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RESEARCH ARTICLE

Effect of Polyethylene Oxide on the Rheological Behavior of Bentonite Suspensions

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ABSTRACT

The effect of Polyethylene Oxide (PEO) with a molecular weight 10000g/mol on the rheological behavior of bentonite suspension was examined in terms of viscosity, yield stress and viscoelastic modulus (G' and G''); characteristic of complex behaviour of montmorillonite in water. A Physica MCR301 rheometer has been used to measure the rheological properties of samples (6% bentonite) as well as bentonite-PEO mixtures at different concentrations of PEO (0.18%, 0.25%, 0.5% and 1%). The polyethylene oxide adsorbs onto clay particles, which changes their basic characteristics depending on the amount of PEO adsorbed.

INTRODUCTION

The bentonite clay is widely used in industrial sectors (chemicals; cosmetics; pharmaceuticals; petroleum industry). The Optimization of the process and the quality of the finished product are closely linked to the rheological behavior of suspensions; these rheological properties strongly depend on the interactions that can be established at the microscopic level between anisotropic particles dispersed in aqueous media. The influence of interactions on the rheological properties of bentonite suspensions was widely studied [1-5]; this interaction forces such as the vander Waals forces are responsible for the formation of flocs and aggregates which gives to the structure a rigid appearance (gel formation) which influences the flow properties; since the viscosity of the suspensions will depend on the flocs size and shape.

The PEO put in the suspension presents an affinity for the bentonite particles and affects its rheological properties by changing the flow shear stress; the conservation and loss viscoelastic modules. In fact; this additive can adopt several mechanisms following its nature; its molecular weight and its concentration: adsorb on the bentonite particles; diffuse in the interfoliar space and bridge the clay particles engendering a systematic flocculation [6,7]. Have shown that the addition of PEO-4000 on suspensions of Na + montmorillonite (5%) allow the gradual recovery of the particles of bentonite thus reducing interactions particle-particle and promoting interactions particle-additive which affects the viscosity and the yield stress (decrease) of the bentonite suspensions. Other work on PEO 6000 and PEO200000 has shown that the PEO influences the gelation kinetics of bentonite suspensions it can slow it down or speed it up depending on the concentration and molecular weight of the polymer added [8,9].

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EXPERIMENTAL

Materials

The clay used in this study is a sodic bentonite its chemical formula is: $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$; had a pH = 9 and a density of 2.4g/cm³. the chemical composition of this bentonite is given in the (Table 1).

The polymer used in this work is Polyethylene Oxide (PEO); nonionic polymer of the polyether's family; having the chemical formula: $\text{HO}-\text{CH}_2-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_2-\text{OH}$ with a molecular weight of 10^4 g/mol.

The ethylene units ($\text{CH}_2 - \text{CH}_2$) constitute the hydrophobic parts of polymer and the oxygen atom forms the hydrophilic part of PEO. This arrangement hydrophilic-hydrophobic is responsible for the particular properties of the polymer; particularly its solubility in water.

Both of bentonite and PEO are obtained from Sigma Aldrich Company

Samples Preparation and Rheological measurements

The bentonite-PEO preparations were performed by adopting the following experimental protocol: to the predetermined quantity of distilled water; the mass of bentonite (6%) was intimately added first. After 8 hours of stirring; the polyethylene oxide corresponding to the desired concentrations (0.18%; 0.25%; 0.5% and 1%) is introduced in the basic bentonite suspension. Homogenization is obtained by stirring for 24 hours.

The rheological measurements were performed by using a Physica MCR301 rheometer; equipped with a coaxial cylinders geometry ($R_1=13.325$; $R_2=14.4645$; with gap length $L=39.997$) it has a peltier temperature control system which allows us to set the temperature during the tests.

To remedy the problem of water evaporation; a cell was used to keep our samples in a moist atmosphere.

Before performing the rheological measurements; each sample is stirred to obtain a homogeneous suspension. To ensure good reproducibility of the measurements; all samples studied are subject to the same mechanical history.

The steady state test consists to apply a rising ramp of shear rate (0.01 to 1000 s⁻¹) for bentonite sample alone and bentonite-PEO suspensions.

To make the connection between the suspension structure and its rheological behavior; we performed tests in

shear stress sweep (for $\omega = 10$ 1/s) and frequency sweep (for $\tau = 0.15$ Pa).

To see the influence of the concentration of PEO on the gelation kinetics of our blend samples; measures of the temporal variation of the viscoelastic moduli G' and G'' for mild conditions were performed ($\tau = 0.15$ Pa; $\omega = 10$ s⁻¹).

RESULTS AND DISCUSSION

Flow curve of bentonite -PEO mixtures

The rheological behavior of the basic bentonite suspension (6%) and bentonite-PEO mixtures at different concentrations of PEO remain shear-thinning with yield stress (Figure 1). However; the PEO causes a decrease in viscosity and yield stress of mixtures which exceeding 0.25% of PEO

In this study; the Herschel-Bulkley model [5] is used for the correlation of experimental results in simple shear:

$$\tau = \tau_c + k\dot{\gamma}^n$$

where τ is the shear stress (Pa) and $\dot{\gamma}$ is the shear rate (1/s) and the rheological parameters of the model to identify are: τ_c yield stress (Pa); the consistency k and n index of flow (Figure 2).

The evolution of rheological parameters (τ_c and k) as function of PEO concentration; is illustrated in (Figures 3a,3b).

The addition of PEO in the bentonite suspension allowing the progressive recovery of bentonite particles by the polymer there by reducing particle-particle interactions [6,7]. Beyond a critical concentration of 0.25% PEO; the additive-particle interactions (which are less rigid than the particle-particle interactions) increase which explain the decrease of the viscosity (same with k) and the yield stress.

Effect of PEO on thixotropic behavior of bentonite

Shear stress and frequency sweep tests: (Figures 4,5) illustrate the evolution of the two moduli G' and G'' of bentonite - PEO samples as a function of shear stress and frequency.

The results obtained revealed that the storage modulus G' 'are greater than the loss modulus G'' ' for every concentration of PEO; it is the viscoelastic solid behavior [8,9]. Any time the modulus G' and G'' of mixtures are still higher than basic bentonite (6%).

Kinetic of structure: Measurements of the temporal variation of viscoelastic moduli G' and G'' for low stress

Table 1: Chemical analysis of bentonite.

Chemical Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂
Concentration %	61.55	21.69	3.80	1.43	2.28	1.82	0.35	0.16

Figure 1 Flow curves for bentonite- PEO mixtures at different concentrations of PEO.

Figure 2 Prediction of flow curves for bentonite- PEO mixtures by HB model.

Figure 3 Evolution of the rheological parameters of the Herschel-Bulkley model as function of PEO concentrations. a) Yield stress. b) Consistency k .

Figure 4 Elastic and loss modulus shear stress sweep as a function of PEO concentrations ($\omega = 10$ 1/s).

Figure 5 Elastic and loss modulus frequency sweep as a function of PEO concentrations ($\tau = 0.15$ Pa).

were performed; (Figures 6,7) shows results obtained. An evolution versus time of the viscoelastic modulus mixtures was recorded. It is found that the bentonite-PEO suspensions have two rheological behaviors: the first corresponds to samples with concentrations of PEO less than the critical one (0.25%) where a decrease in gel time has been observed (faster gelation depending on the concentration of PEO). A second concerns mixtures with PEO concentration greater than the critical (0.25%) where a slowing of the kinetics of gelation has been observed (Table 2).

We can interpret this behavior by the PEO adsorption mechanism on the bentonite particles. Previous work carried out on bentonite -PEO systems; [10-13] studied the influence of several parameters on the adsorption.

Isici and al [14-19] conducted a study on the adsorption of a nonionic polymer on bentonite particles. The polymer

is polyvinyl alcohol (PVA) added at different concentrations. These authors reported that the adsorption of PVA on the surfaces of clay particles changes the load distribution of the electric double layer. Thus the stability and rheological properties of clay suspensions can be adjusted by varying the concentration of PVA added. Somewhat if we increase the polymer concentration; the flattened conformation channels is not possible due to the increase in adsorbed polymer; the thickness of polymer on the surface of the particles becomes larger than the Debye layer. The bridging of two particles by a polymer chain is possible if the surfaces are not saturated in polymer; which causes flocculation of the suspension. In this concentration range; the polymer will have a flocculating effect (in this case $<0.25\%$). If we still increasing the PEO concentration to achieve saturation of the particle surface; such that each particle is surrounded by a polymer layer which is usually repel and in this case we

Figure 6 Elastic and loss modulus time sweep as a function of PEO concentration ($\tau = 0.15$ Pa, $\omega = 10$ s⁻¹).

Figure 7 Evolution of the polymer layer adsorbed on the particle surface, depending on the quantity of polymer added [9].

Table 2: Variation of yield stress (τ_c) and time of gelation as a function of PEO concentration.

% PEO	τ_c	Gel time
0	0.5	5.69
0.18	0.59	4.19
0.25	0.71	3.69
0.5	0.52	5.69
1	0.5	6.19

have the phenomenon of steric repulsion.

The electrostatic range is shown by a dotted circle.

- (1) Small quantity of adsorbed polymer adopts a flattened conformation; the polymer layer is less than the electrostatic scope; which prevents bridging between particles.
- (2) If increasing the concentration; the size of polymer sloop becomes larger than the thickness of the

electrostatic layer; then bridging between two particles is achieved which results in flocculation of the system.

- (3) The polymer concentration in solution is such that the adsorption on the particles is maximum. Although the polymer layer is greater than the layer of electrostatic repulsion; bridging flocculation and therefore is no longer possible. Particles repel by steric repulsion.

CONCLUSION

In this study; we have shown the influence of the polymer PEO with low molecular weight (10000g/mol) on the rheological properties of basic bentonite suspension in steady state (viscosity and stress) and in dynamics (G' and G'').

The results obtained allow us to conclude that the PEO has two different behaviors depending on the concentration

added: for $c < 0.25\%$; the addition of PEO increases the rheological parameters of the suspension (yield stress; viscosity and viscoelastic modulus) and beyond the critical concentration (0.25%) PEO has a reverse effect. The gel time of bentonite-PEO mixtures is also influenced by the concentration of PEO added (acceleration for $c < 0.25\%$ and slowing for $c > 0.25\%$). This behavior can be explained by the modification of the charge distribution of the electric double layer according to the adsorption mechanism of PEO on the clay particles.

There is a very good agreement between the results of tests in steady state and those under dynamic conditions.

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