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# RHEOLOGICAL CHARACTERIZATIONS OF DISPERSIONS OF CLAY PARTICLES IN VISCOELASTIC POLYMER SOLUTIONS

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## ABSTRACT:

In this work, we consider model fluids which are dispersions of clay particles in aqueous solutions of carboxymethyl cellulose. Their rheological properties are measured in both steady and oscillatory shear flows. We present the experimental results obtained for different polymer concentrations and for three different molecular weights of the polymer. The clay is a bentonite sample and the particle concentration is fixed to a value of 5 %. The mechanical properties of these materials is the result of a competition between different mechanisms: association-dissociation of aggregates of particles, adsorption of polymer on the particles and desorption of solvent molecules from the particles, bridging of the particles by long polymer chains.

## ZUSAMMENFASSUNG:

In dieser Arbeit werden Modelldispersionen aus Tonpartikeln in einer wässrigen Carboxymethylzellulose-Lösung betrachtet. Ihre rheologischen Eigenschaften werden sowohl in stationären als auch in oszillatorischen Scherströmungen untersucht. Wir präsentieren die experimentellen Resultate, die für verschiedene Polymerkonzentrationen und für drei unterschiedliche Molekulargewichte des Polymers erhalten wurden. Das Tonmineral ist ein Bentonit, und die Partikelkonzentration beträgt 5 %. Die mechanischen Eigenschaften dieser Materialien resultieren aus einem Wechselspiel verschiedener Mechanismen: Assoziation und Dissoziation der Partikelaggregate, Adsorption des Polymers auf den Partikeln und Desorption der Lösungsmittelmoleküle von den Partikeln sowie Brückenbildung zwischen den Partikeln durch lange Polymerketten.

## RÉSUMÉ:

Nous considérons dans ce travail des dispersions de particules dans des solutions aqueuses de carboxyméthyl cellulose. Les propriétés rhéologiques de ces fluides sont mesurées à la fois en écoulement de cisaillement permanent et oscillatoire. Nous présentons des résultats expérimentaux obtenus pour différentes concentrations en polymère et pour trois masses molaires différentes. L'argile considérée est une bentonite et sa concentration est fixée à 5 %. Les propriétés mécaniques de ces matériaux sont le résultat d'une compétition entre différents mécanismes : association et dissociation des agrégats de particules, adsorption du polymère sur les particules, désorption des molécules de solvant, pontage entre les particules par les longues chaînes de polymère.

**KEY WORDS:** carboxymethyl cellulose, bentonite, particle suspension, rheology, dispersions, viscoelasticity, aging

## 1 INTRODUCTION

The study of the rheological properties of suspensions of solid particles in complex fluid, is of great importance since these kinds of compounds are developed in a lot of applications in areas as different as the development of drilling fluid for oil recovery [1] or fiber science and technology [2]. For instance, dispersions of titanium

dioxide in foam may be used for coating of fabrics [3]. Another example is the introduction of clay particles in a polymer melt in order to improve the fire resistance of the fibers [2–4]. Many results offer a new promising way for flame retarding textiles with a permanent effect at relatively low cost and keeping the basic properties of the textiles [2]. Polymer-clay is very attractive due to the fact that small amount of

clay can lead to great improvement in many properties, such as mechanical, barrier or fire resistance of the polymer [5]. In recent developments, nanofibers and nanocomposites are obtained by electrospinning from polymer solutions with clay nanoparticles as fillers [6].

The characterization of the mechanical properties of clay/polymer nanocomposites is generally performed through linear viscoelastic oscillatory flow measurements [7–8]. The shape of the mechanical spectra may provide useful information on the global exfoliation of the particles and on the percolation threshold as it has been shown for clay/polystyrene nanocomposites [9]. In clay/polymer systems, the structures of the associations of particles are related to the clay/monomer interactions. Weak or stronger gels may be formed, depending on the degree of swelling of the clay galleries by the monomers. Under shear, these associations may break down and different mechanisms have been proposed to understand the rheological properties of such systems [9]. In polymer melts, the solid-like behaviour with no solid-liquid transition observed beyond a critical clay content, is attributed to an incomplete relaxation due to physical jamming or percolation [10–11].

The specific plate-like microstructure of clay is at the origin of different types of particle associations referred as face-to-face (FF), edge-to-face (EF) or edge-to-edge (EE) ones [12]. It depends on pH conditions. For sodium-montmorillonite/water dispersions, the calculation of the total energy of interaction shows a decrease of EF attraction at basic pH while FF associations seem to be predominant. Then, the gel-like structures are less stiff than in acid conditions [13].

Recently, the shear orientation of viscoelastic clay/polymer solutions (laponite/PEO-water solutions) was investigated by coupling classical rheological measurements with the birefringence techniques. This method shows that, when shear rate increases, firstly, particles orient in the flow, and then the polymeric chains are stretched and their anisotropy contributes also to the total birefringence [14]. These laponite/PEO-water solution model systems have been widely studied by different groups and provide useful elements for the comprehension of the microstructures depending on particle-particle and particle-polymer interactions. Daga et al. [15] obtained master curves for  $G'$  and  $G''$  by means of time-temperature and time-concentration superpositions. The competi-

tion between the PEO adsorption on laponite removing polymer from the solution and formation of bridging network may explain the results. Ageing effects are observed: the presence of PEO retards the gelation kinetics of laponite dispersions. The study of transient response to simple shear coupled with light scattering experiments [16] shows that, above a critical shear rate, there is rupture of the particles aggregates, inducing the formation of polymer-clay bonds. At high shear rates, the hydrodynamic forces are sufficient to break the network.

Baghdadi and Sardinha [17] discuss the microstructure depending on the pH and on the polymer length at a given ionic force. Different scenarios are proposed. At pH7, FE associations between particles lead to aggregates and/or percolated structure. With low molecular weight PEO, adsorbed polymer chains form like steric barrier, then breakdown of the structure. Long chains allow bridging between particles. The free chains remaining in the fluid cause a depletion attraction. At pH10, without polymer, FF aggregates dominate. During aging, diffusion of the particles is at the origin of rupture of the aggregates, leading to a higher effective volume fraction; if it is high enough, one observes an elastic behaviour similar to a colloidal glass one. Free chains in the fluid give a depletion force opposing to the homogenisation of the system which behaves like a viscoelastic liquid because of a lower effective volume fraction. High molecular weight polymers allow a gel structure caused by interparticle bridges. In oscillatory flow, in the linear viscoelastic (LVE) regime, the effect of long-term aging (up to 1000 days) has been examined for controlled pH and chain length [18]. The neat laponite dispersions (1–3 %w/w concentration) forms soft solids as aging and the mechanical spectra are in good agreement with the Soft Glass Rheology model [19]. At low polymer concentration, the response of the clay dominates while at high polymer concentrations, the response of the system is governed by the polymer one at high frequencies. This is due to the free chains in solution.

The elasticity of a fluid can be measured through the first normal stress difference  $N_1$  or from rod climbing. Contrary to dispersions in polymer melts, in polymer solutions, the increase of particle concentration leads to an increase of  $N_1$ . This effect, observed with dispersions of kaolinite in a Boger fluid (polyisobutylene-polybutene solution) is due to a screening effect of solvent on particles [20].

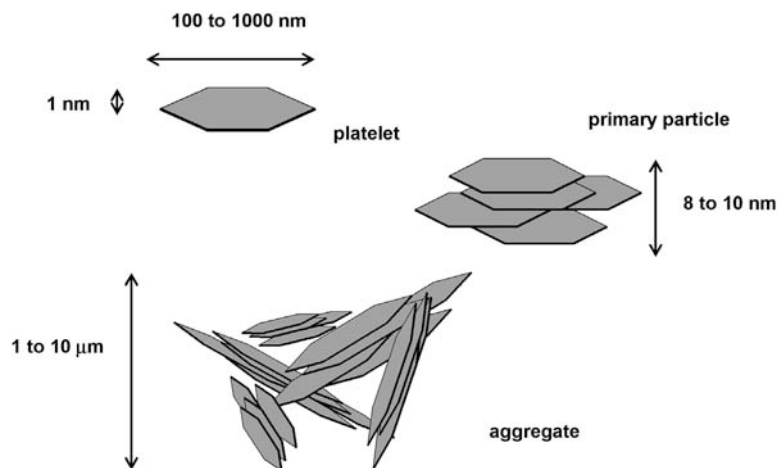
## 2 EXPERIMENTAL

### 2.1 COMPOSITION OF THE DISPERSIONS

Carboxymethyl cellulose (CMC) is a polymer derived from natural cellulose. CMC is a white granular substance soluble both in hot and cold water [21–22]. One of the most important properties of CMC is its ability to act as a thickener [22]. Characteristics which make it useful are: high viscosity at low concentrations, surfactant, and bulking abilities. They are not toxic and do not promote allergic reactions in humans [23]. CMC is used in textile manufacturing as a coating or a sizing agent. It is used in water-based drilling fluids [24]. CMC is also found in detergents, soaps, food products, thickeners, pharmaceuticals, and cosmetics.

Bentonite is a montmorillonite clay of the smectite group. Among its significant properties is its high swelling capacity [25], its ability to adsorb significant amounts of polymer on its surfaces, and the formation of a gel structure with yield stress and viscoelastic properties at low clay concentrations [12]. It is widely used as thickening agent and as key component in various industrial fluid formulations. Among its uses in civil engineering is the soil boring, or the control of the pollutants transport in the environment, and other industrial applications which include cosmetics, chemical, food products, or petroleum [26–27].

In water-based drilling fluids, where bentonite is a major component, CMC is appropriate to increase the stability of mud for drilling purposes and the viscosity of mud fluid as it stabilizes the aqueous suspensions of clay due to its high water retention. It maintains adequate flow properties at high temperature and salinity [22–26]. Montmorillonite is a layered silicate presenting a multiscale organization as shown on Figure 1 according to [9]. The interactions between various polymers and smectite layers have been investigated in detail in several studies. Nowadays, it is well established that, when a polymer is mixed with a clay suspension, the interactions lead to the adsorption of the polymer on the clay surfaces. This adsorption depends on the dimensions and the flexibility of the polymer molecule, which are closely related to its length. It may lead to desorption of solvent molecules from the surface [12].



### 2.2 PREPARATION OF THE SAMPLES

All the products used in this work are provided by VWR Prolabo France. For each mixture, the base CMC powder is firstly, dissolved in 100 g of demineralized water. The mass concentrations of the CMC aqueous solution range from 0.1 to 2.5 %w/w. Three different grades of CMC have been used, respectively named LV (Low Viscosity), MV (Medium Viscosity) and HV (High Viscosity) and corresponding to different molecular weights (90000, 250000 and 700000). After 24 h stirring of the CMC aqueous solution, bentonite powder is dispersed in the solution with a 5 %w/w fixed concentration. These bentonite/CMC solution mixtures are submitted to a continuous agitation during 48 h using magnetic stirrers. After that, the samples are kept at 20°C.

Tests are performed with two constant stress rheometers, AR2000 from TA Instrument and Rheoscope 1 from ThermoHaake equipped with cone-and-plate geometries (AR 2000: acrylic cone, 40 mm diameter, 2° angle; Rheoscope: steel cone, 35 mm diameter, 2° angle). Results obtained from both rheometers are equivalent. The temperature is kept to 20°C. Sample preparation and other parameters like temperature were controlled, because of their influence on the final state of suspensions, and thus on the rheological behaviour. All tests were carefully carried out under the same conditions to allow comparison of the results. The different samples will be named as it follows:

- Bn: Bentonite dispersion in water; concentration =  $n$  %w/w
- CMCnXV: Aqueous solution of CMC; concentration =  $n$  %w/w, XV = LV, MV, or HV
- CMCnXVB5: Bentonite dispersion B5 in an aqueous CMC solution CMCnXV (For instance, CMC1HVB5 means a 5% bentonite dispersion in a 1 % CMC HV aqueous solution).

Figure 1: Schematic representation of montmorillonite multiscale organization [28].

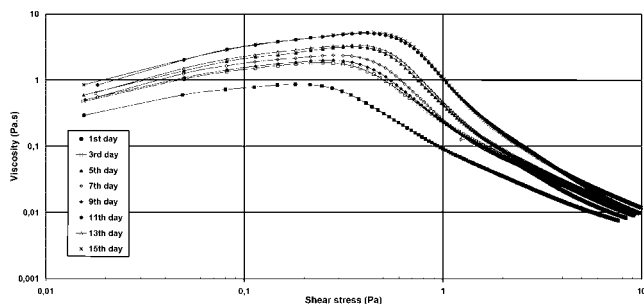
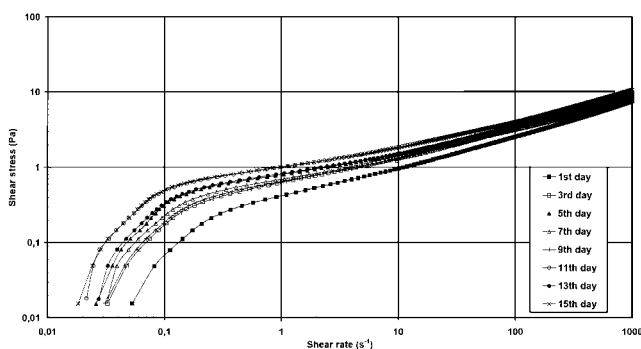
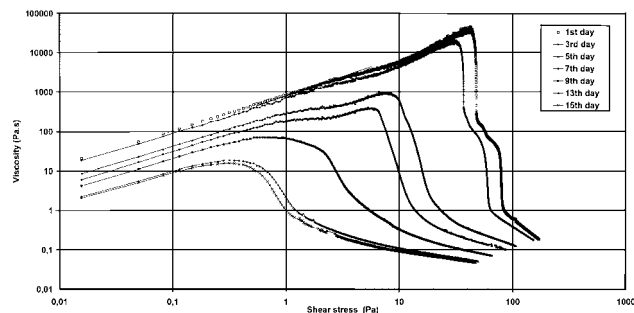
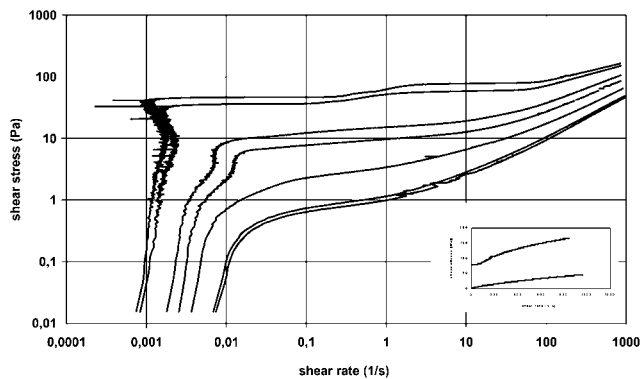


Figure 2 (left above): Rheograms for CMC1HVB5 : from top to bottom: 1<sup>st</sup>, 3<sup>rd</sup>, 5<sup>th</sup>, 7<sup>th</sup>, 9<sup>th</sup>, 13<sup>th</sup>, and 15<sup>th</sup> day. In the insert, linear scale plot for 1<sup>st</sup> and 15<sup>th</sup> day.

Figure 3 (right above): Viscosity versus shear stress for CMC1HVB5.

Figure 4 (left below): Rheograms for B5.

Figure 5 (right below): Viscosity versus shear stress for B5.

### 3 EXPERIMENTAL RESULTS

Rheological properties of dispersions of clay particles in aqueous solutions of carboxymethyl cellulose are measured in both permanent and oscillatory shear flows.

#### 3.1 PERMANENT SHEAR FLOW: AGING STUDY

Experimental results presented in this part, are obtained for polymer concentrations upper or equal to 1 %. Since the stress history of the sample is of great importance [29], experimental procedures have been precisely defined. Measurement protocol is determined in the following way: a pre-shear at 10 s<sup>-1</sup> constant shear rate, during 2 min to homogenize the fluid is followed by a rest of 10 min. After that, a rising continuous ramp with a 0.033 Pa/s slope is applied to the sample. The purpose of this study is to determine the equilibrium of fluids. During aging study of the dispersions the fluid is kept at rest throughout 24 h at constant temperature 20°C and then is gently stirred, each day during 1 hour before measurements [27]. The equilibrium is reached when the rheological properties of the fluid become identical, therefore, when the rheograms become overlaid. Required time to reach the equilibrium state for all concentrations seems to be 15 days. The pH is measured every

day. It ranges between 9 and 10 for all the samples and slightly decreases with aging.

Figure 2 shows the rheograms obtained on dispersion in an aqueous solution of CMC1HV. It displays, in the first day, the existence of an identified yield stress which tends to disappear as the dispersion in polymer solution is growing older. The same tendency is observed for the other concentrations and molecular weights of the polymer. The dispersions are shear-thinning. The ratio shear stress/shear rate defines the shear viscosity for fluid systems. It is plotted vs. the shear stress on Figure 3. The initial increase of the curve corresponds to stresses below the yield stress. A slope of the straight line equal to 1 is associated to a constant shear rate i.e. to a strain proportional to the time. Since the applied stress is a ramp, this leads to a strain proportional to the stress. This behaviour characterizes an elastic solid. In fact, the system behaves as an elastic network, like a gel. Above the yield stress, the systems flow and are shearthinning. The viscosity decreases as the suspension is older. The shape of the curves reveals that different mechanisms occur during the flow. They involve changes of the conformation of macromolecules, rupture of the network crosslinks, rupture of the aggregates and orientation of particles in the flow [14, 16, 30].

The suspension in water is a shear-thinning fluid, but the existence of a yield stress is not as clear as in the previous case (Figure 4). Nevertheless, from a log-log plot, it appears that the established flow occurs only above a critical stress whose value increases when the system is older. Contrary to the dispersion in the polymer solution, the general tendency is an increase of the viscosity of bentonite suspension in water by getting old as shown in figure 5.

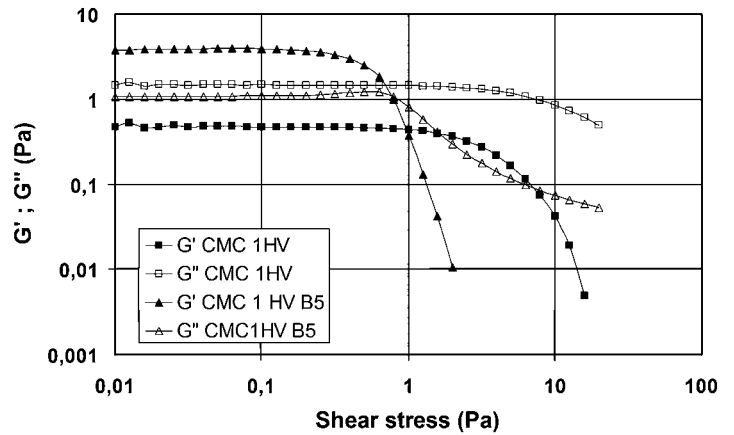
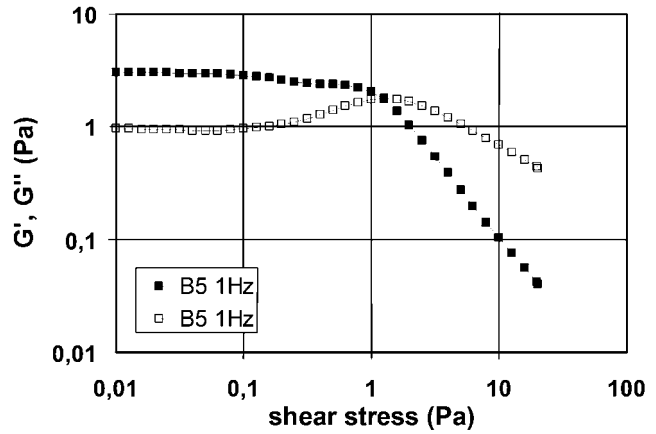
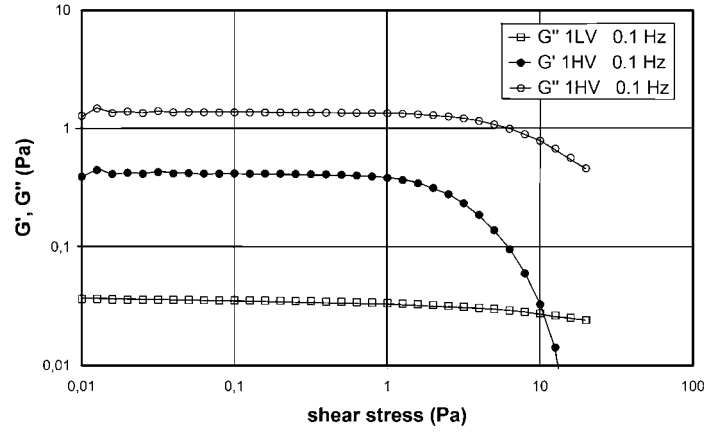
### 3.2 OSCILLATORY SHEAR FLOW

An alternative procedure for investigating the stability or the flocculation of dispersions is through viscoelastic measurement [12, 31]. Measurements of the elastic and viscous moduli  $G'$  and  $G''$  of the CMC aqueous solutions, bentonite/water suspensions and bentonite/CMC-water dispersions were made under oscillatory shear stress. Oscillatory experiments measure the response of viscoelastic materials to small-amplitude oscillatory shear at frequency  $\omega$  (rad/s). In oscillatory shear, the complex shear modulus  $G^*$  is defined as the ratio of the shear stress to the strain. The real and imaginary part of  $G^*$ , respectively  $G'$  and  $G''$  are respectively called the elastic modulus and loss modulus. The elastic modulus  $G'$  represents the elasticity of the material, and hence the solid-like behaviour. While, the loss modulus  $G''$  represents the viscous character, and consequently the liquid-like behaviour of the system. The phase angle shift (loss angle)  $\delta$  is defined by  $\tan\delta = G''/G'$ .

#### Stress sweep at a given frequency: determination of the linear regime

In oscillatory shear flow, a stress sweep at a given frequency gives information on the extend of the linear response domain of the material and also, on the degradation of its mechanical properties when the stress level exceeds some critical value. The determination of the linear region is done at frequencies 0.1, 1, and 10 Hz. The protocol used for sweeping, consists of pre-shear as similar as in permanent flow followed by a sweep versus shear stress in an interval of 0.01 to 20 Pa.

Figure 6 gives the result of the stress sweep for CMC aqueous solution for CMC1HV and CMC1LV, at 0.1Hz frequency. At this frequency,  $G''$  is larger than  $G'$ . The elastic modulus is negligible for the lower molecular weights. For the larger one (HV), the two moduli decrease for a shear stress of



about 1 Pa. Figure 7 shows the behaviour of bentonite dispersion in water. At low shear stress,  $G'$  and  $G''$  are independent of the shear stress and  $G'$  is larger than  $G''$  that means a predominant elastic behaviour. Then, one observes a slight decrease of  $G'$  while  $G''$  increases. Beyond a critical value of the shear stress (about 1.5 Pa), the two moduli sharply decrease and  $G''$  becomes larger than  $G'$ .

Figure 8 presents the comparison between a dispersion in a CMC solution and its continuous phase at the same concentration and the same molecular weight of polymer (CMC 1HV). For the dispersion, in the linear domain,  $G'$  is upper than

from top to bottom:  
Figure 6:  
 $G'$  and  $G''$  versus shear stress  
for CMC1LV and CMC1HV at  
0.1 Hz.

Figure 7:  
 $G'$  and  $G''$  versus shear stress  
for B5 at 1 Hz.

Figure 8:  
 $G'$  and  $G''$  versus shear stress  
for CMC 1HV and CMC  
1HVB5 at 0.1 Hz.

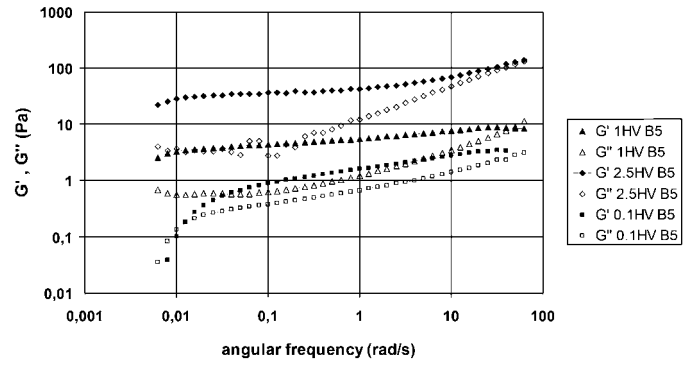
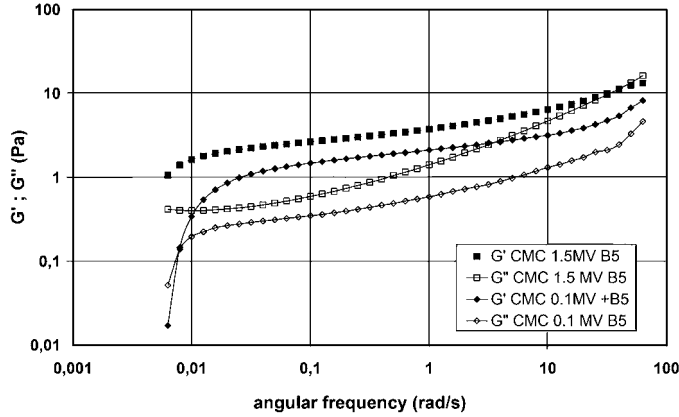
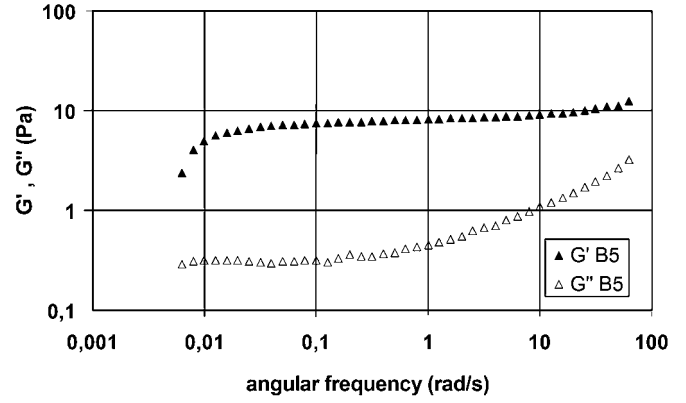
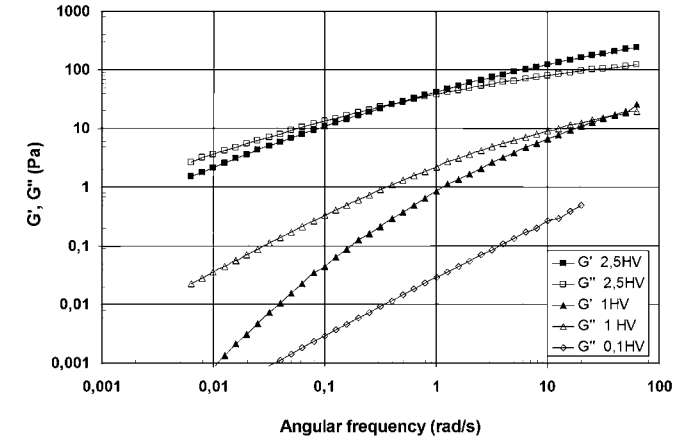


Figure 9 (left above):  $G'$  and  $G''$  versus angular frequency for CMC0.1HV, CMC1HV and CMC2.5HV.

Figure 10 (right above):  $G'$  and  $G''$  versus angular frequency for B5.

Figure 11 (left below):  $G'$  and  $G''$  versus angular frequency for CMC0.1MVB5 and CMC1.5MVB5.

Figure 12 (right below):  $G'$  and  $G''$  versus angular frequency for CMC HV B5 at different polymer concentrations.

$G''$ . Adding bentonite,  $G'$  become tenfold the elastic modulus of the polymer solution. Beyond about 1 Pa,  $G'$  monotonously decreases while  $G''$  slightly increases, becomes larger than  $G'$  and, then, decreases. This indicates the transition from a solid-like behaviour to a liquid-like behaviour. Beyond of this critical value of shear stress, the sample start to flow. Both moduli downfall; the viscous one predominates, and the elastic one becomes negligible. This is in good agreement with the flow curve (Figure 2).

A classification of the different possible large amplitude oscillatory behaviours has been proposed on the basis of a network model involving two parameters  $a$  and  $b$  defining respectively the creation and loss rates of junctions as the shear strain increases [32]. Four types of behaviours can be distinguished. Among of them, Type I corresponds to  $a < 0$  and  $b > 0$  i.e. the creation term decreases while the loss term increases. In this case, the two moduli  $G'$  and  $G''$  decrease when the shear strain exceeds a critical value. Type III is associated to  $a > 0$ ,  $b > 0$  and  $a < b$ : the creation and loss terms increase with the shear strain but the destruction rate is faster than the creation one. Then, above a critical value of the shear strain, a strain hardening of  $G''$  is observed, followed by a strain thinning while  $G'$  is strain thinning. According to this classification, the

curves related to the polymer solutions, with concentrations in the semi-diluted or concentrated regimes correspond to Type I network. The weak overshoot of  $G''$  observed in Figures 7 and 8 corresponds to Type III and can be explained by the balance between formation and destruction of the junctions [32].

### Frequency sweep in the linear domain

The protocol used for frequency sweep consists of pre-shear as similar as permanent flow followed by a frequency sweep from  $10^{-3}$  to 10 Hz. Shear stress amplitude is fixed at 0.02 Pa. The elastic modulus  $G'$  and the viscous modulus  $G''$  are reported in Figures 9 and 10 as functions of frequency, for CMC and bentonite. The polymer solution displays a classical behaviour of a viscoelastic fluid with a terminal region ( $G' \approx \omega^2$  and  $G'' \approx \omega$ ) in the low frequency range and an intersection point at a crossover frequency  $\omega_c$  (Figure 9). The moduli and the maximum relaxation time (given by  $1/\omega_c$ ) increases when the polymer concentration  $c_p$  increases. Then, the terminal region is shifted towards the lower frequencies which cannot be explored with the rheometer. For the lower concentrations i.e. in the dilute regime, the fluid behaves as a viscous one with  $G'' \approx \omega$  and  $G'$  negligible.

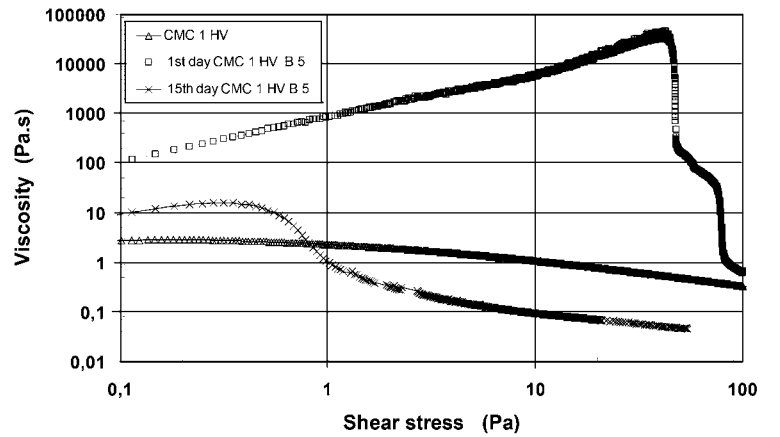
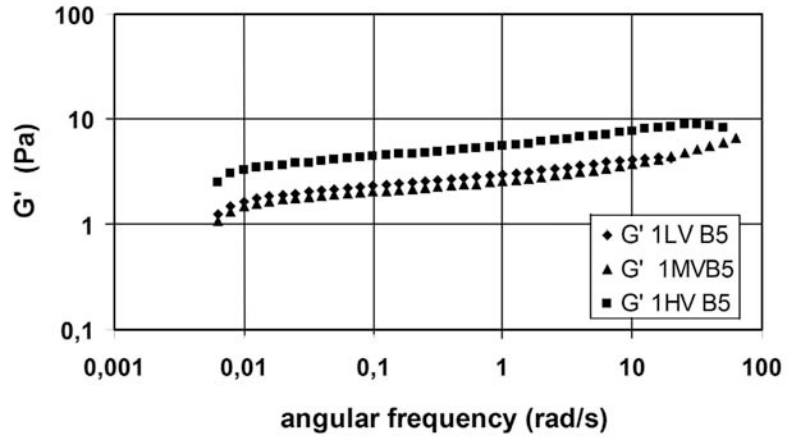
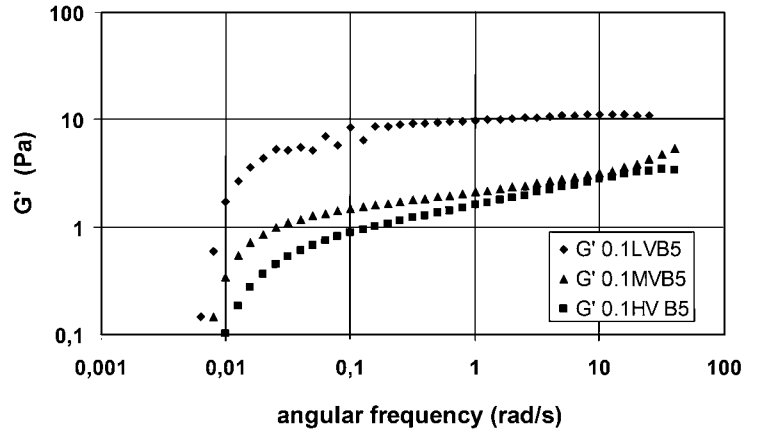
The dispersion B5 exhibit an elastic behaviour with a quasi-plateau modulus  $G'$  which is ten

to twenty fold  $G''$  (Figure 10). This gel-like behaviour is modified when the clay particles are dispersed in the polymer solutions. Figure 11, obtained for the dispersions in CMC0.1MV and CMC1.5MV, shows that  $G' > G''$  except at low and high frequencies.  $G'$  slowly increases with the frequency and with the polymer concentration (Figure 11). One can conjecture from Figure 11 that there are two intersection points of  $G'$  and  $G''$  curves for two characteristic frequencies  $\omega_{c1}$  and  $\omega_{c2}$  related to two relaxation times  $\tau_1$  and  $\tau_2$ . As  $c_p$  increases, these intersection points are shifted towards lower frequencies, resulting in an increase of the relaxation times. The comparison between Figures 9 and 12 shows that the viscoelastic character of the suspending medium is modified by the addition of particles and the material tends to act as an elastic gel when the polymer concentration increases. In the interval  $[\omega_{c1}, \omega_{c2}]$   $G'$  becomes predominant even for the lower polymer concentrations. For 0.1HVB5, the evolution of  $G'$  and  $G''$  with the frequency is quasi parallel with a slow increase like  $G' \propto \omega^\alpha$  and  $\alpha = 0.2$ . When  $c_p$  increases, the exponent  $\alpha$  decreases and  $G'$  tends to a plateau while a minimum of  $G''$  appears. That means a stronger gel.

Comparing to B5 system, as  $c_p$  increases, the moduli increase and become larger than for B5, due to the contribution of the polymer. But the elastic character of the fluids is less marked as in the plateau region,  $G'$  is approximately  $25G''$  for B5,  $2.5G''$  for 0.1HVB5 and  $10G''$  for 2.5HVB5. The influence of the molecular weight of the polymer depends on the polymer concentration. Figure 13 represents  $G'$  for  $c_p = 0.1\%$ . One can observe that the elastic modulus is larger for the lower molecular weight. It is the contrary for  $c_p = 1\%$ : in this case, HV corresponds to higher values of  $G'$  (Figure 14). This gives information on the different natures of the networks involved.

#### 4 DISCUSSION AND CONCLUSION

This work allows the comparison of rheological properties of suspensions of solid particles in water and in viscoelastic aqueous polymer solutions. Clay particles have a particular structure since they are constituted of platelets, layered to form primary particles, aggregated together (Figure 1). During the study of aging, the value of pH, for all the suspensions, is in the range 9 - 10. The pH only slightly decreases in the course of



aging. These values indicate predominant Face to Face type associations with a great ability to trap more water between layers [12 - 14]. Previous works from the laboratory [33], showed that when CMC is mixed to montmorillonite suspensions, the polymer coats the clay particles and prevents the reorganization of the agglomerates by the usual mechanisms (face-to-face connections). In this case, the rheological behaviour of the CMC/bentonite suspensions depends on the structural state of the polymer. Clearly, the effect of aging is not the same for dispersions in water and in polymer solutions.

from top to bottom:  
Figure 13:  
 $G'$  and  $G''$  versus angular frequency for CMC HV, MV, LV B5 ( $c_p = 0.1\%$ ).

Figure 14:  
 $G'$  and  $G''$  versus angular frequency for CMC 1HVB5, 1MVB5, 1LVB5.

Figure 15:  
Viscosity versus shear stress for CMC1HV and CMC1HVB5 at 1<sup>st</sup> and 15<sup>th</sup> day.



In water, there is probably a dissociation of the aggregates and perhaps a partial exfoliation of the clay particles leading to the formation of an open tri-dimensional structure with an elastic behaviour as it can be seen from oscillatory measurements. In the polymer solution, at the beginning of the aging process, a yield stress can be determined especially in the case of high polymer concentration and/or molecular weight. Along aging, this yield stress tends to disappear and the system becomes more fluid. Initially, large aggregates are present in the dispersion. The stirring of the sample every day would lead to the rupture of the aggregates in smaller ones while the penetration of the macromolecules within these aggregates becomes easier together with their adsorption on the clay particles. For a young system, the shape of the curve of Figure 3 means that different mechanisms successively occur to explain the sharp decrease of the viscosity [30, 34]. There is probably formation of a thin depletion layer in the vicinity of the solid surfaces of the rheometer geometry which acts as a lubrication layer. As the shear stress increases, the rupture of the large aggregates induces a further fall of the viscosity. Then, the orientation of the particles and the conformation change of the macromolecules in the flow takes place leading to a shear thinning behaviour.

Rossi et al. [12] explain that, a consequence of the adsorption of polymer on the particles is the desorption of solvent molecules from the surface of particles and water molecules may be transferred from the surface to the bulk. In the equilibrium state, the system does not consist of large bentonite aggregates dispersed in a polymer solution but of small aggregates coated by polymer in a less concentrated polymer solution. This argument combined with the existence of the depletion layer could explain the Figure 15 where the viscosity of CMC1HVB5 is smaller than CMC1HV.

The oscillatory measurement in the linear domain (i.e. in the limit of low shear stresses) characterizes the structure not perturbed by the flow. The addition of particles in a low polymer concentrated solution leads to a rise of the moduli (Figure 12) by two order of magnitude for  $c_p = 0.1\%$ . While for  $c_p = 2.5\%$ , the order of magnitude of the moduli is the same than for the polymer solution but the shape of the mechanical spectra is different. In the first case  $c_p = 0.1\%$ , corresponding to a dilute/semi-dilute regime, the polymer chains connect the particles and aggregates and an elas-

tic network is formed. For low molecular weight chains (LV on Figure 13)  $G'$  is much larger than for HV. The exfoliation is not cancelled by the presence of polymer and there is probably a combination of the effect observed for B5 and the crosslinks formation due to the presence of the polymer. When  $c_p$  increases, in the semi dilute/concentrated regime, the mechanical properties of the network is mainly controlled by the macromolecular chains and the elastic modulus increases with the molecular weight (Figure 14).

In some systems in polymer melts, the absence of terminal zone is related to incomplete relaxation due to physical jamming with a solid-like behaviour, because of the mesoscopic structure of highly anisotropic clay tactoids [10, 35]. From our mechanical spectra, the behaviour appears to be that of physical viscoelastic gels, with a terminal zone shifted towards lower frequencies as polymer concentration increases, corresponding to longer lifetimes of network junctions. The mechanical behaviour of the systems bentonite/aqueous polymer solutions considered here is the result of a competition between different mechanisms:

- Association-dissociation of aggregates of particles
- Adsorption of polymer on the particles and desorption of solvent molecules from the particles
- Bridging of the particles by long polymer chains

Then, different kinds of elastic networks may be formed which are destroyed when the shear stress exceeds some critical value, leading to the flow of the systems.

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