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International Journal of Pharmaceutics 182 (1999) 7–20

international journal of pharmaceutics

Pharmaceutical grade phyllosilicate dispersions: the influence of shear history on floc structure

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Received 27 April 1998; received in revised form 13 January 1999; accepted 17 January 1999

Abstract

The effect of mixing conditions on the flow curves of some clay–water dispersions was studied. Two Spanish fibrous phyllosilicates (sepiolite from Vicálvaro and palygorskite from Turón) and a commercial bentonite (Bentopharm©, UK) were selected as model clays. The disperse systems were made up using a rotor-stator mixer working at two different mixing rates (1000 and 8000 rpm), for periods of 1 and 10 min. Rheological measurements were taken and the corresponding flow curves obtained immediately after interposition and then after a period of 24 h under low shear caused by a roller apparatus. Aqueous sepiolite dispersions showed the highest viscosity and were easily interposed, whereas palygorskite dispersions were more difficult to obtain, resulting in low to medium viscosity gels. Bentonite dispersions provided medium viscosity systems, which greatly increased their viscosity after the low shear treatment (as a result of swelling), whereas the viscosity of the fibrous clays stayed at approximately the same values or even decreased. A linear relation was found between mixing energy and apparent viscosity in the bentonite systems, while apparent viscosity in the sepiolite samples was related to mixing power, with minor influence of mixing times. All the systems studied had thixotropic behaviour, changing from clearly positive to even negative thixotropy in some palygorskite systems. Finally, we studied the effect of drastic pH changes on the system structure. Results showed that rheological properties were highly sensitive to pH in the fibrous dispersions, but less sensitive behaviour was found in the laminar clay systems. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Sepiolite; Palygorskite; Smectite; Disperse systems; Rheology; Mixing performance

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PII: S0378-5173(99)00075-7

1. Introduction

Silica, talc and other phyllosilicates such as kaolinite, smectites and fibrous clays are among the most widely used minerals in the composition of medicines (Hermosín et al., 1981; Alvarez, 1984; Galán et al., 1985). These minerals can either be used as they are or after divers chemical treatments intended to bring out one particular quality. The special characteristics of these clays make them ideal for use as pharmaceutical excipients, or as active ingredients, finding application in several OTC pharmaceutical products as a result of their antacid and antidiarrhoeal properties. Despite their multiple applications, it is generally hard to explain marked differences in the rheological properties of suspensions made up with apparently similar clays, even when all pharmacopoeial specifications are satisfied.

The rheological properties of suspensions can be affected by two categories of factor—hydrodynamic and non-hydrodynamic. All the interactions between the dispersion medium and the particles are usually referred to as hydrodynamic effects. This kind of force is predominant in suspensions of particles larger than 10 μm (Kamal and Mutel, 1985; Mewis, 1985), and are determined by the concentration of the particles (Everett, 1988), their shape (Weinberger and Goddard, 1974), size and size distribution (Henderson et al., 1982) and the rheology of the suspending medium (Metzner, 1985). The second category refers to the non-hydrodynamic effects and includes the colloidal properties of dispersions where the attractive interactions between solid particles are so strong that a rigid network is obtained.

Clays can be defined as materials with particle sizes below 2 μm (i.e. colloidal size). Dispersion of discrete particles with colloidal dimensions in a fluid medium involves a number of different stages including incorporation, wetting, breakdown of particle clusters (aggregates and agglomerates) and flocculation of the disperse particles. The properties of the final product, even at low solid concentration, will vary from that of the fluid medium. If the solid fraction is low enough (i.e. dilute dispersions) quantitative and confirmed theoretical equations can be used to explain the rheology of the systems on the basis of particle–fluid interactions. However, most systems of practical interest are non-diluted, where particle–particle interactions are added to those between particles and fluid medium and consequently only semi-quantitative information becomes available. Moreover, weakly flocculated systems are usually obtained, where the floc structure and consequently the system properties are highly influenced by the shear history. In such systems, divers forces may be active and the final properties will depend on both particle characteristics, such as shape and size, layer charge, exchangeable ions etc. and elaboration and post-treatment conditions such as mixer shear rate and time, types of mixer used, presence or not of later shearing processes, conditioning temperature, pH of the gastrointestinal medium, ionic strength, etc. Several authors have studied the formation and stability of clay gels and the effect of pH and salt concentration on the properties of the resulting product. Two distinct flocculation mechanisms have been described to explain the structural changes when laminar clays are dispersed in a polar medium; internal mutual flocculation between faces and edges of the clay particles (Van Olphen, 1963), and heteroflocculation or coagulation caused by face–face interactions. Permien and Lagaly (1994a,b, 1995) explained the effect of the presence of different substances on the rheology of montmorillonite suspensions on the basis of non-hydrodynamic interactions. Similar studies were made with fibrous clays by Chang et al. (1993). The rheological properties of both sepiolite and montmorillonite suspensions were studied by Simonton et al. (1988), who found that a three-dimensional structure composed of interconnecting fibres may be formed by means of ultrasonic treatment of sepiolite–water dispersions. However, little research has focussed on the effects of hydrodynamic factors, such as size and shape of the particles, on the final product properties. There are also few articles about the effect of shear history on the rheological behaviour of clay dispersions, where the degree of dispersion and flocculation and the structural changes resulting from differences in particle shapes and size distributions have significant influence. Pharmaceutical dispersions consisting of these materials will be shaken several times during their 'life' resulting in changes in the system structure and when administered orally they will find a special pH environment that may severely affect their properties.

The aim of this paper is to examine the effects of mixing conditions (mixing power and mixing time) and subsequent controlled agitation (simulating the pre-administration shake) on the rheology of suspensions consisting of fibrous (sepiolite, palygorskite) or laminar (smectite) clays. Finally, the effect of drastic changes on the pH of the suspensions was studied and gel stability measured. Rheological data are explained on the basis of both hydrodynamic and non-hydrodynamic factors.

2. Materials and methods

2.1. Materials and sample preparation

Two fibrous clays (sepiolite from Vicálvaro, Madrid (SV) and palygorskite from Turón, Ciudad Real (PCR) and a laminar shape clay (Benthopharm©, BTP) were studied. For each sample powder the sieve fraction between 75 and 125 μm was selected by dry sieving and then stored at 40% relative humidity and room temperature (22–25°C) for at least 48 h before carrying out any study.

2.2. Mineralogical and chemical contents and size distributions

Determination of mineral composition was carried out by X-ray diffraction (XRD), using a Philips® PW1710, CuKα radiation and automatic slit, and by the powder method and oriented aggregates treated with ethylene-glycol, dimethylsulphoxide and heating to 550°C. The percentages of the different mineral phases were calculated using data obtained by XRD and chemical analyses, following the method used by Torres-Ruiz et al. (1994) and López-Galindo et al. (1996). Major elements were analysed by X-ray fluorescence, using Philips® PW1404 equipment, Cr/Au tube and Be window. Finally, particle size distribution was determined with Galai® CIS-1 System laser equipment.

2.3. Preparation and study of disperse systems

Dispersions of each clay were made up at 2 and 10% w/v in distilled water using a high shear rotor-stator mixer (Silverson L4RT, Silverson Machines Ltd., UK). Rotor speeds of 1000 and 8000 rpm were used in the interposition for periods of 1 and 10 min (i.e. four different mixing energies). To study the effect of low shearing on the systems' properties, they were then shaken in a roller at 30 rpm for 24 h. On the other hand, the disperse systems studied could be administered orally and it is therefore important to stabilise the effect of drastic pH changes on their structural stability and properties. To assess these effects, the pH of each dispersion was altered by adding different solutions and shaking at 30 rpm until a constant pH was measured (approximately 2 h). The solutions used were obtained by dilution of convenient amounts of 0.1 N HCl or 0.1 NaOH N in water, the ionic strength being adjusted by adding 0.1 M KCl. The pH values of the solutions used to bring about the pH changes (pH = 1.2, 5.8, 13.1) were selected following Dressman et al. (1993) to imitate those of gastric fluid at three extreme conditions (i.e. pH before lunch, after lunch, highly anomalous pH, respectively). The pH values of the disperse systems were then monitored until an equilibrium value was reached.

The rheological properties of the dispersions were measured immediately after mixing, after the 24 h low shearing period, and after alteration of the pH, using a couette type viscometer(Chand 35, Chandler Ltd., USA) at 25°C.

3. Results

3.1. Mineralogical and chemical characterisation

Tables 1 and 2 show the mineralogical and chemical contents of the studied samples, respectively. BTP is a material widely used in pharma-

Table 1
Mineralogical contents of the studied samples

	Quartz	Opal	K-Feldspar	Albite	Calcite	Palygorskite	Sepiolite	Al smectite	Mg smectite	Illite	Clinoptilolite
BG	1	–	–	1	1	–	–	95	–	2	–
BTP	3	13	–	–	2	–	–	78	–	2	2
PCR	7	–	3	–	9	53	–	3	2	23	–
PUC	11	–	–	–	5	73	–	7	–	2	2
PHR	17	–	–	–	6	46	–	15	12	4	–
SV	–	2	2	–	–	–	91	–	3	2	–
SY	–	–	2	–	–	–	93	1	2	2	–

Table 2
Chemical contents of the studied samples

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	PPC
BG	53.78	20.09	1.45	4.69	1.79	0.69	0.52	0.41	0.05	17.40
BTP	62.00	15.30	3.40	1.72	1.53	1.85	0.36	0.14	0.08	13.90
PCR	52.89	12.62	4.17	6.68	5.23	0.14	2.16	0.34	0.02	15.72
PHC	54.90	9.72	3.49	8.27	3.28	0.16	0.76	0.48	0.07	18.60
PHR	58.40	10.30	4.11	10.20	3.62	0.15	0.60	0.50	0.07	11.20
SV	56.44	1.28	0.38	23.50	0.21	0.10	0.64	0.06	0.02	17.32
SY	55.57	1.47	0.43	23.79	0.23	0.17	0.66	0.06	0.02	17.54

ceutical applications as a suspension vehicle. Nevertheless, the mineralogical analysis showed a low smectite content (the main mineral) and a relevant percentage of opal and quartz as impurities. According to the chemical analysis, it also contains a certain amount of Ca^{2+} and Zn^{2+}. The flow behaviour of bentonite dispersions is sensitive to the Na^{+}/Ca^{2+} ratio which, in the case of BTP, was shown to be 1.85/1.53. This ratio means the clay can be defined as a sodium bentonite. The energy required to introduce a water molecule into the inter-laminar space of this type of smectite is low enough to asses the formation of a structure capable of retaining a great amount of water when their water dispersions are stored (i.e. it would be reasonable to obtain a gel after a swelling period). Purity of SV is higher than in the cases of BTP and PCR, with a main mineral content of 91%. Finally, the percentage of palygorskite in PCR is only 53%, with a high content in other clay minerals such as illite and smectite. Attention should be drawn to the presence of an significant percentage of calcite in PCR (9%) that could be eliminated by a simple acid treatment. In both fibrous samples, chemical analysis revealed typical percentages of the minerals studied, with no impurities of any relevance to the aims of this study.

3.2. Disperse systems properties

Clay gels can be obtained by mechanical (Chang, 1992) or ultrasonic agitation (Simonton et al., 1988) of the internal phase in the medium. In this study four different mechanical agitation energies were used to disperse the solids in distilled water. The data obtained from the rheological study have been plotted as flow curves (or rheograms), where the unbroken line corresponds to the increase in shear rate and the broken line to the decrease. In order to facilitate reading of the corresponding yield stresses, a semi-logarithmic plot is included on the right of each rheogram. By using the Bingham equation, it was then possible to obtain the apparent viscosities at 300 rpm, and correlate them to the mixing energy applied to break down the aggregates.

3.2.1. Effect of mineral type, solid content and interposition conditions (Fig. 1)

In the case of BTP dispersions, viscosity depends greatly on the solid fraction, which is only significant in the 10% w/v dispersions. As can be observed in Fig. 1(A), bentonite systems showed non-newtonian behaviour with a yield stress that increased with viscosity between 1 and 16 Pa. Consequently, they can be classified as Bingham bodies. Interposition conditions (mixing time and mixing power) seem to have a similar effect on the break-up of aggregates (i.e. increasing power or time results in an increase in viscosity). Positive thixotropic behaviour can be observed in all cases, with low thixotropic areas no matter what the mixing conditions.

Fig. 1(B) shows the flow curves for PCR. Its mixing-related behaviour is extremely sensitive and systems of significant viscosity could only be obtained with both maximum power and interposition time and even then, viscosity was ten times less than that of BTP. The systems also showed high dependence on the solid fraction, which could be measured when the solid fraction was 10%. In these conditions, a Bingham plastic is

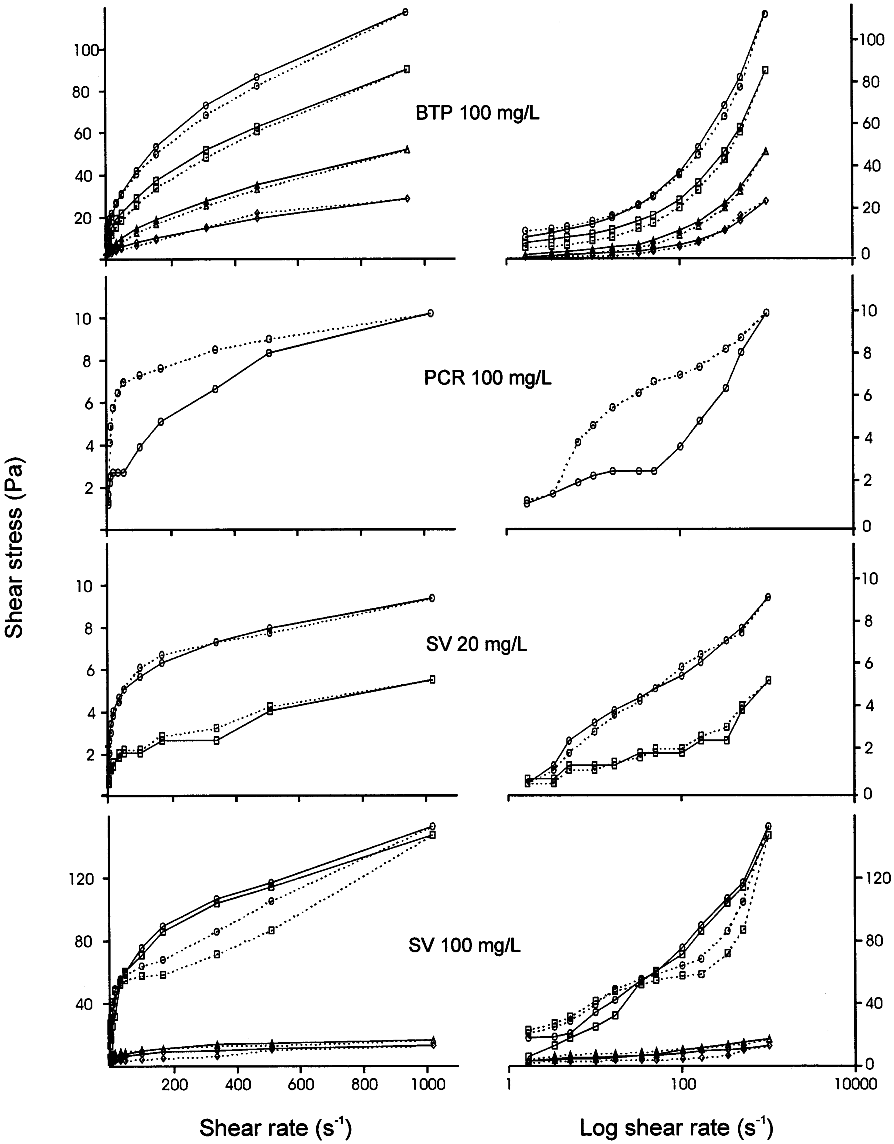

Fig. 1. Effect of mineral type, solid fractions and initial interposition conditions on the rheological properties of the systems (◇ = 1000 rpm × 1 min, ∇ = 1000 rpm × 10 min, □ = 8000 rpm × 1 min, ○ = 8000 rpm × 10 min).

obtained with yield stress around 2 Pa, showing high antithixotropic behaviour.

Finally, SV systems were the most viscous and easy to obtain when high mixing rates were used. Mixing power rather than mixing time seems to be the main factor influencing the properties of the systems. This fact is not obvious when the solid fraction is low, in which case mixing time seems to affect viscosity (Fig. 1C). However, as can be seen in Fig. 1(D), the flow curves of 10% were hardly dependent of mixing rate and time is noted to be a secondary factor. Flow curves corresponded to Bingham plastic with yields stresses around 10 Pa and thixotropic behaviour changing to antithixotropic when the applied shear rate was under 100 s^{-1}.

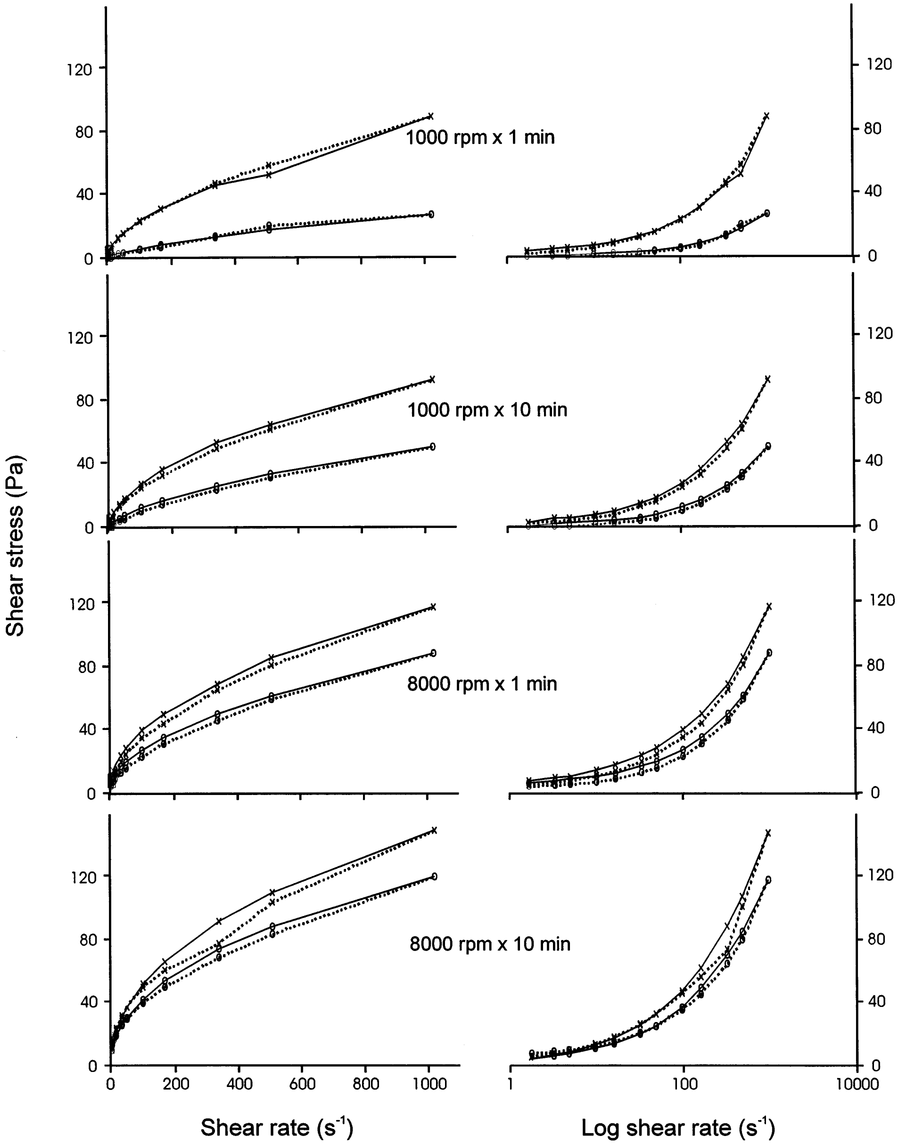

Fig. 2. Effect of low shearing treatment on the rheograms of BTP systems (○ = 0 h, X = 24 h).

3.2.2. Effect of a 'post-shaking' treatment

When flow behaviour was measured in the former flocculated systems after shear treatment (similar to shaking several times prior to administration) the following changes occurred in the rheograms:

BTP system viscosities increased greatly after the 24 h low shearing period (Fig. 2). The increases can be inversely related to the initial mixing energy of interposition (as interposition energy increases, the effect of the subsequent shear period on the viscosity decreases). Thixotropy values remain the same despite the new structure level.

The viscosity of palygorskite suspensions did not increase after low shearing, but a drastic reduction in antithixotropic behaviour was observed (Fig. 3). The initial thixotropy measured

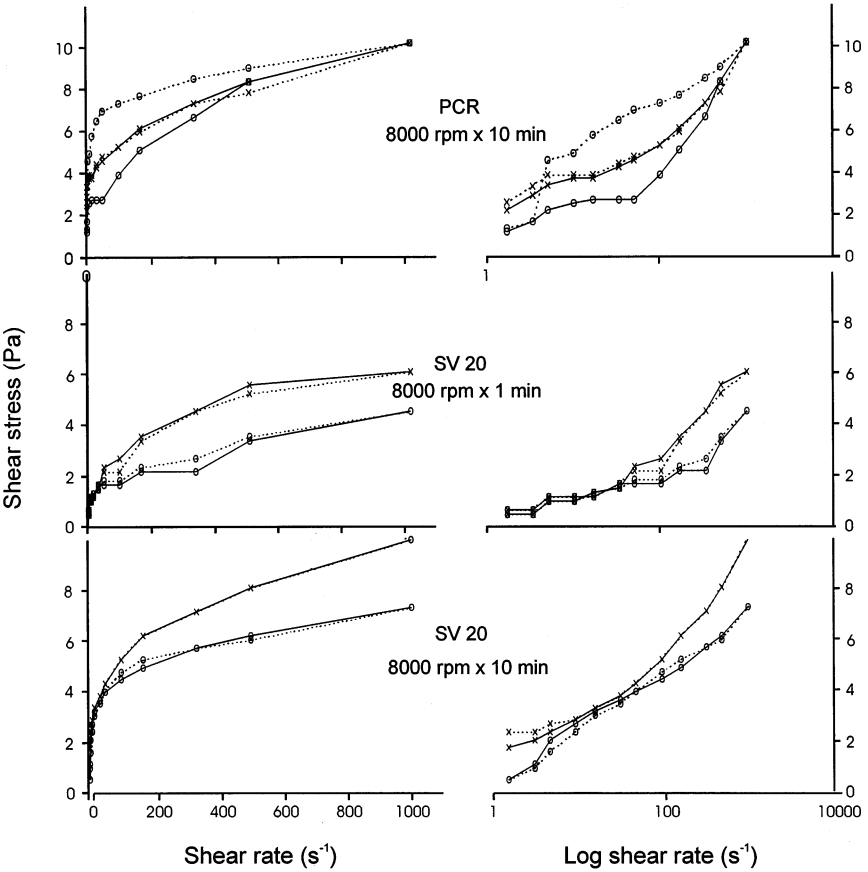

Fig. 3. Effect of low shearing treatment on the rheograms of PCR (100 g l^{-1}) and SV (20 g l^{-1}) systems (○ = 0 h, X = 24 h).

seem to be related to an inadequate choice of increments (5 s before change in shear rate was used in all cases and measurements were taken just before change in rate).

Sepiolite gels obtained using 20% of solid content showed a minor increase in viscosity after shaking (Fig. 3), and in a proportion that does not seem to be related to the initial mixing time. When the solid fraction was 100% w/v (Fig. 4), two different patterns were found: those gels obtained at 1000 rpm (A and B) increased their viscosities, whereas in those obtained at 8000 rpm (C and D), viscosity was found to decrease after the low shearing period whatever the time used. There was also a reduction in thixotropic areas in the high mixing rate gels, which could even collapse, as in the case of D.

3.2.3. Effect of drastic pH changes

The pH levels of the suspensions were monitored until an equilibrium value was reached. Table 3 presents the equilibrium values of each dispersion after 2 h. Higher times resulted in slight variations in the pH values and this period was therefore chosen to estimate the effect of gastric pH on real residence times. The pH affects the structure of gels to a different extent, depending on preparation conditions and the kind of clay. According to the rheograms for BTP and PCR, we can infer that the change in pH did not severely affect severely the structure, resulting in flow curves similar to those of the initial gels (Fig. 5). On the other hand, shear stress values of SV decreased drastically when diluted with the basic solution. Fig. 6 represents the flow curves of the

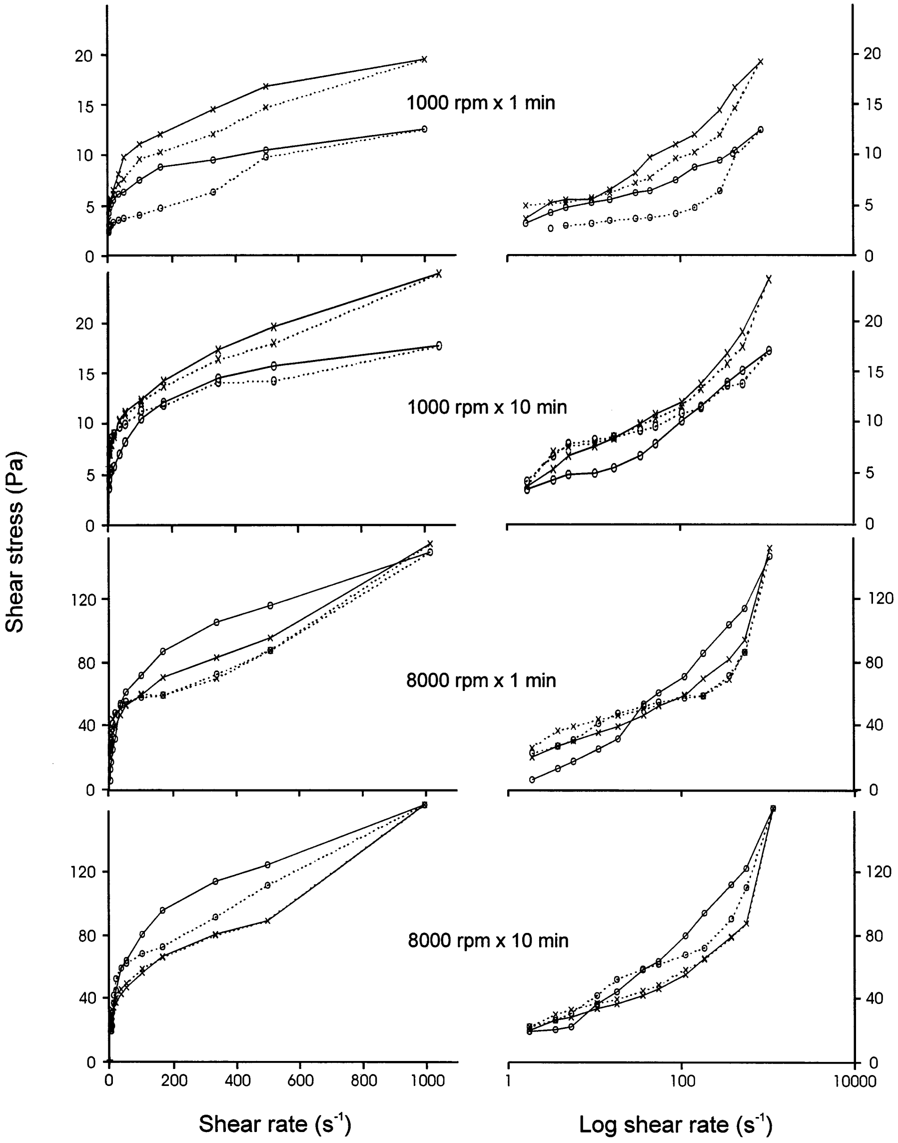

Fig. 4. Effect of low shearing treatment on the rheograms of SV (100 g l^{-1}) systems (○ = 0 h, X = 24 h).

sepiolite suspensions (100% w/v), showing the different effects on the rheology patterns depending on the initial treatment and the disappearance of thixotropy. More detailed observation allows us to distinguish between them. When prepared at 1000 rpm for 1 min, high dependency on the pH could be observed. Addition of the NaOH solution to the suspensions prepared at 1000 rpm for 10 min almost completely inhibited gel formation, so there was no observable yield stress and viscosity is only slightly higher than that of the water. This was not the case of the neutral and acid suspensions where dilution only caused a small decrease in viscosity. Similar behaviour can be observed on the 8000 rpm curves.

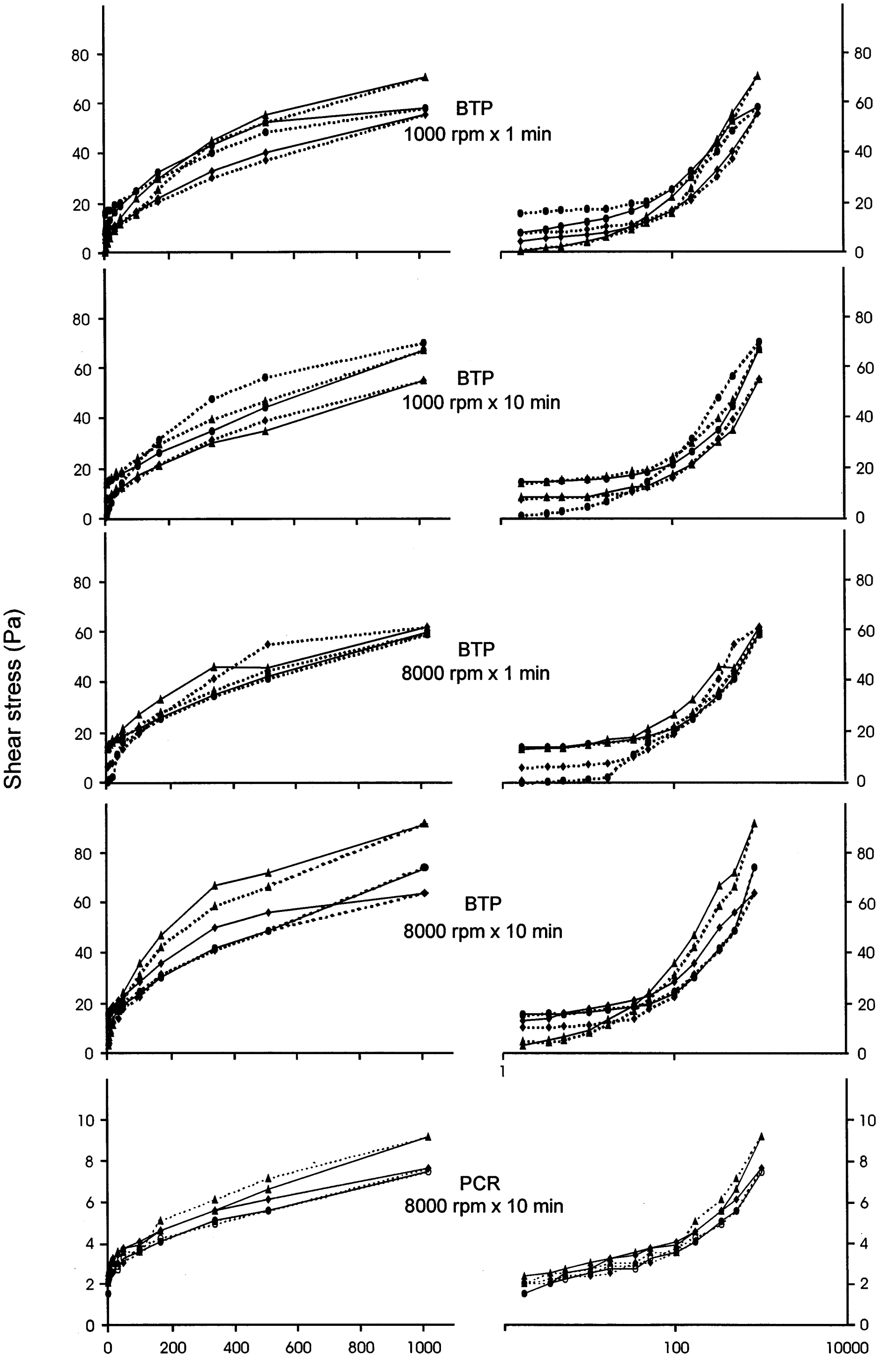

Fig. 5. Effect of pH modifications on the rheograms of BTP and PCR systems (▲ = basic, ◆ = neutral, ○ = acid).

Table 3
Pseudoequilibrium pH of the systems after 2 h of addition of the three different pH solutions

Medium pH	BTP (100 mg l^{-1})	PCR (100 mg l^{-1})	SV (20 mg l^{-1})	SV (100 mg l^{-1})
1.20	7.35	7.55	6.31	6.98
5.80	8.15	8.12	7.78	7.54
13.10	10.12	9.06	11.62	10.61

4. Discussion

The sepiolite gels were more viscous than the smectite and palygorskite ones, forming good pseudoplastic gels in water at 2 and 10% w/v. Dispersion of SV particles seems to be almost total after the first mixing treatment, where BTP required a swelling time of 24 h at least. Flow curves obtained after the 24 h low shearing period showed that dispersion of the laminar particles had not concluded after the initial mixing. The nature of the gelling mechanisms of fibrous and laminar clays are clearly different, as can be seen by the results presented. Their differing structure and chemistry may help to explained these differences.

Firstly, the studied systems are formed by particles of similar sizes but very different shapes—rod-like or prolate spheroids (palygorskite and sepiolite) and disk-like or oblate spheroids (smectite). The presence of hydrodynamic forces tends to align the major axis with the flow and their relative importance may be expressed in terms of the Peclet number (*Pe*). Clearly, *Pe* for fibres is always several orders of magnitude higher than *Pe* for laminar particles. When the system is highly viscous and/or the particle size is not small enough the disperse phase orientation is flow dependent and it is their orientation and resistence to be orientated which mainly determine the system properties.

Secondly, laminar particles of BTP have a structure formed by parallel sheets of negatively-charged tetrahedra and compensated by interlayer cations. Osmotic swelling may occur when the particles or their aggregates are immersed in a medium with a low electrolyte concentration. The negatively-charged faces are attracted to the positively-charged edges and an open structure is formed. Consequently, flocculation (and hence formation of the gel structure) of laminar clays would mainly be obtained through an electrostatic mechanism (i.e. swelling). On the other hand, the exact mechanism of gel formation in fibrous particulate systems is not well understood. Some authors have proposed a mechanism basically caused by physical interaction between the fibres and, therefore, dependent on fibre (Simonton et al., 1988). The presence of superficial silanol groups would have a secondary effect on gel formation. Other authors, however, prefer to explain the formation and stability of fibrous clay gels by electrostatic interactions similar to those responsible for the mechanism in laminar (Chang et al., 1993).

Our results seem to confirm the need for breakdown of aggregates and formation of a structure in both laminar and fibrous clays (which otherwise could not give rise to a gel by mere swelling). Fig. 7 present the results of the correlation study between the two possible mixing energy factors ($N^3 t$ or $N^2 t$) and the apparent viscosities, both for BTP and SV, and clearly show the perfect linearity between energy applied and apparent viscosity in the case of BTP, as well as the influence of shaking power in the case of SV. However, it was not possible to determine which of the two energy factors ($N^3 t$ or $N^2 t$) more closely fitted the correlation. Once this open structure in which the fibres are more or less isolated has been established, the system is sensitive to pH alteration, which demonstrates the importance of electrostatic equilibrium in its stability.

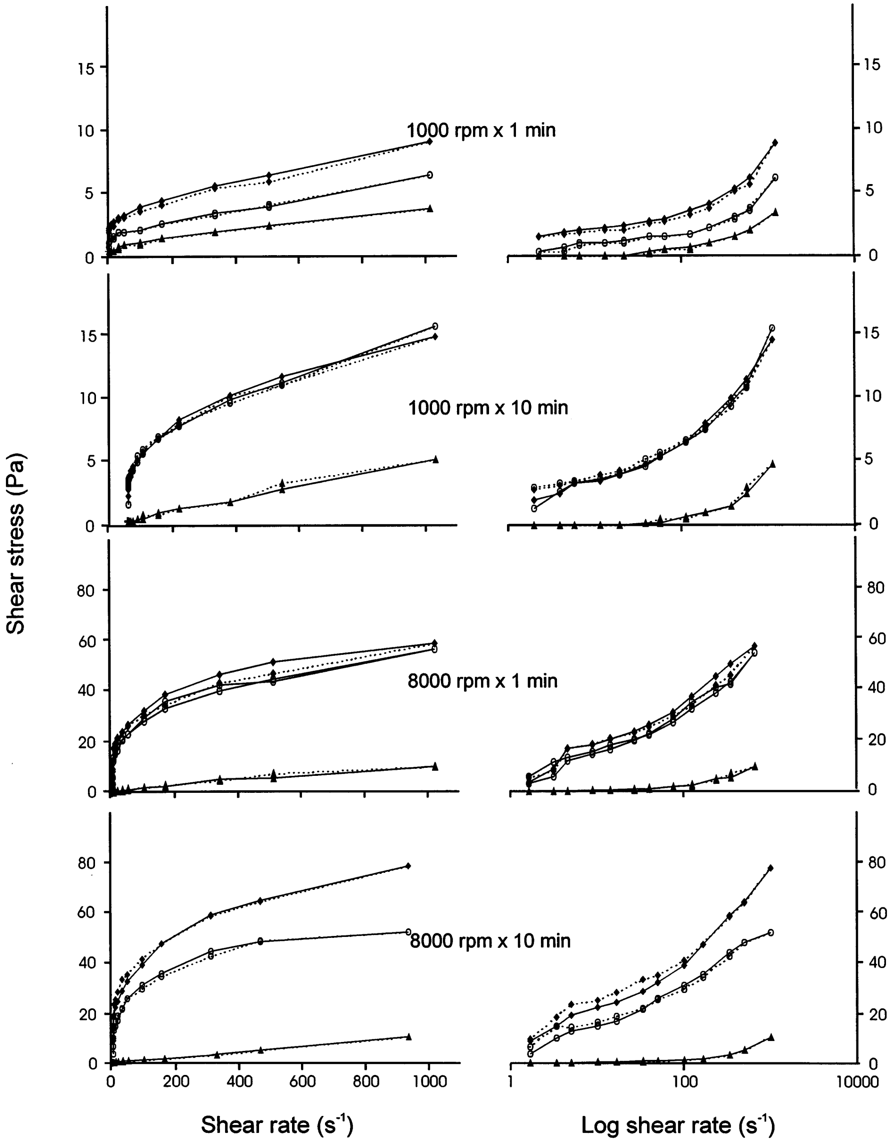

Fig. 6. Effect of pH modifications on the rheograms of SV (100 g l^{-1}) systems (▲ = basic, ◆ = neutral, ○ = acid).

5. Conclusions

Ultrasonic agitation is not necessary to develop high viscosity in fibrous samples, nor is the low shearing period which seems to be an important factor for laminar samples. The difference was related to the special shape of their particles. In our opinion, gel structure in fibrous clay suspensions may be formed by hydrodynamic forces, even when non-hydrodynamic forces could be implied in its final stability. Breakdown of the structure seems to take place by gradual erosion of flocs, whereas reorganisation would occur by the particles sticking together again. The different mechanism of breakdown and recovery of structure leads to the structure's dependence on the shear history. We must assume a specific kind of aggregation between the particles to explain the

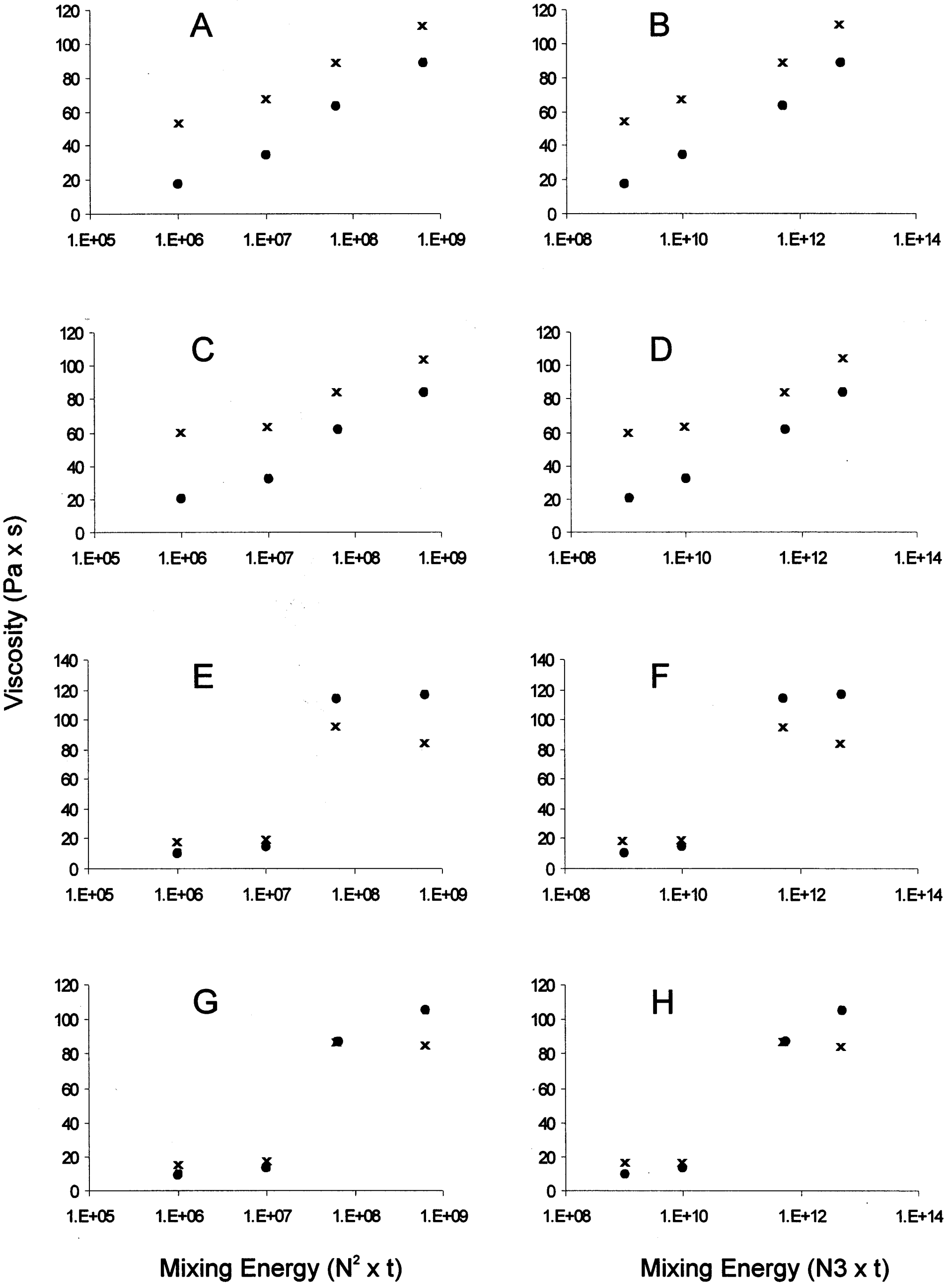

Fig. 7. Correlation study of mixing energies to apparent viscosities measured at 300 rpm for BTP (A, B, C and D) and SV (E, F, G and H) systems. Figures A, B, E and F correspond to increasing values of viscosities correlated to N^2 *t* and N^3 *t*, respectively and figures C, D, G and H to decreasing values correlated to N^2 *t* and N^3 *t*, respectively. The measurements were taken at the following periods: ● = immediately after mixing, X = after 24 h of low shear rolling.

dependence of the flow curves on the pH. Floc structure will be determined by the shapes of their particle components. The formation of floc structures and ultimately the resulting space network of particles and/or flocs will have a profound effect on the flow behaviour of the system. Assuming a reversible structure formation, we consider the flocs to gradually breakdown when shear rate is increased and to restructure when stored. These reversible changes in floc structure require time, resulting in time dependent viscosities, i.e. thixotropy.

Regarding their applications, we must mention that fibrous clays do not require a swelling period to obtain a gel, whereas laminar clays do, which is of major importance when 'in situ' interposition of the dispersion is desired. Moreover, the systems are suitable for oral administration, as their aggregation state does not significantly alter in acid or neutral medium, although its does in a strong basic one.

Acknowledgements

This study was supported by DGES project PB95-1271-C02-01 and Group RNM-0179 of the Junta de Andalucía.

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