

Influence of the adsorption of non-ionic polymer on the rheology and stability of montmorillonite clay suspensions

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Abstract : *In this article, we showed the influence of the non-ionic polymer, polyethylene oxide (PEO) of molecular weight 6×10^3 g/mol and 2×10^5 g/mol on the rheological properties of the montmorillonite clay, bentonite suspensions. The PEO presents an affinity for the bentonite particles gradually coated the particles, and affects their kinetic aggregation. The reduction of clay particle-particle interaction took place until steady values of the yield stress. The stability of the suspension was enhanced with increasing polymer adsorption. The influence of this additive was investigated in terms of viscosity, yield stress, loss and elastic modulus which are principal characteristics of the drilling fluids. The analysis by X-rays diffraction also allowed understanding the rheological behavior of the mixture bentonite-PEO. Indeed, the PEO can adopt diverse possible mechanisms: adsorption on the surface of particles, intercalation between the platelets of clay or favouring flocculation by forming bridges between particles.*

1. Introduction

The bentonite suspensions are fluids which the particularly complex rheological properties [1] are at the origin of various industrial applications. We find them in particular as agent of texture in cosmetics, as mud of drilling in the petroleum industry or acting as waterproofness in the civil engineering. These colloidal suspensions of clay are in the microscopic scale, the seat of fluctuations in position, in orientation and eventually in form. The structure of these systems may adopt much diversified dynamic states of organization in equilibrium and under shear.

Because of its extensive swelling in water, it forms a gel-like structure at relatively low concentrations [2,3] due to the expansion of the clay platelets when saturated with Na^+ or Ca^{2+} ions [4].

In the drilling fluid with water (aqueous solutions of clays and polymers), the clay is a texturing product and viscosifiant which is associated with polymers to allow the drilling fluid to assure the multiple functions: transport the cutting on surface, suspend the cutting when circulation of the drilling fluid is stopped, lubricate and cool the tool etc...

The influence of the interactions on the rheological properties was large studied in systems as the drilling fluids or model fluids [5-7]. Indeed, nanoparticles component of these suspensions, present a very important ratio surface on volume which should increase in theory, all their physical properties (viscosity, yield stress, elastic and loss modulus). In the case of clays, which are constituted by nanoplatelets in charge, we would have the possibility of having a gel of the mixture and thus a raised yield stress. Unfortunately, the dispersal of these platelets is problematic and the obtained properties are mediocre. So numerous research works, concern the improvement of the properties of these clays by addition of additives (polymers) [8-10], to adapt the composition of the fluid to drilling conditions and make a successfully operation.

The scope of the present paper is to provide a complete and comprehensive rheological investigation of bentonite-polyethylene oxide (PEO) system, in particular investigating the influence of this additive on the structure behavior of bentonite suspensions via the viscosity, the yield shear stress of flow, the loss and the elastic modulus which are the main characteristics of water-based drilling fluids. To reach this objective, the rheometry and analysis by X-rays diffractions are used.

2. Experimental methods

The materials used were calcic bentonite (B3378) clay, polyethylene glycol (PEG) and polyethylene oxide. Bentonite is average composition is (% mass): SiO₂-48.35, Al₂O₃-12.15, Fe₂O₃-8.26, CaO-6.68, MgO-5.47, Na₂O-3.65, K₂O-2.39. It possesses a specific surface of 39.3 m²/g, a capacity cationic exchange of 0.88 meq/g, pH=9 and a density of 2,4 g/cm³.

For PEG or PEO which is non ionic polymer of the polyether's family, we selected the molecular weight equal to 6x10³ g/mol and 2x10⁵ g/mol. They respectively possesse a number monomer/chaine 136 and 4545, volumic mass 1173 kg/m³ and 1210 kg/m³, radius gyration 30 Å and 247 Å.

For the preparation of the complex (water-bentonite-PEO), the experimental protocol is the following: in the quantity of demineralised water, we add the bentonite. After 6 hours of agitation, the PEO is introduced into the basic bentonite suspension (6%). The homoge- genization is obtained by magnetic a glass-rod during 48 h. Before making the rheolo- gical measures, every sample is mixed during 45 minutes. To obtain a very well repro-ducibility of the measures, all the samples are subjected, to the same mechanical story (preshear of 15 Pa for 1 minute, followed by a rest of 5 minutes under geometry).

The type of experiment consists in determining the flow curves in simple shear and kinetic structure of gel to different suspensions by rheometer SR-5000 with controlled stress and coaxial cylinder (diameters 32/29.5 mm and high 44.3 mm). By being interested in interaction particles-additives, we coupled with the rheological measures, the analysis by X-rays diffraction realized on Inel XRG-3000.

3- Results and discussions

3.1- Simple shear

In the presence of the polymer (PEG or PEO), the rheological behavior of the bentonite suspension is practically shear-thinning with yield stress (fig. 1 and 2). However, the polymer provokes the decrease of the yield stress of the mixture, even the disappearance of this last one for high concentrations of polymer (τ_c is determined by the intersection point for the first slope with the second slope of the curve in fig. 1 and 2).

The addition of the polymer in the bentonite suspension allows the progressive covering of the bentonite particles, so reducing the interactions particle-particle and favouring the interactions particle-additive [11]. A light reduction of yield stress (τ_c) is observed when the quantity of polymer on the surface increases. This last effect is due to the increase of the continuous phase of the viscosity by the presence of the polymer. Similar observations were reported by Rossi and al. [12,13] on the suspensions of Na+montmorillonite (5%) in the presence of non ionic polymer (PEG-4000). It means, that the presence of the Polymer decreases the interaction between the particles of clay (rigid) for the benefit of the interactions particles-additive (less rigid) which indeed explains the drop of τ_c .

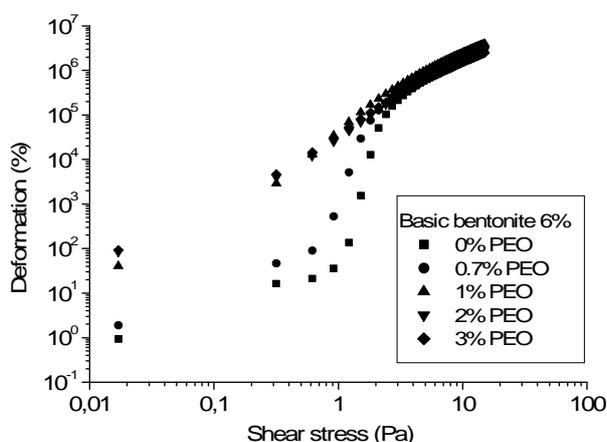


Figure 1 – Deformation as a function of yield stress for mixture bentonite-PEG-6000 suspension.

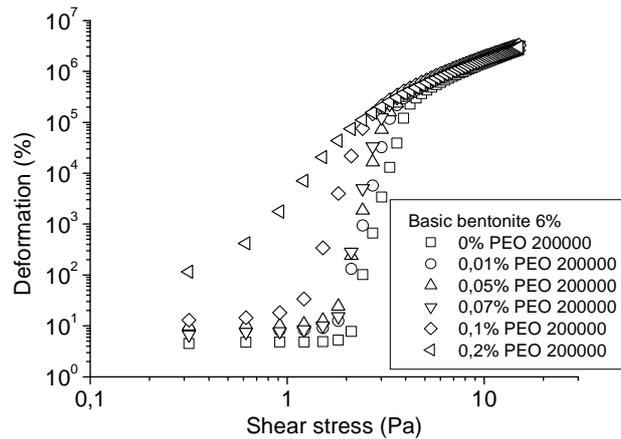


Figure 2 – Deformation as a function of yield stress for mixture bentonite-PEO-200000 suspension.

Besides, we also notice that the quantity of polymer necessary to reduce the yield stress of the bentonite suspensions was very low for PEO (2×10^5 g/mol.) to compared with PEG (6×10^3 g/mol.) Indeed, 0,01% concentration for PEO 2×10^5 g/mol. against 0,7 % concentration for PEG 6×10^3 g/mol.

3.2- Dynamic shear

The tests of sweeping in frequency (fig. 3 and 4) and kinetic structure (fig. 5 and 6) were made to understand the behavior of the complex bentonite-PEG and bentonite-PEO suspensions.

3.2.1. Frequency sweep

After four hours of rest under the geometry, so that the suspensions can reach their equilibrium state, essays of sweeping in frequency revealed that the elastic modulus (G') are superior to the loss modulus (G'') for all the concentrations. It is concerned about the viscoelastic solid behavior (fig. 3 and 4). However, moduli G' and G'' for mixtures always remain lower than the modulus of basic suspension (6% bentonite). That explains the reducing effect of the PEO on these moduli. Besides, we notice that G' is independent from the frequency while the loss modulus increases in high and low frequency.

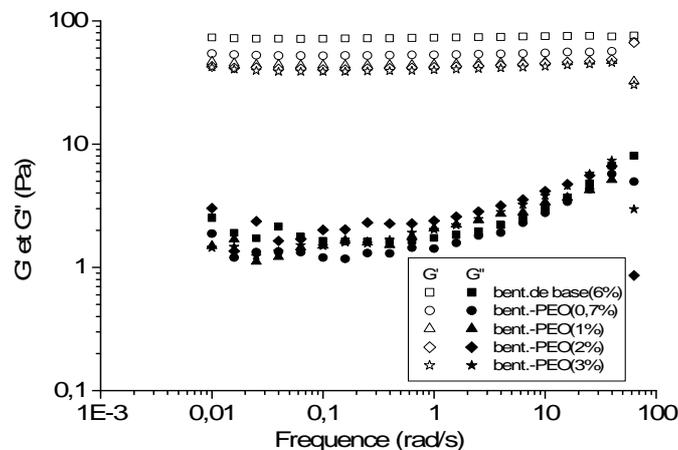


Figure 3- frequency sweep the bentonite-PEO 6000 suspensions.

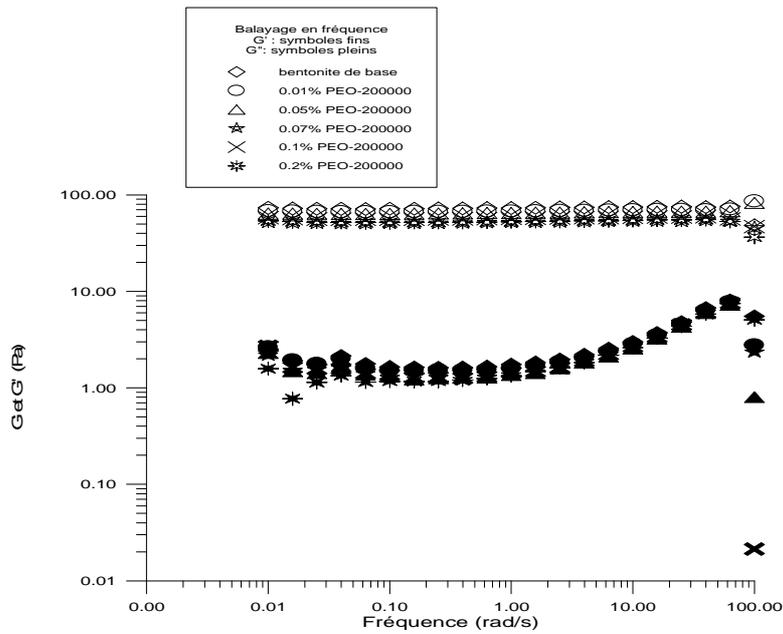


Figure 4- Frequency sweep of bentonite-PEO 200000 suspensions.

3.2.2- Time sweep

In dynamic state, elastic (G') and loss (G'') moduli – time sweep was applied, to highlight the influence of the concentration in PEO on the kinetic of gel to each mixture suspension. Measures of the temporal evolution of elastic and loss modulus (at $\omega=1$ rad/s) for very low deformations (0,5 Pa determined from the stress sweep to highlight the domain of the linear viscoelasticity) were recorded for eight hours in average (fig. 5 and 6). We notice that the most diluted system gels the least fast.

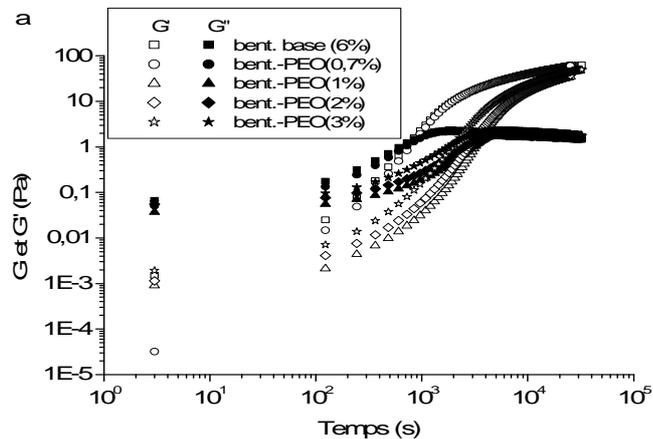


Figure 5- Time sweep of the bentonite-PEO 6000 suspensions

The table 1 shows the evolution of the time gel while just as $G' = G''$, criterion was usually used because of its ease to estimation [14] as a function of the concentration for the bentonite-PEO mixture. This time gel always remain superior to that of the basic suspension for the bentonite in the presence of the PEO 6000, everything to go by an optimum corresponding to the critical concentration (1%). Consequently, we can say that the PEO-6000 slows down the kinetics of aggregation of the system [9,15]. Recently, similar studies on the laponite suspensions of in the presence of PEO of low molecular weight were obtained by Mongondry and al. [16].

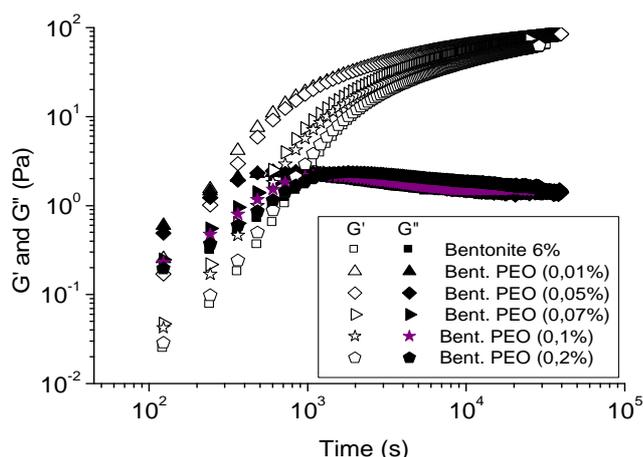


Figure 6- Time sweep of the bentonite-PEO 200000 suspensions.

Table 1- Time gel and viscoelastic moduli of the bentonite-Polymer mixture.

Samples		Gel Time (s)	G' = G'' (Pa)
6% Bentonite +	0% PEG or PEO	800	1.4
	0.7% PEG-6000	843	1.31
	1% PEG-6000	3363	1.2
	2% PEG-6000	3004	1.27
	3% PEG-6000	2163	1.33
	0.01% PEO-200000	220	1.29
	0.05% PEO-200000	265	1.35
	0.07% PEO-200000	484	1.39
	0.1% PEO-200000	527	1.4
	0.2% PEO-200000	723	1.42

On the other hand, for bentonite suspensions in the presence of the PEO 200000, the time gel always remains lower for all the concentrations to compared with the basic suspension (6% bentonite). The elastic modulus G' also increases with the concentration in polymer by favoring the interaction of polymer-polymer to the interaction particle-polymer.

3.3. Discussions

Towards the previous results, there are then two observed characteristic rheological behaviors: the first one is that corresponding to the concentrations lower than 1%, where the particles of clay do not interact between them directly or by intervention of the polymer. The electrostatic repulsion being strong, the PEG is chosen then between one or several of the particles by adsorbing without being able to bridge. In that case, the PEG allows stabilizing the particles of clay. The second behavior, beyond the critical concentration where the time of gel decrease without exceeding that of the basic suspension (800s). We can think that there is possible appearance of the phenomenon of bridge between the particles of clay which favours system flocculation while increasing the concentration of the polymer. These chains of polymer adsorbed on the surface of the particle can interact with those which are in solution. Also, if the chain is long enough and the saturation of particles is not reached, they can adsorb on several particles at the same time (we pass then to a state where particles are suspended by the chains of polymer as long as the saturation of particles is not reached).

Concerning the PEO-200000, the time gel increases with the concentration in polymer. We can envisage the following scenario: when the PEO is in low quantity, the interaction between bentonite particle and the chains of PEO limits itself at the same time in phenomena of adsorption and bridge of bentonite particles. Indeed, the kinetics of structure at this moment is very fast (see table 1) but by having a low elastic modulus (few bentonite particles are bridged). On the other hand, as the concentration in PEO-

200000 increases and thus the quantity of available polymer in solution is more important, it pulls two possible mechanisms in competition: On one hand, the adsorption and the bridge of bentonite particles and on the other hand, an aversion by steric effect between the chains of polymers (no mess because the polymer is the same nature, but possibility to bridge several bentonite particles). So, the kinetic structure of the system bentonite-PEO is delayed but this time with a more important of elastic modulus (because there were enough of bridge bentonite particles). Similar results were obtained by [Isci and al. \[17\]](#), where the authors bring back that the adsorption of the polyvinylalcohol (PVA), a neutral polymer by the surfaces of calcic bentonite particles change the charges distribution of the electrical layer double. So, the rheological properties and the stability of the suspensions can be adjusted by varying the concentration of the PVA in the system.

In summary, the hydrodynamics behavior of a polymer in a suspension depends on interactions polymer - particles, but it is also linked to the interactions polymer - polymer from a certain concentration. This critical concentration is called geometrical covering of concentration c^* , it bounds two domains of concentrations: diluted and semi-diluted [\[18\]](#). The semi-diluted regime can divide itself there two under regimes: no tangle and tangle [\[19\]](#).

In diluted solutions ($c \ll c^*$), every macromolecule is considered as isolated and the interactions between the polymer and the solvent are dominating. The interactions between chains of polymers are minimized and the macromolecule extends at the maximum.

On the other hand, for more concentrated solutions, tangle of molecules appear and the interactions polymer-polymer become dominant. In this case, the solution is called semi-diluted and the concentration is superior in c^* . When polymers are the same nature, we shall have rather aversion by steric effect. Polymers push away and are mutually excluded the space which they fill. Should the opposite occur, the interactions are essentially attractive and polymers incur mutually and fasten.

The change of rheological behavior of the suspensions observed on the previous figures could be due to the microstructural relations between the polymer chains and the clay particles. Indeed, the non ionic polymers can coat the particles of clay or can insert between the layers of particles clay [\[6,20\]](#). An analysis by X-rays diffraction could specify the nature of this rheological behavior.

3.4. Analysis by X-rays diffraction

To understand better the rheological behavior of the complex bentonite-polymer, we made an analysis by X-rays diffraction (XRD) of our samples, dried in the ambient temperature under hood, on the Inel XRG-3000 using a radiation CuK filtered by iron (source 40 kV and 20 mA). It had revealed the d-spacing of the (001) peak following:

Samples	6% benonite +					
	0	0.7	1	2	3	-
Concentration of PEG (%)	0	0.7	1	2	3	-
d-spacing (001) peak (Å)	11.80	13.83	14.03	17.57	17.57	-
Concentration of PEO (%)	0	0.01	0.05	0.07	0.1	0.2
d-spacing (001) peak (Å)	11.80	12.09	12.62	12.09	12.51	12.8

We can notice an increase of the interfoliar distance by the bentonite-PEG system. By being careful and by taking into account rheological results, we can think that the molecules of POG-6000 adsorb and diffuse in the interfoliar space by the presence of the water (layer double) and to the ionic exchange [\[21\]](#). This diffusion is possible because the molecular dimension of the polymer is nearby of the interfoliar space. The mechanism envisaged possible is the following: for low concentrations in polymer ($\leq 1\%$), the adsorbed chains will have a flattened configuration so that the polymer does not exceed the Debye length of the particle. In that case the electrostatic repulsion will continue to impose the stability of the system. If we increase a little the concentration in polymer ($> 1\%$), the conformation flattened by chains is not possible because the number of adsorbed polymer increase. The thickness of polymers on the surface of the particles of bentonite becomes then superior to the Debye layer where the electrostatic repulsion quickly loses of their strength. So the particles bridge probability by a chain of polymer becomes much stronger as well as the surfaces are not saturated in polymer; what involves the flocculation of the suspension (the d-spacing is practically stable, while the time of gel decreases).

For the bentonite suspensions in the presence of the PEO 200000, the molecular dimensions are very big to be able to skip into the interfoliar space [22-24]. The only solution is an adsorption of the macromolecules PEO 200000, on the surfaces of clay particles hydrated or favouring flocculation by forming bridges between particles by engendering a systematic flocculation.

4. Conclusion

In this paper, the influence of polyethylene glycol and polyethylene oxide of molecular weight respectively 6×10^3 g./mol and 2×10^5 g./mol and shear rate on rheological properties of bentonite suspensions is studied. The obtained results show that the polymer presents an affinity for the bentonite particles and reduce the yield stress of flow and the viscoelastic moduli.

The analysis by X-rays diffraction also allowed understanding the rheological behavior of the mixture bentonite-polymer. Indeed, this polymer can adopt diverse possible mechanisms: PEG can adsorb on the surface of the bentonite particles, intercalate between the platelets of clay on the other hand, the PEO can adsorb on the surface of the bentonite particles or favouring flocculation by forming bridges between particles but cannot diffuse in the interfoliar space seen its molecular weight (important molecular dimension).

Concluding, the non-ionic polymers gradually coated the clay particles for a suspension, the reduction of particle-particle interaction took place until steady values of the yield stress. The stability of the suspension was enhanced with increasing polymer adsorption.

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