

**TECHNICAL UNIVERSITY OF CRETE  
DEPARTMENT OF MINERAL RESOURC ENGINEERING**



**Rheological Properties of Palygorskite-Smectite and Sepiolite-Smectite Mixed Clay Suspensions**

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**A thesis submitted to Technical University of Crete, in partial fulfilment of the requirements for the Degree of International Masters in Advanced Clay Science**

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**Abstract:**

Clay minerals are widely used in the formulation of drilling fluids because of their ability to form stable and viscous suspensions. Both bentonites and fibrous clays (sepiolite and palygorskite) are used by the industry for this purpose. Although usually clay suspensions contain a single clay mineral phase, often fibrous clays occur in association with smectite. Since bentonites display different rheological behaviour than the fibrous clays especially in the presence of electrolytes, it is useful to explore the rheological properties of mixed suspensions. So far only few studies have been carried out on this topic (e.g. Neaman & Singer, 2000); hence the rheological properties of clay mixtures are far from being understood. In this study, six well characterized smectite samples with different layer charge, namely low charge (layer charge  $< 0.425$  e/hfu), intermediate charge (layer charge between 0.425 and 0.47 e/hfu) and high charge smectites (layer charge  $> 0.475$  e/hfu) were selected and mixed at different proportions (0, 10, 20, 40, 60, 80, 90 and 100%) with palygorskite from Grevena, Greece and sepiolites from Vicalvaro basin, Spain and Euboea, Greece. The rheological properties of 5% mixed palygorskite-smectite and sepiolite-smectite suspensions as a function of smectite concentration were studied in aqueous medium at pH 7 in order to investigate how the rheological characteristics of palygorskite and sepiolite are affected by the presence of smectite. The results of this work showed that the influence of smectite on rheological properties of palygorskite and sepiolite suspensions depends on the proportion of the smectite admixture and layer charge and charge localisation. The interaction between the two end members seemed to occur at lower percentage (10 to 20%) of smectite in the mixture. The layer charge of smectite influence the degree of dissociation and the thickness of smectite quasicrystals, which consequently determine the number of particle involves in the interaction and the strength of particle-particle linkage.

Key words: Layer charge, rheological behaviour, quasicrystals

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# **1 Introduction**

## **1.1 Problem background**

Clay minerals are among the main additives used often to optimize the rheological properties of suspensions, since they increase significantly the stability and viscosity of the flowing suspension. They form gel-like structures at low solid content (Luckham and Rossi, 1999). This property has great importance in different application. Smectite, sepiolite, and palygorskite are utilized in a variety of industrial applications, such as drilling fluid, paper coating and pharmaceutical products in which rheological properties play a significant role (Galan et al., 1994; Galan, 1996; Luckham and Rossi, 1999; Chafe and Bruyn, 2005; Murray, 2007; Cinar et al., 2009; Christidis 2011; Tunc et al., 2011). In the drilling industry, these properties enable the clay suspension to suspend the large dense particles of the drilling cuttings and require relatively low pump power during circulation (Luckham and Rossi, 1999).

Although most clay minerals form stable and viscous suspensions when dispersed in water, the mechanisms of gel formation for each clay mineral differing because of their unique structures, size, shape and composition (Viseras et al., 1999; Heller and Keren, 2001; Cinar et al., 2009; Paineau. et al., 2011). In swelling clay minerals like montmorillonite, the net negative layer charge generated due to isomorphous substitution is compensated by the interlayer exchangeable cations. The hydration of the interlayer cation, which causes swelling and separation of clay layers, controls the movement of water and affects the rheological properties of swelling clays. Therefore, in such clay minerals the swelling potential and colloidal behaviour (particle-particle interaction) controlled by the layer composition, layer charge and the nature of exchangeable interlayer cation (Simonton et al., 1988; Miyahara et al., 1998; Christidis et al. 2006; Cinar et al., 2009). In contrast in fibrous non-swelling clay minerals, such as palygorskite and sepiolite, the fiber length and number of silanol groups on the surface of the fiber play an important role in aggregating fibers together (Simonton et al., 1988) and forming a random network that entraps water and increases viscosity (Christidis 2011).

Several studies (Brandenburg and Lagaly, 1988; Simonton et al., 1988; Lagaly, 1989; Galan, 1996; Christidis, 1998; Neaman and Singer, 2000; Heller and Keren, 2001; Amorim L. et al., 2004; Christidis et al., 2006; Kelessidis et al., 2007; Kelessidis and Maglioni, 2008; Tunc et al., 2011) have been carried out in the past to understand the rheological properties of standard clays and clay minerals (bentonite, kaolinite, sepiolite and palygorskite). In contrast, only limited works have been performed related to the rheological behaviour of mixed clay suspension. The influence of montmorillonite addition on the rheological behaviour of palygorskite and kaolinite suspensions was investigated by Neaman and Singer (2000) and Keren (1989) respectively. However, still the rheological properties of mixed clays suspension is far from being understood.

Although most studies have been focused on the rheological properties of standard clays, clay minerals usually occurs as mixtures of more than one type of clay minerals and other non-clay minerals. For example, palygorskite and sepiolite occurs in association with smectite in most of known world palygorskite and sepiolite deposits (Table 1 and 2). Therefore it is worthwhile to understand the rheology of suspensions containing mixtures of clay minerals. In addition, so far previous works related to the rheological property of smectite-sepiolite mixed clay suspension have not been reported. Thus, the purpose of this study is to cover this lack of background research work on these topics.

## **1.2 Objective**

This study aims at evaluating the rheological properties of clay suspension containing palygorskite-smectite and sepiolite-smectite mixtures. Different well characterised smectitic clays (bentonites) with different layer charge (High charge ( $> 0.475$  e/hfu), intermediate charge ( $0.425 - 0.470$  e/hfu) and low charge ( $< 0.425$  e/hfu)) were mixed at different proportion with palygorskite and sepiolite to check if the flow behaviour of sepiolite and palygorskite is affected by presence of smectite with different layer charge.

### **1.3 Thesis structure**

This thesis is divided in six chapters:

- ❖ Chapter one provides an introduction to the topic, the importance of the intended work and the overall objective of the Thesis.
  
- ❖ Chapter two deals with literature review and summarize various aspects related to current topic. In this chapter, the rheological features of fluids including flow types and different mathematical functions used for description of different flow behaviours are presented. The flow property of clay slurries both for fibrous and platy clay and factors controlling flow property of clay suspensions are also reviewed.
  
- ❖ Chapter three presents the material and methods used in this Thesis. The chapter also describes the materials used and the applied sample handling steps.
  
- ❖ Chapter four encompasses the results of the work: mineralogical composition, layer charge, free swelling and rheological parameters.
  
- ❖ Chapter five: Deals with the discussion of the overall outcome of the research work.
  
- ❖ Chapter six: includes the summary of main conclusions drawn from this study, as well as recommendations for further work.

## 2 Literature review

### 2.1 Flow behaviour of suspension

The flow behaviour of any system is represented in terms of the relationship between the shear stress and shear rate. A flow curve or rheogram is the graphical representation of shear stress versus shear rate in which the suspension of any material is subjected to ascending or descending shear rates. The viscosity of a fluid is defined as the ratio of the shear stress to the shear rate or the resistance of fluid for flow. The principle of rheological measurements can be explained by the model shown in Figure 2.1. Consider a thin layer of fluid contained between two parallel planes at distance  $dy$  apart in which one plane is fixed (reference plane) and the other moves with a constant velocity when a tangential force is applied to the plane, so that the fluid squeezed between the planes. The shear stress ( $\tau$ ), shear rate ( $\dot{\gamma}$ ) and viscosity ( $\mu$ ) of the fluid are defined as follows:

$$\text{Shear stress } (\tau) = \frac{\text{Force (F)}}{\text{Surface area (A)}} = \tau = \mu \left( -\frac{dV_x}{dy} \right) = \mu \dot{\gamma} \quad (2.1)$$

$$\text{Shear rate } (\dot{\gamma}) = \frac{\text{Velocity}}{\text{Distance}} = \left( -\frac{dV_x}{dy} \right) \quad (2.2)$$

$$\text{Viscosity } (\mu) = \frac{\text{Shear stress}}{\text{Shear rate}} = \tau \left( -\frac{dy}{dV_x} \right) \quad (2.3)$$

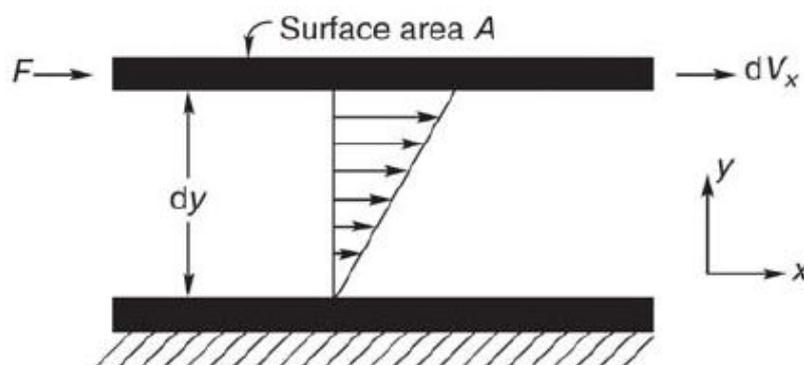


Figure 2.1: Schematic representation of the principle of viscosity measurement (Lagaly, 1989).

Depending up on the relationship of shear stress and shear rate, the fluids are generally classified into Newtonian and non-Newtonian (pseudoplastic, dilatant, yield-pseudoplastic and Bingham plastic) (Luckham and Rossi 1999; Aswad 1996) as discussed below. The mathematical functions that are commonly used to describe the rheogram of different flow behaviour of clay suspensions are also discussed. These rheological models are generally grouped in to single parameter (Newtonian), two parameter (Bingham-plastic model and Power-law model) and three parameter model (Herschel–Buckley model).

A) Newtonian:

In Newtonian fluid viscosity is constant over the entire shear range (Fig.2.3) and flow initiates as soon as the stress applied. It is independent of the shear rate and shear time. In other words, it is characterised by a linear relationship between shear stress and shear rate. The proportionality constant (slope) is the viscosity. It is represented by mathematical function with single parameter (equation 2.4). The rheogram of such fluids at a given temperature is a straight line with constant slope which passes through the origin as shown (Figure 2.2). Newtonian fluid includes water, air, diluted clay suspensions, ethanol, and benzene (Brandenburg and Lagaly, 1988; Aswad, 1996).

$$\tau = \mu \left( -\frac{dV_z}{dy} \right) \quad (2.4)$$

where  $\mu$  is viscosity.

B) Non-Newtonian:

Unlike the Newtonian fluids, the viscosity of the non-Newtonian fluids varies with shear rate and is dependent on shear rate i.e. the slope of the shear stress versus shear rate curve will not be constant as the shear rate changes. Such fluids may also develop yield stress in which a certain minimum shear stress is required for the system to flow. Yield stress develops due to particle-particle interactions, which form networked structures due to dominant attractive forces between particles. An example of such fluids includes polymer melts and

solutions of polymers, as well as liquids in which fine particles like clay particles are suspended (Aswad, 1996). Non-Newtonian behaviour includes:

- a) Pseudoplastic (shear-thinning) behaviour: The majority of non-Newtonian fluids are in this category. It is characterised by apparent viscosity which decreases gradually with increasing shear rate and has no yield stress (Fig.2.2 & Fig.2.3). The shear thinning flow of materials is attributed to the alignment of particles in the direction of shearing. It is described by the Ostwald-Reiner power-law model, in which  $0 < n < 1$ .

$$\tau = K \left( -\frac{dV_x}{dy} \right)^n \quad (2.5)$$

where K is a measure of the consistency of the fluid; and n is the flow-behaviour index, which is a measure of the decrease of effective viscosity with shear rate.

- b) Dilatant (shear-thickening) behaviour: The apparent viscosity increases with increasing shear rate and has no yield stress. It is represented by Ostwald-Reiner power-law model where  $n > 1$ .

$$\tau = K \left( -\frac{dV_x}{dy} \right)^n \quad (2.6)$$

where K is a measure of the consistency of the fluid; and n the flow-behaviour index, which is a measure of the decrease of effective viscosity with shear rate.

- c) Yield-pseudoplastic behaviour: These types of fluids show shear thinning or thickening behaviour similar to the pseudoplastic fluids except for the existence of yield stress. They behave like solids below the yield stress and exhibit fluid behaviour when the shear stress exceeds yield stress. It is

described by Yield-power-law model (Herschel-Buckley) with three parameters ( $\tau_y$ ,  $n$  and  $K$ ).

$$\tau = \tau_y + K \left( -\frac{dV_z}{dy} \right)^n \quad (2.7)$$

Where  $\tau_y$ ,  $n$  and  $k$  are the yield point, the flow behaviour index and the consistency index, respectively.

d) Bingham plastic behaviour: It is characterised by yield stress followed by linear shear stress - shear rate relationship. These slurries are considered to be viscoplastic, i.e they behave like solids below a critical stress (the yield stress). It is described by Bingham-plastic model.

$$\tau = \tau_y + \eta_B \left( -\frac{dV_z}{dy} \right) \quad (2.8)$$

where  $\tau_y$  and  $\eta_p$ , are the yield stress and the plastic viscosity, respectively.

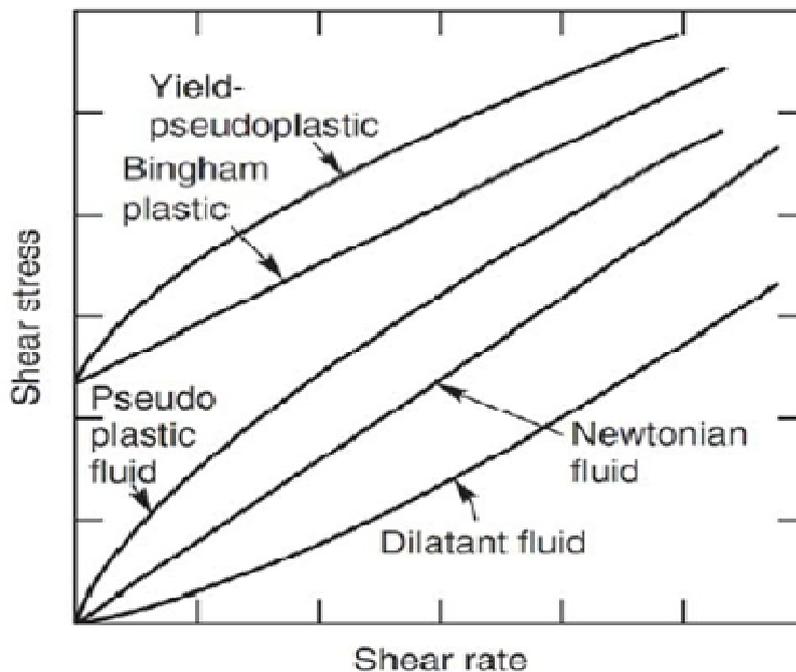


Figure 2.2: Rheograms depicting different flow behaviour (Adapted from Aswad, 1996)

## **2.2 Review on the rheological properties of clay**

### **2.2.1 Introduction**

The clay suspensions behave differently from other colloidal systems due to their disk-like shape and heterogeneous charge distribution (Laxton and Berg, 2006). The rheological parameters of clay suspension (viscosity, shear stress, yield value) can be used to evaluate particle-particle interaction (Neaman and Singer, 2004). Several studies have been carried out on the rheological properties of clay suspensions (Brandenburg and Lagaly, 1988; Christidis, 1998; Luckham and Rossi, 1999; Heller and Keren, 2001; Neaman and Singer, 2000; 2004; Christidis et al., 2006; Tarchitzky and Chen, 2006; Kelessidis et al., 2007; Kelessidis and Maglion, 2008) due to their widespread industrial applications. One of the very important applications of bentonite, sepiolite and palygorskite clay suspensions is their use as water-based drilling fluids in drilling operation with different functions: they carry the drilled cuttings and transport them back to the surface; suspend the drilled cuttings when the circulation is stopped; cool and clean the bit; reduce the friction between the drilling string and the sides of the hole; prevent the inflow of fluids from the permeable rocks that are drilled; maintain the stability of the wellbore; and form a thin, low permeability filter cake which seals the pores and other openings in formations penetrated by the bit (Galan et al., 1994; Luckham and Rossi, 1999; Christidis, 2011). Kaolinite suspensions are used in the slip casting processes during the manufacture of ceramics and in coating paper (Aswad, 1996; Murray, 2007; Christidis, 2011).

Clay minerals display a wide range of colloidal properties, such as thixotropy, viscoelasticity and yield stress, when mixed with water. These properties vary for different clay minerals depending up on their composition, interaction forces between particles, morphology and size of particle (Olphen H., 1964; Brandenburg and Lagaly, 1988; Lagaly, 1989; Tarchitzky and Chen, 2002; Paineau et al., 2011). In addition, factors like clay concentration, pH and type and concentration of electrolyte affect the flow behaviour of clay suspension (Luckham and Rossi, 1999; Yildiz et al., 1999; Keren, 2001; Kelessidis et al., 2007; Christidis, 2011; Paineau et al., 2011). In general, the rheological properties of suspensions can be affected by two categories of

factors: hydrodynamic and non-hydrodynamic (Viseras et al., 1999). All interactions between the dispersion medium and the particles are usually referred to as hydrodynamic effects. Non-hydrodynamic effect includes the colloidal properties of dispersions where the attractive interactions between solid particles are so strong that a rigid network is obtained. In the next sections the structure, rheological properties and factors controlling flow behaviour of smectite, palygorskite and sepiolite and previous works related to current study will be presented.

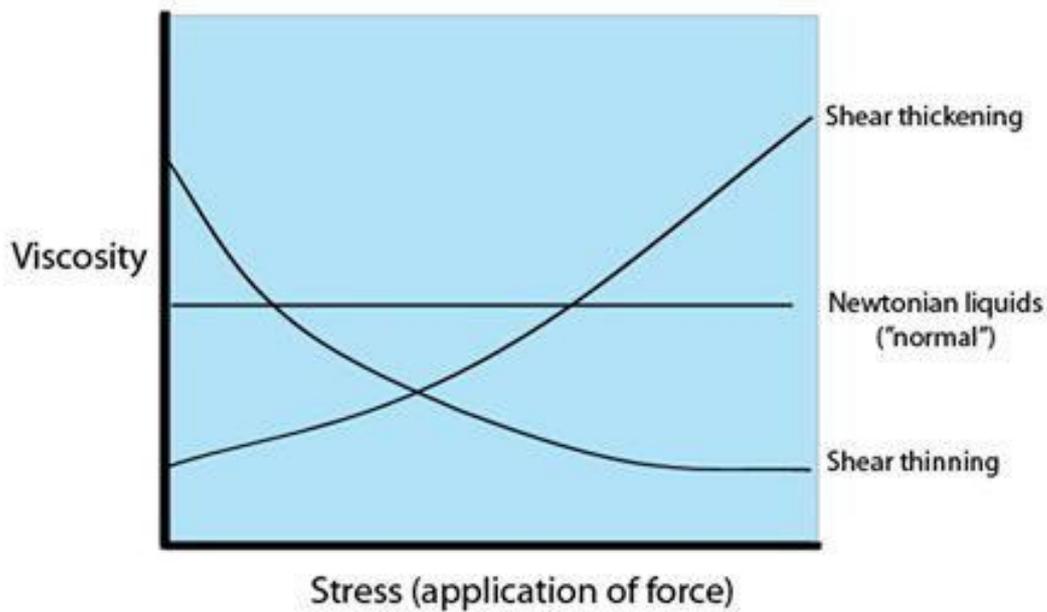


Figure 2.3: Viscosity Vs. stress of different type of fluids (Aswad, 1996).

## 2.2.2 Rheological properties of bentonite suspension

### 2.2.2.1 Introduction

Bentonite is clay rock which is predominantly composed of smectite (Murray, 2007; Christidis, 2011) and its properties and industrial applications are depend on the type and amount of smectite present. Smectite is 2:1 layered aluminosilicate clay mineral composed of two tetrahedral sheets and one octahedral sheet (Fig. 2.4). Isomorphous substitutions of polyvalent cations ( $\text{Si}^{4+}$  or  $\text{Al}^{3+}$ ) by cations of lower valence ( $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  respectively) in the layers which occur in both the tetrahedral and the octahedral sheets, induces a charge deficit that is balanced by cations intercalated between the

structural units ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). The thin sheets are held together by electrostatic forces between alternate layers and bridging cations (Dijkstra et al., 1997). The hydration capacity and charge of these cations determines the swelling potential and separation of the smectite platelets in the presence of water, which in turn controls the flow behaviour (viscosity) of suspension (Dijkstra et al., 1997; Luckham and Rossi, 1999; Paineau et al., 2011). The degree of separation of clay sheet to individual platelets is higher for Na-smectite than Ca-smectite due to relatively weak interlayer bonding in the former (Fig. 2.5). Hence, the physical properties (including rheological parameters) of Ca-bentonite in practical applications are improved by soda activation.

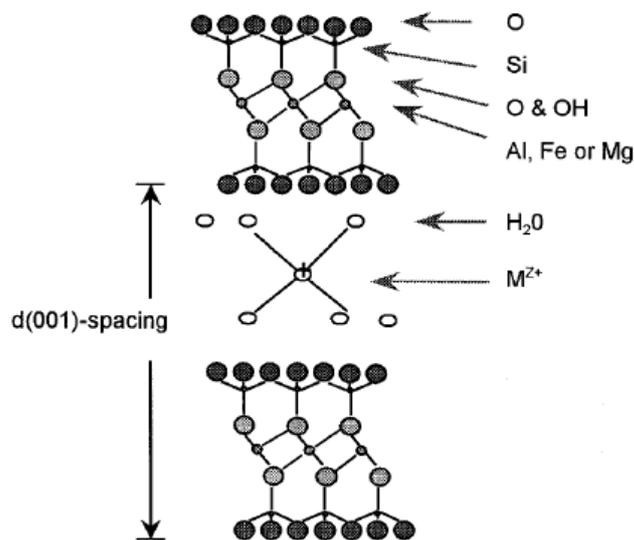


Figure 2.4: Structure of swelling 2:1 clay minerals like smectite

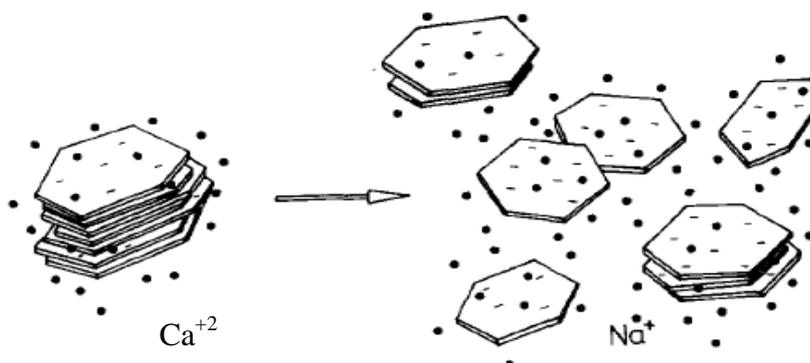


Figure 2.5: Model illustrating the degree of dispersion of smectite quasicrystal in the presence of  $\text{Ca}^{2+}$  (left) and  $\text{Na}^+$  (right) as interlayer cation (Lagaly, 1989).

The clay layer contains negative permanent charges of high density at the face of the layer. At the same time, the broken bonds located at the edge of the sheet yields pH dependent charge (adsorb  $H^+$  or  $OH^-$  according to the pH value of the solution). This charge distribution determines the nature of contact between clay sheets (Miyahara et al., 1998). According to van Olphen (1964), there are three ways of clay platelet association: face to face (FF), leading to thicker plates, and edge to face (EF) or edge to edge (EE), resulting in voluminous flocks or gels (Fig. 2.6). These associations determine the rheological properties of clay suspensions and are influenced by the electrolyte concentration, the Ca/Na ratio and pH of the medium (Brandenburg and Lagaly, 1988; Lagaly, 1989; Luckham P. and Rossi S., 1999; Heller and Keren, 2001; Laxton and Berg, 2006; Christidis, 2011;). For example, calcium ions promote face to face (FF) contacts and stabilize band-like structures (Lagaly, 1989). Alternative to attractive gel type formation, if the forces are strongly repulsive the particles remain isolated and dispersed and form repulsive gels. Such gels possibly form when the clay concentration and electrolyte concentration are very low. If the particle-particle interactions are highly repulsive so that no structure forms, the resulting slurry often exhibits Newtonian behaviour.

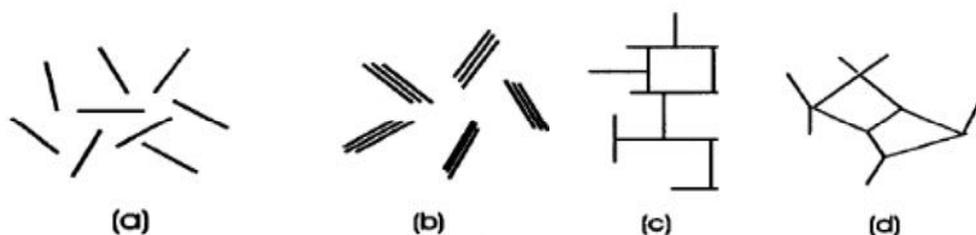


Figure 2.6: Mode of clay particle association: a) Dispersed b) Face-to-face (FF) c) Edge-to-face (EF) and d) Edge-to-edge (EE) (after Luckham and Rossi, 1999).

## 2.2.3 Factors affecting clay rheological properties

### 2.2.3.1 Electrolyte concentration

In the presence of electrolyte the diffused double layer is compressed, the particles come closer and the strength of interparticle interaction increases (Akae and Low, 1988; Abend and Lagaly, 2000; Horpibulsuk et al., 2011). The effect on the flow behaviour of suspension depends on the concentration of the clay. In very diluted salt

solutions, the single silicate layers of montmorillonite are surrounded by the diffuse layers of counter-ions and are repelled from each other by the electrostatic forces forming a stable colloidal dispersion (Abend and Lagaly, 2000). Heller and Keren (2001) reported that edge-to-edge (EE) associations between Na-rich montmorillonite platelets prevail when the electrolyte concentration is below the critical electrolyte concentration, whereas face-to-face (FF) association prevails at concentrations above this critical value. At very low electrolyte concentrations, the edge-to-face (EF) network break down resulting in lower rheological properties due to compression of double layer and reduction of effective charge that determine the electrostatic attraction between edge and face. Further addition of electrolyte concentration (lower than the critical concentration) and compression of double layer, restores the edge-to-face attraction that enhances the rheological properties (van Olphen, 1964; Heller and Keren, 2001).

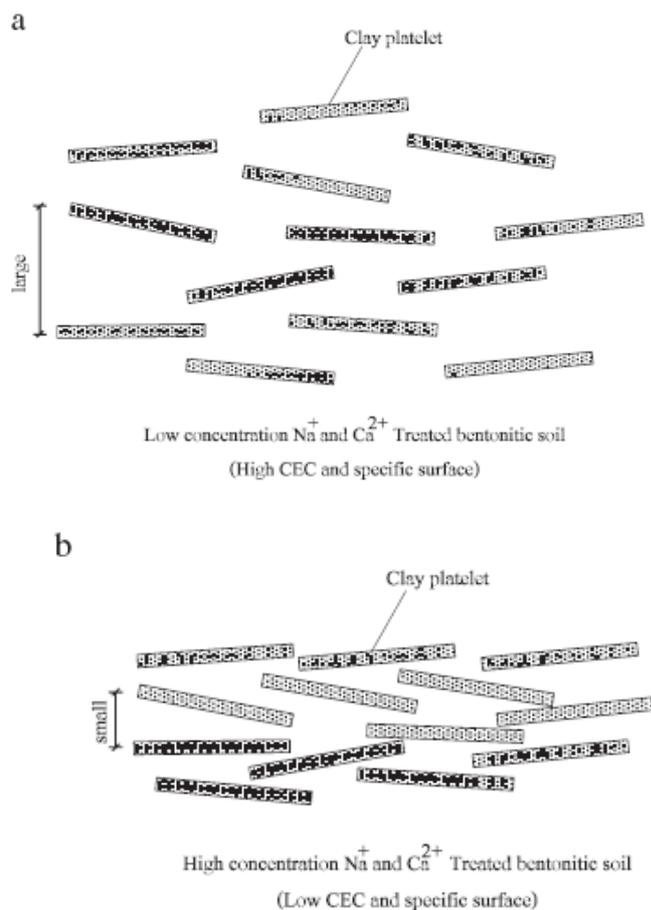


Figure 2.7: Effect of ion concentration on the clay fabric of bentonite (after Horpibulsuk et al., 2011).

### 2.2.3.2 pH

The rheological properties of smectite are highly sensitive to the pH of the medium, because it affects the mode of association of clay particles (Chang et al., 1993; Janek and Lagaly, 2001; Tarchitzky and Chen, 2002; Laribi et al., 2006; Christidis, 2011). Acidic pH and basic pH induce positive and negative edge charge, respectively of the particle edges. Janek and Lagaly (2001) observed sharp increase of viscosity and yield value of bentonite suspension in acidic pH compared to neutral pH conditions. This is due to induced positive edge charge and edge-to-face (EF) particle interaction that forms card house structure (Fig. 2.8). Yildiz et al. (1999) investigated the effect of pH on the rheological properties of bentonite suspensions with and without salt addition and reported lowest yield stress at pH of 7 which increases in acidic and basic pH. In general, at a pH value below the iep (isoelectric point) of the particle edges, edge-to-face attraction predominates due to induced positive edge charge and the rheological parameters increase (Yildiz et al., 1999). At higher pH, the rheological behaviour of bentonite suspensions deteriorates due to change in platelets association from edge-edge and edge-face to face-face (Tarchitzky and Chen, 2002). At extremely high pH, the ionic strength also raises leading to a decrease of the electrical double layer repulsion and flocculation and viscosity (Chang et al., 1993).

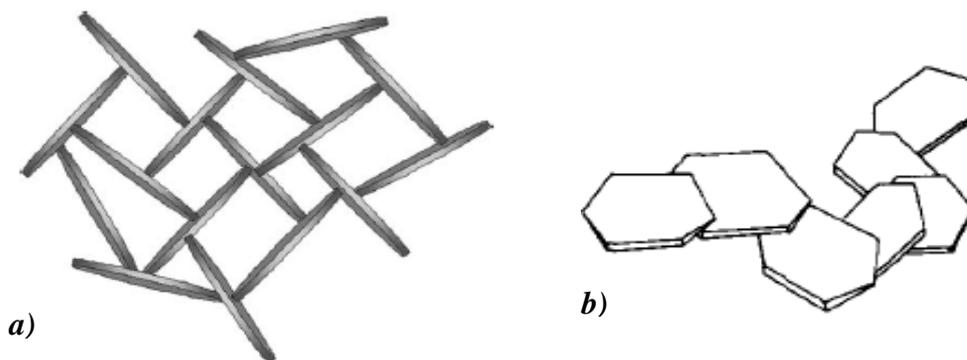


Figure 2.8: Microstructure due to clay network a) Card house (edge-to-face (EF)) ((Laxton and Berg, 2006)) and b) Band-like structure (face-to-face (FF)) (Lagaly, 1989).

### 2.2.3.3 Layer charge and clay concentration

In addition to the aforementioned factors, the flow behaviour of smectite suspension is also affected by the composition, layer charge and concentration of the clay used. Suspensions of low charge smectites develop in general greater viscosity and gel strength than suspensions of high charge smectites (Christidis et al., 2006). This is because the high charge smectites form thick quasicrystals due to strong electrostatic attraction, which develop considerably smaller diffuse double layers and thus binds less water molecules. On the other hand, low charge smectites form thin quasicrystals and allow entrance of more water molecules in the interlayer space. The clay concentration is another factor that controls the flow behaviour of suspension. In general increase of clay concentration enhances all rheological properties (van Olphen, 1964; Luckham and Rossi, 1999; Heller and Keren, 2001). This is because at high clay concentration, flocculation causes the formation of a continuous gel structure instead of individual flocs. For Na<sup>+</sup>-montmorillonite, this concentration is usually above 3% (w/w) (Luckham and Rossi, 1999). Abend and Lagaly (2000) determined the influence of solid content and ionic strength on the state of dispersion from rheological measurements (Fig.2.9).

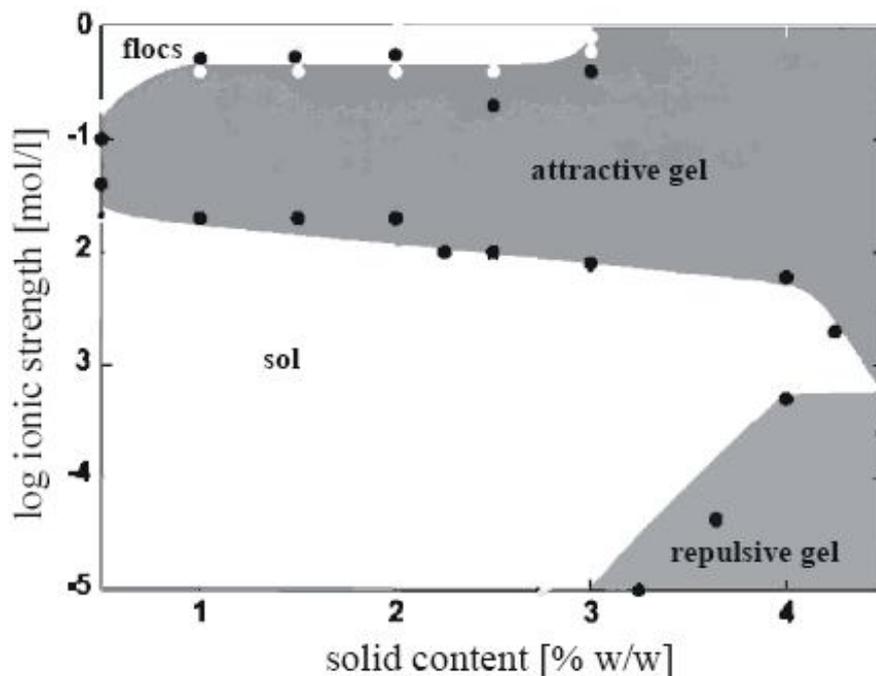


Figure 2.9: The phase diagram showing the influence of solid content and ionic strength on the state of dispersion (Abend & Lagaly, 2000)

## 2.2.4 Rheological properties of palygorskite and sepiolite

### 2.2.4.1 Introduction

Sepiolite and palygorskite are 2:1 layer silicates with micro-fibrous morphology. They differ from other 2:1 layer clay minerals in that each T:O:T unit is linked to the next by inversion of  $\text{SiO}_4$  tetrahedral (Fig. 2.10) forming 2:1 phyllosilicate ribbons containing zeolitic water (Serna et al., 1975; Murray, 2007; Christidis, 2011). This arrangement yields open micro-channels parallel to the fibre axis, which contribute to high porosity and specific surface area, with dimensions of  $4 \text{ \AA} \times 10.6 \text{ \AA}$  and  $4 \text{ \AA} \times 6 \text{ \AA}$  for sepiolite and palygorskite, respectively (Christidis, 2011). In general, they are characterised by a micro-fibrous morphology, low surface charge and high specific surface area (Neaman and Singer, 2004). The world known palygorskite and sepiolite deposits and their mineralogical assemblage are listed in Table 1 and 2 respectively.

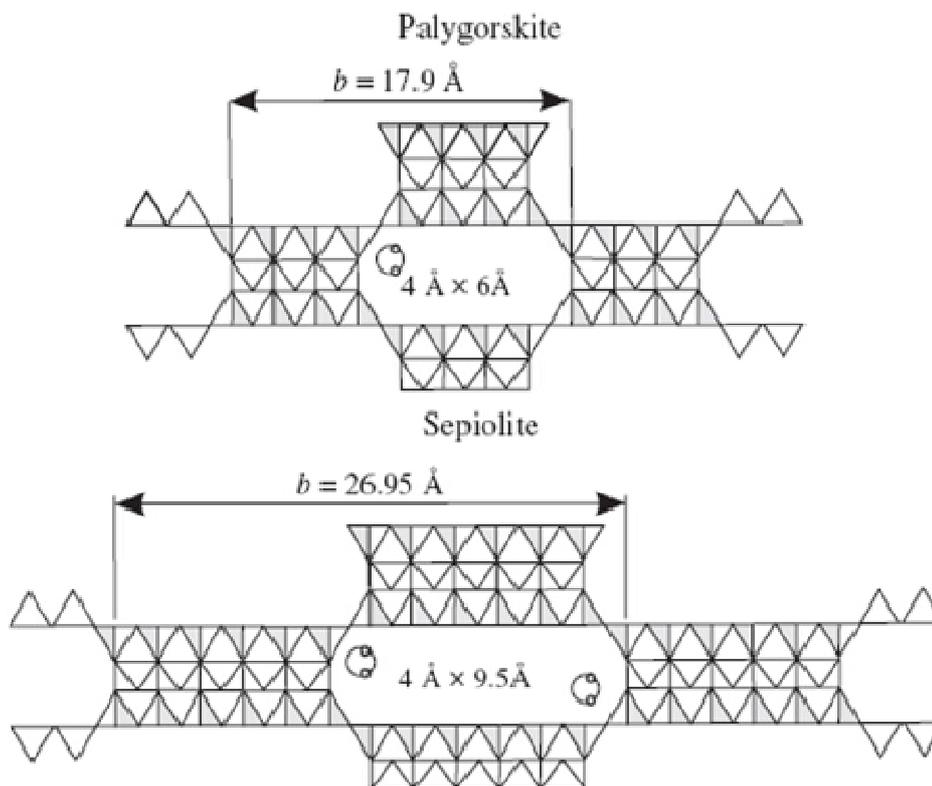


Figure 2.10: Schematic structural diagrams of palygorskite and sepiolite (Adapted from Christidis, 2011).

Table 2.1: Summary of world palygorskite deposits (Galan E. and Singer A., 2011)

<b>Deposit (Country, Age)</b>	<b>Fibrous clay Minerals (Thickness)</b>	<b>Mineralogical association</b>	<b>Environment</b>	<b>origin</b>
Bercimuel (Spain) Miocene	Palygorskite 1-1.5 meter Two beds	Palygorskite (kaolinite, illite, quartz, smectite, mixed layers)	Alluvial	Diagenetic (dissolution- precipitation), Al- smectite
Torrejon el rubio (Spain) Paleogene	Palygorskite 0.5 – 4 m One bed	Palygorskite (Illite, sepiolite, chlorite, dolomite, saponite, quartz, feldspar)	Lacustrine- palustrine (alteration profile)	Diagenetic (dissolution- precipitation), chlorite
Andhra Pradesh (India) Paleogene	Palygorskite 0.5 – 3 m	Palygorskite (?)	Lacustrine	Diagenetic (dissolution- precipitation), illite
Garford Paleochannel (Australia)	Palygorskite Up to 2 m	Palygorskite (Illite, smectite, dolomite)	Lacustrine	No data
Guanshan (China) Meocene	Palygorskite 3 – 6 m	Palygorskite (smectite > quartz >> sepiolite, mica, dolomite)	Lacustrine- fluvial (alteration profile)	Diagenetic (basaltic ash and basalt)
Grevena (Greece) Pliocene- Pleistocene	Palygorskite 10 – 18 m	Palygorskite (smectite, serpentine, quartz, sepiolite, amphibole)	Lacustrine	Diagenetic (saponitic sand, ultra mafic rock)

Table 2.2: Summary of world sepiolite deposits (Galan E. and Singer A., 2011)

<b>Deposit (Country, Age)</b>	<b>Fibrous clay Minerals (Thickness)</b>	<b>Mineralogical association</b>	<b>Environment</b>	<b>origin</b>
Vicalvaro- Vallecas- Cabanas de la Sagra (Spain) Miocene	Sepiolite Lower -1-5 m Upper - 10 m Two beds	Sepiolite (> 95%) (Saponite, stevensite, illite, quartz, dolomite, feldspar)	Alluvial	Depositional neof ormation Diagenetic
Batallons (Spain) Miocene	Sepiolite Lower - 9 m Upper - 2 m Two beds	Sepiolite (> 95%) (Palygorskite, saponite, illite, quartz, calcite, feldspar)	Palustrine	Depositional neof ormation Diagenetic
Eskisehir (Turkey) Miocene	Sepiolite 0.5 – 5 m Beds	Sepiolite (90%) (illite, quartz, dolomite, feldspar)	Lacustrine	Depositional neof ormation Diagenetic
Eskisehir (Turkey) Miocene	Loulinghite 0.6 - 6 m	Loulinghite (sepiolite, analcime, smectite, illite, calcite, feldspar, palygorskite, opal)	Lacustrine - Volcanosedim entary	Diagenetic
Mara Orera (Spain) Miocene	Sepiolite 0.5 – 0.6 m	Sepiolite (Palygorskite, Mg- smectite, calcite, dolomite, zeolite)	Palustrine- Lacustrine	Depositional neof ormation
Amargosa (USA) Pliocene- Pleistocene	Sepiolite Up to 1.5 m	Sepiolite (saponite, illite, kerolite- stevensite, calcite, dolomite)	Lacustrine	Depositional neof ormation

#### **2.2.4.2 Rheology of palygorskite and sepiolite**

Similar to bentonite, fibrous palygorskite and sepiolite clay minerals are commonly utilized in a variety of rheological applications (Galan, 1996; Neaman and Singer, 2004; Cinar et al., 2009; Murray, 2007), since the particles allow gels to be formed at low solids concentrations. However, the nature of the gelling mechanisms of fibrous clay minerals and layer silicates like montmorillonite are very different due to differences in their structure and chemistry (Simonton et al., 1988). Aggregates of sepiolite and palygorskite fibres usually form bundles (Serna et al., 1975; Galan, 1996; Christidis, 2011) and separation of the massive bundles into individual fibres is not achieved by hydration of interlayer cations like in montmorillonite, but is done simply by mechanical means. Simonton et al. (1988) suggested that silanol groups on the surface of the sepiolite fibres play an important role in gluing fibres together so the gel structure can develop.

The advantage of palygorskite and sepiolite in drilling mud over other clays like bentonite is their ability to maintain the desired rheological properties at high electrolyte concentrations over a wide pH range (Galan, 1996). At  $\text{pH} \leq 7$  the rheological parameters remain relatively constant and unaffected even at high electrolyte concentrations, but at  $\text{pH} \geq 9$  they are influenced significantly by electrolyte addition (Neaman and Singer, 2000). In addition, sepiolite is the only clay mineral which can form stable suspension at higher temperature. As a result it is used in drilling muds for geothermal wells (Galan, 1996). Sepiolite gels can be quickly and easily prepared compared to montmorillonite (Simonton et al., 1988).

The flow properties of palygorskite and sepiolite suspensions are affected by factors like suspension concentration, particle morphologies, pH, and the type and concentration of electrolytes (Galan, 1996; Yildiz et al., 1999; Neaman and Singer, 2000; Tunc et al., 2011; Cinar et al., 2009). Neaman and Singer (2000) investigated the rheology of aqueous suspensions of six palygorskites with different fibre length under different conditions (pH, clay concentration, electrolyte concentration and adsorbed ions). Their finding indicates that the rheological parameters of palygorskite

suspensions (plastic viscosity, Bingham yield value, and apparent viscosity) increase with the sphericity (length/ width ratio) of individual palygorskite fibers and with clay concentration. These rheological parameters are also higher for clays saturated with divalent ions than those for clays saturated with monovalent ions.

The pH of the solution medium controls the arrangement of fibers and the viscosity of palygorskite and sepiolite suspensions. Face-to-face particle association occurs at low pH values, giving rise to close-packed domains of fibers, while at high pH values the fibers adopt a random orientation (Neaman and Singer, 2000). Recently, Cinar et al. (2009) investigated the effects of different acids (HCl, H<sub>2</sub>SO<sub>4</sub> and citric acid) on the rheological properties of sepiolite and reported the optimum apparent viscosity value to be obtained at pH 8 - 9. In acidic pH, partial collapse of the structure due to the release of Mg ions and in alkaline pH, the increase OH ion adsorption on the surface and interparticle repulsion cause peptization that demolishes the network structure, decreasing significantly viscosity.

### **2.2.5 Rheology of mixed clay minerals**

Opposite to standard clays, only few works has been conducted on the rheological property of mixed clays. Keren (1989) investigated the rheological characteristics of mixed kaolinite-montmorillonite suspensions as a function of adsorbed ion (Na<sup>+</sup> or Ca<sup>2+</sup>) and montmorillonite concentration. Addition of small amount of Na<sup>+</sup> and Ca<sup>2+</sup> saturated montmorillonite to kaolinite transforms the flow behaviour of kaolinite from Newtonian to non-Newtonian at pH range from 4 to 7 due to an association between kaolinite and montmorillonite platelets.

Neaman and Singer (2000) studied the rheology of mixed palygorskite–montmorillonite suspensions to determine the effect of montmorillonite on the flow behaviour of palygorskite and reported that the degree of interaction between particles depended on the montmorillonite concentration in the mixture (Figure 2.11). Small montmorillonite additions (up to 10 wt. %) increased the rheological parameters (plastic viscosity and Bingham yield point) of palygorskite that contained smectite impurities. Addition of 20 - 40 wt. % and ≤ 40 wt. % montmorillonite to palygorskite

suspension containing smectite impurities and no smectite impurities, respectively, resulted in a nearly Newtonian flow. Further addition  $\geq 40$  wt. % montmorillonite increased sharply the rheological parameters of suspensions.

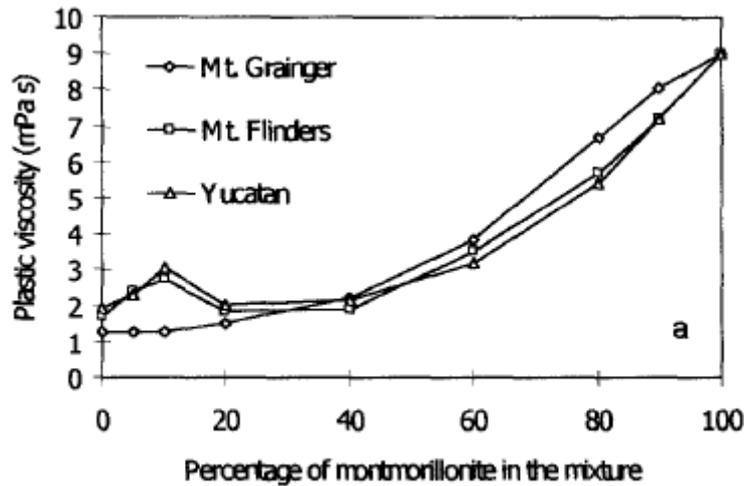


Figure 2.11: Effect of montmorillonite concentration on plastic viscosity of palygorskite (Neaman and Singer, 2000)

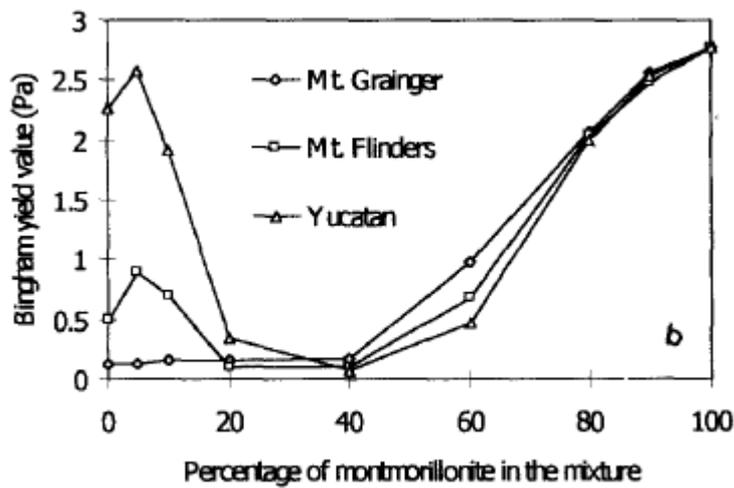


Figure 2.11: Effect of montmorillonite concentration on Bingham yield point of palygorskite (Neaman and Singer, 2000)

### **3. Materials and methods**

#### **3.1. Materials**

Since the primary purpose of this study was to investigate the rheology of mixed clay suspensions, six representative bentonite samples having different origins were selected based on their layer charge (low charge ( $< 0.425$  e/hfu), intermediate charge ( $0.425$ - $0.470$  e/hfu), and high charge smectite ( $> 0.470$  e/hfu)). Subsequently they were used to prepare palygorskite-bentonite and sepiolite-bentonite mixed suspension. Montmorillonites from Wyoming (SWy-2), Texas (STx-1b), Nevada (Kinney) and Arizona (SAz-2) were obtained from the Clays Repository of the Clay Mineral Society. Sepiolite (ES5) from Vicalvaro basin, Spain, sepiolite from Euboea, Greece (GSp), nontronite (DA 04) and palygorskite (DA01) from Grevena, Greece were used for preparing the mixture. Table 3.1 lists the materials used in this study and summarize information about the source, layer charge, cation exchange capacity and pre-treatment used (Na-activation).

#### **3.2 Initial sample characterization**

##### **3.2.1 X-ray diffraction**

The natural materials contain different clay and non-clay minerals which can influence the rheological properties; therefore knowing the mineralogical composition of the sample is vitally important. Bulk mineralogy of the samples was determined by X-ray powder diffraction (XRD), on randomly oriented samples, with a Brucker AXS D8 Advance, using  $\text{CuK}\alpha$  radiation and a step size of  $0.021$  degrees.

For bulk mineralogical analysis, the samples were first dried in oven for 2 hours at  $60^\circ\text{C}$ , crushed moderately to powder using pestle and mortar and were side loaded to sample holder to prepare randomly oriented powder. Before extraction of the  $< 2\text{-}\mu\text{m}$  size fraction for oriented slide, the samples were first dispersed overnight in distilled water, centrifuged repeatedly for 10 minutes and washed several times with distilled water until the conductivity (concentration of electrolytes) allowed formation of a stable suspension. Then, clay fraction ( $< 2\ \mu\text{m}$ ) was extracted from the higher portion of the stable suspension (1.5 cm) using pipet and settled onto glass slides to form oriented slides. Following the air-dried analysis, the samples were placed in a

desiccator where they were exposed to ethylene glycol vapour and heated overnight at 60°C. This helps in distinguishing smectite, which expands to 17 Å, from other non-swelling clay minerals.

Table 3.1: Summary of materials used in this experimental work

<i>samples</i>	<i>Pre-treatment</i>	<i>Layer charge(e/hfu)</i>	<i>CEC (meq/100g)</i>
SWy-2 Wyoming, USA (Na-montmorillonite)	-	0.38	84.48
STx-1b Texas, USA (Ca-montmorillonite)	Na activation	0.44	76.2
DA04 Grevena Greece (Nontronite)	Na activation	0.39	74.45
SAz-2 Arizona, USA (Ca-montmorillonite)	Na activation	0.55	129.3
Kinney (Ca-montmorillonite)	Na activation	0.49	136.54
AK-1.2 Milos, Greece (Ca-montmorillonite)	Na activation	0.42	86.16
ES5 Vicalvaro basin, Spain	-	-	14.45
DA01 Grevena, Greece	-	-	24.36
GSp Euboea, Greece	-	-	21.36

### 3.2.2 Energy dispersive X-ray fluorescence spectrometry (EDS-XRF)

The chemical composition of the studied samples was determined by energy dispersive X-ray fluorescence (XRF) spectrometry. Finely ground materials were dried overnight in the oven at 105°C; then, after cooling in a desiccator, they were transferred in previously annealed porcelain crucibles. Calcination for 2 hours at 1000°C was performed in the furnace and the materials were cooled again in the desiccator. 1.5 g of the calcined material was mixed with 7.5 g of di-lithium tetraborate, transferred into a platinum crucible, melted for 25 min and then poured into a

casting dish to produce the glass bead. The glass beads were measured for major elements with “S2 RANGER, XFlash® LE by Bruker AXS”EDS-XRF in the Laboratory of Inorganic and Organic Chemistry and Organic Petrography, Department of Mineral Resources Engineering of Technical University of Crete (TUC).

### **3.3 Layer charge measurement**

The layer charge of smectites for the bentonite samples was determined using the method of Christidis and Eberl (2003). The measurement was done using the Layer Charge computer code of Eberl and Christidis (2002). The method is based on the comparison of XRD traces of K-saturated, ethylene glycol solvated smectite with simulated XRD-traces calculated for three-component interlayering (fully expandable 17.1 Å layers, partially expandable, 13.5 Å layers and non-expandable 9.98 Å layers) (Christidis and Eberl, 2003) (Figure 3.1). The method is faster than the other methods (structural formula and alkylammonium method) and less affected by presence of impurities compared to the other methods.

The method has two options to find the calculated pattern that best matches the measured pattern: a peak position method and a whole-profile fitting method. According to Christidis and Eberl (2003), the peak position method is less accurate for high charge smectite. On the other hand, the presence of other clay and non-clay minerals with diffraction maxima in the proximity of K-smectite maxima (e.g. illite, quartz) can result poor fit if whole-profile fitting option is selected. Therefore, in this work both methods were applied and similar results were obtained with good fit.

Prior to layer charge determination, the less than 2 µm fractions of the bentonites were separated by sedimentation and saturated twice with 1M KCl solution to allow all exchangeable ions to be replaced by potassium ions. After K saturation, the samples were washed five times with deionized water followed by high speed centrifugation to remove free chloride ions. Oriented specimens of K-saturated clays were prepared for X-ray diffraction (XRD) analysis by sedimentation of a clay suspension onto a glass slide and subsequent air drying and then saturation in ethylene glycol vapour at 60°C for 16 h.

The samples were then grouped according to their layer charge (High charge, intermediate charge and low charge) for the intended work. The classification scheme for dioctahedral smectite according to layer charge and XRD characteristics proposed by Christidis et al. (2006) is indicated in Figure 3.2.

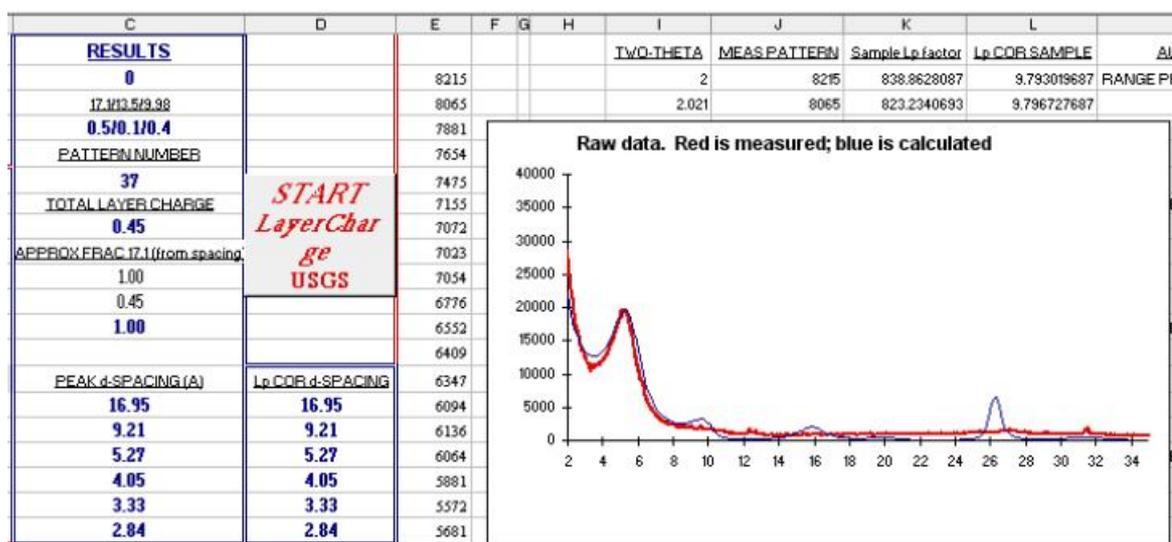


Figure 3.1: Layer charge measurement for sample DA04 using the LayerCharge computer code of Eberl and Christidis (2002) (Red = measured, blue = calculated).

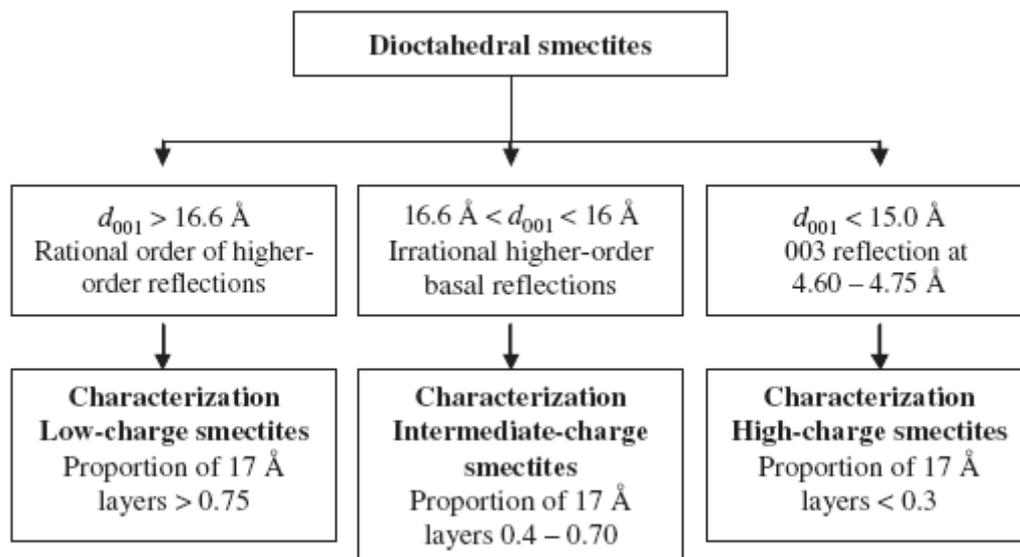


Figure 3.2: Classification scheme of di-octahedral smectites by XRD, according to their layer charge characteristics (Christidis, 2011).

### 3.4 Free swelling test

The free swelling test was carried out to determine the optimum  $\text{Na}_2\text{CO}_3$  concentration necessary for activation of Ca-bentonite prior to rheological measurements. The test was carried out according to the method of Inglethorpe et al. 1993 (Industrial minerals laboratory manual of British Geological survey). However, in this study 2 g of clay and 100 ml graduated cylinder was used instead of 1 g of clay and 10 ml graduated cylinder.

The materials were dried at  $60^\circ\text{C}$  for more than 12 h, crushed with mortar and passed through a  $75\ \mu\text{m}$  sieve. Subsequently they were activated with 1, 2, 3, 4, 5 and 6 wt.%  $\text{Na}_2\text{CO}_3$  and then 2 g of the original and the Na-activated clay was added into 100 ml graduated cylinders filled with deionized water (Figure 3.3). The volume of swollen gel was recorded after 24 hours and the reading was multiplied by 5 to express it as ml gel per 10 g of clay. The concentration of  $\text{Na}_2\text{CO}_3$ , which caused maximum free swelling volume (swelling index), is considered to be the optimum concentration (Christidis et al., 2006).

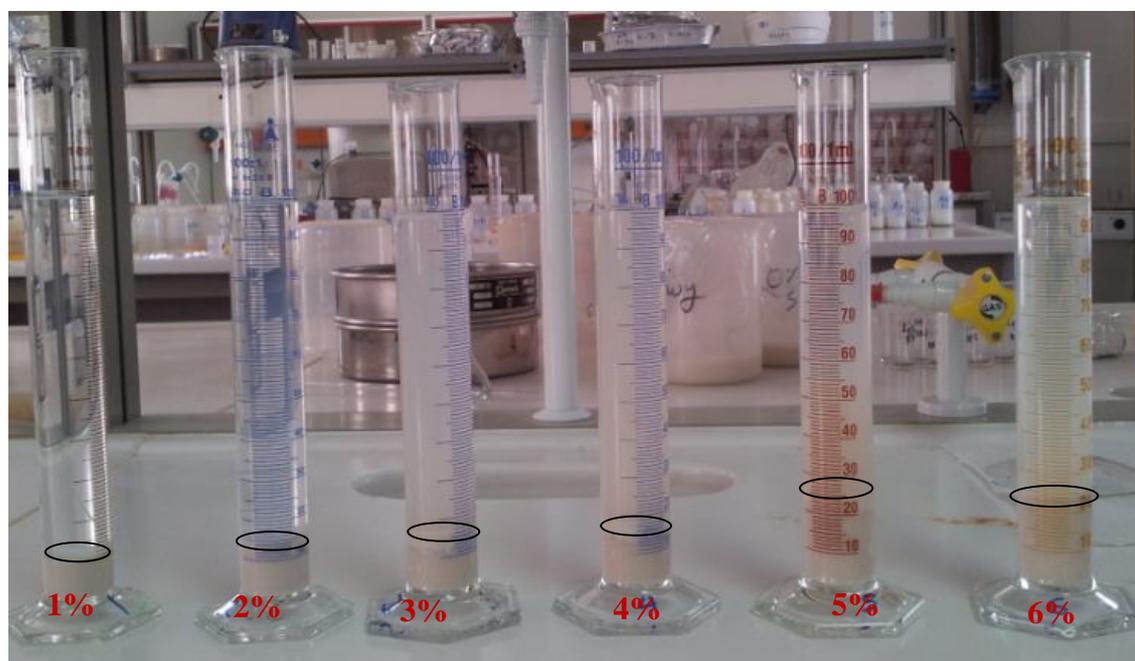


Figure 3.3: Image showing free swelling test after activation with 1, 2, 3, 4, 5 and 6%  $\text{Na}_2\text{CO}_3$

### 3.5 Rheological measurements

#### 3.5.1 Couette-type viscometer

There are two types of viscometers to obtain data required to plot the rheograms: the rotational viscometer and the tube viscometer. In this study, all measurements were performed with a Couette-type rotational fann type viscosimeter (Grace - M3500 viscometer) at Fluid Mechanics Laboratory of the Technical University of Crete. It has a rotating outer cylindrical cup (rotor sleeve) coaxial with an inner fixed bob which is connected to a torsion spring (Figure 3.4). In such viscometers, fluid is placed in the annular space between the outer cylinder and the inner cylinder and sheared by rotation of the outer cylinder while keeping the inner cylinder stationary. The outer cup can be rotated at a known speed which produces shear rates and transmitted via the suspension to the rotor. A meter attached to the torsion spring (Figure 3.4), which resists the force tending to rotate the bob, measures the torque acting on the bob. The viscometer is connected to a computer and the shear stress at each shear rate was recorded digitally. The readings thus obtained were used to calculate the rheological parameters (plastic viscosity, apparent viscosity and yield point) using equations 3.1, 3.2 and 3.3.

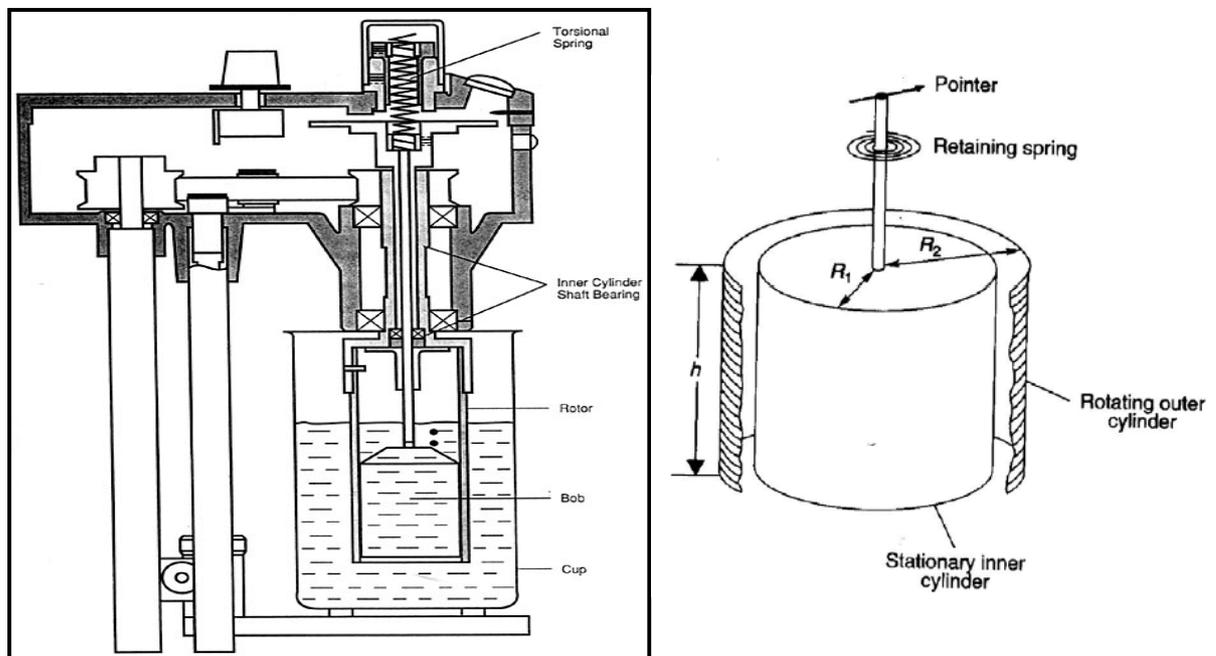


Figure 3.4: Schematic diagram of a Couette-type coaxial cylindrical viscometer (left) and section view of rotational viscometers (outer and inner cylinder) (right)

### 3.5.2 Preparation of suspension

Prior to rheological measurement, the materials were oven-dried at 60°C, ground and passed through a 75 µm sieve and treated with the optimum concentration of Na<sub>2</sub>CO<sub>3</sub> that was determined from free swelling test. Even though the presence of impurities like iron-oxides and organic matter affects the rheology of clay suspension, no attempt was made to purify any of these materials used in this study.

The suspensions of palygorskite-smectite and sepiolite-smectite mixtures at a concentration of 5 wt % were prepared by suspending the mixture of the two end members at proportions of 0, 10, 20, 40, 60, 80, 90 and 100 % wt. in deionized water according to Inglethorpe et al. (1993) (Industrial minerals laboratory manual of British Geological survey). The mixtures were ultrasonified for 2 minute to disintegrate clay aggregate and obtain homogeneous suspensions. Then they were stirred for 20 minutes with a Hamilton Beach® mixer, transferred to beakers, sealed to prevent evaporation and left to age for 16 hours. The pH of the dispersions was adjusted to neutral (pH 7) by careful addition of diluted HCl or NaOH in small steps. The pH of the dispersion was measured with “Inolab pH meter”. After aging, the suspensions were stirred again for 5 minutes immediately before determination of rheological properties. The rheological properties (Plastic viscosity, apparent viscosity and yield value) were determined from the following equations:

$$\text{Plastic viscosity (cP)} = [600 \text{ rpm reading}] - [600 \text{ rpm reading}] \quad (3.1)$$

$$\text{Apparent viscosity (cP)} = [600 \text{ rpm reading}] \div 2 \quad (3.2)$$

$$\text{Yield value} \left( \frac{\text{lb}}{100 \text{ ft}^2} \right) = [300 \text{ rpm reading}] - \text{Plastic viscosity} \quad (3.3)$$

Table 3.2: The specifications of Grace - M3500 viscometer

<b>Viscometer</b>	
<b>Rotating cap (rotor sleeve)</b>	
Internal diameter	1,450 in (36,83 mm)
Total length	3,425 in (70 mm)
Distinctive mark	2,30 in (58,4 mm) from the base
Two rows of holes 1/8 in (3,18 mm) at a distance of 120 deg (2,09 rad) between them, on the periphery of the circular lid, just below the mark.	
<b>Inner stationary cylinder (Bob)</b>	
Diameter	1,358 in (34,49 mm)
Length of cylinder	1,496 in (38,00 mm)
It has a flat base, while the top growth has tapered, tapering gradually.	
<b>Speeds</b>	
Ranges from 0.02 to 600 rpm	

## 4. Results

### 4.1. Mineralogical composition

The mineralogical composition of the samples used in this study is summarized in Table 4.1. The XRD traces of the samples are given in appendix A.

#### 4.1.1. Bentonites

All the bentonites samples contain dioctahedral smectite (Ca or Na-smectite) as the major phase, which is confirmed by the shift of its characteristic peak, after treatment with ethylene glycol, from 12-15 Å to 17 Å and the presence of (060) diffraction peak at 1.49 - 1.50 Å. Apart from smectite (nontronite), DA04 and SWy-2 samples presented sharp peaks at 3.34 Å and 7.32 Å, which is characteristic of the presence of abundant quartz and serpentine respectively. Other trace amount of non-clay minerals was also observed in the bentonite samples (Table 4.1).

#### 4.1.2. Fibrous clays

The XRD analysis result showed palygorskite is the dominant clay mineral in DA01 sample both in bulk and clay fraction. It also contains serpentine, quartz and minor smectite and amphibole. Sepiolite is the dominant clay mineral in Spanish sepiolite (ES5) and Greek sepiolite (GSp) sample with minor amount of illite, smectite and dolomite.

### 4.2. Chemical composition

The chemical analysis of the samples is given in Table 4.2. All mineralogical data given in this study are referred to the ignited mass basis. Loss-on-ignition (LOI) is determined by heating three grams of the sample ( $m_{\text{initial}}$ ) in the furnace up to a specified temperature (1000°C) in order to remove all the volatile components ( $m_{\text{volatiles}}$ ) (equation 4.1). The result showed the Fe-rich nature of sample DA04 and DA01 (> 10% Fe<sub>2</sub>O<sub>3</sub>). In contrast, the Al<sub>2</sub>O<sub>3</sub> % is very low (< 4%) in these samples compared to other samples. Even though this chemical data was for bulk sample, the proportion of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> together with the x-ray result (i.e. 060 reflections < 1.51 Å) indicted these two samples are Fe-rich di-octahedral clays.

$$\text{LOI} = \frac{m_{\text{volatiles}}}{m_{\text{initial}}} 100 \quad [\%] \quad (4.1)$$

Table 4.1: Mineralogical assemblage of the studied samples

<i>Sample</i>	<i>major</i>	<i>minor</i>	<i>trace</i>
DA04	Nontronite	Serpentine, quartz	Palygorskite, dolomite, amphibole
DA01	Palygorskite	Serpentine, quartz	Smectite, amphibole, dolomite
ES5	Sepiolite		Illite, smectite, dolomite
SWy-2	Na-montmorillonite	Quartz,	Mica, feldspar
STex-1b	Ca-montmorillonite		Calcite, mica, quartz
SAz-2	Ca-montmorillonite		Quartz, mica, feldspar
Kinney	Ca-montmorillonite		Quartz, beidellite
AK 1.2	Ca-montmorillonite		Plagioclase, calcite, brookite
GSp	Sepiolite		Smectite, mica

Table 4.2: Bulk chemical composition of the studied samples

<i>Sample</i>	<i>DA01</i>	<i>Swy-2</i>	<i>Saz-2</i>	<i>Stex-1b</i>	<i>Kinney</i>	<i>DA04</i>	<i>ES5</i>	<i>AK 1.2</i>	<i>GSp</i>
Na <sub>2</sub> O (%)	0.0	2.2	2.5	2.0	1.4	0.6	0.0	1.9	0.0
MgO (%)	23.9	6.9	11.8	9.0	12.1	18.4	35.8	6.5	21.4
K <sub>2</sub> O (%)	0.2	0.5	0.1	0.1	0.2	0.3	0.4	0.3	0.0
CaO (%)	0.7	1.7	3.4	2.1	1.4	2.3	0.0	1.7	1.4
TiO <sub>2</sub> (%)	0.3	0.1	0.2	0.2	0.1	0.4	0.1	0.8	0.0
MnO (%)	0.3	0.0	0.1	0.0	0.1	0.2	0.0	0.0	0.0
Fe <sub>2</sub> O <sub>3</sub> (%)	10.8	4.7	2.0	1.5	1.5	14.5	0.8	7.6	0.1
Al <sub>2</sub> O <sub>3</sub> (%)	3.3	16.6	16.0	13.6	17.5	3.7	2.4	16.0	1.2
SiO <sub>2</sub> (%)	50.9	59.5	53.2	64.5	52.8	50.4	50.6	53.9	66.9
P <sub>2</sub> O <sub>5</sub> (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0
LOI	9.5	7.7	10.7	7.0	13.0	9.2	10.0	11.0	9.0
Total	99.9	100.0	100.0	100.0	100.1	99.9	100.0	100.0	100.0

### 4.3. Layer Charge characterisation

The layer charge characterisation of bentonite samples was performed based on the classification scheme proposed by Christidis et al., (2006), which includes intermediate layer charge (0.425 – 0.470 e/hfu) in addition to high charge ( $> 0.475$  e/hfu) and low charge ( $< 0.425$  e/hfu) classification proposed by Christidis and Eberl (2003). This classification scheme is based on the magnitude of layer charge, the XRD characteristics of K-saturated, ethylene glycol solvated oriented clay fractions and the rheological properties (Christidis et al., 2006).

Representative XRD traces of the clay fractions of the oriented K-saturated samples after ethylene glycol solvation are shown in Figure 4.1. According to this classification scheme, low charge smectites are those which have layer charge lower than 0.425 e/hfu and with XRD traces characterised by first order diffraction maxima between 16.6 and 17.1 Å and well defined rational higher order basal reflections (Figure 4.1. a) SWy-2 and c) AK-1.2). Low charge smectites also contain high proportion ( $> 0.75$ ) of low charge layers (17 Å). For tetrahedrally charged smectites, such as beidellite and nontronite, the layer charge is  $< 0.365$  e/hfu instead of 0.425 e/hfu, since they yield XRD traces like montmorillonite with less low charge layers.

High charge dioctahedral smectites are characterised by layer charges greater than 0.475 e/hfu ( $> 0.415$  e/hfu for tetrahedrally charge smectites) and XRD traces with first order maximum at 14 Å and a 003 diffraction maximum at 4.6–4.7 Å (Figure 4.1. c) Kinney). The fraction of low charge layers (17 Å) is less than 0.3.

The third category includes smectites with intermediate layer charge, characterised by layer charge between 0.425 e/hfu and 0.470 e/hfu (0.365 and 0.415 for beidellite and nontronite) and XRD traces with first order reflections from 16.6 to 16.0 Å and irrational higher order basal reflections (Figure 4.1. b) STex-1b). For this class of smectites, their rheological properties vary according to their layer charge and the proportion of the low charge layers (Christidis et al., 2006).

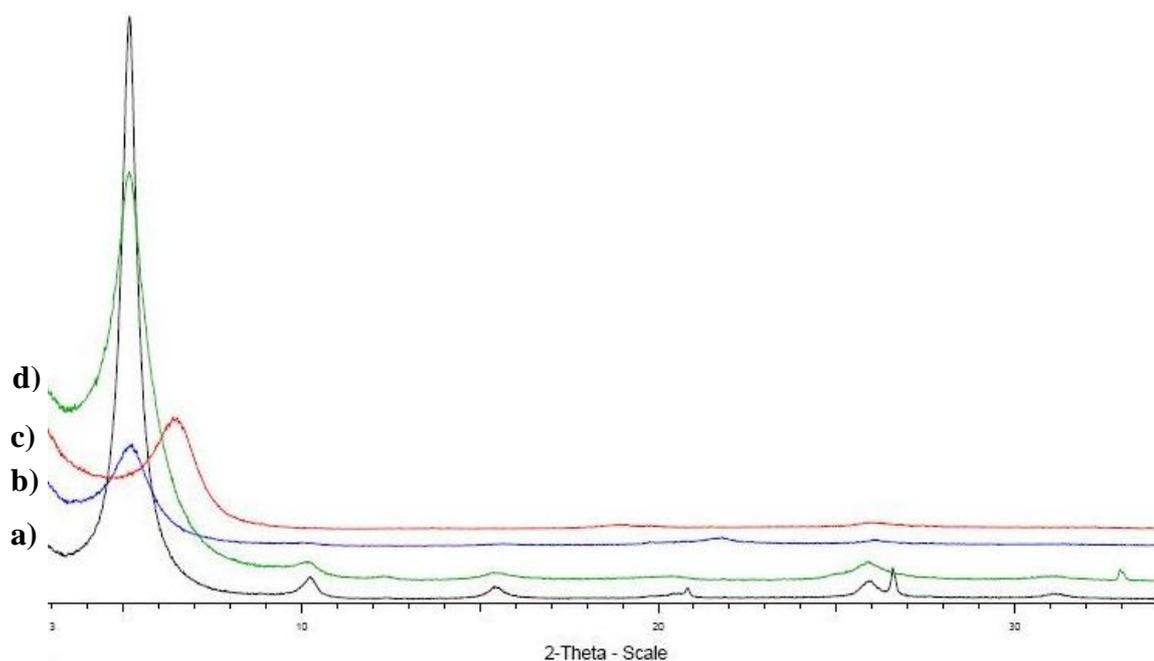


Figure 4.1: XRD patterns of K-saturated and ethylene glycol-salivated oriented clay fractions a) SWy-2 (low charge) b) STex-1b (intermediate charge) c) Kinney (high charge) and D) AK 1.2 (low charge).

#### 4.4. Free swelling index

In practical applications the swelling and rheological properties of Ca-bentonites are commonly improved by exchanging the interlayer  $\text{Ca}^{+2}$  by  $\text{Na}^{+}$ . This is because the presence of Na-ion in the interlayer initiates disaggregation of the smectite particles into thinner lamellae. For industrial application, the exchange process is commonly performed by addition of sodium carbonate (Lagaly, 1989) in the presence of moisture. The free swelling indices of the bentonites of this study after soda ( $\text{Na}_2\text{CO}_3$ ) activation are shown in Table 4.3. The values in brackets indicate the percentage (wt.%) of  $\text{Na}_2\text{CO}_3$  added to obtain maximum swelling volumes. This behaviour shows the capacity of the natural clays to transform to the sodium-rich form.

Table 4.3: Free swelling indices of the studied bentonites

<i>Sample</i>	<i>Swelling index (ml/10 g of clay)</i>
DA04	100 (5)
STex-1b	100 (5)
Kinney	150 (5)
AK-1.2	130 (4.5)
SAz-2*	111 (5)
SWy-2*	205 (1)

\*Data from Christidis et al., 2006

Figure 4.2 shows the swelling at different wt.% of Na<sub>2</sub>CO<sub>3</sub> activation. The amount (%) of Na<sub>2</sub>CO<sub>3</sub> added to attain maximum swelling was: 5% for sample SAz-2, STex-1b, Kinney and DA04 and 4.5% for sample AK-1.2. Further addition of soda above this optimum percentage reduced the swelling values. This is probably due to the increase of salt concentration (free electrolyte) by excess sodium carbonate and contraction of diffused double layer. Similar effect of excess sodium carbonate on the rheological property was also reported by Yildiz et al. (1999).

The amount of sodium carbonate added to attain the maximum swelling depends on the abundance of Na in the exchangeable sites, the layer charge (CEC) of smectite and the smectite content in the bentonite (Christidis et al., 2006). Generally, sodium rich and low charge smectite (like SWy-2) require less Na<sub>2</sub>CO<sub>3</sub> (< 2%) to develop maximum free swelling volume. In contrast calcium rich and high charge smectites (SAz-2, STex-1b, AK-1.2 and Kinney) required higher amounts of Na<sub>2</sub>CO<sub>3</sub> (4-5%). High layer charge, localisation of charge in tetrahedral sheet and interlayer Ca<sup>2+</sup> also affect the delamination of clay aggregates to individual particles. As a result complete activation of Ca-smectite and high charge smectite to Na-smectite may not be achieved (Yildiz et al., 1999). The effect of charge localisation on swelling can be explained, for example by comparison of sample DA04 (nontronite) with samples that have relatively higher layer charge (SAz-2 and Kinney). Due to the presence of significant tetrahedral charge, DA04 developed lower swelling volume comparable to high charge smectites (SAz-2).

## 4.5 Rheological characterisation

### 4.5.1 Palygorskite-smectite mixture

#### 4.5.1.1 Flow behaviour and diagram

The flow diagrams (rheogram) for 5% solid suspension of palygorskite-smectite mixture at different proportion of smectite (0, 10, 20, 40, 60, 80, 90 and 100%) are shown in Figure 4.3 to 4.7. All the suspensions exhibited pseudoplastic non-Newtonian flow behaviour except for suspensions with  $\geq 80\%$  intermediate charge (DA 04 and STex-1b) and high charge smectite (SAz-2 and Kinney) which exhibited Bingham plastic type flow. This non-Newtonian flow behaviour with yield stress arises from the presence of particle-particle interaction at such higher solid concentration (Luckham and Rossi, 1999).

The obtained shear stress ( $\tau$ ) and shear rate ( $\dot{\gamma}$ ) values of pseudoplastic flow curves fitted well to the Herschel-Buckley (Yield-power-law model), power-law model and the Bingham plastic flow curves fitted well to the Bingham plastic model (regression coefficient  $> 0.975$  for all studied systems). The selected figures for the fitting are included in the appendix C. The equation for the Bingham, power-law and Herschel-Buckley models are shown in equations 2.8, 2.5 and 2.7, respectively. All the suspensions exhibiting pseudoplastic behaviour display shear thinning characteristics (i.e.  $0 < n < 1$ ).

Suspensions with Bingham plastic type of flow (DA01 - SAz-2 (100%), DA01 - SAz-2 (90%), DA01 - SAz-2 (80%), DA01 - STex-1b (100%), DA01 - STex-1b (90%), DA01 - Kinney (100%), DA01 - Kinney (90%), DA01 - DA04 (90%) and DA01 - DA04 (90%)) showed a yield stress  $< 2$  Pa (Appendix B). Below the yield stress, particle-particle interactions are strong enough to provide a networking structure (micro-aggregates), able to resist shear distortion and the slurry behaves as a solid. When the stress exceeds the yield stress, the networking between clay particles totally distorts, the particles align in the shearing direction and the slurry continuously deforms (Luckham and Rossi, 1999; Neaman and Singer, 2000), behave as a fluid and the viscosity remains constant.

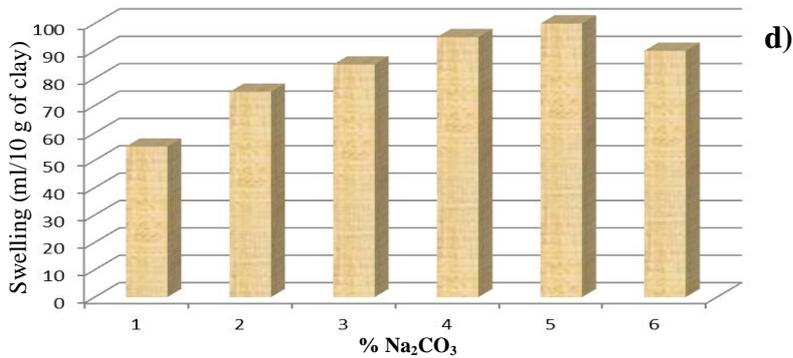
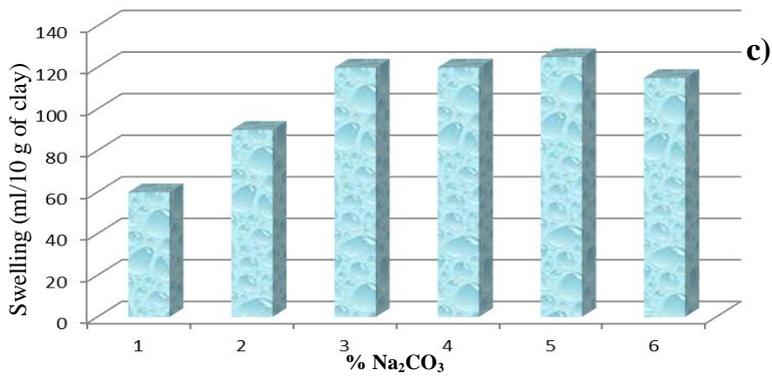
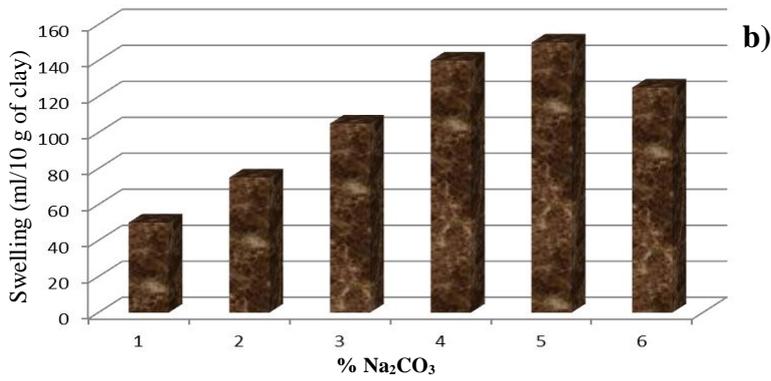
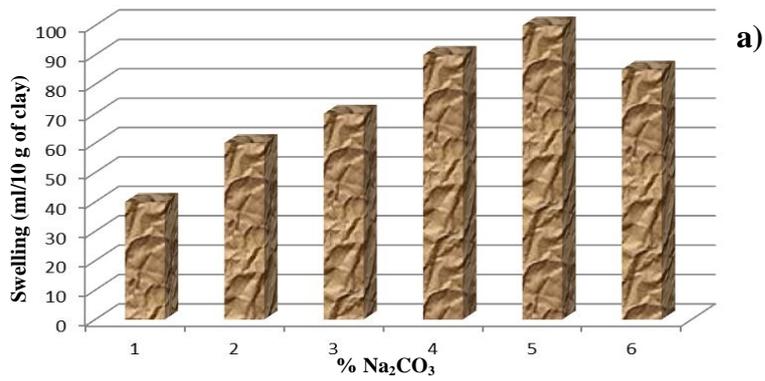


Figure 4.2: Determination of the free swelling index (ml gel/10 g clay) for a) DA04, b) Kinney, c) STex-1b and d) AK-1.2.

The flow diagrams of suspension of the remaining mixtures consists of two parts (with and without yield stress): the first part is characterized by a progressive decline in viscosity as shear rate increases (at a low shear rate) and the second part is characterized by constant viscosity (at higher shear rate). The first part is attributed to progressive destruction of networking structures and decrease of micro-aggregate size with increasing shear rate (Luckham and Rossi, 1999; Neaman and Singer, 2000) and the orientation of the individual platelets in the direction of flow (Heller and Keren, 2001). An alternative explanation for the observed decrease in viscosity with shear rate can be the release of molecular water held by the three-dimensional structures during destruction of the particle association.

The linear part of the rheograms is attained after complete disruption of particle-particle interaction (Luckham and Rossi, 1999; Yildiz et al., 1999) at a certain shear rate depending on the sample. After this shear rate the structural components align themselves in the direction of flow (Yildiz et al., 1999; Heller and Keren, 2001) and the suspensions exhibit Newtonian flow behaviour. The shear rate at which the linear segment of the flow curve attained was shifted to lower and higher shear rate as the proportion of high charge and low charge smectite in the mixture increased, respectively (Figures 4.3 to 4.7).

According to parameters obtained from fitting to power-law and Herschel-Buckley model (Appendix B), the consistency coefficient ( $K$ ) of the mixed palygorskite-smectite suspensions decreased with addition of SAz-2 and DA04 at all proportions in the mixture, with addition  $\geq 20\%$  of STex-1b and Kinney and with addition  $\geq 40\%$  of SWy-2 and AK-1.2 in the mixture. In addition it increased with addition of 10% SWy-2, 20% SWy-2, 10% AK- 1.2, 20% AK-1.2, 10% STex-1b and Kinney in the mixture. The consistency coefficient is a measure of the consistency of the suspension (Luckham and Rossi, 1999). The higher the value, the stronger is the association between clay particles (Morariu et al., 2009).

Even though all the suspensions with pseudoplastic flow showed shear thinning behaviour ( $0 < n < 1$ ), the value for flow index ( $n$ ) was higher for smectite dominating

suspensions ( $> 40\%$  smectite in the suspension) compared to palygorskite dominating suspensions. This indicates that palygorskite dominating suspensions are more pseudoplastic or deviate from Newtonian flow. The lowest value of  $n$  (0.11 – 0.17) were observed for 10%, 20% and 40% of low charge smectites (SWy-2 and AK-1.2) in the mixed suspensions. The consistency coefficient ( $K$ ) also tends to increase for these proportions of smectite in the suspension (Appendix B).

Palygorskite dominating ( $\leq 40\%$  smectite) suspension did not show yield stress value and fitted well to the power-law model. In contrast smectite dominating suspensions showed relatively higher yield stress value, especially for the low charge smectites such as SWy-2 ( $> 11$  Pa) and fitted well to Herschel-Buckley model. This suggests that flow is easily initiated in palygorskite dominated suspensions compared to smectite dominated suspensions. Besides, addition of  $\leq 40\%$  smectite has no effect on the yield stress value of the mixed suspensions, but it modified the consistency coefficient ( $K$ ) and flow index ( $n$ ) values.

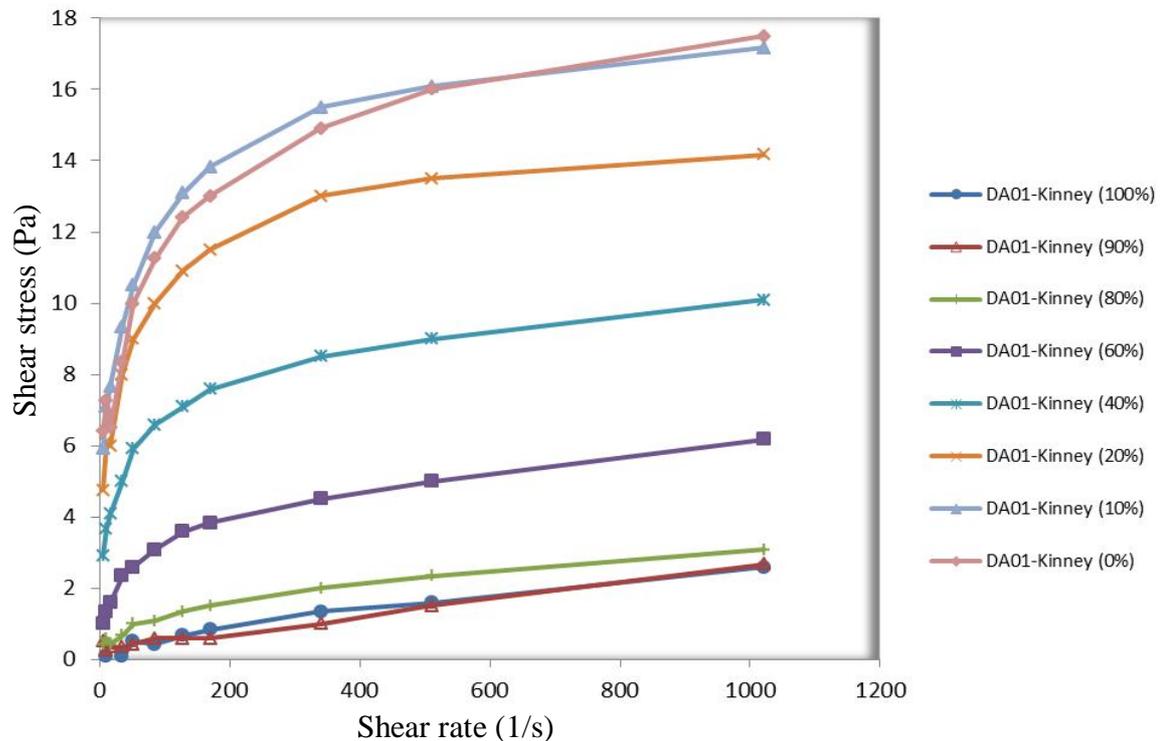


Figure 4.3: Rheograms of DA01 (palygorskite)-Kinney (smectite) mixed suspension.

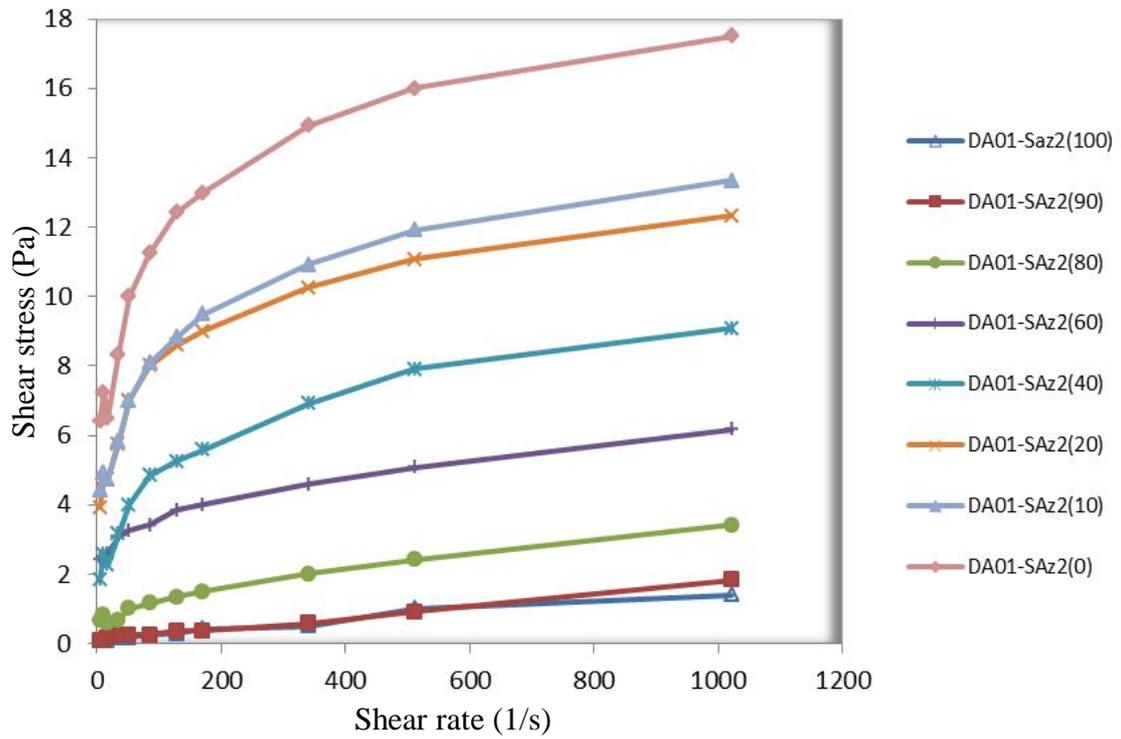


Figure 4.4: Rheograms of DA01 (palygorskite)-SAz-2 (smectite) mixed suspension.

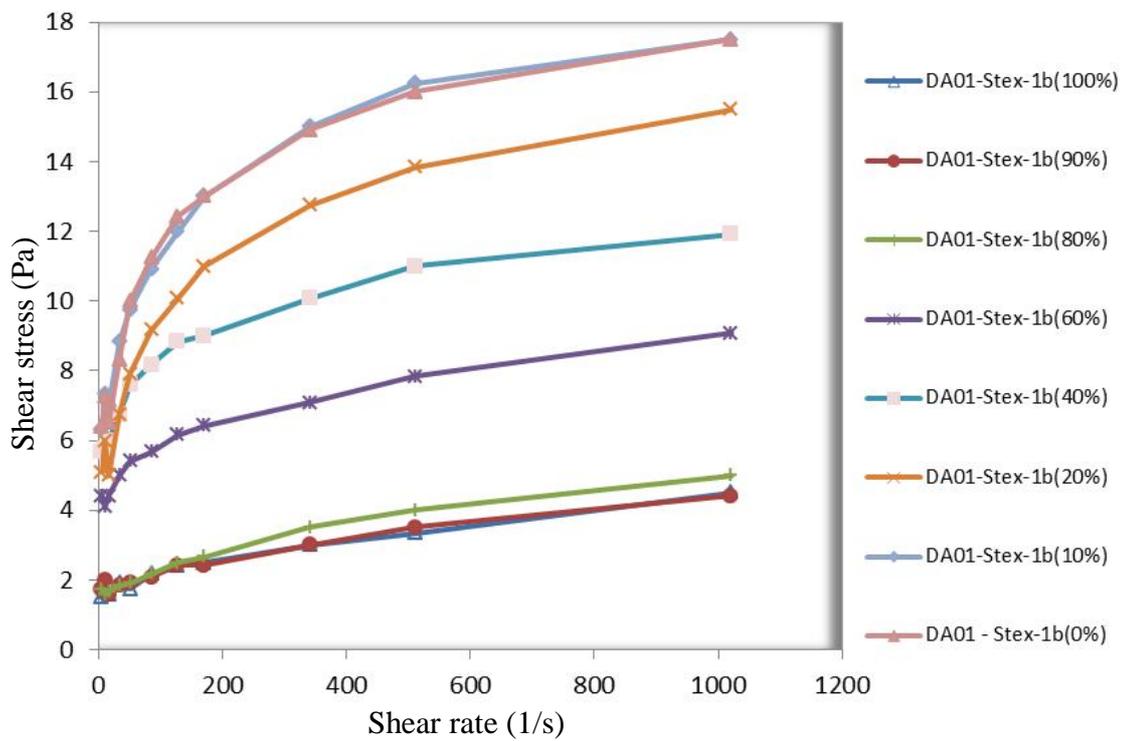


Figure 4.5: Rheograms of DA01 (palygorskite)-STex-1b (smectite) mixed suspensions.

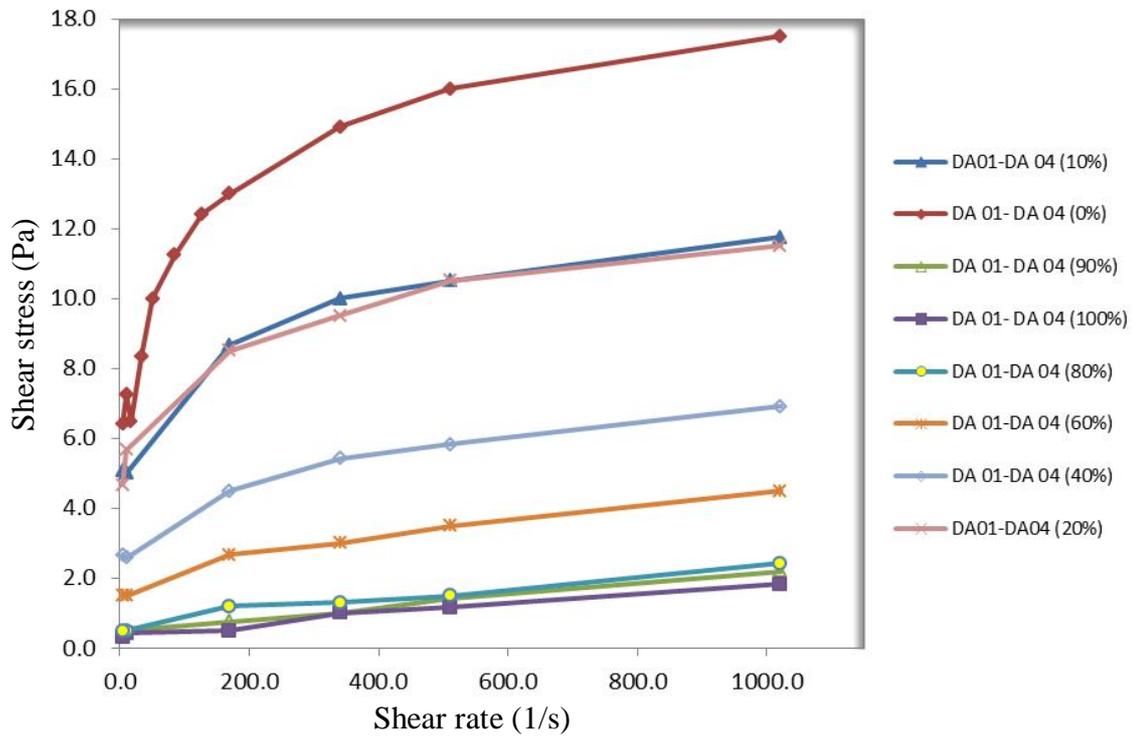


Figure 4.6: Rheograms of DA01 (palygorskite) – DA04 (smectite) mixed suspensions.

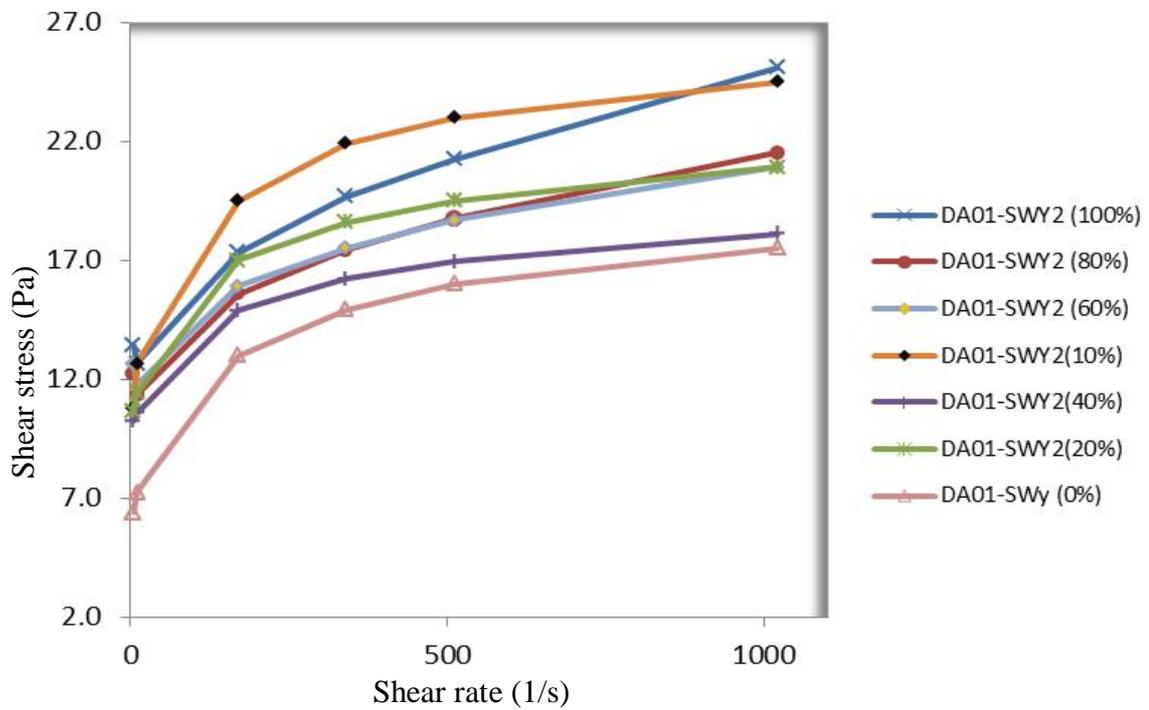


Figure 4.7: Rheograms of DA01 (palygorskite) – SWy2 (smectite) mixed suspensions.

#### **4.5.1.2 Rheological parameters**

##### **4.5.1.2.1 Plastic viscosity, apparent viscosity and yield point**

The rheological parameters (plastic viscosity, apparent viscosity and yield point) for different mixtures of palygorskite and smectite are listed in Table 4.4. The values were determined according to API specification 13A (1993) based on the reading at 300 and 600 rpm. The pure palygorskite end member (DA01) and the low charge smectite end member (SWy-2) develop suspensions of high viscosity which meet the API specifications (i.e. viscometer dial reading at 600 rpm is  $> 30$ ) at concentration of 5%. Intermediate (STex-1b and DA04) and high charge (SAz-2 and Kinney) smectite develop low viscosity. Sample AK 1.2 with low layer charge (0.42 e/hfu) also has lower viscosity. This indicates the rheological properties of the smectite are not controlled only by layer charge. Other factors, such as charge distribution and localisation (tetrahedral or octahedral charge), presence of non-clay impurity and particle size of the smectite, should also need to be considered.

The layer charge and rheological parameters for the bentonite samples are inversely related (Figure 4.8). However, SWy-2 with low layer charge and DA04 with tetrahedral charge deviated from the general trend. Similar results were also reported by Christidis et al. (2006). The reason for this inverse relation is because the magnitude of layer charge controls the electrostatic component of interaction of the smectite particles, which in turn controls the size of quasicrystals and amount of water molecules bound in the interlayer region (Yildiz et al., 1999; Christidis et al., 2006). In fact, high charge smectites form thick quasicrystals (Christidis et al., 2006) that may influence the self-organization and interaction of particles in the suspension.

Plots of the rheological parameters of mixture suspensions vs. percentage of smectite in the mixture are shown in Figure 4.9, 4.10 and 4.11. For low charge smectites (SWy-2 and AK-1.2), the rheological parameters tend to improve for 10% smectite in the mixture. The change is more prominent for apparent viscosity and yield value. At this concentration the yield value attained maximum value being higher than both end members. Further increase of smectite content to 20% and 40% resulted to a sharp

Table 4.4: Rheological parameters of suspensions of palygorskite mixed with different bentonites (according to API 13A, 1993)

SAMPLE	RHEO. PROPERTY	% OF SMECTITE IN THE MIXTURE							
		0	10	20	40	60	80	90	100
DA04	Apparent viscosity (cP)	17.12	11.58	11.30	6.77	4.40	2.36	2.20	1.80
	Plastic viscosity (cP)	3.42	2.61	2.00	2.12	1.96	1.79	1.50	1.30
	Yield point (Pa)	13.12	8.59	8.90	4.45	2.34	0.87	0.60	0.50
SWy-2	Apparent viscosity (cP)	17.12	24.31	20.55	18.20	20.55	21.04	21.44	24.54
	Plastic viscosity (cP)	3.42	3.60	2.94	2.94	4.89	5.38	5.71	7.50
	Yield point (Pa)	13.12	19.83	16.87	14.62	14.99	14.99	15.07	16.32
STex-1b	Apparent viscosity (cP)	17.12	17.36	15.17	11.74	8.89	4.97	4.40	4.40
	Plastic viscosity (cP)	3.42	3.42	3.26	2.94	2.45	2.12	1.63	1.79
	Yield point (Pa)	13.12	13.26	11.40	8.43	6.17	2.73	2.65	2.50
Kinney	Apparent viscosity (cP)	17.12	17.12	14.27	9.87	5.87	3.02	2.20	2.61
	Plastic viscosity (cP)	3.42	2.94	2.61	2.45	1.96	1.79	1.47	1.47
	Yield point (Pa)	13.12	13.09	11.16	7.10	3.75	1.17	0.70	1.09
SAz-2	Apparent viscosity (cP)	17.12	13.05	12.07	8.89	5.95	3.34	1.79	1.57
	Plastic viscosity (cP)	3.42	2.77	2.45	2.28	1.96	1.79	1.63	1.17
	Yield point (Pa)	13.12	9.84	9.21	6.32	3.83	1.48	0.36	0.37
KA-1.2	Apparent viscosity (cP)	17.12	19.57	15.17	10.27	6.69	5.14	4.32	3.51
	Plastic viscosity (cP)	3.42	2.94	2.94	2.61	2.12	2.45	2.28	2.12
	Yield point (Pa)	13.12	15.93	11.71	7.34	4.37	2.58	1.95	1.33

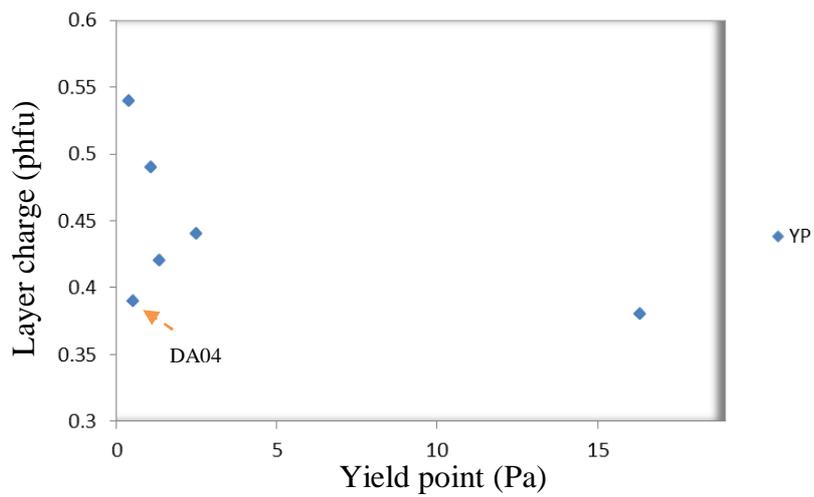
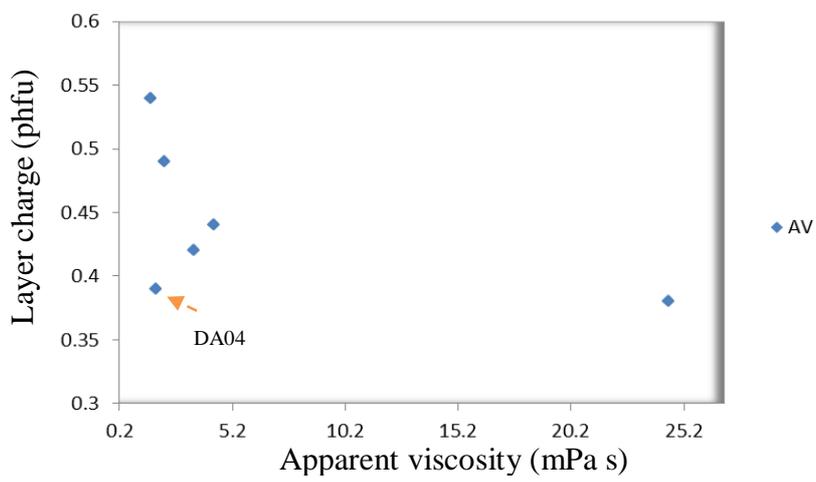
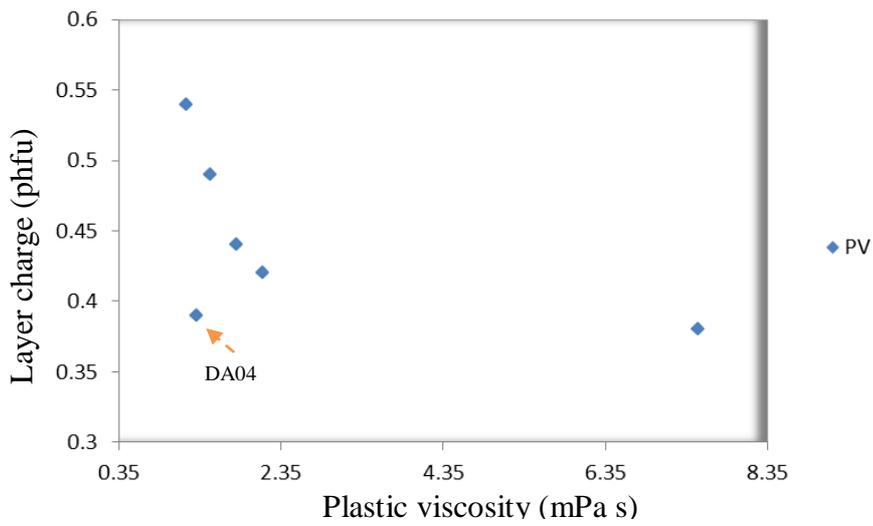


Figure 4.8: Variation of rheological parameters of smectites with layer charge a) plastic viscosity b) apparent viscosity and c) yield point. (DA04 tetrahedral charge).

decrease of the rheological parameters. As the concentration of the smectite in the mixture exceeds 40%, these parameters improved and deteriorated for SWy-2 and AK-1.2, respectively. In contrast, for intermediate charge (STex-1b and DA04) and high charge smectites (SAz-2 and Kinney), the rheological parameters decrease with increasing proportion of smectite in the suspension. However, the rate at which the parameters decrease is dependent on the magnitude of the layer charge. Sample DA04 with intermediate charge showed exceptional behaviour i.e. it developed viscosity even lower than the high charge smectites (e.g. Kinney). The reason for this low viscosity is probably due to the localisation of charge in the tetrahedral sheet (Bleam, 1990; Christidis et al., 2006). In tetrahedrally charged smectites, the charge is located close to the surface and consequently holds strongly the clay layers together. Therefore, the degree of dissociation and swelling is low. Besides, the presence of high percentage of impurities like serpentine, iron oxides and quartz in the sample also contributes to the low viscosity.

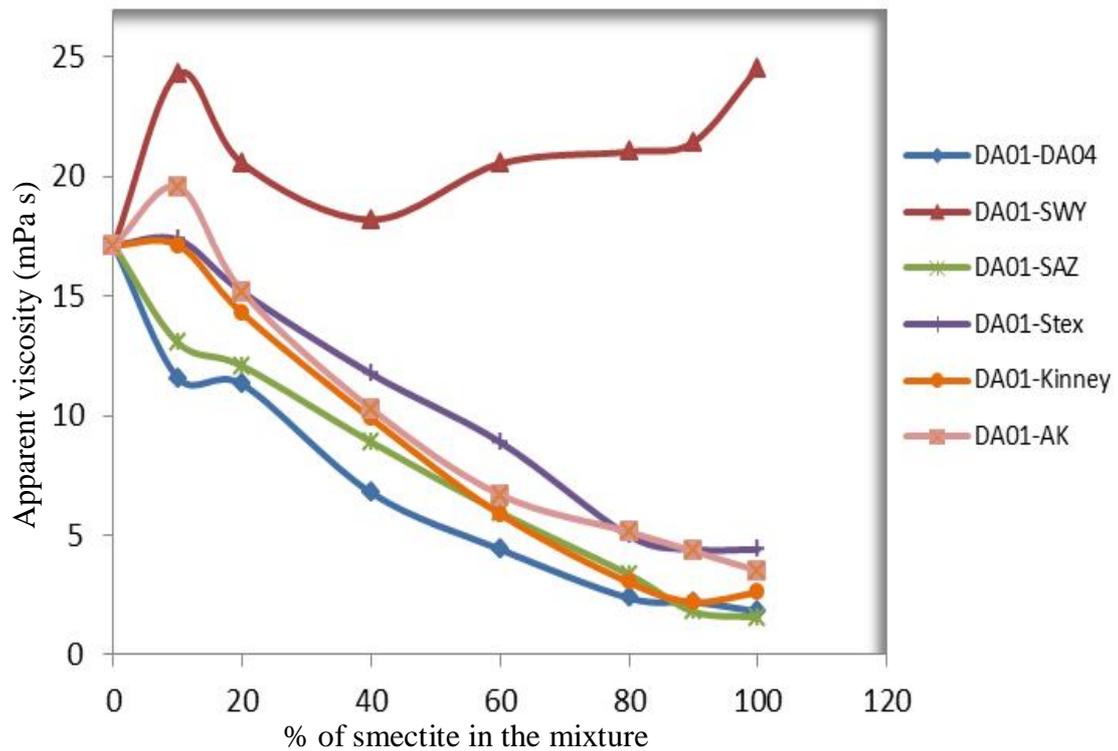


Figure 4.9: Effect of smectite content with different layer charge on apparent viscosity of palygorskite suspensions.

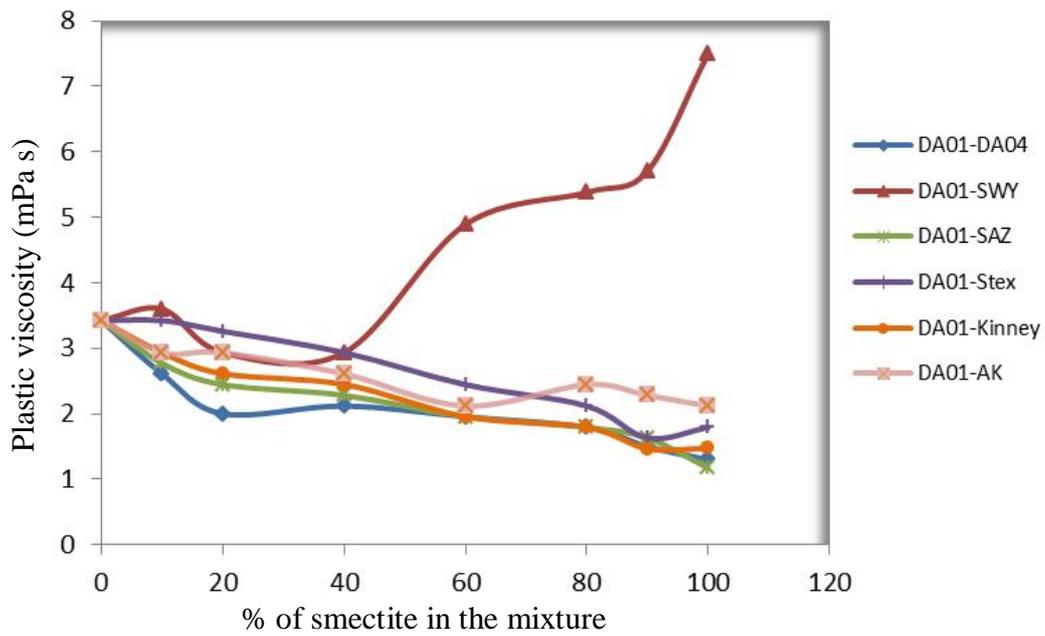


Figure 4.10: Effect of smectite content with different layer charge on the plastic viscosity of palygorskite suspensions.

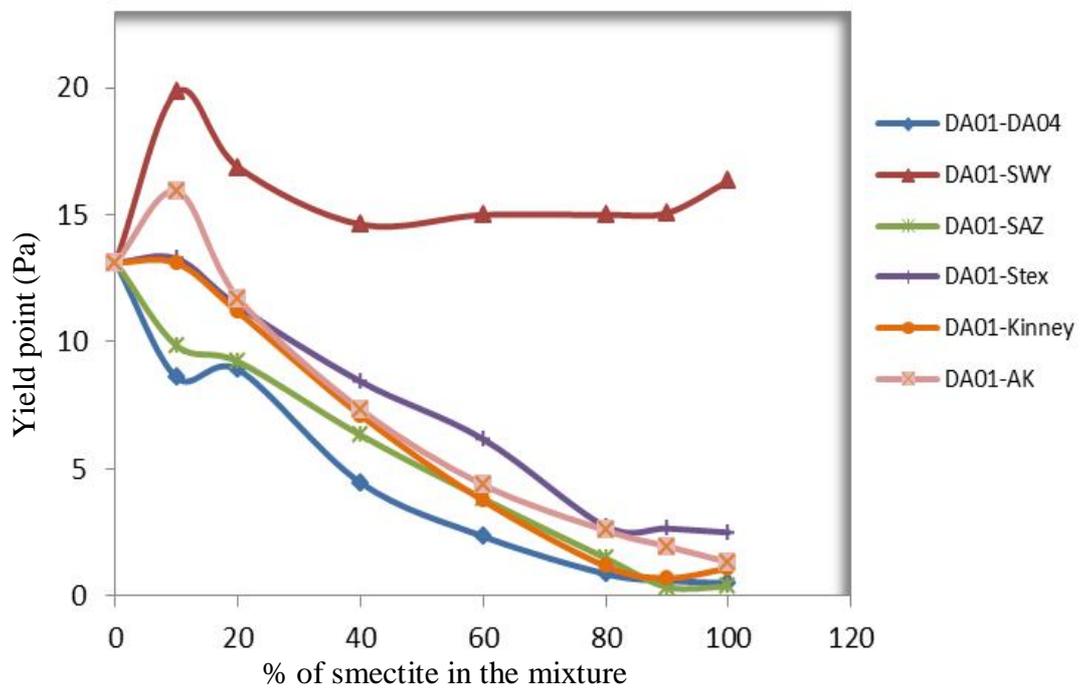


Figure 4.11: Effect of smectite content with different layer charge on the yield point of palygorskite suspensions.

#### 4.5.1.2.2 Bingham plastic and yield value

The alternative method used in this study to investigate the rheological properties of the mixture was by determining Bingham plastic viscosity and Bingham yield point. As mentioned before most of the suspensions showed non-Newtonian pseudoplastic and Bingham plastic flow behaviour. Such flow behaviour can be described using the Bingham model (Neaman and Singer, 2000; Tunc et al., 2011). In this method, the linear segment of the pseudoplastic flow curve, which occurs after the disruption of all the particle linkage, is considered. The linear segments of the flow curves were extrapolated to intercept the vertical axis. Values of Bingham plastic viscosity and Bingham yield point were obtained from the slopes and intercepts, respectively, of this segment. The values are included in Table B.3 (Appendix B).

Figure 4.12 shows the variation of the Bingham plastic viscosity values of the mixed suspensions as a function of smectite content in the mixture. The general trend is almost similar to the other rheological parameters (plastic viscosity, apparent viscosity and yield value) mentioned before. The plastic viscosity values of the suspensions showed increasing tendency for low percentage (< 10%) of low charge smectite (SWy-2) and intermediate charge smectite (STex-1b). For > 20% smectite in the mixture, the value decreases continuously with percentage of smectite for all mixtures except for SWy-2. The plastic viscosity decreased to a minimum value at 40% SWy-2 and increased at concentrations higher than 40% in the mixture. Similar results have been reported by Neaman and Singer (2000) for mixture of palygorskite and Wyoming bentonite. However, the Newtonian flow reported by these authors for 20 – 40% smectite content in the mixture due to prevention of the two end members from interacting with each other and forming network was not observed in this work. Under the current experimental condition (i.e. high (5%) solid concentration), low percentage of smectite may not prevent palygorskite particles to form networks and exhibit Newtonian flow.

The Bingham yield points obtained from the intercept of the linear part of shear stress versus shear rate graph were also plotted as a function of the proportion of smectite

(Figure 4.13). The effect of layer charge and its localisation was more evident in the case of the Bingham yield point. For low charge smectites (SWy-2 and AK-1.2), addition of 10% smectite increased the yield point of the suspension even to a value higher than the two end members. Significant change was not observed after addition of 10% smectite in the case of STex-1b and Kinney. The Bingham yield point decreased sharply after addition of 10% of SAz-2 and DA04 in the mixture. Further addition ( $\geq 20\%$ ) of smectite caused decrease of yield point for all smectite concentrations, except for SWy-2 in which it increased gradually for smectite content in the mixture  $> 40\%$ .

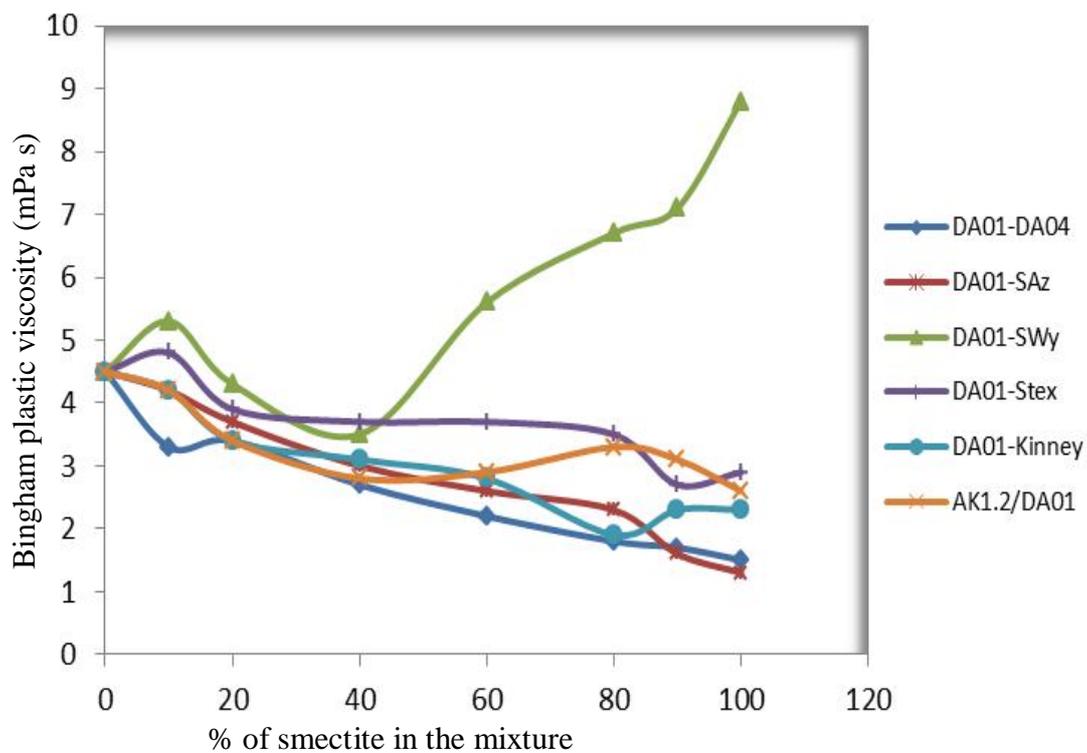


Figure 4.12: Effect of smectite content with different layer charge on Bingham plastic viscosity of palygorskite.

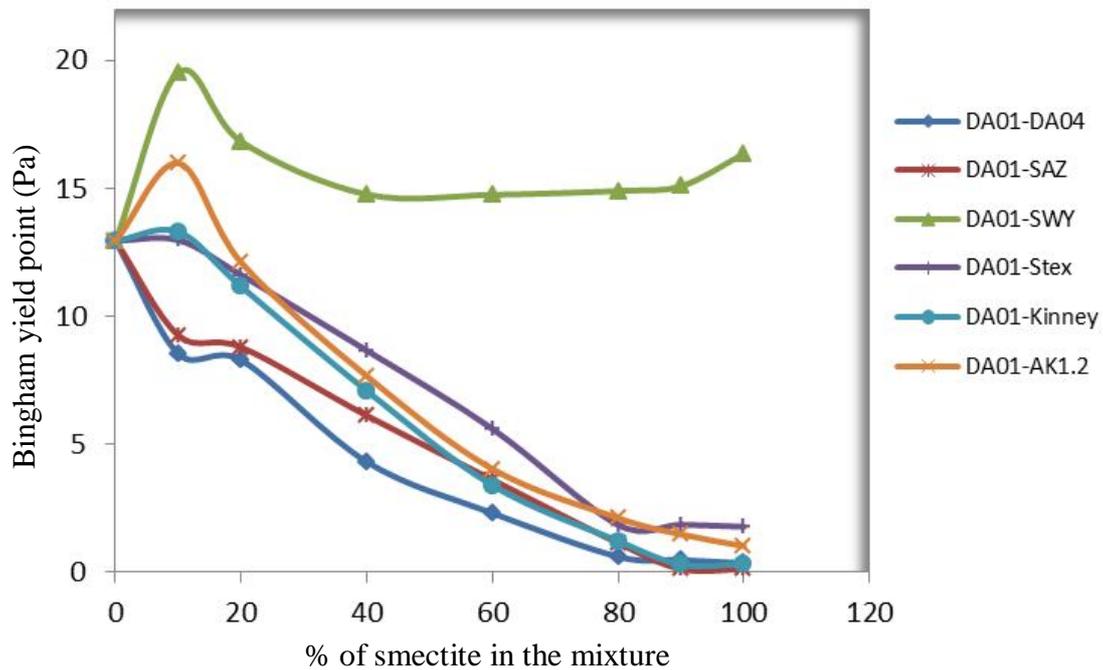


Figure 4.13: Effect of smectite content on the Bingham yield point of palygorskite-smectite suspensions.

#### 4.5.1.3 Effect of NaCl on the rheological properties of mixed palygorskite-smectite suspensions

One of the advantages of fibrous clay over bentonite in water based drilling fluid is that their rheological properties are not affected by the presence of salt (Galan, 1996; Murray, 2007). In this study the rheological properties of palygorskite-smectite mixed suspensions was measured after addition of 2M NaCl and was compared with electrolyte free suspensions. Figures 4.14 and 4.15 show the influence of addition of 2M NaCl on the apparent viscosity and yield point of selected mixed suspensions (DA01-SteX-1b and DA01-Kinney) with different proportion of smectite. For lower percentages of smectite ( $\leq 40\%$ ), the effect electrolytes on apparent viscosity and yield point is insignificant. In other words, the presence of salt does not influence significantly the flow behaviour of suspensions rich in palygorskite. The effect of electrolyte on the suspension is more pronounced for higher percentage of smectite in the mixture ( $> 40\%$ ) (i.e. both apparent viscosity and yield value increased by more

than two times). However, the plastic viscosity value increased irrespective of percentage of smectite in the mixture (Appendix B).

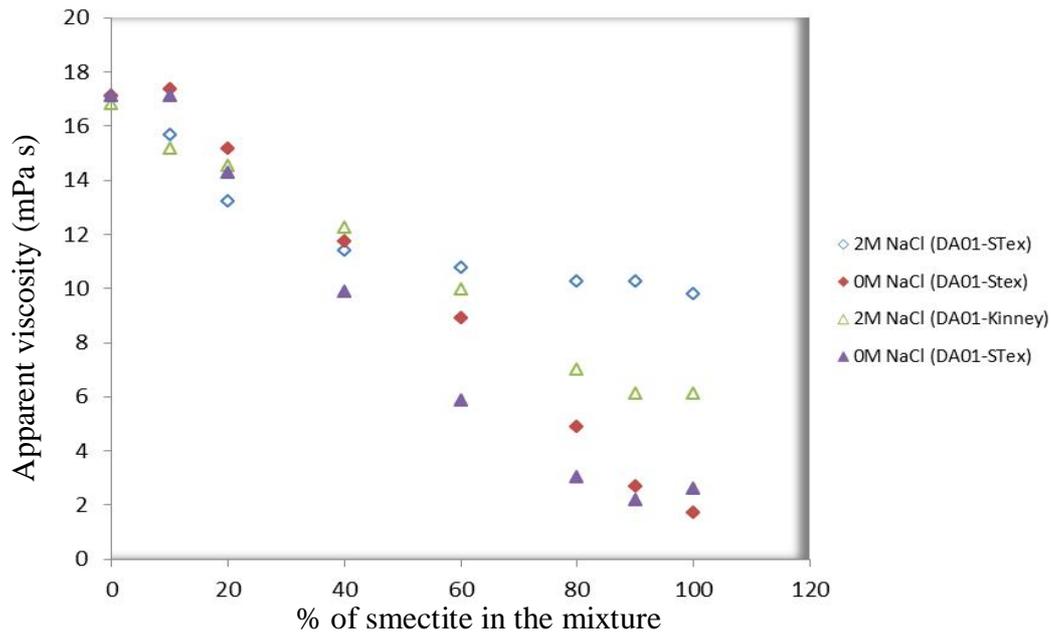


Figure 4.14: Effect of addition of NaCl (2M) on apparent viscosity of palygorskite mixed with STex-1b and Kinney bentonite suspension.

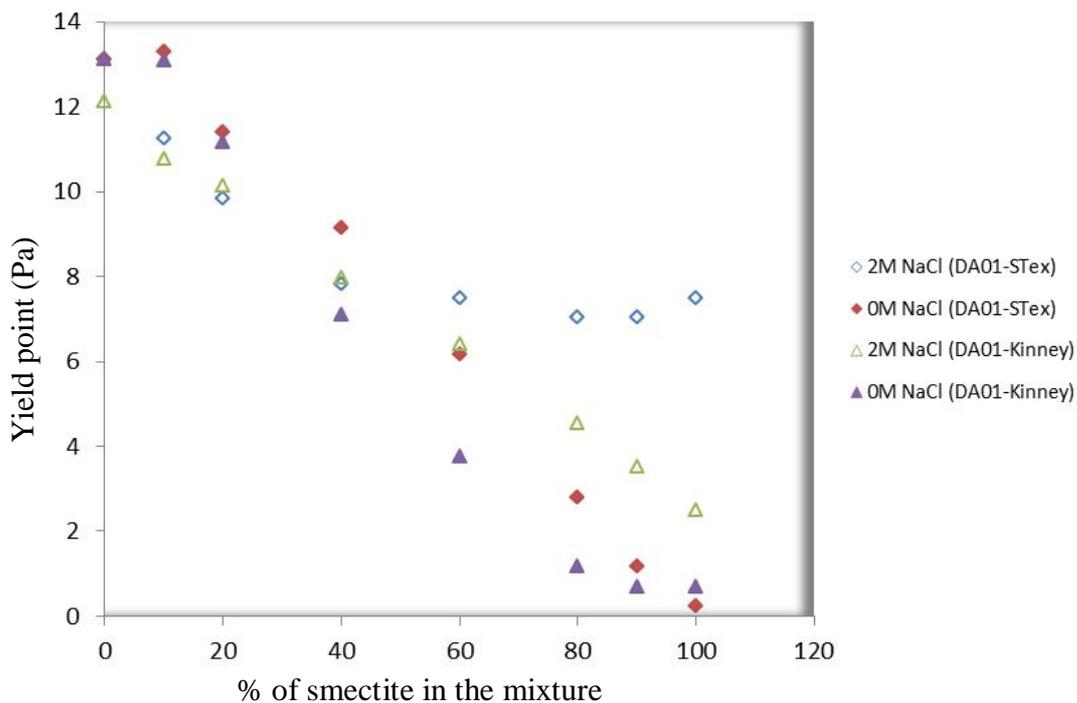


Figure 4.15: Effect of electrolyte (NaCl) on yield point of palygorskite mixed with STex-1b and Kinney bentonite suspensions.

## 4.5.2 Sepiolite-smectite mixture

### 4.4.2.1 Flow diagrams

Sepiolite is the other clay mineral characterised by fibrous morphology. Similarly sepiolite sample from Spain (ES5) and Greece (GSp) were mixed with three types of smectites (low, intermediate and high charge smectite). The shear stress versus shear rate graph of sepiolite – smectite mixed aqueous suspensions containing 5 wt.% solids is shown in Figures 4.16, 4.17, 4.18 and 4.19. All sepiolite suspensions (both GSp and ES5) mixed with low charge smectite (SWy-2) at different proportions showed non-Newtonian pseudoplastic flow behaviour. The suspensions of sepiolite mixed with intermediate (STex-1b) and high charge (SAz-2) smectite exhibited pseudoplastic flow for  $\leq 80\%$  smectite in the suspension. However, as the fraction of intermediate and high charge smectite in the mixture increased (0 – 80%), the shear rate at which the flow curve became linear shifted to lower value. Further addition of smectite ( $\geq 80\%$ ) transformed the flow behaviour to Bingham plastic type of flow with yield point  $< 2$  Pa.

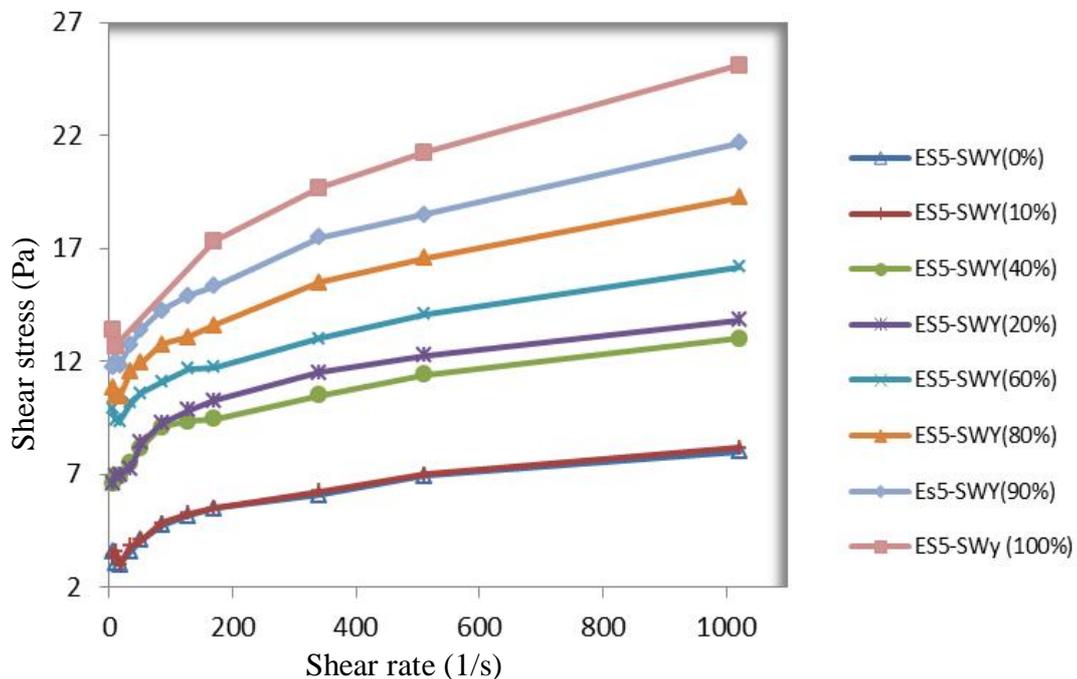


Figure 4.16: Rheograms of ES5 (Spain sepiolite) – SWy-2 (smectite) mixed suspension.

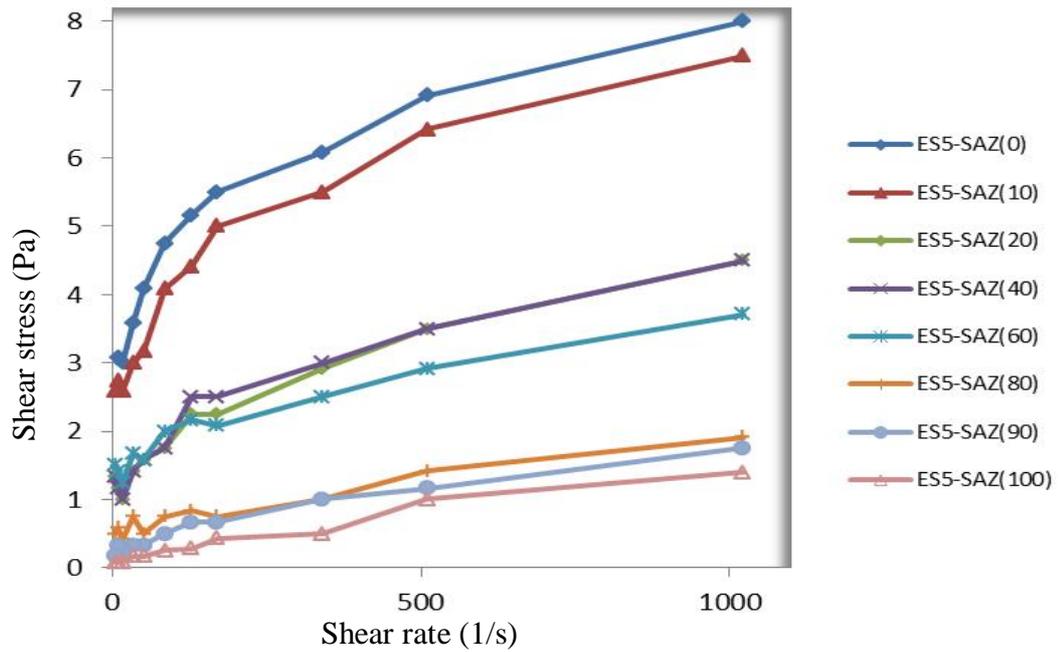


Figure 4.17: Rheograms of ES5 (Spain sepiolite) – SAz-2 (smectite) mixed suspension.

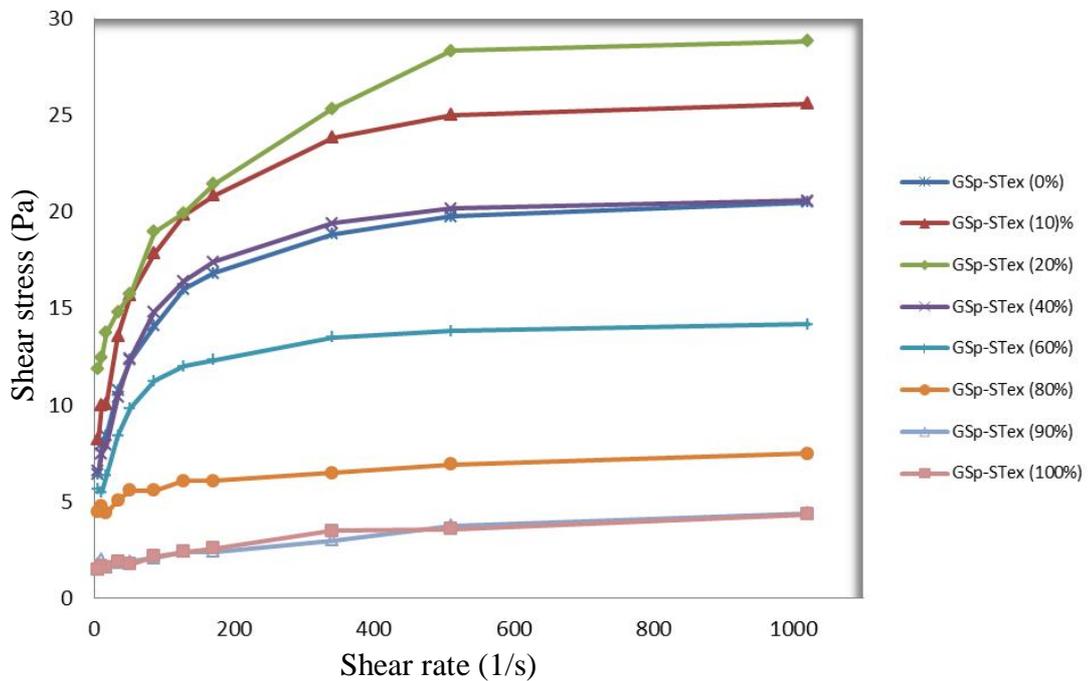


Figure 4.18: Rheograms of GSp (Greece sepiolite) – STex-1b (smectite) mixed suspension.

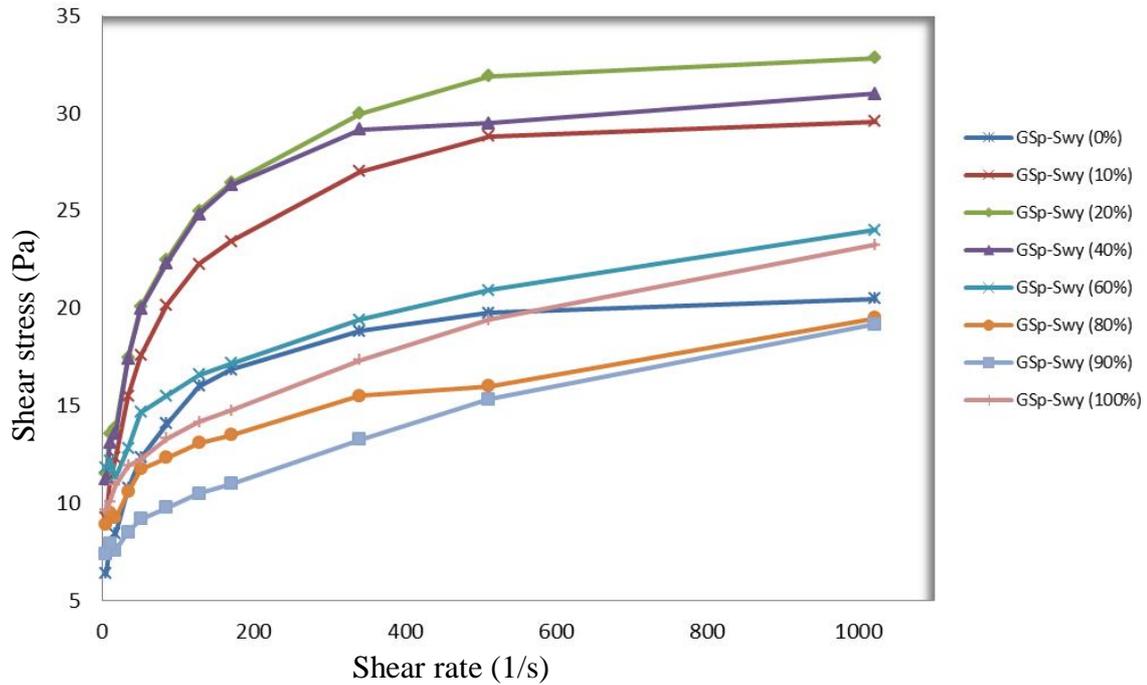


Figure 4.19: Rheograms of GSp (Greece sepiolite) – SWy-2 (smectite) mixed suspension.

The obtained shear stress ( $\tau$ ) and shear rate ( $\dot{\gamma}$ ) values of pseudoplastic flow were fitted well to the Herschel-Buckley (Yield-power-law model) and power law models and Bingham plastic flow were fitted to Bingham plastic model (regression coefficient  $> 0.96$  for all studied systems). The selected figures for the fitting are included in appendix C.

All the sepiolite-smectite mixed suspensions exhibiting pseudoplastic behaviour showed sheared thinning characteristics (i.e.  $n$ , varied between 0.27 and 0.5 for ES5 and 0.18 and 0.5 for GSp) (Appendix B). The lowest value for the flow property index ( $n$ ) was observed at 10 % to 40% of smectite in the mixture for low charge smectite (ES5-SWy-2 and GSp-SWy-2) and intermediate charge (GSp-STex-1b and ES5-STex-1b). The flow behaviour index is a measure of deviation from Newtonian flow behaviour. As  $n$  increases, pseudoplastic behaviour decreases (Grigelmo-Miguel et al., 1999). This indicates that deviation from Newtonian flow behaviour is higher at smectite contents 10%-40% in the mixture. For ES5-SAz-2 mixture, the pseudoplastic

behaviour decreased with proportion of smectite up to 60% in the mixture. Smectite content > 80% transformed the flow behaviour to Bingham plastic flow type.

The consistency coefficient (K) of sepiolite end members is relatively higher than the smectite end member. Especially Greek sepiolite (GSp) showed higher consistency coefficient ( $> 5 \text{ Pa s}^n$ ). The highest K value of the mixed suspension was observed at the lowest flow behaviour index (n) value, which occurred at 10% to 40% of smectite in mixture. However, the change was very sharp in the case of Greek sepiolite (GSp) compared to the Spanish sepiolite (ES5). This sharp change in K and low n value is attributed to the interaction of particles of the two end members.

All the suspensions exhibiting pseudoplastic and Bingham plastic flow behaviour in the case of Spanish sepiolite (ES5) showed yield stress values between 11.9 Pa (SWy-2 (100%)) and 0.12 Pa (SAz-2(100%)). The yield stress value decreased with increasing proportion of intermediate (STex-1b) and high charge smectite (SAz-2) in the mixture. In contrast it increased exponentially with the proportion of low charge smectite (SWy-2) in the mixture. Sepiolite dominating suspensions ( $\leq 40\%$  smectite) in the case of Greece sepiolite (GSp) did not show yield stress value.

#### **4.4.2.2 Rheological parameters**

##### **4.4.2.2.1 Plastic viscosity, apparent viscosity and yield point**

The rheological parameters (plastic viscosity, apparent viscosity and yield point), which were determined according to API specifications (API 13A, 1993), for mixed sepiolite and smectite suspensions at different proportions are listed in Table 4.6. The ES5 end member developed relatively lower apparent viscosity and yield value. In contrast GSp developed suspensions of high apparent viscosity which meet the API specifications (i.e. viscometer dial reading at 600 rpm is  $> 30$ ). However, the plastic viscosity was higher for ES5 (Spain sepiolite) than for GSp (Greek sepiolite). This difference in rheological properties between the two sepiolites is related to difference in their physical properties (fibre length, specific surface area and CEC). GSp was reported to have higher fiber length (5.1  $\mu\text{m}$ ) (Simonton T. et al., 1988) and CEC (21 meq/100 g) than ES5. BET specific surface area of GSp (214  $\text{m}^2/\text{g}$ ) is also higher than specific surface area of ES5 (147  $\text{m}^2/\text{g}$ ).

Table 4.6: Rheological parameter of suspension of sepiolite (ES5 & GSp) mixed with different smectite (according to API 13A, 1993).

SAMPLE	RHEOLOGICAL PROPERTY	% OF SMECTITE IN THE MIXTURE							
		0	10	20	40	60	80	90	100
ES5 & SWy-2	Apparent viscosity (cP)	7.83	7.83	13.5	12.7	15.8	18.8	20.9	24.5
	Plastic viscosity (cP)	2.12	1.96	3.10	3.10	4.08	5.22	5.71	7.50
	Yield point (Pa)	5.47	5.62	9.99	9.21	11.2	13.0	14.6	16.3
ES5 & STex-1b	Apparent viscosity (cP)	7.83	7.34	6.36	6.36	5.87	3.83	4.40	4.40
	Plastic viscosity (cP)	2.12	2.12	1.96	1.96	1.96	1.79	1.63	1.79
	Yield point (Pa)	5.47	2.65	1.95	3.75	4.22	4.22	5.00	5.47
ES5 & SAz2	Apparent viscosity (cP)	7.83	7.34	4.40	4.40	3.63	1.88	1.63	1.37
	Plastic viscosity (cP)	2.12	1.96	1.96	1.96	1.56	0.98	0.98	0.78
	Yield point (Pa)	5.47	5.15	2.34	2.34	1.99	0.86	0.62	0.56
GSp & SWy-2	Apparent viscosity (cP)	20.1	28.95	32.13	30.33	15.9	15.33	18.8	24.5
	Plastic viscosity (cP)	1.47	1.47	1.79	2.94	6.03	7.01	7.50	7.50
	Yield point (Pa)	17.8	26.31	29.05	26.24	9.45	7.96	10.8	16.3
GSp & STex-1b	Apparent viscosity (cP)	20.1	25.0	28.2	20.1	13.8	7.34	4.32	4.40
	Plastic viscosity (cP)	1.47	1.14	0.98	0.82	0.65	1.14	1.30	1.79
	Yield point (Pa)	17.8	22.9	26.0	18.5	12.7	5.93	2.89	5.47

Figures 4.20, 4.21 and 4.22 show the variation of the rheological parameters of the sepiolite-smectite mixed suspensions as a function of smectite percentage. Addition of 10% of all smectites to ES5 did not change the rheological parameters significantly, whereas the rheological parameters sharply increased after addition of 20% of low charge smectite (SWy-2) in the mixture. In the case of GSp, addition of 10% to 20% of both low charge (SWy-2) and intermediate charge (STex-1b) smectite increased sharply apparent viscosity and yield value. This sharp increase is probably due to

interaction between sepiolite and smectite particles (Neaman and Singer, 2000). Further addition (40%) of low charge smectite (SWy-2) decreased slightly the rheological parameters in both sepiolite suspensions. Addition of > 40% of low charge smectite (SWy-2) to ES5 resulted to an increase of all rheological parameters. In contrast the apparent viscosity and yield value decreased, to even lower values than the two end members, (suspensions containing 40-80% SWy-2) in the case of GSp. The rheological parameters deteriorate with increasing proportion of high charge (SAz-2) and intermediate charge (STex-1b) smectite. However, the decrease of the rheological parameters with increasing smectite content is still more pronounced for high charge smectite compared to intermediate charge smectite.

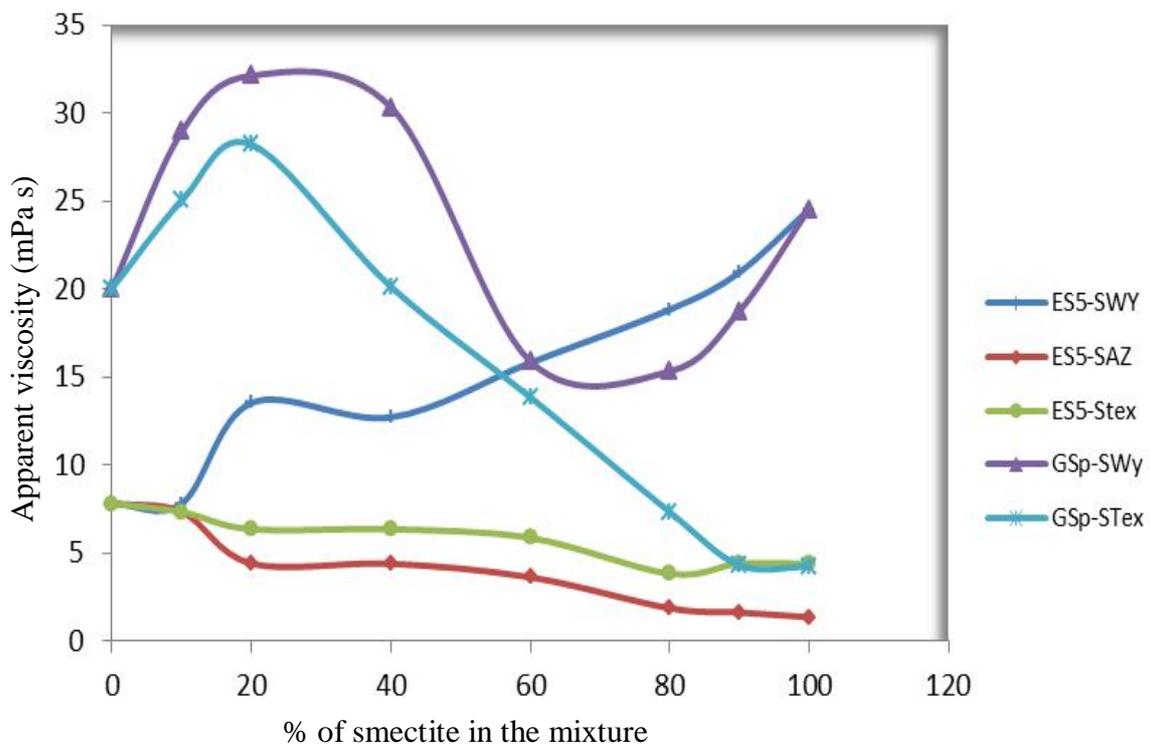


Figure 4.20: Effect of low (SWy-2), intermediate (STex-1b) and high charge (SAz-2) smectite concentration on apparent viscosity of mixed suspensions of sepiolite-smectite.

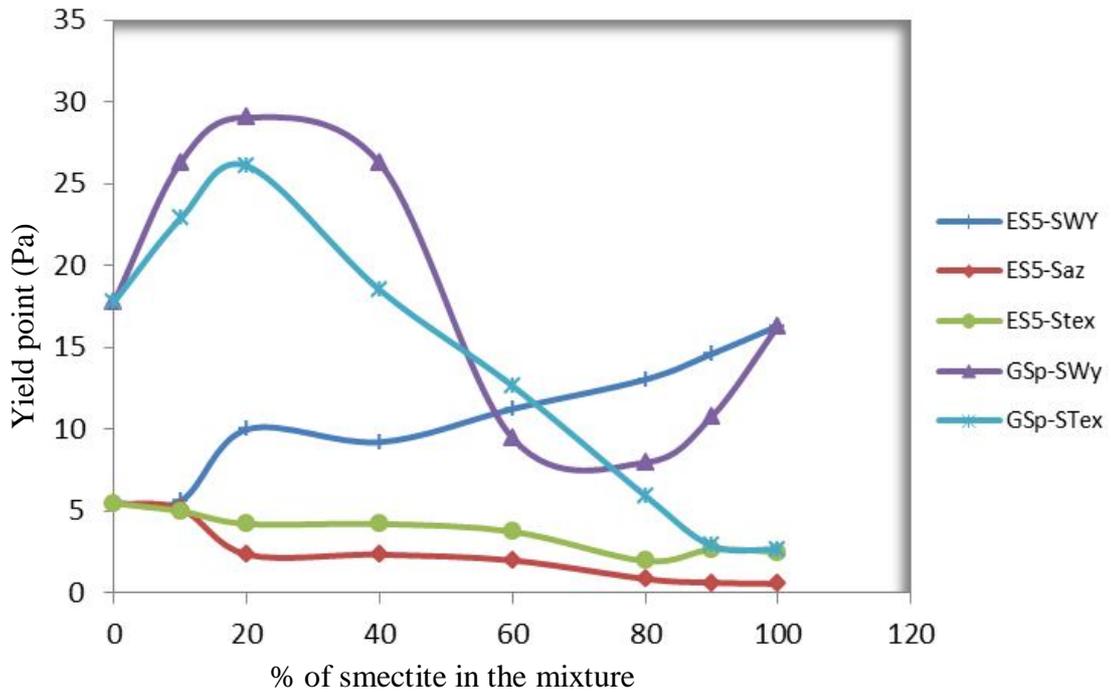


Figure 4.21: Effect of low (SWy-2), intermediate (STex-1b) and high charge (SAz-2) smectite concentration on the yield point of mixed suspensions of sepiolite-smectite.

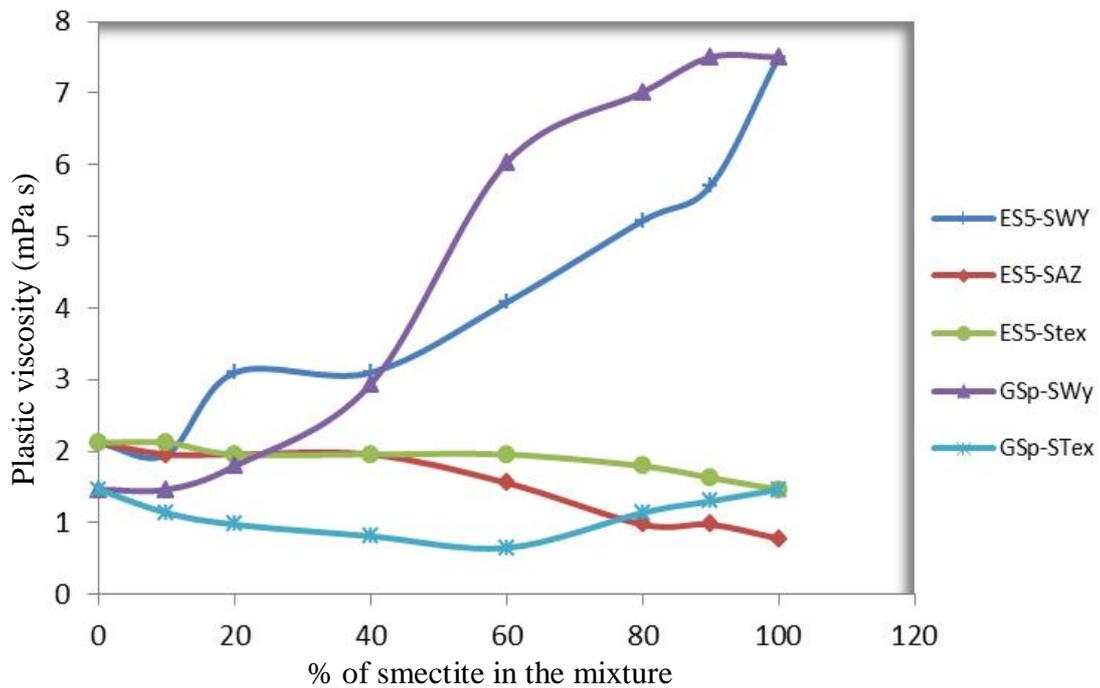


Figure 4.22: Effect of low (SWy-2), intermediate (STex-1b) and high charge (SAz-2) smectite concentration on plastic viscosity of mixed suspensions of sepiolite-smectite.

#### 4.4.2.2.2 Bingham plastic viscosity and yield point

Unlike the above method, which is based on the reading at two points (API 13A, 1993), the linear part of the curve are considered to determine Bingham plastic viscosity and yield point. The Bingham yield point and plastic viscosity obtained from the intercept and slope of linear part of shear stress versus shear rate graph were plotted as a function of smectite concentration ( Figures 4.23 and 4.24). The data is given in table B.1 (appendix B). Similarly general trends that depend on the proportion and the layer charge of the smectite were obtained.

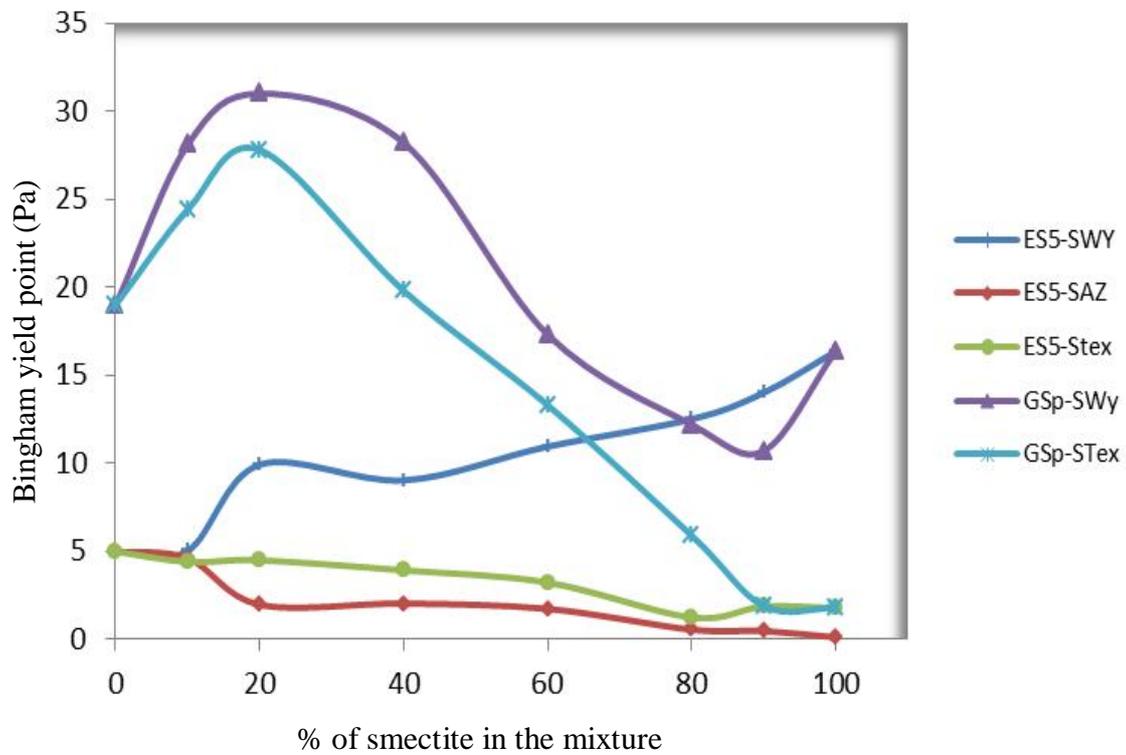


Figure 4.23: Effect of low (SWy-2), intermediate (STex-1b) and high charge (SAz-2) smectite concentration on Bingham yield point of mixed suspension of sepiolite-smectite.

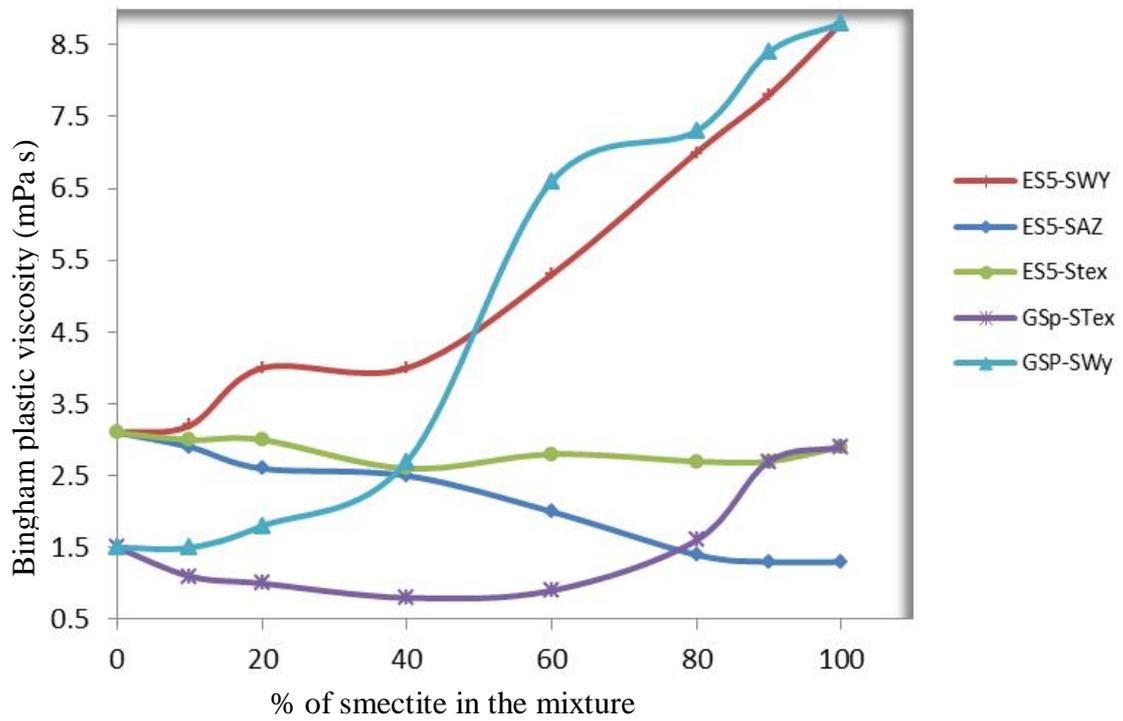


Figure 4.24: Effect of low (SWy-2), intermediate (STex-1b) and high charge (SAz-2) smectite concentration on Bingham plastic viscosity of mixed suspension of sepiolite-smectite.

## 5 Discussion

Fibrous clays occur in association with smectite, especially in soil clay minerals (Neaman and Singer 2000; Galan and Singer, 2011). The rheological properties of palygorskite-montmorillonite mixed clay suspensions depend on the fraction of montmorillonite in the mixture (Neaman and Singer, 2000). However, our current studies showed that in addition to proportion of smectite, the layer charge of the smectite plays a role on the rheological properties of the mixed suspensions. In the present study, palygorskite and sepiolite were mixed with different types of smectite. The bentonites used consist of smectites with layer charges that fall in the three groups (low charge, intermediate charge and high charge) of smectites proposed by Christidis et al. (2006).

The results in Figures 4.9 to 4.13 and Figures 4.20 to 4.24 demonstrate that the rheological properties of fibrous clays (palygorskite and sepiolite) mixed with smectite are determined both by the proportion and the layer charge of the smectite in the suspension. Layer charge is one of the factors which affect the rheological property (viscosity, gel strength, yield stress and thixotropy) (Christidis et al., 2006) and swelling potential (Stucki and Kostka, 2006; Laird D, 2006) of bentonites. According to our observation, it also seems to affect the rheological properties of the mixed palygorskite-smectite and sepiolite-smectite suspensions. This can be explained for example by observing the variation of yield stress value (both yield point and Bingham yield point) in mixed suspensions containing different smectites. In concentrated suspensions like in this experimental condition (5% solid), the gelation is expected to be due to particle-particle association that result yield stress. The yield stress value of suspension depends on the number of particle-particle linkages (van Olphen, 1964; Heller and Keren, 2001) and on the strength of particle-particle linkage (Neaman and Singer, 2000). This particle linkage in the mixed suspension could be between similar clay particles (smectite-smectite, palygorskite-palygorskite and sepiolite-sepiolite) or between different clay particles (smectite-palygorskite and smectite-sepiolite). Therefore, the degree of delamination of smectite aggregates to individual particles during wetting, that was controlled by the magnitude and localisation of layer charge (Laird , 2006), can probably influence the

yield point of the suspension. Low charge smectite like SWy-2, forms thin quasicrystals (Christidis et al., 2006; Laird, 2006). Hence the number of particles involved in particle-particle interaction is greater. In contrast, in high charge smectite (SAz-2 and Kinney) the quasicrystals tend to be larger and stable, due to an increased interparticle attraction (Laird, 2006). This is also true for tetrahedrally charged smectite (DA04). Thus, the number of smectite particles involved in interaction (smectite-smectite, smectite-palygorskite or smectite-sepiolite) is lower in suspension containing high charge smectite compared to low charge smectite. These could be the possible reasons for the variable rheological parameters observed with different proportions of low charge and high charge smectite in the mixtures.

In addition, formation of larger aggregates of smectite crystals in case of high charge smectites is expected to weaken the possible palygorskite-smectite and sepiolite-smectite networks and lead to lower yield points (van Olphen, 1964; Christidis et al., 2006; 2010) This could be explained by comparison of the effect of addition of 10 - 20% of three smectites (SWy-2, STex-1b and SAz-2) on the yield point of mixed sepiolite-smectite and palygorskite-smectite suspensions (Figures 4.11, 4.13, 4.21 and 4.23). At first place without the presence of particle-particle interaction between the two end members (sepiolite and palygorskite with smectite), this abrupt change in yield point at concentration of 10 to 20% of smectite in the suspension would not have occurred. However, the strength of particle-particle linkage is determined by the size of smectite quasicrystals (van Olphen, 1964) that interact with palygorskite and sepiolite fibres, which in turn depend on the magnitude and localisation of layer charge (Christidis et al., 2006). The thicker the floc, the weaker is the particle-particle linkage which breaks easily at lower rate of shear. The water molecules entrapped by the formation of networking will be freed when the linkages break. This could be the possible explanation for the sharp decrease of rheological properties in the case of high charge (e.g. SAz-2) and tetrahedrally charged (DA04) smectite compared to low charge (SWy-2) and intermediate charge (e.g. STex-1b) smectite. The aforementioned explanation (i.e. thin lamellae and large number of particles involved in the interaction) could be a possible additional explanation for the sharp increase of viscosity parameters in the case of low charge smectite (SWy-2 and AK-1.2). The

shifting of shear rate at which the flow curve became linear to the lower (left) and higher (right) value with increasing proportion of high charge and low charge smectite in the mixture, respectively, also attests to the influence of smectite layer charge on the strength of particle-particle linkage.

In addition to the type of smectite in the mixture, it seems that the fibre length, CEC and specific surface area of the fibrous clay end members also affect the rheological properties of the mixed suspensions. The longer the individual fibres and the higher the cation exchange capacity (CEC), the higher is the rheological properties of fibrous clays (Simonton et al., 1988; Neaman and Singer, 2000). The surface silanol groups are involved in binding sepiolite fibre together and hence, influence viscosity and yield stress of sepiolite gels (Simonton et al., 1988). Addition of 10 - 40% smectite (SWy-2 and STex-1b) in the mixture on the magnitude of apparent viscosity and yield value is more pronounced in the case of Greek sepiolite (GSp) compared to Spanish sepiolite (ES5) (Figure 4.20, 4.21 and 4.23). This indicates that the differences in the characteristics amongst the two sepiolites (GSp and ES5) affected the magnitude of particle-particle interaction. The presence of large silanol groups (CEC) together with high specific surface area and fibre length (Simonton et al., 1988) for GSp appeared to contribute to the interaction with smectite particles.

The response of fibrous clays and smectite to the presence of electrolyte is expected to be different. This is because the mechanisms of gel formation in the two clays are different due to their different morphological and structural characteristics (Galan, 1996; Christidis et al., 2010). This study has also shown that the effect of electrolyte on the rheology of the mixed suspension of palygorskite-smectite depends on the relative concentrations of the two end members in the mixture (Figure 4.14 and 4.14.). The random networking between fibres (Simonton et al., 1988) and edge-to-edge particle association under current experimental pH condition (Brandenburg and Lagaly, 1988; Heller and Keren, 2001; Tarchitzky and Chen, 2002) control the development of viscosity in fibrous clays and smectites respectively. The random networking between palygorskite fibres does not seem to be significantly affected by addition of electrolyte. In the suspensions dominated by smectite (> 40%), the high

electrolyte concentration (2M NaCl) exerts attractive forces between the particles due to suppression of the diffused double layers and transforms particle associations from edge-to-edge to face-to-face causing coagulation (Yildiz et al., 1999; Abend and Lagaly, 2000). However, the effect of coagulation on the rheological properties of the slurry depends on the solid content of the suspensions (Abend and Lagaly, 2000; Heller H. and Keren, 2001). At lower solid contents ( $< 3\%$ ) the flocs formed settle independently to sediment and viscosity decreases. In contrast at solid content  $> 3\%$ , the flocs connect to fill the space and form a three-dimensional network of particles instead of settling independently. In other words it forms attractive gel (Abend and Lagaly, 2000). The high viscosity of smectite dominated 5% palygorskite-smectite mixed suspensions after addition of 2M NaCl may be explained by this ionic strength effect. Recently, Christidis et al. (2010) also reported that the addition of electrolyte ( $\leq 1\text{M NaCl}$ ) to a suspension with 6.2% solid content had no effect on the rheological properties of palygorskite suspension, while it deteriorated the rheological properties of smectite bearing palygorskite suspension. This also indicates that the effect of electrolyte on the rheological property of the mixed suspension depends on the relative concentration of the electrolyte. Low electrolyte concentration causes compression of the diffuse double layer that in turn contributes to the free movement of the individual platelets (Heller and Keren, 2001). As a consequence the viscosity drops. Higher electrolyte concentration in concentrated suspension similar to this experimental condition may promote coagulation and increase rheological parameters (Abend and Lagaly, 2000). In this work the effect of electrolyte on the rheological property of sepiolite-smectite was not checked. However, since the mechanism of gel formation of sepiolite is similar to palygorskite due to the similar morphology of the two clay minerals, the effect of electrolyte on sepiolite-smectite mixed suspension is expected to be similar.

## **6 Conclusion and recommendation**

### **6.1 Conclusion**

The rheological properties of fibrous clays (palygorskite and sepiolite) mixed with smectites having different layer charge was investigated. The result from both palygorskite-smectite and sepiolite-smectite mixed suspensions showed that the degree of interaction between smectite and fibrous clay particles and its effect on the viscosity parameters of the suspensions depend on the concentration, layer charge and charge localisation of the smectite in the mixture. The interaction between the two end members seems to occur at lower percentage (10 to 20%) of smectite in the mixture. The mechanism by which the layer charge and charge localisation of smectite affects the system behaviour by influencing the degree of dissociation and the thickness of smectite quasicrystals, which consequently determine the number of particles involved in the interaction and on the strength of particle-particle linkages. In the case of smectites with low layer charge, the interaction of smectite particles with palygorskite and sepiolite fibres is higher and the particle-particle linkage is stronger because the smectite particles dissociate to thin quasicrystals or isolated to single smectite layers. An increase in layer charge resulted to lower swelling and dissociation of smectite particles and favoured the stability and formation of thick smectite quasicrystals. As a consequence, the interaction is relatively low and the particle-particle linkage broke easily. Tetrahedrally charged smectite (nontronite) was found to behave similar to high charge smectite. From the results of this study it seems that the physical and chemical properties of the fibres (fibre length, specific surface area and cation exchange capacity (CEC)) also affect the interaction of fibrous clays with smectite and consequently the rheological properties of the mixtures.

### **6.2 Recommendation**

- The explanation of the behaviour of the systems in the region where interaction occurs (10 to 20% smectites) requires a more sophisticated analysis of the ways in which the particles interact. Therefore, incorporating some additional tests such as high resolution imaging (SEM or TEM) can add significant information to the interpretation and analysis of the behaviour of the studied system.

- Adding more samples to the dataset can result in better understanding of the rheological properties of palygorskite-smectite and sepiolite-smectite mixed suspensions. Especially it is recommended to investigate the rheological properties of sepiolite-trioctahedral smectite mixed suspension, since sepiolite usually occurs in association with tri-octahedral smectite such as stevensite and saponite.

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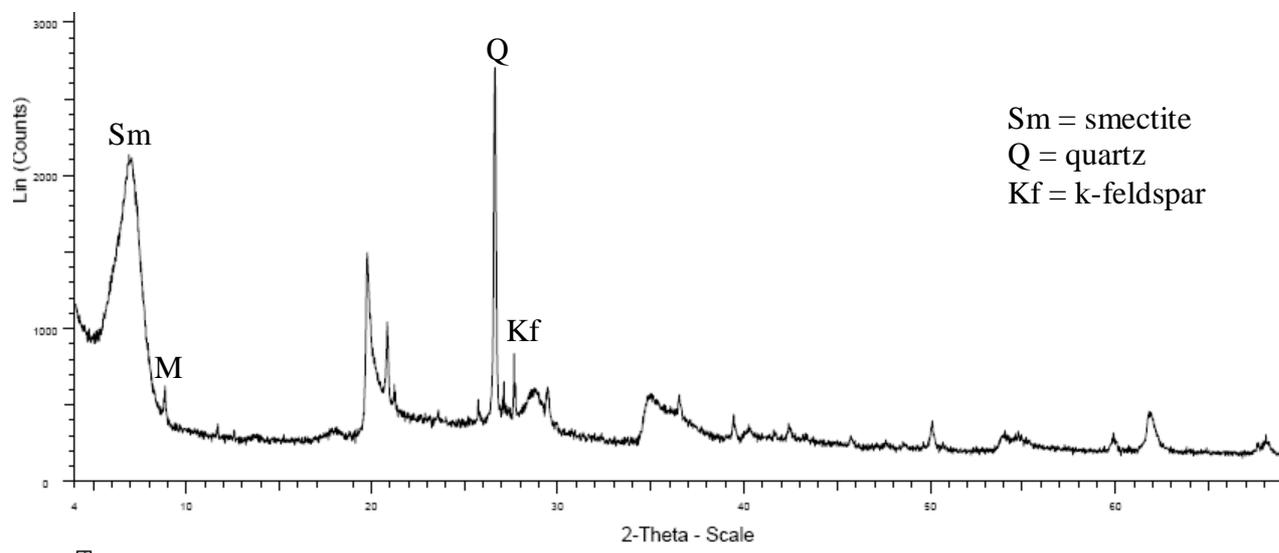
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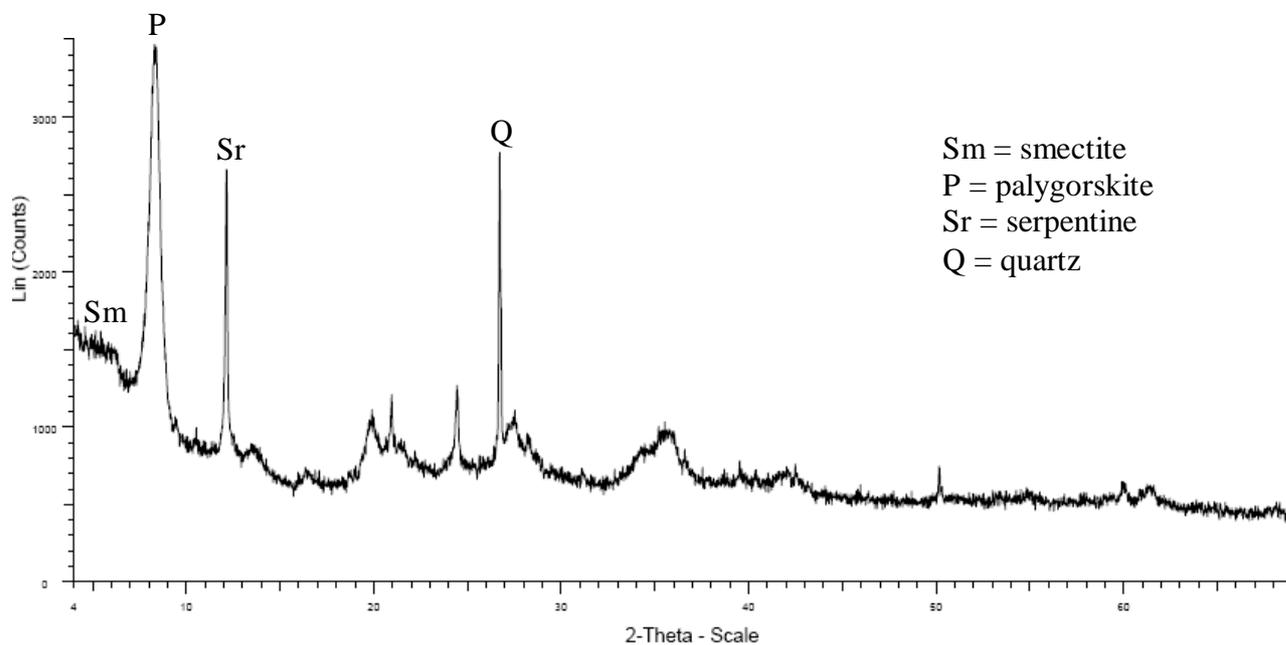
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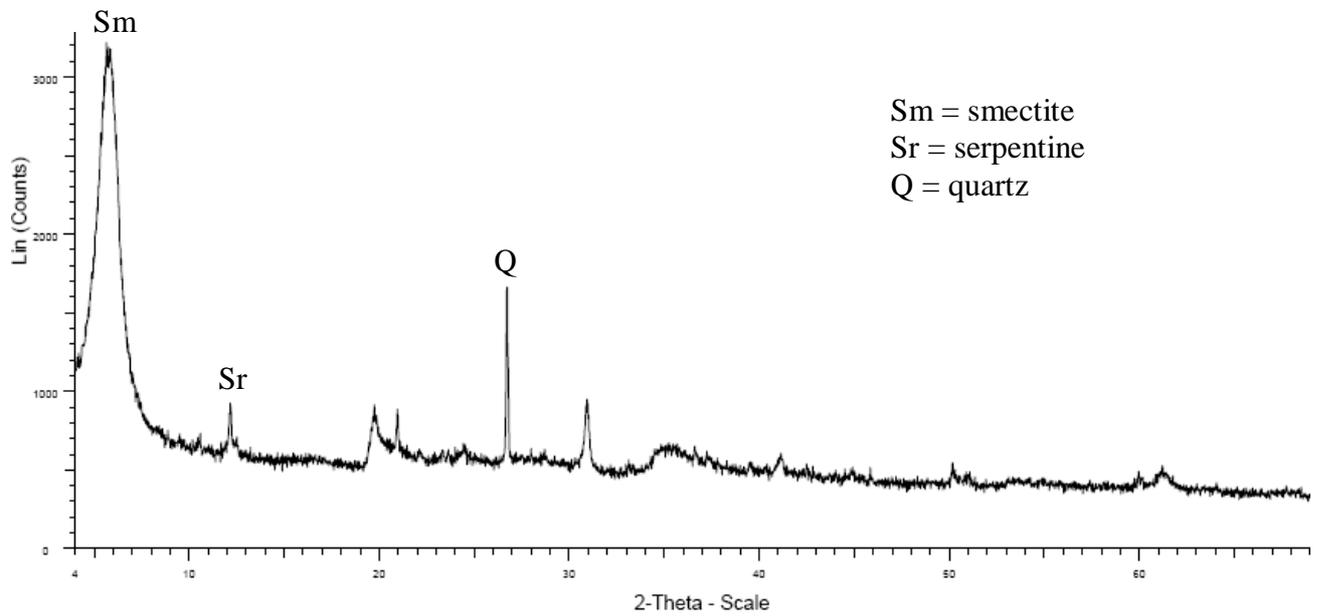
## Appendix A



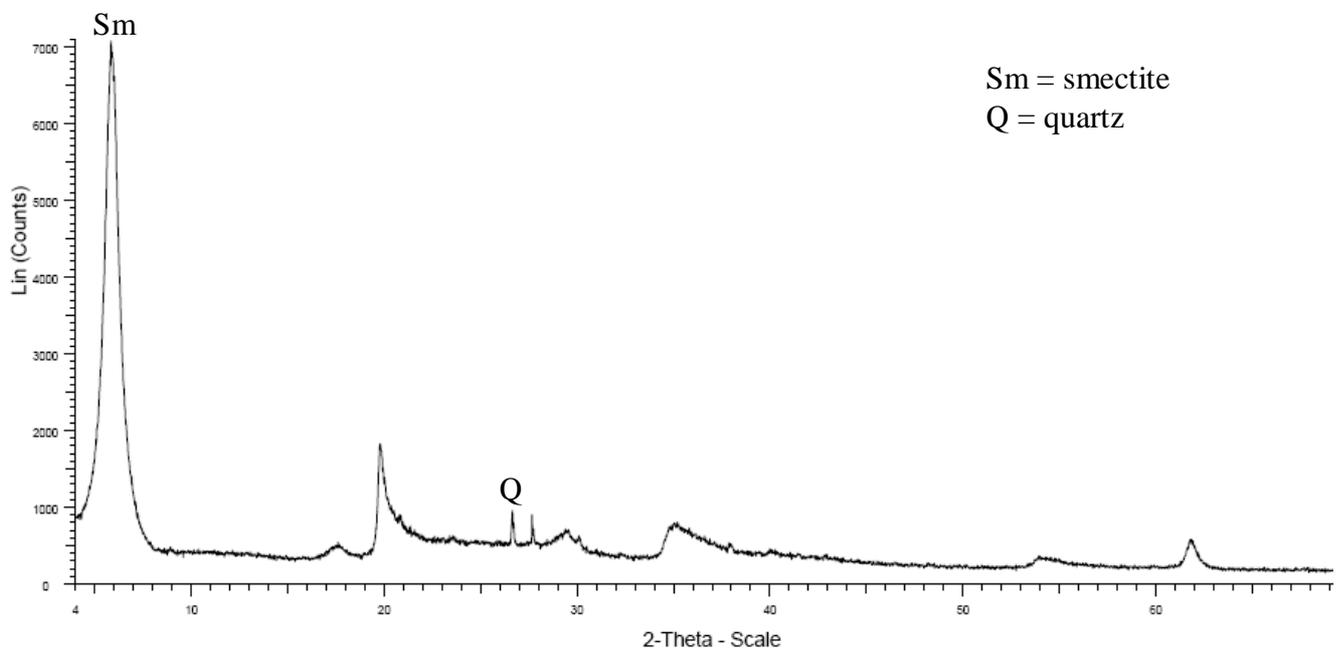
A.1. X-ray diffraction patterns of SWy-2



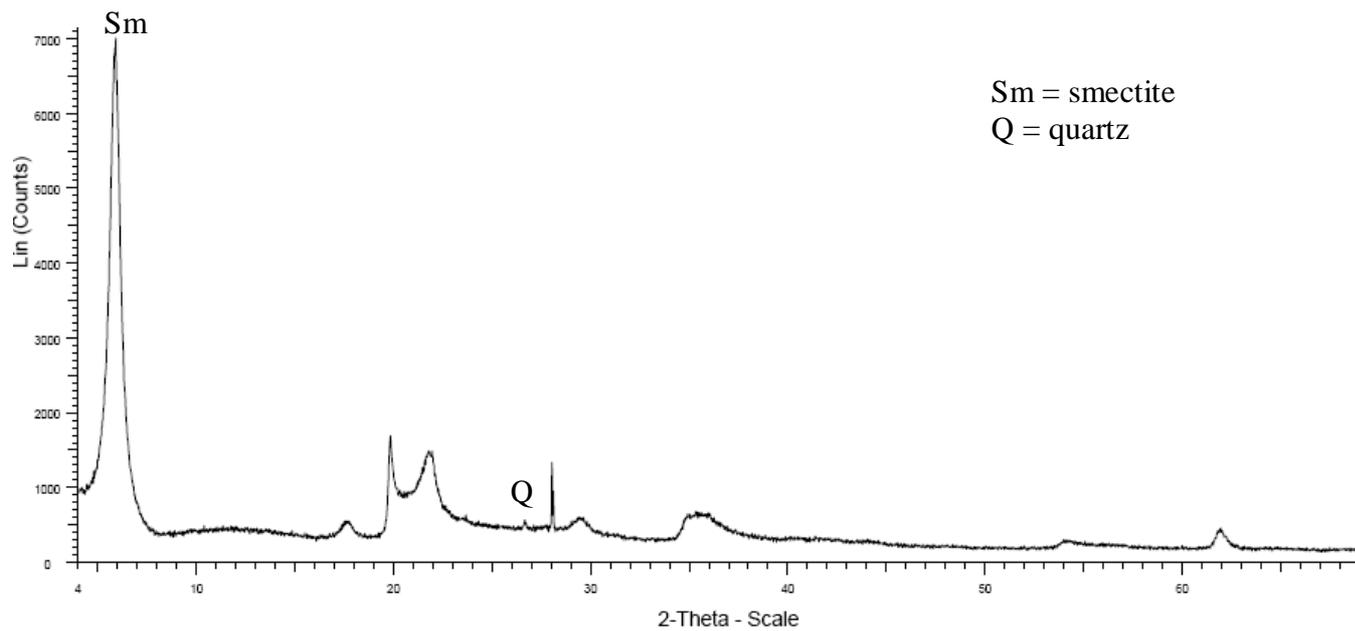
A.2. X-ray diffraction patterns of DA01



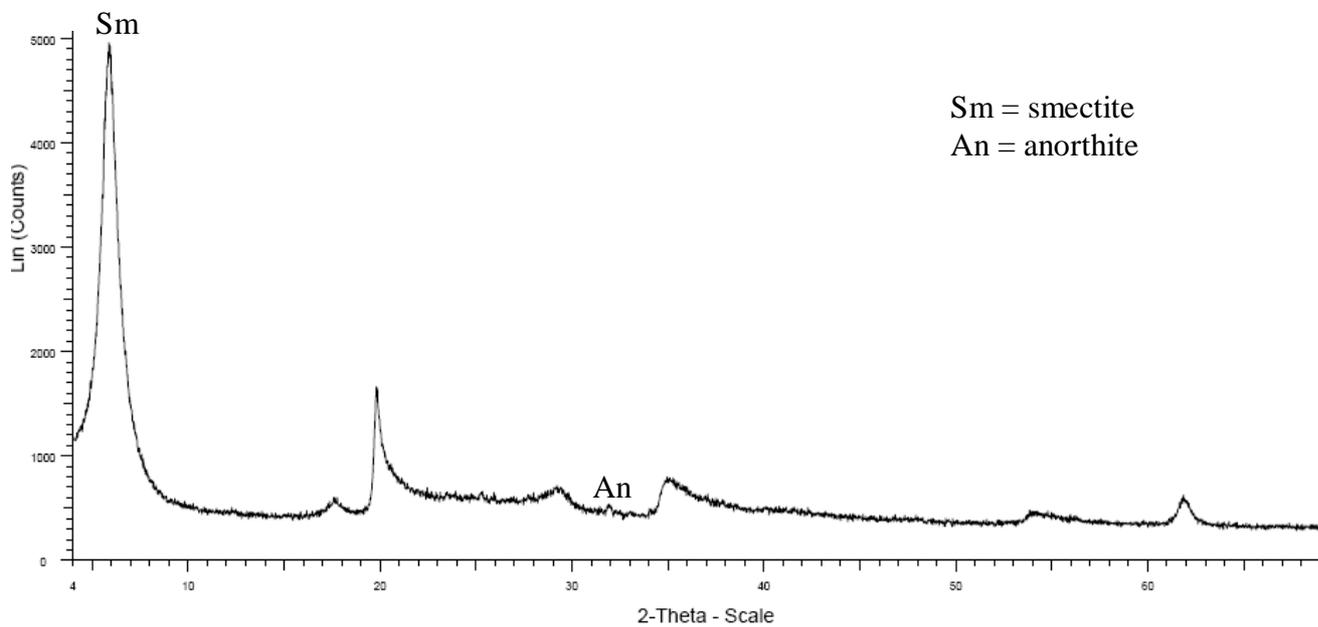
A.3. X-ray diffraction patterns of DA04



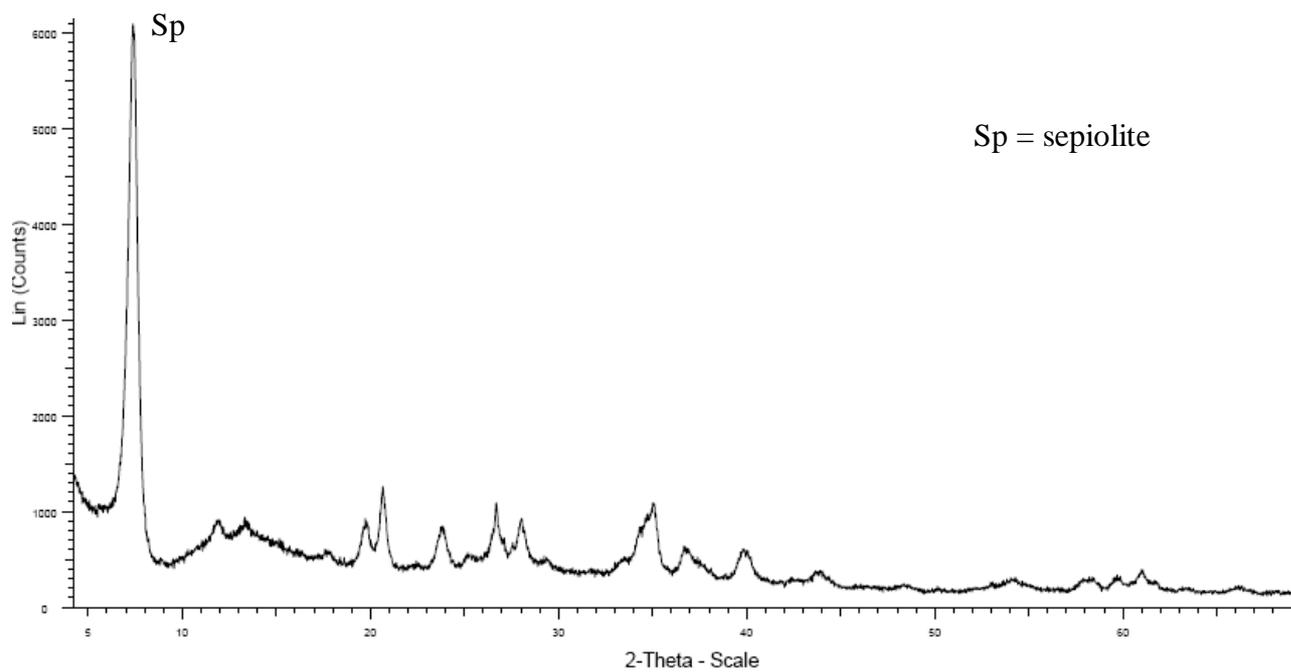
A.4. X-ray diffraction patterns of SAz-2



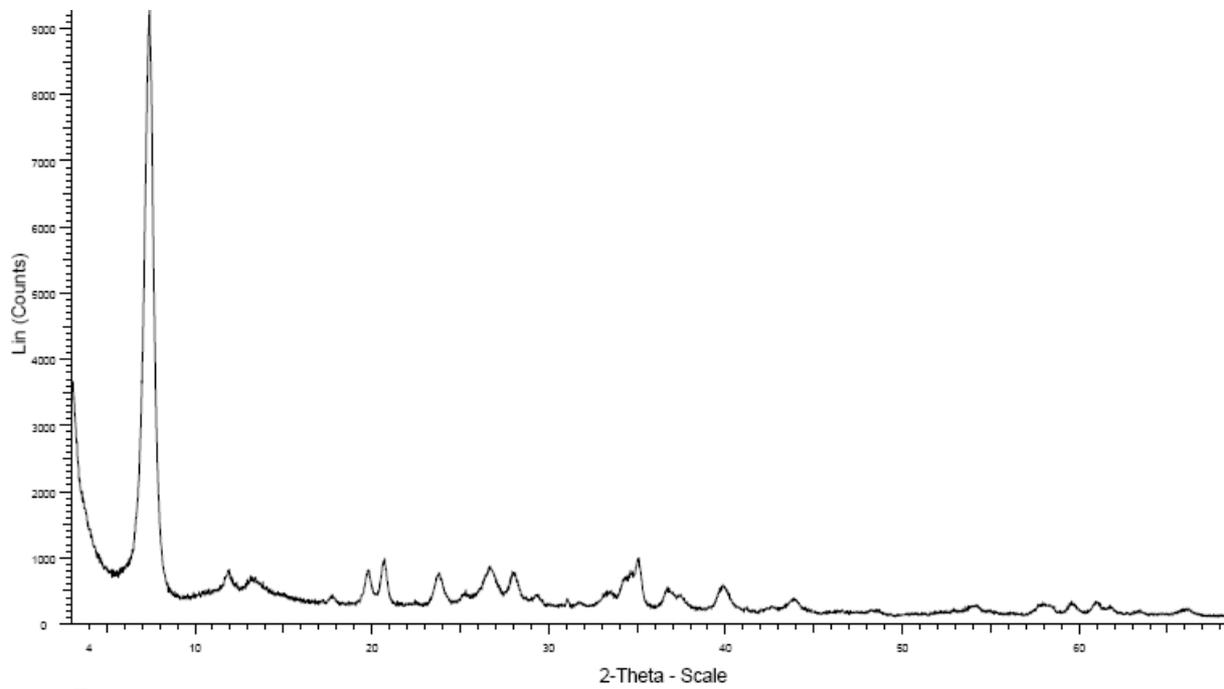
A.5. X-ray diffraction patterns of STex-1b



A.6. X-ray diffraction patterns of AK-1.2



A.7. X-ray diffraction patterns of ES5



A.8. X-ray diffraction patterns of GSP

## Appendix B

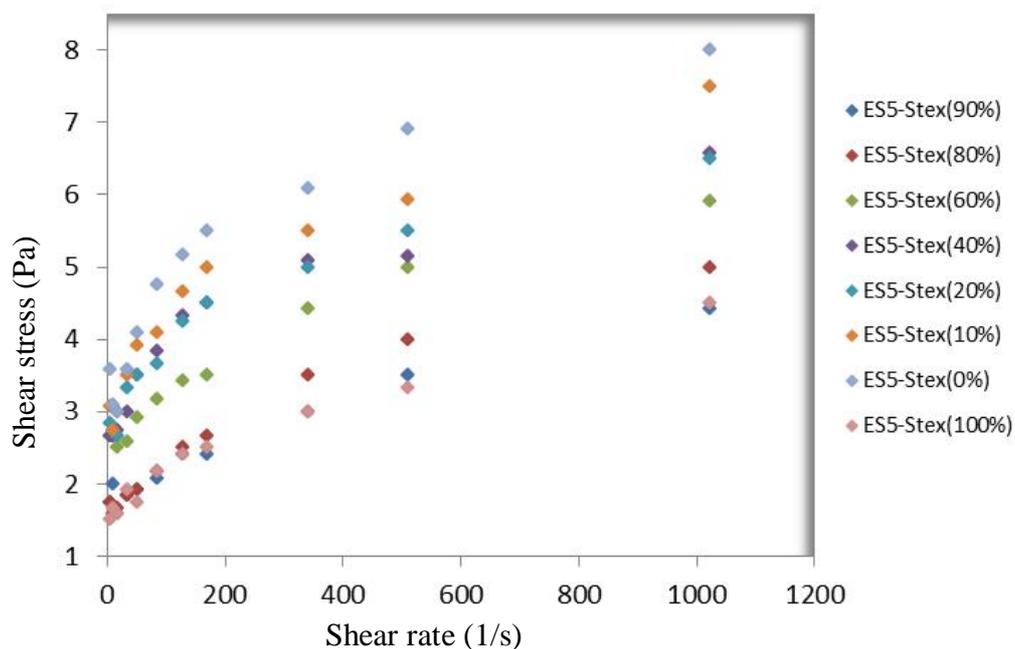


Figure B.1: Rheograms of ES5 (Spain sepiolite) – SAz-2 (smectite) mixed suspension

Table B.1: Bingham rheological parameters of sepiolite-smectite mixed suspension

SAMPLE	RHEOLOGICAL PROPERTY	% OF SMECTITE IN THE MIXTURE							
		0	10	20	40	60	80	90	100
ES5 & SAz-2	Plastic viscosity (cP)	3.1	2.9	2.6	2.5	2	1.4	1.3	1.3
	Yield point (Pa)	4.99	4.6	1.96	2.0	1.7	0.55	0.47	0.11
ES5 & SWy-2	Plastic viscosity (cP)	3.1	3.2	4	4	5.3	7	7.8	8.8
	Yield point (Pa)	4.99	5.03	9.92	9.03	10.95	12.5	14	16.3
ES5 & STex-1b	Plastic viscosity (cP)	3.1	3	3	2.6	2.8	2.7	2.7	2.9
	Yield point (Pa)	4.99	4.4	4.49	3.9	3.23	1.24	1.86	1.78
GSp & STex-2	Plastic viscosity (cP)	1.5	1.1	1	0.8	0.9	1.6	2.7	2.9
	Yield point (Pa)	19	24.4	27.8	19.8	13.3	5.9	1.9	1.78
GSp & SWy-2	Plastic viscosity (cP)	1.5	1.5	1.8	2.7	6.6	7.3	8.4	8.8
	Yield point (Pa)	19	28.1	31	28.2	17.3	12.2	10.7	16.35

Table B.2. Model parameters of the mixed suspension (palygorskite-smectite & sepiolite-smectite)

SMECTITE	MODEL PARAMETERS	% OF SMECTITE IN THE MIXTURE (DA01-SMECTITE)							
		0	10	20	40	60	80	90	100
Saz-2	YV (Pa)	-	-	-	-	2	0.44	0.09	0.13
	K (Pa s <sup>n</sup> )	4.35	3.15	3	1.3	0.2	0.12	0.0012	0.0013
	n	0.21	0.21	0.21	0.28	0.44	0.45	1	1
Stex-1b	YV (Pa)	-	-	-	-	3.39	0.58	0.92	0.2
	K (Pa s <sup>n</sup> )	4.35	4.8	3.74	3.92	0.42	0.27	0.0029	0.0014
	n	0.21	0.19	0.21	0.16	0.38	0.39	1	1
Swy-2	YV (Pa)	-	-	-	-	11.9	11.9	12.2	11.97
	K (Pa s <sup>n</sup> )	4.35	8.83	8.61	8.36	0.36	0.13	0.24	0.4
	n	0.21	0.15	0.13	0.11	0.47	0.64	0.53	0.5
DA04	YV (Pa)	-	-	-	-	1.1	0.59	0.48	0.39
	K (Pa s <sup>n</sup> )	4.35	3.61	3.71	1.71	0.15	0.0018	0.0017	0.0015
	n	0.21	0.17	0.16	0.2	0.44	1	1	1
AK-1.2	YV (Pa)	-	-	-	4.04	3.27	1.88	1.32	0.97
	K (Pa s <sup>n</sup> )	4.35	6.98	6.24	1.59	0.3	0.1	0.04	0.01
	n	0.21	0.16	0.13	0.19	0.35	0.48	0.62	0.85
Kinney	YV (Pa)	-	-	-	-	-	-	0.3	0.25
	K (Pa s <sup>n</sup> )	4.35	4.78	4	2.29	0.7	0.22	0.0023	0.0024
	n	0.21	0.19	0.19	0.22	0.32	0.38	1	1

SMECTITE	MODEL PARAMETERS	% OF SMECTITE IN THE MIXTURE (ES5-SMECTITE)							
		0	10	20	40	60	80	90	100
Saz-2	YV (Pa)	2.43	1.68	0.38	0.3	0.26	0.56	0.34	0.12
	K (Pa s <sup>n</sup> )	0.46	0.48	0.35	0.43	0.33	0.0014	0.0015	0.0013
	n	0.36	0.36	0.35	0.33	0.3	1	1	1
Stex-1b	YV (Pa)	2.43	1.43	1.52	1.7	1.92	1.04	0.51	0.18
	K (Pa s <sup>n</sup> )	0.46	0.74	0.73	0.52	0.17	0.003	0.0026	0.0014
	n	0.36	0.3	0.28	0.32	0.45	1	1	1
Swy-2	YV (Pa)	2.43	2.86	4.2	6.95	8.98	9.88	11.05	11.97
	K (Pa s <sup>n</sup> )	0.46	0.27	1.5	0.21	0.37	0.37	0.29	0.4
	n	0.36	0.44	0.27	0.48	0.41	0.46	0.52	0.5

SMECTITE	MODEL PARAMETERS	% OF SMECTITE IN THE MIXTURE (GSP-SMECTITE)							
		0	10	20	40	60	80	90	100
Stex-1b	YV (Pa)	-	-	-	-	-	3.27	1.99	0.18
	K (Pa s <sup>n</sup> )	5.34	6.78	8.67	5.37	4.1	0.86	0.0026	0.0014
	n	0.21	0.2	0.18	0.21	0.2	0.23	1	1
Swy-2	YV (Pa)	-	-	-	-	10	7.11	6.68	11.97
	K (Pa s <sup>n</sup> )	5.34	7.44	9.23	9.14	0.91	1.02	0.34	0.4
	n	0.21	0.19	0.19	0.21	0.4	0.36	0.52	0.5

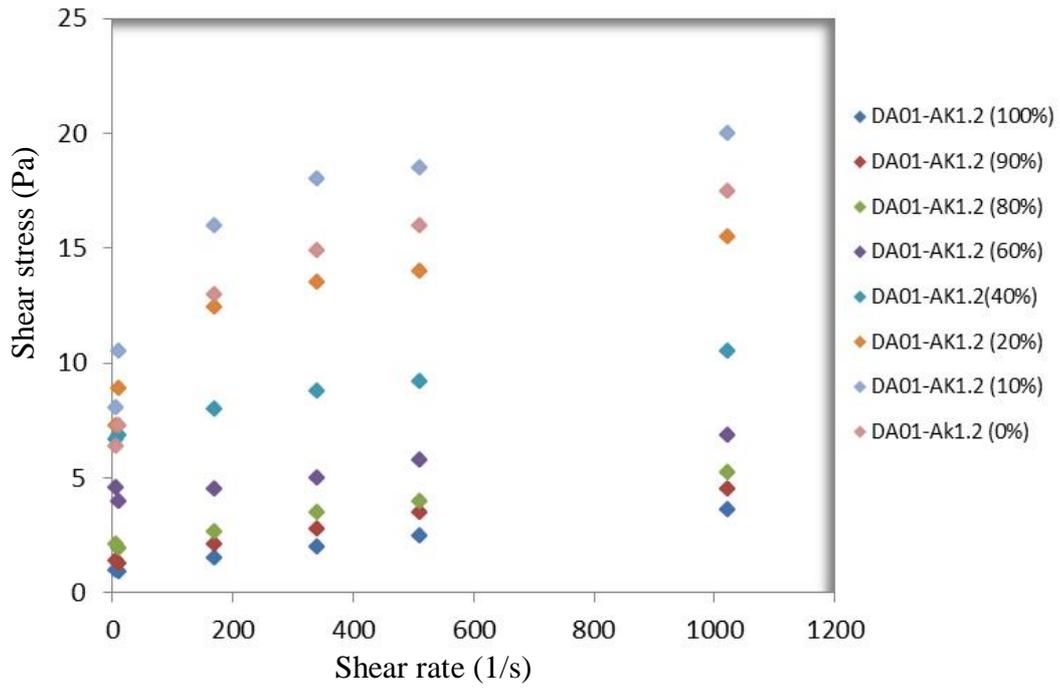
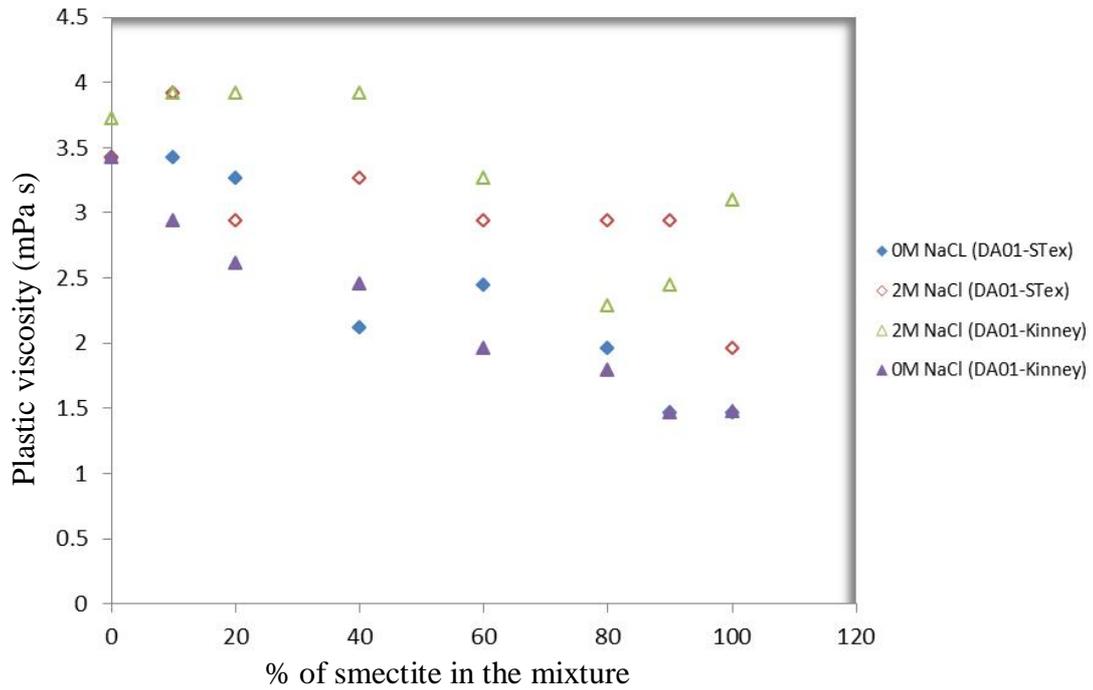
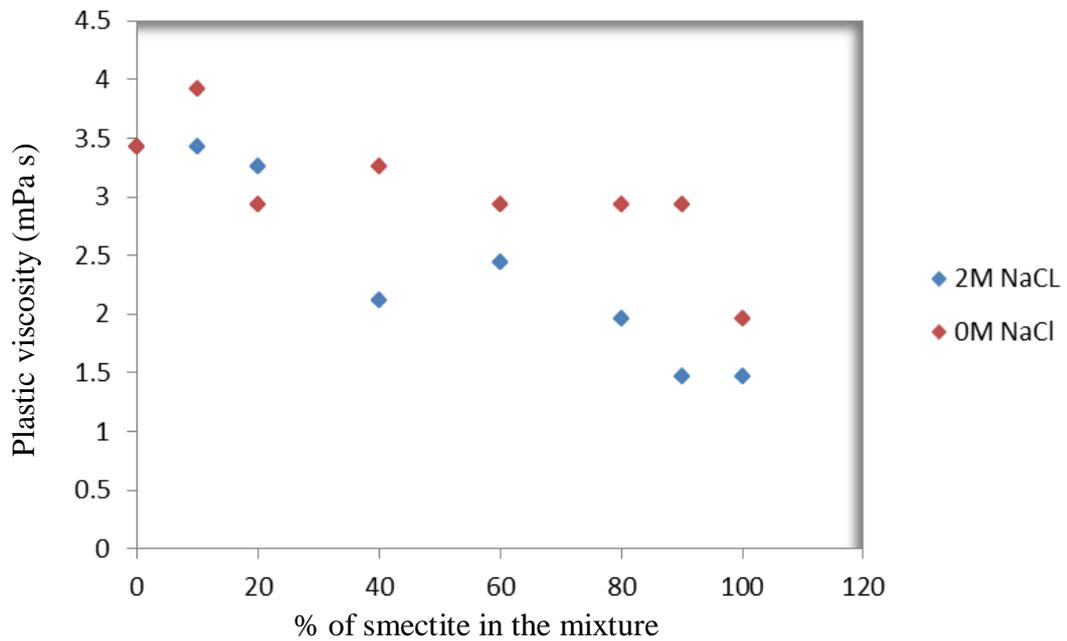


Figure B.2: Rheograms of DA01 (palygorskite) – K1.2 (smectite) mixed suspension.



B.3: Effect of electrolyte on the plastic viscosity of STEx-1b-DA01 and DA01-Kinney mixed suspension



B.4: Effect of electrolyte on the plastic viscosity of STex-1b-DA01 mixed suspension

Table B.3: Bingham plastic viscosity and yield stress of palygorskite-smectite mixture

SAMPLE	RHEOLOGICAL PROPERTY	% OF SMECTITE IN THE MIXTURE							
		0	10	20	40	60	80	90	100
DA04	Plastic viscosity (cP)	4.5	3.3	3.4	2.7	2.2	1.8	1.7	1.5
	Yield point (Pa)	13.0	8.5	8.3	4.3	2.3	0.6	0.5	0.4
SWy-2	Plastic viscosity (cP)	4.5	5.3	4.3	3.5	5.6	6.7	7.1	8.8
	Yield point (Pa)	13.0	19.5	16.8	14.8	14.8	14.9	15.1	16.4
STex-1b	Plastic viscosity (cP)	4.5	4.8	3.9	3.7	3.7	3.5	2.7	2.9
	Yield point (Pa)	13.0	13.0	11.6	8.7	5.6	1.9	1.9	1.8
Kinney	Plastic viscosity (cP)	4.5	4.2	3.4	3.1	2.8	1.9	2.3	2.3
	Yield point (Pa)	13.0	13.3	11.2	7.1	3.4	1.2	0.3	0.3
SAz-2	Plastic viscosity (cP)	4.5	4.2	3.7	3.0	2.6	2.3	1.6	1.3
	Yield point (Pa)	13.0	9.3	8.8	6.1	3.6	1.1	0.1	0.1
KA-1.2	Plastic viscosity (cP)	4.5	4.2	3.4	2.8	2.9	3.3	3.1	2.6
	Yield point (Pa)	13.0	16.0	12.1	7.7	4.0	2.1	1.5	1.0

### Appendix C: Selected figures for fitting to rheological models

