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Rheological properties of montmorillonitic clay suspensions: Effect of firing and interlayer cations

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Abstract

The effect of a prior firing of three montmorillonite clays, exhibiting different nature of interlayer cations, on the rheological behaviour of related aqueous suspensions (5 and 10 mass% of solid content) was examined. Calcinations were performed at 150 °C, 250 °C, 300 °C or 450 °C for 30 min. The rheological properties were characterized at 25 °C in the flow mode using the Herschel–Bulkley model.

The alkaline interlayer cation (Na) tended to increase the yield stress of montmorillonite suspensions in comparison with earth-alkaline ones (Ca, Mg). As expected, increasing solid content led to increasing yield stress.

For calcinations until 200 °C, the relevant suspensions exhibited an increasing yield stress due to a gel-like behaviour in relation with a card-house-like structure. Furthermore, calcination above 300 °C favoured the decrease of the corresponding yield stress. This behaviour seemed to be related to the modification of the surface properties of the clay platelets, more precisely to the beginning of clay dehydroxylation.

Keywords: Montmorillonites suspensions; Rheology; Calcination temperature; Interlayer cations; Surface interactions

1. Introduction

Montmorillonite is the most often studied swelling clay mineral, widely used in many industrial applications because of their high aspect ratio, plate morphology, high cation exchange capacity (CEC), natural abundance and low cost. Several million tons of montmorillonites are used in the form of colloidal dispersions. Colloidal dispersions of montmorillonites are thickening and thixotropic agents which are introduced in drilling fluids, paints emails, gelling, decoloring, water pollutant elimination, radioactive waste repository, cracking, pesticide formulations, cosmetic and pharmaceutical preparations. They are expandable layered silicates and can be intercalated and/or exfoliated into nanocomposites.[1–3]

Montmorillonites belong to the smectite family, which represents some 2:1 phyllosilicates. The layer structure of these silicates is characterized by an octahedrally coordinated metallic ion (usually aluminium or magnesium) sheet sandwiched between two tetrahedral silicate sheets. The isomorphic substitution of octahedral Al by a divalent metal ion commonly occurs in montmorillonites and leads to a negatively charged unit layer. This charge deficit is balanced by the presence of interlayer cations which have the capability to interact with surrounding medium, namely with external cations (exchangeable cations) and with water to form a hydrated interlayer cation.[1] Moreover, pH-dependent charges develop on the surface hydroxyls at the edges. Interlayer cations are exchangeable and the exchange is reversible for simple cations.[4] When the exchangeable cations are hydrated and water molecules enter the space between the structural layers, the basal spacing between two layers (i.e., (0 0 1) d-spacing) increases and the volume of the clay expands (the swelling behaviour).

On account of a large variety of physical and chemical properties of montmorillonite: swelling, adsorption, ion exchange, surface acidity, etc., montmorillonites are not used in ceramic as significant components, but are often present as impurities (except for earthenware and pottery manufacturing). The swelling properties and the CEC (see below) of these clays cause instabilities in the rheological behaviour of related slurries or pastes, which are not suitable for applications in the ceramic industry.

The magnitude of clay swelling depends on the nature of the exchangeable cations, the nature of the solution and the clay compositions. Moreover, clay swelling is strongly

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Table 1
Chemicals ((a) technical fact sheet, (b) X-ray fluorescence)) and mineralogical (c) compositions (mass%) of B. Maghnia, Smectite CPA and M. Sarde.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Technical fact sheet								
B. Maghnia	55–65	12–18	–	0–2	1–5	2–3	0.76–1.75	1–3
Smectite CPA	60	20	0.4	6.6	1.7	4.6	3.9	0.4
M. Sarde	58–62	15–18	0.1–0.3	3–4	3–4	5–6	0.5–1	0.1–0.3
X-ray fluorescence								
B. Maghnia	64.86	17.96	0.29	2.85	0.51	3.58	1.62	1.56
Smectite CPA	53.81	18.16	0.61	6.22	3.93	3.63	4.06	0.57
M. Sarde	56.57	17.90	0.36	4.25	2.65	5.96	1.24	<0.20

	Montmorillonite	Illite	Quartz	Calcite	(Ca·Fe)SiO_3	Orthoclase
Mineralogical compositions						
B. Maghnia	~75%	–	~15%	–	–	~10%
Smectite CPA	~60%	~27%	~5%	~3%	~5%	–
M. Sarde	~90%	<8%	<2%	–	–	–

enhanced in fresh water. When the salinity of the aqueous solution used increases, the swelling ability of clay decreases.[5] The hydroxyl groups of montmorillonite play a major role in their interaction with water and other polar molecules in the presence of an interlayer cation.[6,7] Chatterjee et al.[8] have shown that the activity order for the exchangeable cations among all the monovalent and divalent series is: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Cs^{+} > Rb^{+} > Na^{+} > Li^{+} > K^{+}$. Therefore, smectites with divalent interlayer cations exhibit less swelling than those with monovalent cations.

Thermal analyses of natural montmorillonites showed three main steps of weight loss. In the first step ($T < 200\,°C$) a weight loss, corresponding to both physisorbed and interlayer water loss, takes place. After this step, a slight gradual weight decrease in the range 200–600 °C, which is attributed to the water loss of both montmorillonite and associated phases present in the sample. Finally, a third main weight loss occurs at temperatures in the range 600–700 °C, related to the release of structural OH of montmorillonite.[9]

The shape of montmorillonite particles can change with environmental or experimental conditions and can never be considered as invariable. Plasticity of clays is attributed to aggregation of clay mineral particles to a card-house structure. The particles are linked by edge/face, edge/edge and face/face contacts to a three-dimensional network throughout the whole system. The presence of water film between clay platelets and the conception of the card-house model were determinant for the understanding of the plasticity and flow properties of clay dispersions.[10]

The rheological behaviours of montmorillonite materials in water are very sensitive to many parameters, such as concentration, layer charge, exchangeable cations, particle size, morphology, temperature and chemical environment (pH, ionic strength).[11] Literature usually provides general rules for sodium and calcium bentonites: the presence of organic and inorganic compounds; the role of pH in the presence of different electrolytes, deflocculants or inorganic salts.[2,12–17] But to our knowledge, the behaviour of montmorillonite suspensions prepared from montmorillonite powder previously heated at different temperatures has not yet been investigated. Such study may provide interesting hints for future development regarding the use of smectites in silicate-based ceramic materials.

In the present work, we study the effect of a pre-treatment of montmorillonite powder at 150 °C, 250 °C, 300 °C or 450 °C on the rheological behaviour of aqueous suspensions of three varieties of montmorillonite clays. Correlations between the rheological behaviour of montmorillonite clays, thermal evolution and mechanical properties will be discussed.

2. Experimental part

2.1. Materials

Three commercial montmorillonite clays were used, namely: B. Maghnia (BENTAL-ENOF Spa[a]) from Algeria, Smectite CPA (Le Comptoir Provençal des Argiles[b]) from France and M. Sarde (Argiles du Bassin Méditerranéen[c]) from Italy. Their chemical analyses were given by technical fact sheets provided by the suppliers (Table 1a) and also estimated by X-ray fluorescence (Table 1b) by SFC (Société Française de la Céramique). The mineralogical composition was estimated using both XRD and chemical composition (Table 1b) characterizations.

Montmorillonite clays were heated at 5 °C min^{-1} from room temperature up to 150 °C, 250 °C, 300 °C and 450 °C for 30 min.

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[a] Entreprise Nationale des Produits Miniers Non-Ferreux et des Substances Utiles, 31 Rue Mohamed Hattab – Belfort, Alger Algérie. Tel.: +213 21 52 52 36/52 17 73/52 32 44; http://www.enof-mines.com; 73% montmorillonite, 7% illite and 20% quartz, CEC ~ 91 meq/100 g, granulometry < 74 μm.

[b] Comptoir Provençal des Argiles (CPA), 124 rue Philémon Laugier ZI Saint Martin, 83400 Hyères les Palmiers, France. Tel.: +33 04 94 00 66 20; http://www.provence-argile.com; 70% smectite, 15% illite, 5% kaolinite, 5% calcite and 5% quartz, CEC ~ 70 meq/100 g, granulometry < 75 μm.

[c] Argiles du Bassin Méditerranéen, Z.A. du Bas Jasson – 83250 La Londe. Tel.: +33 04 94 66 62 94; http://www.argiles-abm.com; 98% montmorillonite and 2% quartz, CEC ~ 120 meq/100 g, granulometry < 77 μm.

2.2. Methods

The BET surface areas were determined from N_2 adsorption experiments using a Micromeritics model Tristar® analyzer. Each clay sample (~1.5 g) has undergone drying and degassing for 12 h at 110 °C.

The densities of montmorillonite powders were estimated using an AccuPyc II 1330 Pycnometer. The size of the sample chamber used was 3.5 cm^3.

Natural pH measurements were performed at 21 °C, using fresh suspensions (made of 1 g of clay in 15 mL of deionized water), with a MeterLab PHM 240 (Radiometer COPENHAGEN) pH-meter.

Grain size measurements were conducted using a laser granulometer, Mastersizer2000, from Malvern. Aqueous suspensions of each powder were sonicated prior to the analysis in order to break the coarse agglomerates.

The thermal behaviours were studied using a coupled DTA-TGA Setsys 2400 apparatus (Setaram) equipped with a DTA-1500 head system. The device was used in the temperature-scanning mode and all experiments were performed under dried air from room temperature to 1000 °C with a heating rate of 10 °C min^{-1}. Experiments were carried out in a Pt crucible with 100 mg of powder under ambient atmospheric pressure and a pure alumina powder, served as a reference material.

X-ray diagrams (XRD) were obtained on powdered samples with a Brucker-AXS D 5000 powder diffractometer using $K\alpha_1$ radiation of Cu and a graphite back-monochromator. XRD experiments were achieved in step-scan mode from 2° to 35° (2θ) with a counting time of 2 s per 0.02° step. Crystalline phases were identified by comparison with PDF (powder diffraction files) standards from ICDD.

Scanning electron microscope (SEM) observations of powders were carried out at an acceleration voltage between 10 and 30 kV using a Hitachi S-2500. Prior to their observation a metal layer (Pt) was deposited on the samples.

2.3. Rheological measurements

The rheological behaviour of suspensions was characterized using a cone–plate geometry (40 mm 2° steel cone and Peltier plate) mounted on a controlled stress rheometer AR1500ex from TA® Instruments. A shear stress (τ)–shear rate (γ) sweep was applied to each suspension varying the shear stress between 0 and 50 Pa at 25 °C. The flow curves were analysed and fitted to the Herschel–Bulkley model expressed by Eq. (1):

$$\tau = \tau_0 + (k(\dot{\gamma})^n) \qquad (1)$$

where τ and τ_0 are, respectively, the shear stress and the yield stress, k the consistency (viscosity in the case of a Newtonian or Bingham fluid), $\dot{\gamma}$ refers to the shear rate, and n is the power law exponent (rate index).

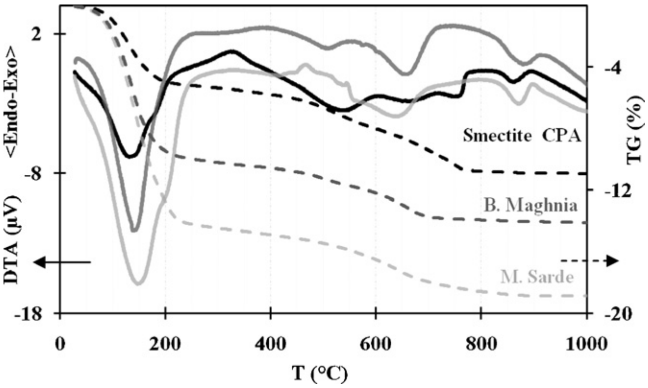

Fig. 1. Thermoanalysis curves of smectite CPA, B. Maghnia and M. Sarde as received.

As received and previously fired at 150 °C, 250 °C, 300 °C and 450 °C montmorillonites were dispersed in deionized water. After ultrasonication (2 min), the samples were shaken for 2 h

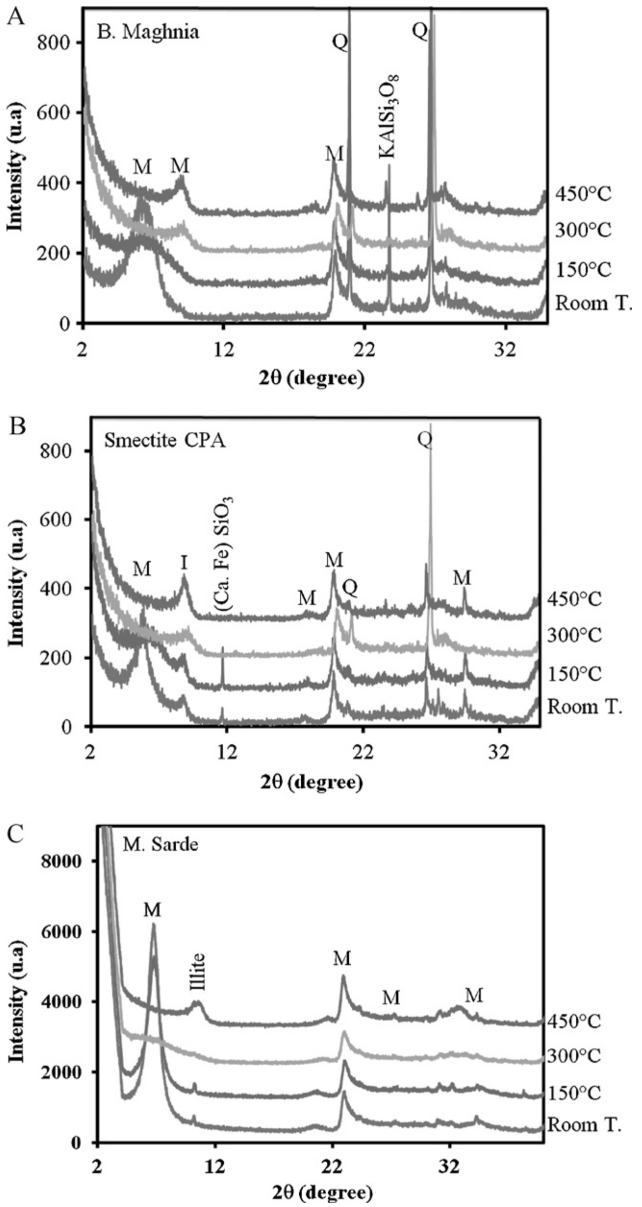

Fig. 2. X-ray diagrams of B. Maghnia (A), smectite CPA (B) and M. Sarde (C) at room temperature and after heating at 150 °C, 300 °C and 450 °C for 30 min (M, montmorillonite – PDF file: 00 058 2038; I, illite – PDF file: 00 002 0050; Q, quartz – PDF file:04 012 0490).

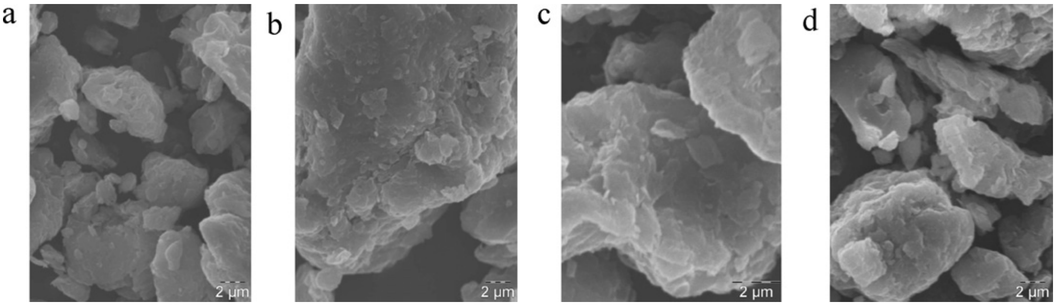

Fig. 3. Scanning electron microscopy of B. Maghnia platelets at room temperature (A), after a 30 min treatment at 150 °C (B), 300 °C (C) and 450 °C (D).

prior to rheological measurements. Ultrasonication was required to get reproducible results and to break agglomerate of montmorillonite. Rheological measurement was performed using 1 mL aliquot of each suspension.

Thixotropic behaviour was indicated by a hysteresis loop between the flow curves at increasing and decreasing rates.[2] The degree of thixotropy was measured by the area of the hysteresis loop.

3. Results and discussion

3.1. Thermal behaviour of raw materials

DTA-TG curves of as-received montmorillonite clays are presented in Fig. 1. Under the same experimental conditions, the three montmorillonitic clays yielded different behaviours. However, three main phenomena were observed:

- Dehydration at temperature <250 °C associated with two endothermic reactions for Smectite CPA and M. Sarde, and one endotherm in the case of B. Maghnia.[18,19] The resulting mass losses were 5%, 10% and 14% for Smectite CPA, B. Maghnia and M. Sarde, respectively. These differences are due to the effective montmorillonite mineral content within the raw clays; the higher the montmorillonite content [a–c], the greater the mass loss during dehydration. According to the technical fact sheet and mineralogical compositions, the montmorillonite content are 60–70 mass% in Smectite CPA, 73–75 mass% in B. Maghnia and 90–98 mass% in M. Sarde (thus the observed order in dehydration mass loss Smectite CPA < B. Maghnia < M. Sarde). Despite the relatively close montmorillonite content in Smectite CPA and B. Maghnia, the great difference observed in mass loss can be justified by the presence of other 2:1 phyllosilicates (illite) and associated phases ($((Ca\cdot Fe)\ SiO_3)$) in Smectite CPA which are less sensitive towards surrounding water as can be observed through XRD analyses (Fig. 2) and mineralogical composition (Table 1c). The nature of the interlayer cation has a strong effect on the sensitivity of montmorillonites towards hydration. From literature,[20,21] it has been showed that for a given water content, the interlayer spacing increases in the order Na-montmorillonite < Na/Mg-montmorillonite < Mg-montmorillonite < Ca-montmorillonite. This trend was explained by the fact that with Na cations only planar inner-sphere water complexes were formed while in the case of Mg and Ca cations, both inner-sphere and outer-sphere water complexes were formed. Combining this result with the general behaviour described by Chatterjee et al.[8] about the less activity of monovalent cations on the swelling of clays, the great content of K-cations in Smectite CPA (15% illite; technical fact sheet) compared to that of B. Maghnia may explain the obtained difference in mass loss. Regarding the dehydration temperature, previous studies showed that the nature of interlayer cation played a significant role on K- and Na-montmorillonite which were completely dehydrated around 200–300 °C, whereas with polyvalent exchangeable cations higher temperatures are required.[22,23]
- Dehydroxylation related to two typical endothermic peaks was observed between 400–590 °C and 570–770 °C. The difference in temperature may be related to the binding energy of hydroxyl groups within the clay mineral network/lattice. The associated mass losses were 5, 4 and 3% for Smectite CPA, B. Maghnia and M. Sarde, respectively. These results indicate

Table 2
Specific surface area BET, natural pH value, granulometry distribution ($d_{0.1}$, $d_{0.5}$, $d_{0.9}$) and density at different temperatures.

	Bentonite Maghnia				Smectite CPA				M. Sarde			
T (°C)	25	150	300	450	25	150	300	450	25	150	300	450
pH value	8.6	8.4	8.5	7.5	8.3	8.2	8.1	7.9	8.9	8.9	8.6	7.5
ρ (g/cm^3)	∼2.3	∼2.5	∼2.6	∼2.7	∼2.3	∼2.5	∼2.7	∼2.7	∼2.3	∼2.4	∼2.7	∼2.7
BET (m^2/g)	∼75				∼113				∼90			
Granulometry	$d_{0.1}$	$d_{0.5}$	$d_{0.9}$		$d_{0.1}$	$d_{0.5}$	$d_{0.9}$		$d_{0.1}$	$d_{0.5}$	$d_{0.9}$	
25 °C (µm)	∼0.7	∼4.2	∼29.7		∼0.7	∼3.2	∼18.5		∼1	∼4.7	∼36	

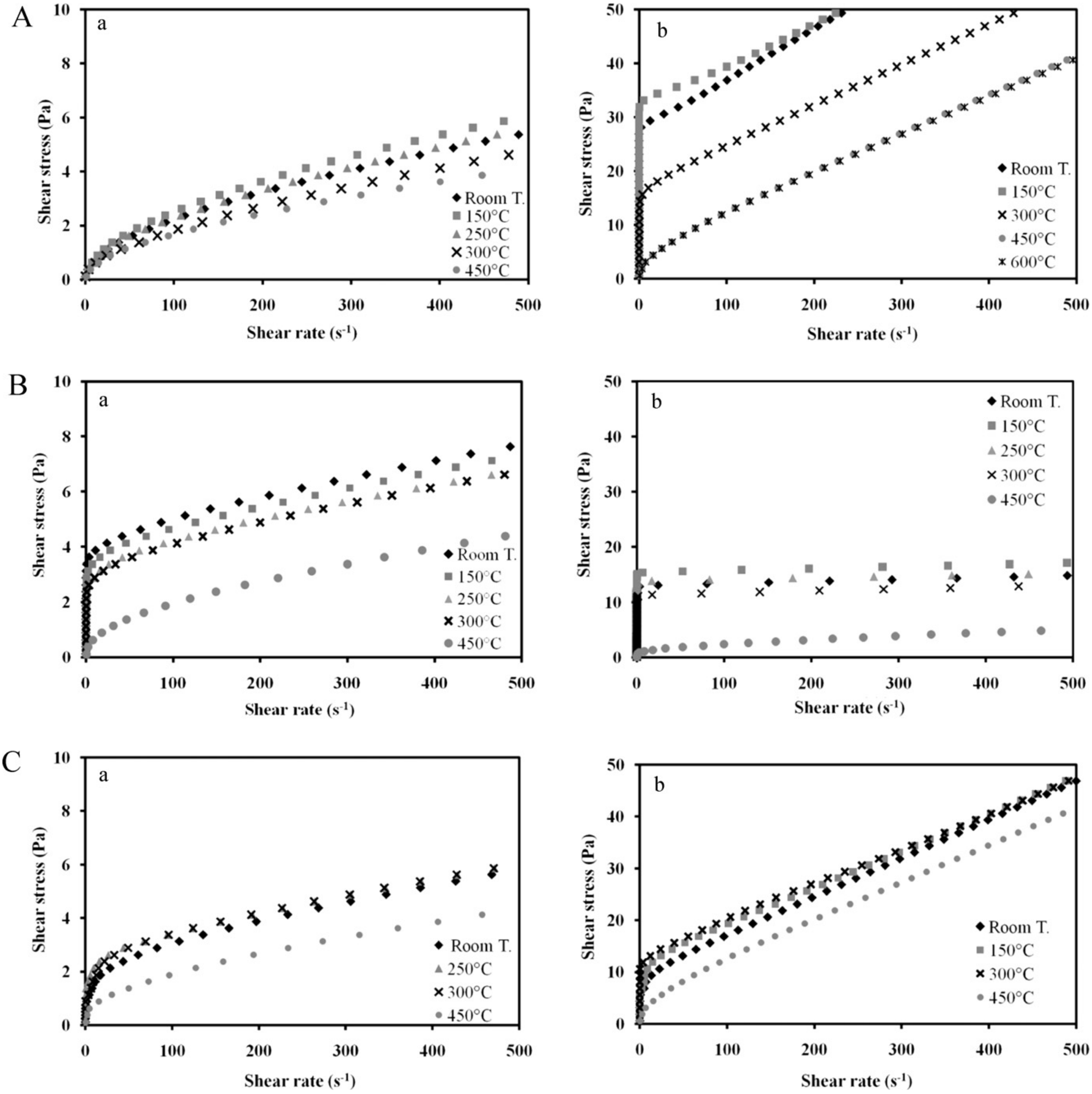

Fig. 4. Flow curves of aqueous suspension containing 5% (a) and 10% (b) (w/w) of B. Maghnia (A), Smectite CPA (B) and M. Srade (C) treated at various temperatures.

that the Smectite CPA possess the greater structural hydroxyl content within the phyllosilicates.

- Structural reorganization associated to a S-shaped endothermic–exothermic peak[24] was observed in the range 830–940 °C.

3.2. Effect of the firing temperature on the characteristics of montmorillonites

As previously mentioned, the calcination temperatures used in this study are 150, 250, 300 and 450 °C. The X-ray diagrams obtained for the three montmorillonitic clays are presented in Fig. 2. The (0 0 1) basal spacing recorded before any treatment characterized the hydrated state of the interlayer space, which is usually above 1.2 nm according to literature.[17] By increasing the pre-heating temperature up to 450 °C, thermal dehydration of montmorillonite gave rise to a gradual decrease of the (0 0 1) basal spacing which drops to 0.96–0.99 nm, depending on the interlayer cations, due to the collapse of dehydrated interlayers of the clay.

Besides, it was noted that the pH values of fresh suspensions remained unchanged when the montmorillonitic clays have been

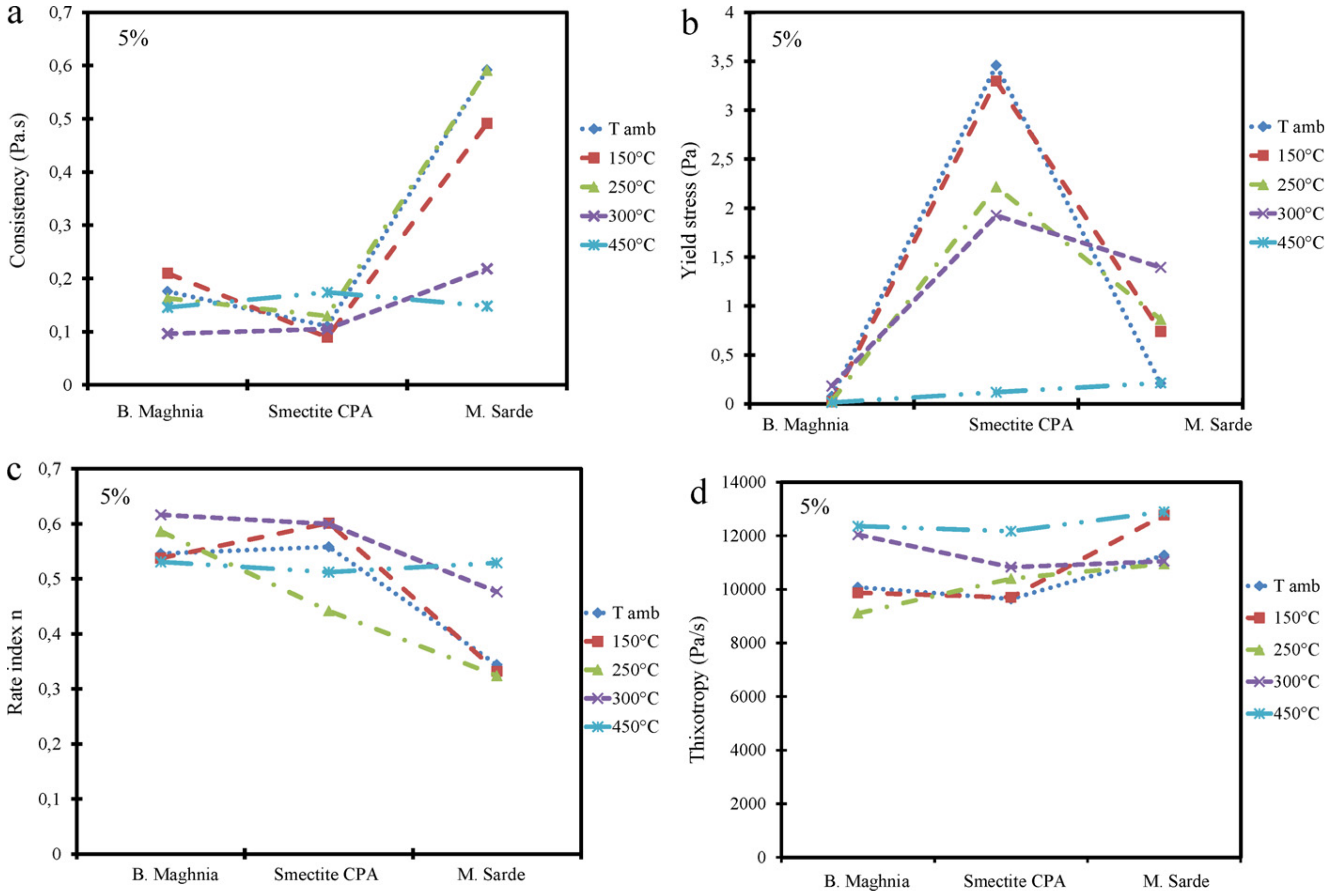

Fig. 5. Plot of yield stress (a), consistency (b), rate index (c) and thixotropy (d) vs. montmorillonite clays for 5 mass%.

previously calcined up to 300 °C (Table 2). At higher calcinations temperature (450 °C), a significant decrease in pH values is observed (for example, from 8.9 to 7.5 for B. Maghnia), which can be assigned to the fact that the donor character of the basal surfaces of clay particles is decreased, leading to less affinity towards H^+ ions present in water. Moreover, interlayer cations became less exchangeable under these conditions. Smectite CPA showed a different behaviour, since its pH value is less sensitive to preheating (variation from 8.3 to 7.9 ± 0.1). This specific trend may result from the presence of illite (Fig. 2B) and from the fact that interlayer cations are mainly potassium, which are less active cations compared to calcium, sodium and magnesium cations.[6,8]

BET surface areas were not affected by the pre-heating performed on the studied clays. It appeared that Smectite CPA exhibits the highest value, which indicates the presence of fine-sized particles as can be observed through granulometry distribution measurements (Table 2).

3.3. Rheological behaviour

The influence of the calcination temperatures on the rheological behaviour at 25 °C of aqueous suspensions containing 5 or 10 mass% of the different montmorillonitic clays are presented in Figs. 4–6. The yield stress, consistency and ratio index were derived from the flow curves using the Herschel–Bulkley relation (Eq. (1)).

3.3.1. Influence of solid content

The shear stress increased with concentration as expected in all cases for as-received clays (Fig. 4). The effect is more important with B. Maghnia since the yield stress increased from 0.1 to 28 Pa when the solid content was varied from 5 to 10 mass%. While for the same solid content variation, the yield stresses determined for Smectite CPA and M. Sarde increased from 3.5 to 13 Pa and 0.2 to 7 Pa, respectively. Such difference appeared as a combined effect of the clay platelets shape, the presence of associated mineral (quartz) and the interlayer cations activities. In fact, clay particles are generally packed to form coarse aggregates as can be observed on SEM images of B. Maghnia (Fig. 3), this peculiar arrangement controls the self-organization within the suspension and the flowing during rheological measurement. Furthermore, considering the lowest BET specific surface area of B. Maghnia, it is likely that the coarse quartz particles with acidic surfaces may interact with the montmorillonite basal surfaces (basic character), giving rise to an increase in the yield stress.

The consistency tends to decrease while the rate index increases until 300 °C with increasing solid content for as-received B. Maghnia and M. Sarde. This behaviour is justified by

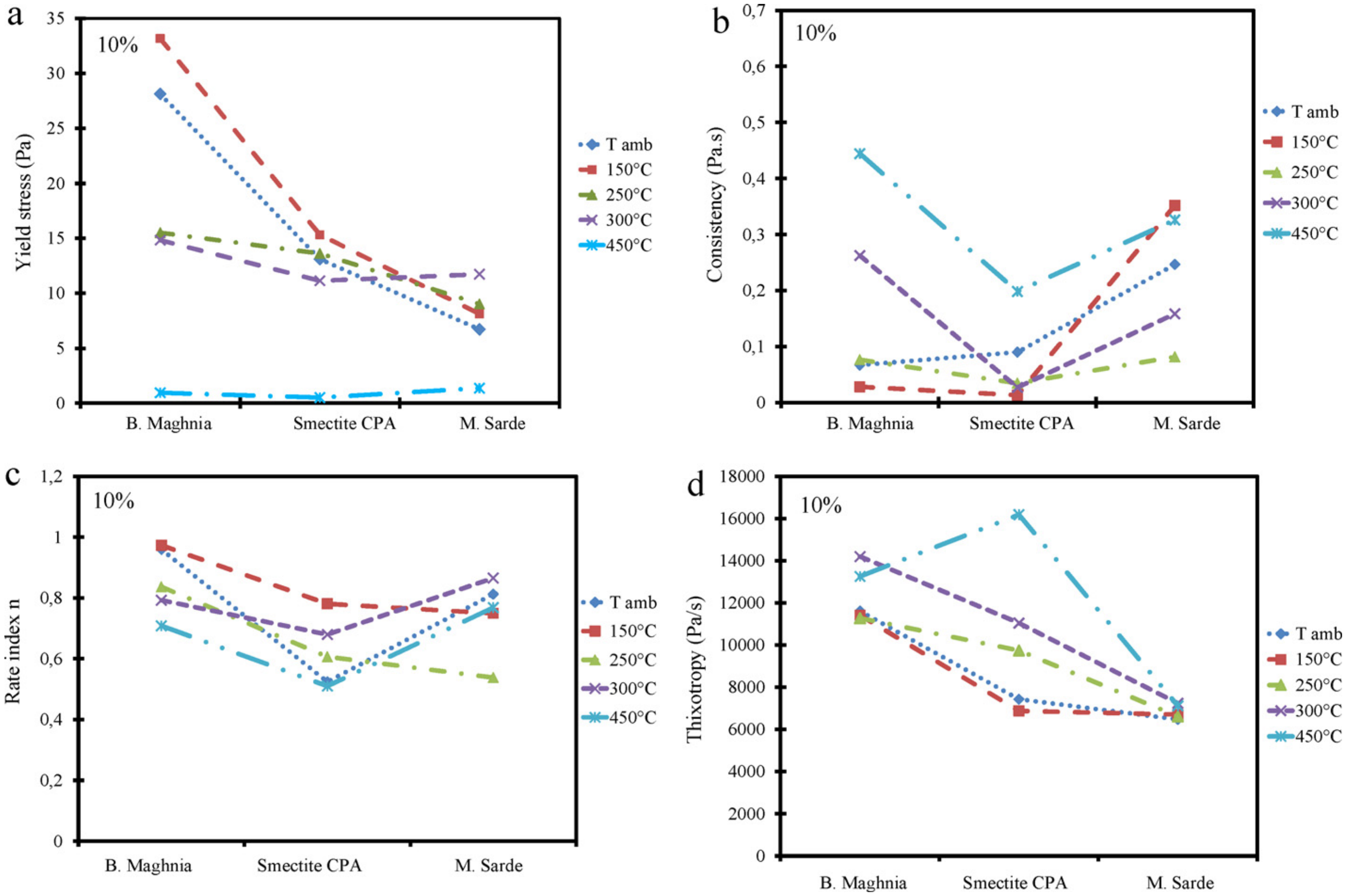

Fig. 6. Plot of yield stress (a) consistency, (b) rate index, (c) and thixotropy (d) vs. montmorillonite clays for 10% mass.

the higher activity of Mg^{2+} ions, which are released in solution and act as structuring agents towards clay particles. Moreover, when the solid content is increased, the saturation of the solution is quickly reached such that the structuring effect of Mg^{2+} cations is no longer efficient, thus the decrease in consistency observed here. In addition, it is noted that the rate index of B. Maghnia becomes slightly shear thickening ($n > 1$) above 80 s^{-1} for a solid content of 10 mass%. With increasing solid content, the formation of particle agglomerates is enhanced and they tend to behave as isotropic elements, which justifies the modification of the rate index. For Smectite CPA, the consistency and rate index were less affected by increasing solid content, this reflected the low activity of interlayer K/Ca cations. The studied suspensions exhibited a common shear-thinning behaviour since each rate index (n) was in most cases <1.

The thixotropy was not very sensitive towards solid content for as-received Smectite CPA and B. Maghnia, while it strongly decreased with increasing solid content for M. Sarde. The latter trend was assumed as a result of the effective montmorillonite mineral content in the starting clay (98 mass% in M. Sarde).

3.3.2. Influence of the calcinations temperature

3.3.2.1. Evolution of yield stress. The calcinations of montmorillonitic clays led to various behaviours as can be observed on Figs. 4–6. All suspensions exhibited a maximal yield stress, this behaviour was enhanced for suspensions with 10 mass% solid. The maximum yield stress was reached for calcination temperatures of 300 °C for M. Sarde (12 Pa) and 150 °C for B. Maghnia (33 Pa) and Smectite CPA (15 Pa). These trends reflected the difference regarding the interaction between clay particles within the suspensions.

At a first approximation, the surface charge of clay platelets seemed to be modified depending on the calcination temperature. This assumption is not coherent with the decrease in pH value (Table 2) previously mentioned, since it is well known from literature[11] that the edge charge density at pH > 6 is low and negative, the basal surface charge remaining also positive. Therefore, the cardhouse-like structure formation due to edge(−)/face(+) interactions is well appropriated in this case.

A second assumption is consistent with the effect of interlayer cations released and activity within the suspension. It had been shown in literature that a significant proportion of exchangeable cations are localized at the edges of clay platelets. In the case of Na-Montmorillonites, coagulation occurred through face-to-edge bridging promoted by the presence of exchangeable cations at the edges or basal surfaces. It was also noted that for low salt concentrations, face-to-edge attraction prevailed while with high salt concentrations, face-to-face attraction was promoted. Such interactions may likely occur within our suspensions, thus justifying the presence of a maximal yield stress. The higher maximal yield stress obtained with B. Maghnia may result from the presence of Mg/Na cations, which are more efficient compared to Ca/K cations in Smectite CPA. For high montmorillonite mineral content (M. Sarde), it seemed that the pre-heating should be performed at higher temperature to induce a significant modification of surface interactions that governs the structuring of suspension. A greater value was expected for M. Sarde since it presented higher Mg and Ca contents, but it was not the case probably because near 300 °C, the dehydration was completed and the interlayer started to collapse leading to a strong limitation of interlayer cations mobility.

3.3.2.2. Consistency. The evolution of the consistency of the suspensions with respect to the calcination temperature appeared as the reverse of general trend observed for yield stress. For each type of montmorillonite, a minimal consistency was noted at calcination temperatures of 300 °C for M. Sarde (0.16 Pa s) and 150 °C for both B. Maghnia (0.03 Pa s) and Smectite CPA (0.01 Pa s) in 10 mass% solid suspensions (Figs. 5b and 6b). This peculiar trend can be justified by considering that when the higher self-organization state was reached within the suspensions (maximal yield stress), the clay platelets acquired a high velocity, due to the high shear stress applied to break down the inter-particles bonding, and therefore flowed more easily (high fluidity). After these minima, the consistency was increased with further increased of the preheating temperature. Such behaviour seemed to result from the presence of less structuring cations in solution which caused the formation of less inter-particles bridging (lower yield stress required) and the persistence of loose agglomerates that decreased the flowing rate of the suspension, thus the lower fluidity observed.

3.3.2.3. Rate index. The rate index was <1 for all suspensions (Figs. 5c and 6c), which was a characteristic of shear-thinning behaviour regardless of the calcination temperature. Also maximal rate index values were observed and well correlated with maximal yield stresses obtained for B. Maghnia and Smectite CPA (preheating temperature of 150 °C). M. Sarde exhibited a maximal rate index for a preheating at 250 °C. This can indicate that the clay particles were significantly modified in the range 250–300 °C for M. Sarde, which is consistent with the behaviour of a pure montmorillonite (low associated minerals).

3.3.2.4. Thixotropy. The thixotropy did not follow a monotone evolution (Figs. 5d and 6d). Actually, minimal values were obtained for B. Maghnia and Smectite CPA for calcinations at 300 and 150 °C, respectively. While in the case of M. Sarde, thixotropy was almost constant. Such trends are consistent with the ability of self-organization within the suspensions due to combined effect of released interlayer cations in solution and associated phases in the starting clays. That is admixed crystalline and non-crystalline phases, in particular carbonates and iron oxides, cementing materials like silica and humic compounds, can strongly affect the rheological behaviour of clays.[10]

4. Conclusion

The characterization of the rheological behaviour of three montmorillonitic clays at 25 °C have evidenced the effect of interlayer cations and associated mineral. Actually, the yield stress tends to decrease when the interlayer cations are predominantly monovalent, due to their less structuring action.

Moreover, the presence of associated minerals such as quartz tends to promote the increase of yield stress because of the acido–basic like surface interactions with the basal surfaces of montmorillonite.

The calcination of montmorillonitic clays up to 300 °C prior to their rheological characterization does not significantly affect the rheological behaviour.

Calcinations at 450 °C, lead to irreversible interlayer modification of montmorillonites structure and therefore the related suspensions exhibit lower yield stress and shear-thinning behaviour.

The result of this investigation may be a good clue for the possible introduction of smectites in ceramic body, with the aim to improve their rheological behaviour regarding the shaping process without decreasing the final properties of related ceramic products.

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