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Research paper

Rheological properties of palygorskite–bentonite and sepiolite–bentonite mixed clay suspensions

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ABSTRACT

This study examines the influence of layer charge and smectite content on the rheological properties of mixed bentonite–palygorskite suspensions. Eight bentonite samples containing smectite with layer charge ranging between 0.38 and 0.54 e/huc were used to prepare 5% w/v mixed palygorskite–bentonite aqueous suspension at pH 7. The influence of smectite on the apparent viscosity and yield point of palygorskite suspensions depends on the proportion of the smectite in the mixture and the layer charge and charge localization of the smectite. The interaction between the two end member clay minerals is maximum at low percentage (10 to 20%) of bentonite in the mixture. Low charge and high charge smectite tended to improve and deteriorate, respectively, the yield point and apparent viscosity of the suspension. This behaviour seemed to be related to the influence of layer charge of smectite on the degree of delamination and the thickness of smectite quasicrystals, which consequently determine the number of particles involved in the interaction and the strength of particle–particle linkages.

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1. Introduction

Clay minerals have remarkable rheological properties and are used to increase the stability and viscosity of flowing suspensions. They tend to form gel-like structures at low solid contents (Luckham and Rossi, 1999). This property is of great importance in different applications. Smectite, and palygorskite are utilized in a variety of industrial applications, such as drilling fluids, paper coating and pharmaceutical products in which rheological properties play a significant role (Chafe and Bruyn, 2005; Christidis, 2011; Cinar et al., 2009; Galan, 1996; Galan et al., 1994; Luckham and Rossi, 1999; Murray, 2006; 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 water circulation (Kelessidis et al., 2007; 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 differ because of their unique structures, particle size and shape and composition (Cinar et al., 2009; Heller and Keren, 2001; Paineau et al., 2011; Viseras et al., 1999). In swelling clay minerals like montmorillonite, the net negative layer charge generated due to isomorphic 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 molecules and affects the rheological properties of swelling clays. Therefore, in such clay minerals the swelling potential and colloidal behaviour (particle–particle interaction) are controlled by the layer composition, the layer charge and the nature of exchangeable interlayer cation (Christidis et al., 2006; Cinar et al., 2009; Miyahara et al., 1998; Simonton et al., 1988). In contrast, in fibrous non-swelling clay minerals, such as palygorskite and sepiolite, the fibre length and number of silanol groups on the surface of the fibre play an important role in aggregating fibres together (Simonton et al., 1988) and forming a random network that entraps water and increases viscosity (Christidis, 2011).

Several studies have been carried out in the past to understand the rheological properties of standard clays and end member clay minerals, namely bentonite, kaolinite, sepiolite and palygorskite (Abend and Lagaly, 2000; Amorim et al., 2004; Brandenburg and Lagaly, 1988; Christidis et al., 2006; Galan, 1996; Heller and Keren, 2001; Kelessidis et al., 2007; Kelessidis and Maglion, 2008; Lagaly, 1989; Neaman and Singer, 2000; Paineau et al., 2011; Simonton et al., 1988; Tunc et al., 2011 among many others). In contrast, there is limited work on the rheological properties of mixed clay suspensions. 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 behaviour of mixed clays suspension is far from being understood. The limited information is considered important because most clays used in drilling fluid applications usually contain more than one type of

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Table 1
Origin, layer charge and cation exchange capacity (CEC) of the materials used in this experimental work.

Samples	Pre-treatment	Smectite (%)	Layer charge (e/huc)	CEC (meq/100 g)
SWy-2 Wyoming, USA (Na-montmorillonite)	–	78.5	0.38	84.5
STx-1b Texas, USA (Ca-montmorillonite)	Na activation	89	0.44	76.2
DA04 Grevena, Greece (Nontronite)	Na activation	81.1	0.39	74.5
SAz-2 Arizona, USA (Ca-montmorillonite)	Na activation	93	0.55	129.3
Kinney Nevada, USA (Ca-montmorillonite)	Na activation	96.4	0.49	136.5
AK-1.2 Milos, Greece (Ca-montmorillonite)	Na activation	92.7	0.42	86.2
AE2 Milos, Greece (Ca-montmorillonite)	Na activation	74.8	0.52	98.9
Melo Melo, Brazil (Ca-montmorillonite)	Na-activation	81	0.49	84.5
ES5 Vicalvaro basin, Spain	–	–	–	14.5
DA01 Grevena, Greece	–	–	–	26.4
GSp Euboea, Greece	–	–	–	21.4

clay minerals along with non-clay minerals. For example, palygorskite and sepiolite occur in association with smectite in most of the known world palygorskite and sepiolite deposits (Galan and Singer, 2011). Therefore it is worthwhile to understand the rheological behaviour of suspensions containing mixtures of clay minerals.

The purpose of the present work is to study the effect of bentonite addition on the rheological behaviour of aqueous suspensions of palygorskite and sepiolite. The bentonites used contained smectites with different layer charge and the rheological parameters considered were apparent viscosity at 600 rpm and yield point. In addition, since to the authors' knowledge, previous work related to the rheological

properties of smectite–sepiolite mixed clay suspension have not been reported so far, this work attempts to cover the lack of background research work on these topics.

2. Materials and methods

2.1. Materials

Three fibrous clays were used in the present study: palygorskite (sample DA01) from Grevena, Greece and sepiolites from Vicalvaro basin, Spain (sample ES5) and Euboea, Greece (sample GSp). Eight bentonite samples of different origins, SWy-2 from Wyoming, USA, STx-1b from Texas, USA, DA04 from Grevena, Greece, SAz-2 from Arizona, USA, Kinney from Nevada, USA, AK-1.2 from Milos, Greece, AE2 from Milos, Greece and Melo from Melo, Uruguay, were selected based on the different layer charge of smectite. Subsequently they were used to prepare palygorskite–bentonite and sepiolite–bentonite mixed suspension. Table 1 lists the materials used in this study and summarizes information about the source, layer charge of smectite present, cation exchange capacity and pre-treatment used (Na-activation).

2.2. Experimental methods

The bulk mineralogy of the samples was determined with X-ray diffraction (XRD), using a Bruker D8 Advance diffractometer, with $\text{CuK}\alpha_1$ radiation, 40 KV, and 40 mA. The random powder mounts of samples were scanned with a step size of $0.02^\circ 2\theta$ and counting time per step of 0.3 s. The mineral phases were quantified using a Rietveld-based refinement routine using the TOPAS 3.0® software. The routine is based on the calculation of a single mineral-phase pattern according to the crystalline structure of the respective mineral, and the refinement of the pattern using a non-linear least squares routine. The quantification errors calculated for each phase according to Bish and Post (1993) are estimated to be ~1% (Table 2).

The bentonite samples were classified according to the layer charge of the smectites present, following the characterization scheme of Christidis et al. (2006), namely high charge (>0.475 e/huc) intermediate charge (0.425–0.470 e/huc) and low charge (<0.42 e/huc) smectites. The layer charge of smectites for the bentonite samples was determined with the method of Christidis and Eberl (2003), using the LayerCharge computer code. Prior to layer charge determination, the less than $2\ \mu\text{m}$ fractions of the bentonites were separated by

Table 2
Mineralogical composition of the studied materials. Values in brackets correspond to quantification error for each mineral, estimated by TOPAS 3.0® software.

	SWy-2	STx-1b	DA04	SAz-2	Kinney	AK-1.2	AE2	Melo	ES5	DA01	GSp
Smectite (0.2–1.6%)	78.5	89	81.1	93	96.4	92.7	74.8	81	–	3	–
Palygorskite (1.4%)	–	–	–	–	–	–	–	–	–	80.1	–
Sepiolite (0.7%)	–	–	–	–	–	–	–	–	95	–	99.1
Kaolinite (0.2–0.5%)	–	–	–	–	–	1	4.3	–	–	–	–
Illite (0.5%)	–	–	–	1.2	–	–	1	–	1.1	–	–
Chlorite (0.1–0.4%)	1.5	–	1.1	–	–	–	–	–	–	–	–
Biotite (0.1%)	0.6	–	–	–	–	–	–	–	–	–	–
Quartz (0.09–0.9%)	10.5	2.8	5.1	1.2	3.5	–	0.8	18.9	–	5.3	0.5
Opal-CT (0.8%)	–	4.6	–	–	–	–	–	–	–	–	–
Calcite (0.1%)	1.2	–	–	–	–	–	1.3	–	–	0.6	–
Dolomite (0.01–0.1%)	–	–	7.1	–	–	–	9.1	–	–	0.4	0.4
Siderite (0.02%)	–	–	–	–	–	1.1	–	–	–	–	–
Albite	1.6	3.6	1.3	4.6	–	2	–	–	–	–	–
K-Feldspar (0.7%)	5.1	–	–	–	–	1.8	8.7	–	3.9	–	–
Lizardite (0.2%)	–	–	1.7	–	–	–	–	–	–	7.4	–
Talc (0.6%)	–	–	1.4	–	–	–	–	–	–	3	–
Gypsum (0.09%)	0.2	–	–	–	–	–	–	–	–	–	–
Hornblende (0.08%)	–	–	0.4	–	–	–	–	–	–	0.2	–
Brookite (0.01%)	–	–	–	–	–	0.9	–	–	–	–	–
Pyrite (0.05%)	–	–	0.8	–	–	0.5	–	–	–	–	–

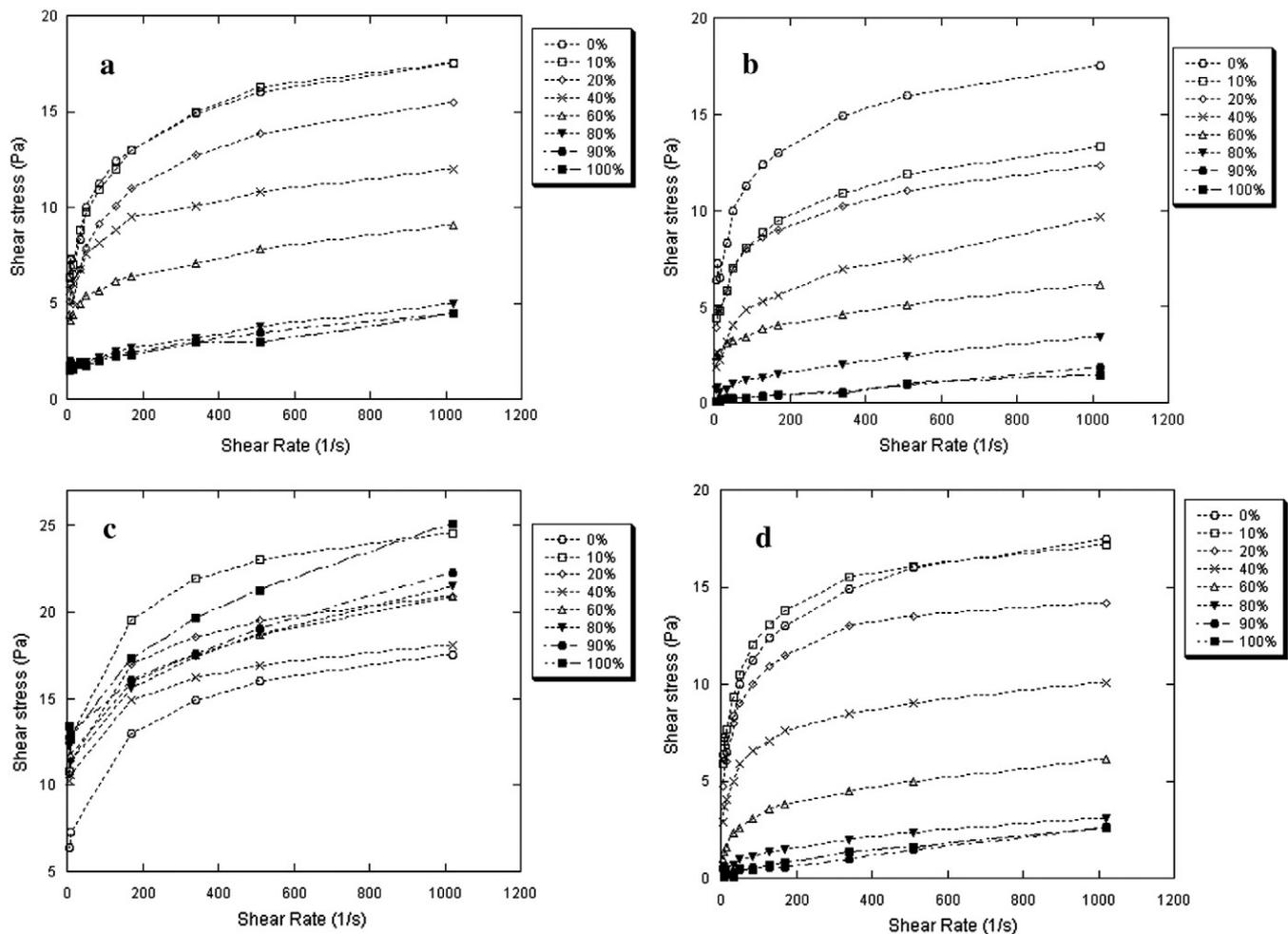


Fig. 1. a). Flow curves of aqueous suspensions containing 5% DA01-STex-1b mixtures. The numbers indicate the percentage of smectite (STex-1b) in the mixture. b). Flow curves of aqueous suspensions containing 5% DA01-SAz-2 mixtures. The numbers indicate the percentage of smectite (SAz-2) in the mixture. c). Flow curves of aqueous suspensions containing 5% DA01-SWy-2 mixtures. The numbers indicate the percentage of smectite (SWy-2) in the mixture. d). Flow curves of aqueous suspensions containing 5% DA01-Kinney mixtures. The numbers indicate the percentage of smectite (Kinney) in the mixture.

sedimentation in deionized water and saturated twice with 1 M KCl solution to allow all exchangeable ions to be replaced by potassium ions. After K saturation, the samples were washed with deionized water until no chloride detected (AgNO_3 test). Oriented specimens of K-saturated clays were prepared for XRD analysis by settling of the clay suspension onto glass slides and subsequent air drying and then saturation in ethylene glycol vapour at 60 °C for 16 h.

The cation exchange capacity (CEC) of the clays was determined by ammonium acetate exchange at pH 7. Briefly, 2 g of sample previously dried at 105 °C was saturated twice by 10 mL of 1 M ammonium acetate solution in 50 mL polyethylene centrifuge tubes. After the second saturation the samples were left overnight to allow all the exchangeable cations to be replaced by NH_4^+ , and washed five times with ethanol to remove the excess ammonium ions. The adsorbed NH_4^+ was extracted by leaching each sample three times with 25 mL 1 M KCl solution and its concentration was determined spectrophotometrically with a DR 2800 UV-vis spectrophotometer (N-NH₃, Method 8038 (Program 380) –Nessler) at 425 nm.

Before mixing the two end members (fibrous clay and bentonite), the Ca-bentonite samples were activated with Na_2CO_3 . The optimum concentration of Na_2CO_3 for the activation was determined from free swelling tests (Inglethorpe et al., 1993). Activation with Na_2CO_3 was preferred to NaCl, since the method is routinely used by the industry (Christidis, 2011).

The suspensions of palygorskite–bentonite and sepiolite–bentonite mixtures at a concentration of 5% wt were prepared by dispersing 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). The mixtures were ultrasonified for 2 min to disintegrate clay aggregates and obtain homogeneous suspensions. Subsequently, they were stirred for 20 min with a Hamilton Beach® high speed mixer, transferred to beakers, sealed to prevent evaporation and left to age for 16 h. The pH of the dispersions was adjusted to 7 by the addition of diluted HCl or NaOH in small steps (Inolab pH meter). All the suspensions formed a gel after ageing, except the suspensions containing >80% intermediate charge smectites (DA04 and STex-1b) and high charge smectites (SAz-2 and Kinney) which formed a sol, i.e., the particles form a stable colloidal dispersion. After ageing, the suspensions were stirred again for 5 min immediately before determining the rheological properties (API 13A, 2006).

The rheological data were measured with a Couette-type rotational Fann type viscometer (Grace-M3500) at Drilling Engineering and Fluid Mechanics Laboratory of the Technical University of Crete. The instrument has a rotating outer cylindrical cup (rotor sleeve) coaxial with an inner fixed bob which is connected to a torsion spring. 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. At each shear

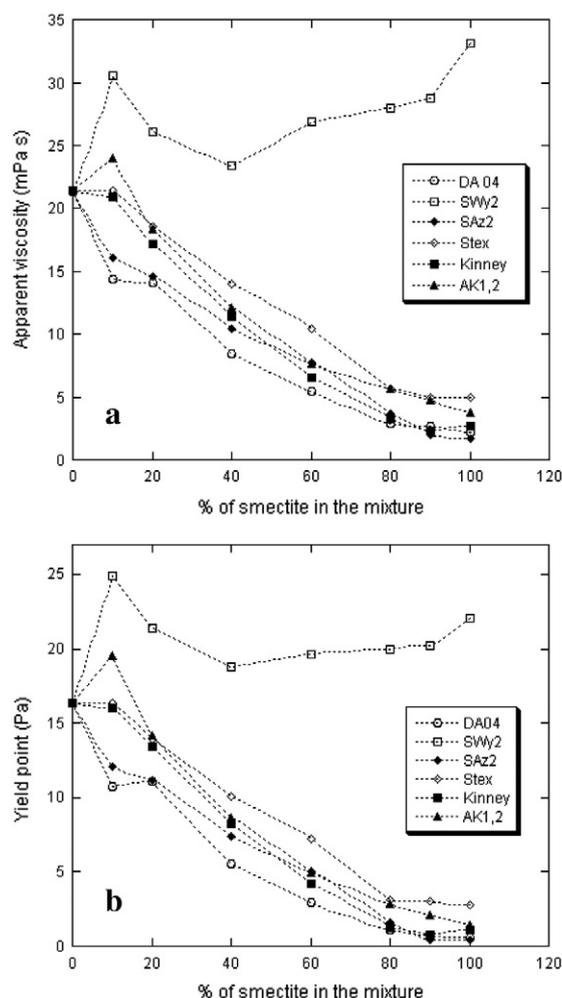


Fig. 2. a). Effect of smectite content with different layer charge on the apparent viscosity (600 rpm) of palygorskite suspensions. b). Effect of smectite content with different layer charge on the yield point of palygorskite suspensions.

rate, five shear stress data were recorded digitally every 12 s which were then averaged. The apparent viscosity and yield point were determined according to API specification (API 13A, 2006) from the high shear rate range (at 300 and 600 rpm).

3. Results

3.1. Mineralogical composition of the samples

The mineralogical composition of the studied samples and the abundances (% wt) of the minerals present are listed in Table 2. The bentonites consist principally of smectite (75–95%), quartz (1–19%), K-feldspar (2–9%) and plagioclase (1–5%). Minor phases present in the samples are dolomite, kaolinite, chlorite and traces of calcite, serpentine, talc, biotite, illite, hornblende and pyrite. STex-1b contains opal-CT (~5%), SWy-2 traces of gypsum and AK1.2 traces of brookite and siderite. The palygorskite sample consists principally of palygorskite (82%), serpentine, quartz smectite and talc and traces of calcite, dolomite and hornblende. The sepiolite samples are almost pure; GSp contains traces of dolomite and quartz, whereas ES5 contains minor feldspar and traces of illite.

The CEC values of the different samples are listed in Table 1. A weak trend holds between smectite content and the CEC (data not shown). In general, the CEC values reflect both the smectite content and the layer

charge of the smectites. The low CEC of the DA04 is attributed both to the relatively low smectite content and the relatively low layer charge of the nontronite present. GSp has a higher CEC than ES5. Finally, the relatively high CEC value of DA01 is partly attributed to the minor smectite present.

3.2. Rheological properties

3.2.1. Palygorskite–bentonite suspensions

3.2.1.1. Flow behaviour. The selected flow diagrams for 5% solid suspensions of palygorskite–bentonite mixtures at different proportions of bentonite (0, 10, 20, 40, 60, 80, 90 and 100% wt) are shown in Fig. 1. All the suspensions exhibited pseudoplastic non-Newtonian flow behaviour (i.e. apparent viscosity decreases with increasing rate of shear stress) except for suspensions containing > 80% intermediate charge smectites (DA 04 and STex-1b) and high charge smectites (SAz-2 and Kinney) which exhibited Bingham plastic type flow. Addition of 10% low charge smectite (SWy-2 and AK1.2) shifted the flow curve to higher shear stress, whereas it did not affect the behaviour of Tex-1b and Kinney bentonites.

For the flow curves with pseudoplastic behaviour, the shear rate at which the linear segment of the flow curve attained was shifted to lower shear rates, as the proportion of high and intermediate charge smectites increased up to 80%, and to higher shear rate as the proportion of low charge smectite increased (Fig. 1). Further addition (>80%) of high charge and intermediate charge smectite in the mixture transformed the flow curves to linear (Bingham plastic type flow) with Bingham yield stress <2 Pa.

3.2.1.2. Evolution of apparent viscosity and yield point. The variation of apparent viscosity at 600 rpm and yield point with the percentage of smectite for 5% palygorskite–bentonite suspensions is shown in Fig. 2. For low charge smectites (SWy-2 and AK-1.2), the apparent viscosity and yield point tend to improve for 10% smectite in the mixture. At this concentration the yield point attained maximum value being higher than both end members. Further increase of smectite content to 20% and 40% resulted to a sharp decrease of apparent viscosity and yield point. As the concentration of the smectite in the mixture exceeds 40%, these parameters improved in SWy-2 and deteriorated in AK-1.2.

For 10% addition of STex-1b and Kinney, the apparent viscosity and yield point did not show significant change, whereas they decreased sharply after 10% addition of DA04 and SAz-2 in the mixture (Fig. 2). Further addition of both intermediate charge (STex-1b and DA04) and high charge smectites (SAz-2 and Kinney) deteriorated both the apparent viscosity and yield point. However, the rate at which the parameters decrease depends on the magnitude of the layer charge. Sample DA04, which contains nontronite with intermediate charge showed exceptional behaviour i.e. it developed apparent viscosity and yield point even lower than the high charge smectites (e.g. Kinney).

The apparent viscosity at different shear rates and for different % wt smectite in the mixture is shown in Fig. 3 for the 5% suspensions of palygorskite mixed with low charge smectite (SWy-2 and AK 1.2), high charge smectite (SAz-2) and tetrahedrally charged smectite (DA04). The apparent viscosity followed the same trend at all shear rates. It showed an increasing and decreasing trend for mixtures containing 10% of low charge and high and tetrahedrally charged smectite, respectively. Also, the apparent viscosity decreased with increasing shear rate, indicating shear thinning flow behaviour. The effect of smectite addition on the apparent viscosity of the mixture suspension is lower at higher shear rates compared to low shear rates, decreasing gradually with increasing shear rates. An attempt to correlate the layer charge of smectite with the relative change of apparent viscosity and yield point at smectite content, where sharp change in suspension behaviour is observed (10% smectite), yielded strong negative correlation ($r > 0.94$)

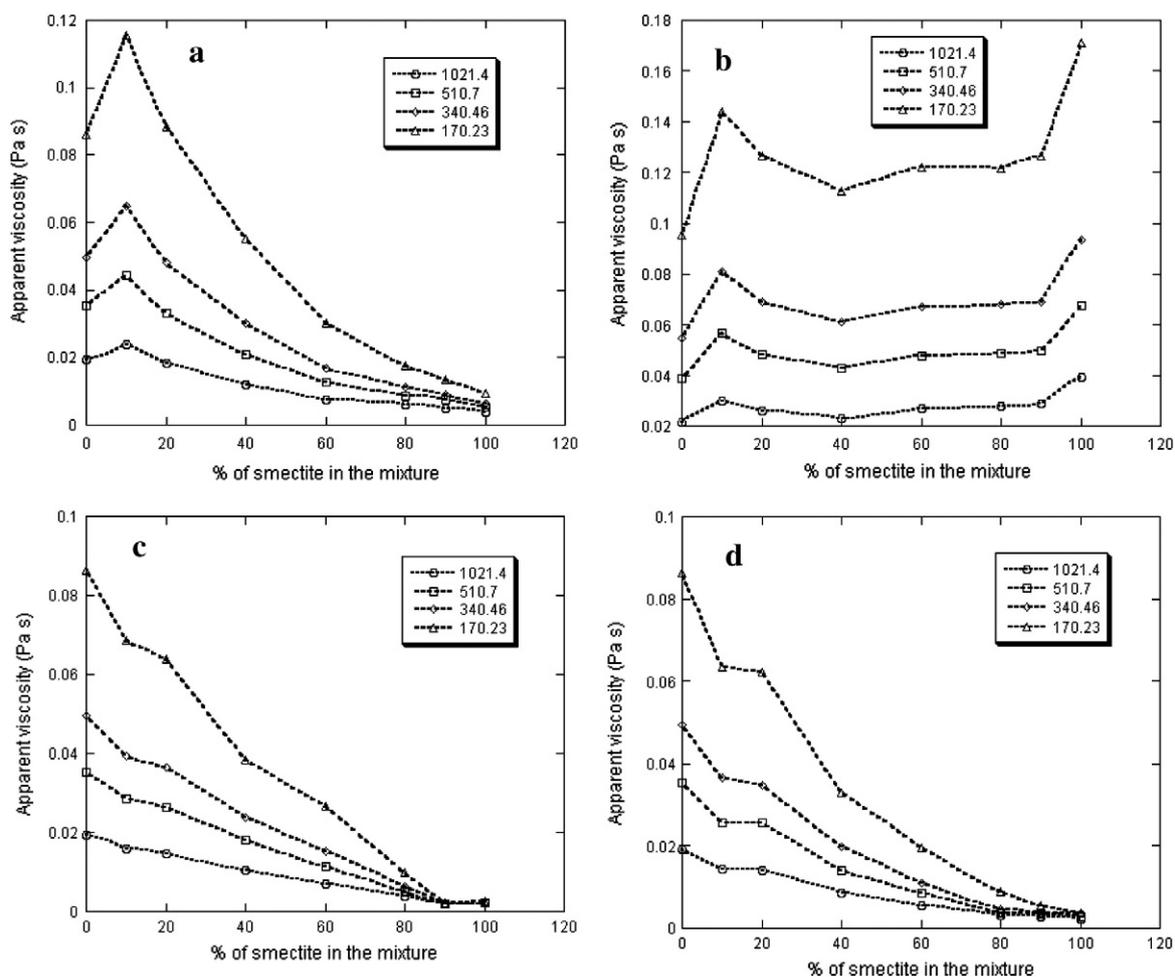


Fig. 3. a). Variation of apparent viscosity for 5% DA01-AK1.2 mixed suspension at different shear rate with percentage of smectite in the mixture. b). Variation of apparent viscosity for 5% DA01-SWY-2 mixed suspension at different shear rate with percentage of smectite in the mixture. c). Variation of apparent viscosity for 5% DA01-SAZ-2 mixed suspension at different shear rate with percentage of smectite in the mixture. d). Variation of apparent viscosity for 5% DA01-DA04 mixed suspension at different shear rate with percentage of smectite in the mixture.

when tetrahedrally charged smectite (DA04), which deviate from the overall trend, was not considered in the correlation (Fig. 4).

3.2.2. Sepiolite–bentonite suspensions

3.2.2.1. Flow behaviour. The selected flow diagrams of sepiolite–bentonite mixed aqueous suspensions containing 5% wt solids are shown in Fig. 5. All sepiolite suspensions (both for GSp and ES5) mixed with bentonite containing low charge smectite (SWy-2) at different proportions showed non-Newtonian pseudoplastic flow behaviour. In the case of Spanish sepiolite (ES5), the flow curve gradually shifted to higher shear stress as the proportion of low charge smectite (SWy-2) in the mixture increased. However, addition of 20% SWy-2 shifted the flow curve to shear stress value higher than 40% SWy-2 in the mixture. Addition of 10 to 40% of SWy-2, in GSp sepiolite suspensions, shifted the flow curve to shear stress value even higher than the two end members (GSp and SWy-2).

The suspensions of sepiolite mixed with bentonite containing intermediate (STex-1b) and high charge (SAz-2) smectite exhibited pseudoplastic flow for $\leq 80\%$ smectite in the suspension. As the fraction of bentonite containing 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 except for GSp sepiolite suspensions with 10 to 40% intermediate charge smectite (STex-1b) in the mixture,

which shifted to higher shear rate. Further addition of smectite ($>80\%$) transformed the flow behaviour to Bingham plastic type of flow with yield stress < 2 Pa.

The ES5 sepiolite end member developed suspensions with relatively low apparent viscosity and yield point. In contrast GSp sepiolite developed suspensions of high apparent viscosity which meet the API specifications (API 13A, 1993). 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 has been reported to have higher fibre length ($5.1 \mu\text{m}$) (Simonton et al., 1988) and CEC ($21 \text{ meq}/100 \text{ g}$) than ES5 ($3.4 \mu\text{m}$ & $14.5 \text{ meq}/100 \text{ g}$). The BET specific surface area of GSp ($214 \text{ m}^2/\text{g}$) is also higher than the specific surface area of ES5 ($147 \text{ m}^2/\text{g}$).

3.2.2.2. Evolution of apparent viscosity and yield point. The variation of apparent viscosity at 600 rpm and yield point with percentage of bentonite in 5% sepiolite–bentonite mixed suspension is shown in Fig. 6. Addition of 10% of all bentonites to ES5 did not affect the apparent viscosity and yield point significantly, whereas both parameters sharply increased and decreased after addition of 20% of bentonite containing low charge smectite (SWy-2) and high charge smectite (SAz-2), respectively. In the case of GSp, apparent viscosity and yield point increased sharply after addition of 10–20% bentonite containing SWy-2, STex-1b and Melo smectite, whereas they decreased sharply after addition

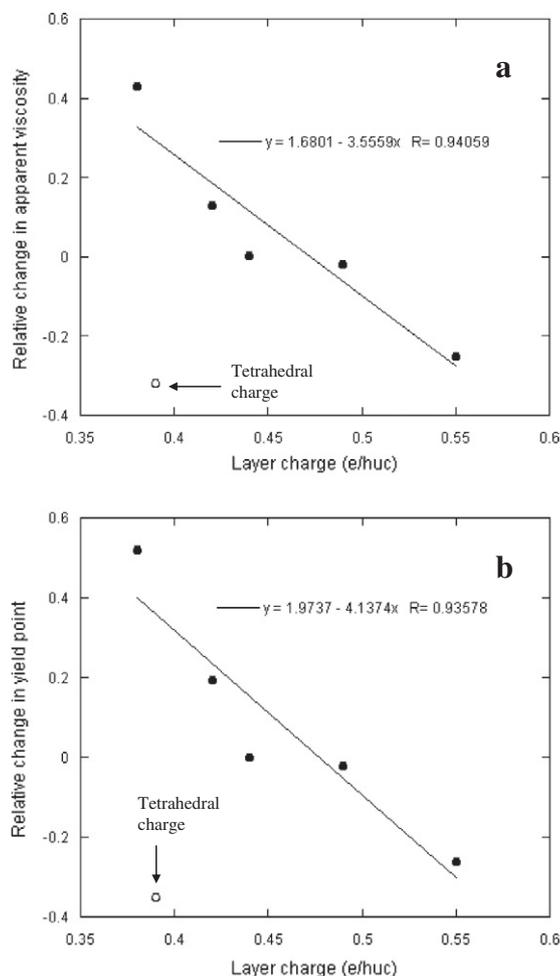


Fig. 4. a). Effect of layer charge of smectite on apparent viscosity of palygorskite–bentonite suspension at 20% of smectite in the mixture. b). Effect of layer charge of smectite on yield point of palygorskite–bentonite suspension at 20% of smectite in the mixture.

of 10% AE2 bentonite. This sharp change in apparent viscosity and yield point is attributed to the interaction of clay particles between the two end members, sepiolite and smectite (see below).

Further addition of smectite (>20%) caused the apparent viscosity and yield point to increase or decrease gradually depending on the properties of the pure smectite end member. Addition of >40% low charge smectite (SWy-2) to ES5 resulted to an increase of apparent viscosity and yield point. In contrast, both parameters decreased, to even lower values than the two end members, for suspensions containing 40–80% SWy-2 in the case of suspensions with GSp. The long fibres of Greek sepiolite (GSp) in this region (60–80% of smectite) may probably partially prevent the smectite particles from interacting and forming network. The apparent viscosity and yield point deteriorate with increasing proportion of bentonites containing high charge (SAz-2, Melo and AE2) and intermediate charge (STex-1b) smectite. In general, the decrease of apparent viscosity and yield point with increasing smectite content is still more pronounced for high charge smectite compared to intermediate charge smectite.

The evolution of apparent viscosity at different shear rates and for different percentages of bentonite in the mixture for the selected 5% sepiolite–smectite mixed suspensions is shown in Figs. 7 and 8. The apparent viscosity at all shear rates followed general trend similar to that observed for 600 rpm, that depends on the proportion and layer charge of the smectite in the mixture.

The relative change of the apparent viscosity and yield point of sepiolite suspension at the lower percentage of smectite (20%) in the mixture is well correlated with the layer charge of the smectite (Fig. 9). In mixed suspensions containing the two sepiolites (ES5 and GSp), the relative change is negatively correlated with layer charge. However, the change seems to depend on the nature of the sample (fibre length, specific surface area and CEC). The suspension of ES5 showed negative relative change both in the presence of high charge smectite (SAz-2) and intermediate charge smectite (STex-1b), whereas GSp showed positive relative change in the presence of intermediate charge smectite (STex-1b) and high charge smectite (Melo).

4. Discussion

Fibrous clay minerals occur in association with smectite, especially in soil clays (Galan and Singer, 2011; Neaman and Singer, 2000). Although previous work has shown that the rheological properties of palygorskite–montmorillonite mixed clay suspensions depend on the fraction of montmorillonite in the mixture (Neaman and Singer, 2000), the present study has clearly shown that in addition to the proportion of smectite, the layer charge of smectite also affects the apparent viscosity and yield point of the mixed palygorskite–smectite and sepiolite–smectite suspensions. The bentonites used consist of smectites which cover the whole range from low charge to high charge smectites according to the classification scheme of Christidis et al. (2006). In concentrated suspensions used in the current experimental setup (5% solids), the gelation is expected to be due to particle–particle association that results yield point in addition to hydration of clay particles. The yield point of a suspension depends on the number and on the strength of particle–particle linkages (van Heller and Keren, 2001; Neaman and Singer, 2000; Olphen, 1964). These particle linkages in the mixed suspensions could be between similar clay particles namely smectite–smectite (S–S), palygorskite–palygorskite (P–P) and sepiolite–sepiolite (SE–SE) or between different clay particles, namely smectite–palygorskite (S–P) and smectite–sepiolite (S–SE). Therefore, the degree of delamination of smectite aggregates to individual platelets during dispersion, that is controlled by the magnitude and localization of layer charge (Laird, 2006), might affect the yield point of the suspension. Low charge smectite like SWy-2 is expected to form thin quasicrystals (Christidis et al., 2006; Laird, 2006). Hence a greater number of particles will be involved in particle–particle interaction. In contrast, in high charge smectites (SAz-2, AE2, Melo and Kinney) the quasicrystals tend to be larger and stable, containing a larger number of layers, 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 the S–S, S–P and S–SE interactions is smaller in suspensions containing high charge smectite compared to their counterparts with low charge smectite.

Bentonite DA04 which contains nontronite with intermediate charge displayed similar apparent viscosity and yield point to high charge smectites. The reason for the lower apparent viscosity and yield point is attributed 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, swelling and the degree of delamination of the clay particles are low, contributing to inferior rheological properties. Hence, in the case of nontronite the large size of quasicrystals hindered the development of viscous suspensions at any smectite proportion.

Formation of larger aggregates of smectite crystals in the case of high charge smectites and tetrahedrally charged smectites is expected to weaken the possible S–P and S–SE networks and might lead to lower yield points (van Christidis et al., 2006, 2010; Olphen, 1964). This could be explained by comparison of the effect of addition of 10–20% of the different bentonites on the yield point of mixed sepiolite–smectite and palygorskite–smectite suspensions (Figs. 2–8). The abrupt

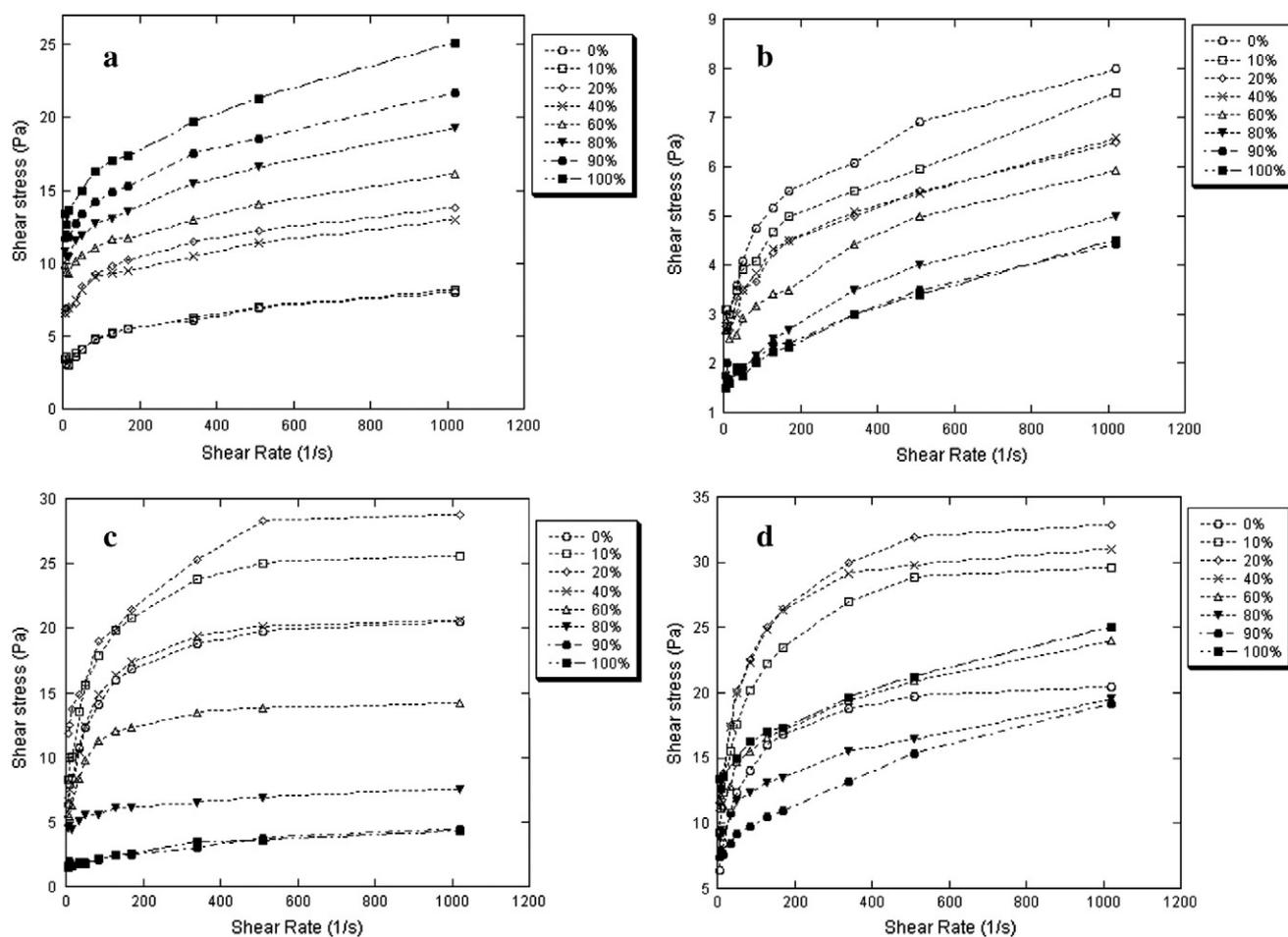


Fig. 5. a). Flow curves of aqueous suspensions containing 5% ES5-SWy-2 mixtures. The numbers indicate the percentage of smectite (SWy-2) in the mixture. b). Flow curves of aqueous suspensions containing 5% ES5-STex-1b mixtures. The numbers indicate the percentage of smectite (STex-1b) in the mixture. c). Flow curves of aqueous suspensions containing 5% GSp-STex-1b mixtures. The numbers indicate the percentage of smectite (STex-1b) in the mixture. d). Flow curves of aqueous suspensions containing 5% GSp-SWy-2 mixtures. The numbers indicate the percentage of smectite (SWy-2) in the mixture.

change in yield point and apparent viscosity at concentration of 10 to 20% of smectite in the suspension would not have occurred without particle–particle interactions between the two end members (sepiolite or palygorskite with smectite). However, the strength of particle–particle linkages is determined by the size of smectite quasicrystals (van Olphen, 1964) that interact with palygorskite and sepiolite fibres, which in turn depends on the magnitude and localization of layer charge (Christidis et al., 2006). The linear relationship obtained between layer charge and the relative change in apparent viscosity and yield point at 10–20% smectite content in the mixture, together with the deviation of tetrahedrally charged smectite (DA04) from the general trend (Figs. 4 and 9), also confirmed the role of layer charge and charge localization of the smectite on the nature of linkage between the two end members. The thicker the smectite floc is, 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 released when the linkages break. This might explain the sharp decrease of apparent viscosity and yield point in the case of high charge (e.g. SAz-2, AE2) 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 alternative for the sharp increase of viscosity in the case of low charge smectite (SWy-2 and AK-1.2).

The non-Newtonian flow behaviour (pseudoplastic and Bingham plastic type flow) of the suspensions is attributed to complex particle–particle association and formation of network between clay particles (S–S, P–P, S–P, SE–SE and S–SE). The flow curves with pseudoplastic flow behaviour consist of two parts: the first part is characterized by a progressive decline in apparent viscosity as shear rate increases (at a low shear rate) and the second part is characterized by constant apparent 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). The linear part of the rheograms attains after complete disruption of particle–particle linkage (Luckham and Rossi, 1999; Yildiz et al., 1999). After this shear rate the structural components align themselves in the direction of flow (Heller and Keren, 2001; Yildiz et al., 1999) and the suspensions exhibit constant apparent viscosity. However, the shear rate needed for complete disruption of particle linkage depends on the smectite layer charge as indicated by the shift of shear rate at which the flow curve became linear to the lower (left) value (Figs. 1a,b,d and 5c) with increasing proportion of high and intermediate charge smectite. Besides, for the suspensions with low charge smectite (SWy-2) and with low content (<20%) of high and intermediate charge smectite, the linear part of the flow curve was not attained in the studied shear

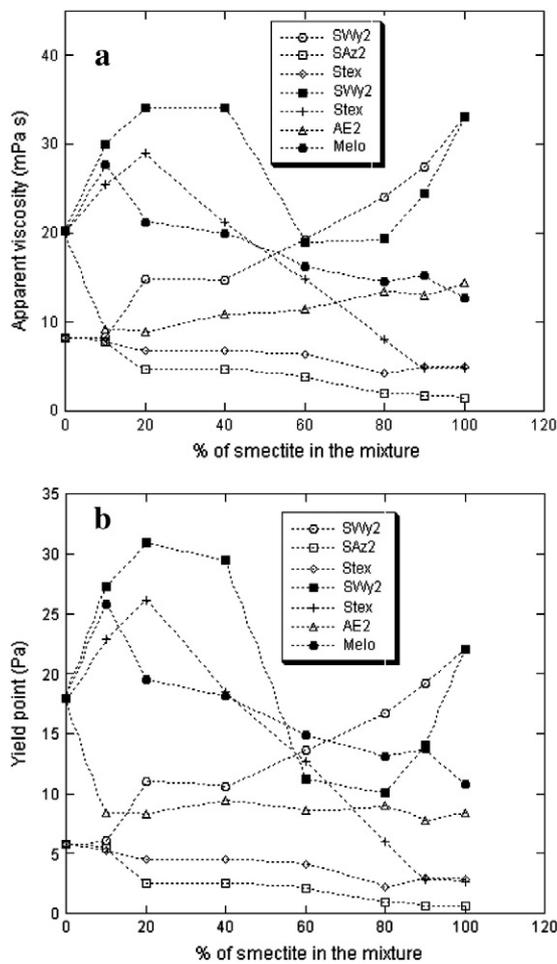


Fig. 6. a). Effect of smectite content with different layer charge on the apparent viscosity (600 rpm) of sepiolite suspensions. b). Effect of smectite content with different layer charge on the yield point of sepiolite suspensions.

rate range. This supports the above discussed influence of smectite layer charge on the number and strength of particle–particle linkage.

Apart from the type of smectite in the mixture, it seems that the fibre length, the cation exchange capacity (CEC) and the 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 CEC, the greater are the apparent viscosity and yield point of fibrous clays (Neaman and Singer, 2000; Simonton et al., 1988). The surface silanol groups are involved in binding sepiolite fibres together and hence, affect the apparent viscosity and yield point of sepiolite gels (Simonton et al., 1988). Addition of 10–20% smectite (SWy-2, Melo and STex-1b) in the mixture has a greater influence on the apparent viscosity and yield point of GSp compared to ES5 (Figs. 6–8). This indicates that the differences in the intrinsic characteristics between the two sepiolites affected the magnitude of particle–particle interaction. The presence of a greater number of silanol groups which control the CEC (Table 1) together with high specific surface area and fibre length of GSp might contribute to a more intense interaction with smectite particles (Simonton et al., 1988). This possibility will be tested further with additional sepiolite samples having different fibre lengths.

5. Conclusions

The rheological properties of suspensions of fibrous clays (palygorskite and sepiolite) mixed with bentonites containing smectites with different layer charge was investigated. The degree

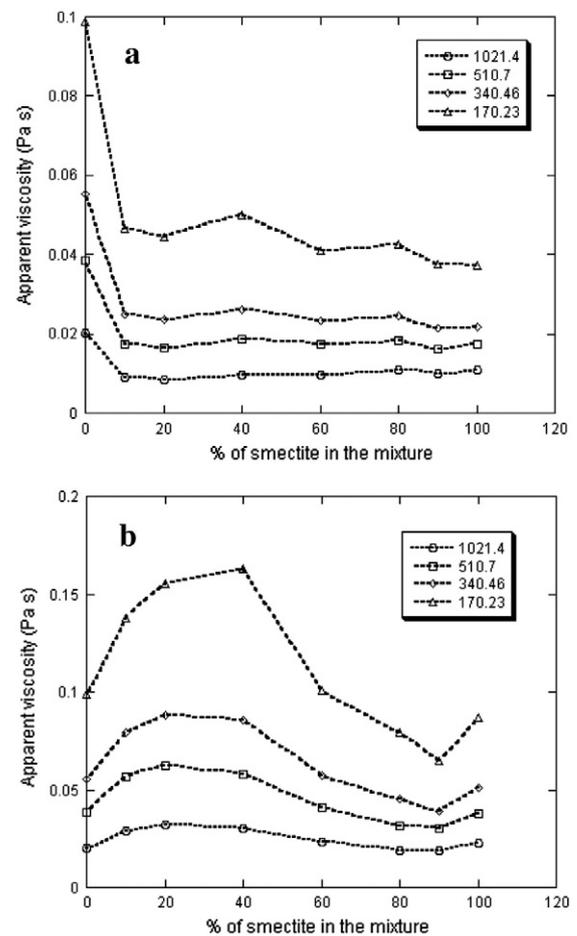


Fig. 7. a). Variation of apparent viscosity for 5% GSp-AE 2 mixed suspensions at different shear rate with percentage of smectite in the mixture. b). Variation of apparent viscosity for 5% GSp-SWy-2 mixed suspensions at different shear rate with percentage of smectite in the mixture.

of interaction between smectite and fibrous clay particles and its effect on the apparent viscosity and yield point of the suspensions depend on the concentration, layer charge and charge localization of the smectite in the mixture. Maximum interaction between the two end member clay minerals occurs at 10–20% bentonite in the mixture. This is important inasmuch as palygorskite and sepiolite clays often contain 10–20% smectite. The layer charge and charge localization of smectite affect the system behaviour by influencing the degree of delamination 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 with palygorskite and sepiolite fibres and thus the particle–particle linkages are stronger because the smectite particles delaminate to thin quasicrystals or to isolated single smectite layers. An increase in layer charge resulted to lower swelling and delamination of smectite particles and favoured the stability and formation of thick smectite quasicrystals. Tetrahedrally charged smectite (nontronite) behaved similar to high charge smectite. The physical and chemical properties of the fibres (fibre length, specific surface area and CEC) also affect the interaction of fibrous clays with smectite and consequently the rheological properties of the mixtures.

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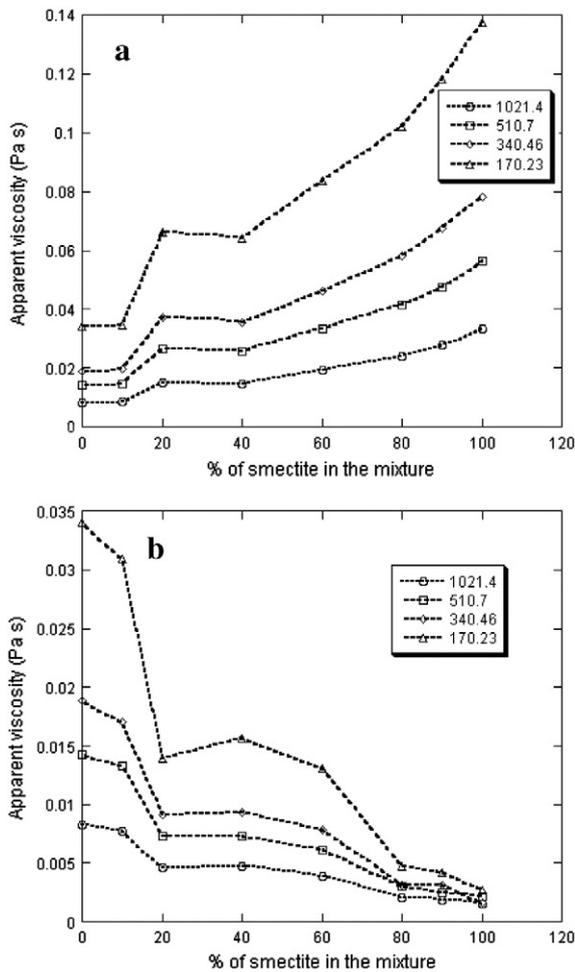


Fig. 8. a). Variation of apparent viscosity for 5% ES5-SWy-2 mixed suspensions at different shear rate with percentage of smectite in the mixture. b). Variation of apparent viscosity for 5% ES5-SAz-2 mixed suspensions at different shear rate with percentage of smectite in the mixture.

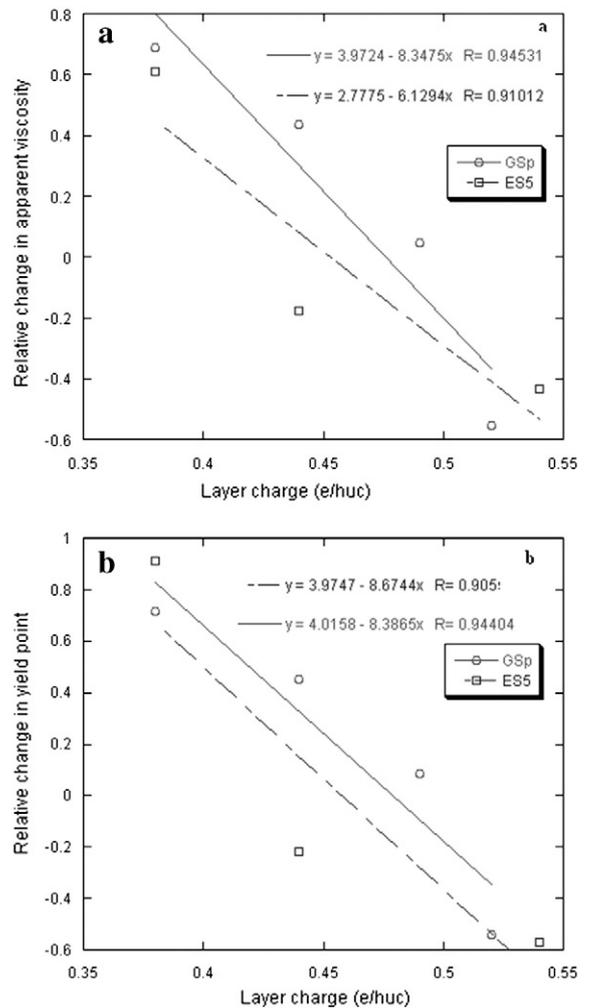


Fig. 9. a). Effect of layer charge of smectite on apparent viscosity of sepiolite–bentonite suspension at 20% of smectite in the mixture. b). Effect of layer charge of smectite on yield point of sepiolite–bentonite suspension at 20% of smectite in the mixture.

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