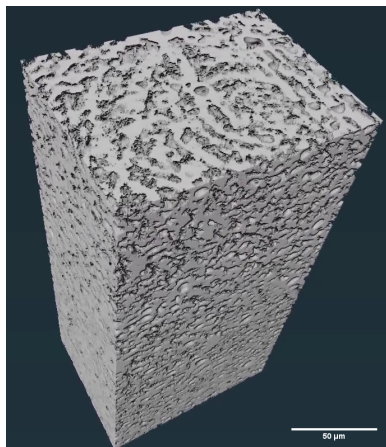
(b) Attapulgite 10% wt. - Old



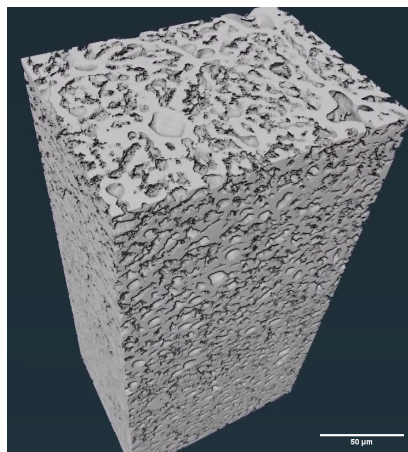
(c) Bentonite 10% wt. - Fresh



(d) Bentonite 10% wt. - Old



(e) Attapulgite 5% wt. + Bentonite 5% - Fresh



(f) Attapulgite 5% wt. + Bentonite 5% - Old

Figure A.4: 3D visualisation of the X-Ray tomography reconstruction after image processing: the clay is dark, the pores are bright

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