

INFLUENCE OF LOW MOLECULAR WEIGHT POLYMERS ON THE RHEOLOGY OF BENTONITE SUSPENSIONS

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INFLUENCE DE POLYMÈRES DE FAIBLE MASSE
MOLÉCULAIRE SUR LA RHÉOLOGIE
DE SUSPENSIONS DE BENTONITE

Dans cette communication, nous démontrons comment les polymères synthétiques de masse moléculaire relativement faible modifient notablement les propriétés rhéologiques de suspensions de bentonite dans l'eau en fonction de polymère et/ou du degré de couverture superficielle de la particule d'argile. Les comportements de deux types de polymères non ioniques sont décrits : une série de polymères à oxyde de polypropylène — oxyde de polyéthylène nonylphénol avec longueur de chaîne EO variable et une série composée d'un copolymère à bloc ABA d'oxyde de polypropylène — oxyde de polyéthylène avec longueur de chaîne EO variable.

Les isothermes d'adsorption de suspensions d'argile diluées ont montré une plus grande teneur en polymère de plus faible masse moléculaire (en $\mu\text{mol}/\text{m}^2$) dans chaque série. La quantité adsorbée augmente dans la proportion de NPE > PEO > PE. Les mesures de taux de rupture et de contrainte de la rupture oscillatoire et de la rupture stabilisée des suspensions d'argile concentrées (3 à 6 %/v) facilitent l'interprétation des interactions de particule. Le seuil d'écoulement, la viscosité plastique et le module élastique ont montré un maximum pour une couverture superficielle de 50 % environ par les polymères NPE, suivi d'une diminution provoquée par la stabilisation de la suspension. Dans le cas des polymères PE, ces paramètres ont diminué de manière continue au fur et à mesure du recouvrement de la particule d'argile. L'étalonnage du module élastique avec une teneur d'argile croissante permet de calculer l'exposant n à partir de la loi de puissance $G' = k\phi^n$ qui donne une description qualitative du degré de dispersion des différents polymères. Les résultats préliminaires de l'effet de la température et de la pression sur les suspensions de bentonite et polymère sont également présentés.

INFLUENCE OF LOW MOLECULAR WEIGHT POLYMERS
ON THE RHEOLOGY
OF BENTONITE SUSPENSIONS

In this communication we demonstrate how relatively low molecular weight synthetic polymers significantly alter the rheological properties of Bentonite/water suspensions depending upon the polymer dosage and/or degree of surface coverage on the clay particle. The behaviour of two types of nonionic polymers are reported; a series of nonylphenol poly(propylene oxide)-

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poly(ethylene oxide) polymers with varying EO chain length and a series consisting of an ABA block copolymer of poly(propylene oxide)-poly(ethylene oxide) with varying EO chain length.

Adsorption isotherms of dilute clay suspensions showed a higher uptake of the lowest molecular weight polymer (in $\mu\text{mol}/\text{m}^2$) for each series. The adsorbed amount G increases in the order $\text{NPE} > \text{PEO} > \text{PE}$. The oscillatory shear and steady state shear stress-shear rate measurements of concentrated clay suspensions (3-6% w/v) facilitate the interpretation of the particle-particle interactions. The yield stress, plastic viscosity and elastic modulus showed a maximum at about 50% surface coverage by the NPE polymers, and a subsequent decrease due to stabilisation of the suspension. For the PE polymers these parameters continuously decreased as the surface of the clay particle was covered. Scaling of the elastic modulus with increasing clay content allows the determination of the exponent n from a power-law fit $G = K\phi^n$ which qualitatively describes the degree of dispersion for the different polymers. Preliminary results of the effect of temperature and pressure on Bentonite/polymer suspensions are also presented.

INFLUENCIA DE LOS POLÍMEROS DE REDUCIDA MASA MOLECULAR SOBRE LA REOLOGÍA DE SUSPENSIONES DE BENTONITA

En la presente comunicación, se trata de demostrar cómo los polímeros sintéticos de masa molecular relativamente reducida, modifican en proporciones apreciables las propiedades reológicas de las suspensiones de bentonitas en el agua, en función de la concentración de polímeros y/o del grado de cobertura superficial de la partícula de arcilla. Se describen los comportamientos de dos tipos de polímeros no iónicos: una serie de polímeros de óxido de polipropileno — óxido de polietileno nonilfenol, con longitud de cadena EO variable y una serie compuesta por un copolímero de cloque ABA de óxido de propileno — óxido de polietileno con longitud de cadena EO variable.

Las isoterms de adsorción de suspensiones de arcilla diluida han demostrado una mayor concentración de polímeros de masa molecular más reducida (en $\mu\text{mol}/\text{m}^2$) en cada serie. La cantidad adsorbida aumenta según la proporción de $\text{NPE} > \text{PEO} > \text{PE}$. Las mediciones del índice de ruptura y tensiones de la ruptura oscilatoria y de la ruptura estabilizada de las suspensiones de arcilla concentrada (3 a 6 %/v) facilitan la interpretación de las interacciones de partícula. El límite de flujo, la viscosidad plástica y el módulo elástico han venido a demostrar un valor máximo para una cobertura superficial de un 50 % aproximadamente, por los polímeros NPE, seguido de una disminución provocada por la estabilización de la suspensión. Al tratarse de los polímeros PE, estos parámetros llegan a disminuir de forma continua, a medida que se produce el recubrimiento de la partícula de arcilla. La calibración del módulo elástico con una concentración de arcilla incremental, permite calcular el exponente n a partir de la ley de potencia $G' = k\phi^n$ que permite obtener una descripción cuantitativa del grado de dispersión de los distintos polímeros. También se presentan los resultados preliminares del efecto de la temperatura y de la presión sobre las suspensiones de bentonita y polímero.

INTRODUCTION

Bentonite clay is a key component in the formulation of water based drilling fluids. Because of its extensive swelling in water, it forms a gel-like structure at relatively low concentrations (4-5% w/w) due to the expansion of the clay platelets when saturated with Na^+ ions [1]. The development of this structure is responsible for the yield stress of the suspension, which is convenient for suspending the cuttings when circulation of the drilling fluid is stopped and the formation of a "mud-cake" along the walls of the borehole. Moreover, at higher shear rates the shear-thinning properties of these suspensions give the fluid a sufficiently low viscosity to transport these cuttings back to the surface. However, high temperatures and salt conditions encountered in the well may modify the rheological properties and this makes the use of polymers necessary.

High molecular weight polymers (CMC, gums, polyacrylamides) have been traditionally used in the formulation of water-based drilling fluids for reducing filtration, facilitating clay stabilisation, improving debris suspension capacity and drillstring lubrication in the drilling operation [2]. Low molecular weight synthetic ethylene-oxide based surfactants have been found to exhibit an inhibiting effect on the dispersion of shale cuttings [3] and [4]. The complex formulation of these suspensions have made it difficult to explain the influence of a particular component on their rheological behaviour. Also, the exclusive use of steady state shear stress shear rate measurements does not provide all the information that is needed to understand the particle/particle interaction in clay/polymer systems. High temperature-high pressure studies have been performed on complex drilling fluids [5], but the effect of a low molecular weight polymer in the clay suspension has not yet been analysed. It is the objective of this work to determine the effect of relatively low molecular weight nonionic polymers on the rheological behaviour of bentonite suspensions.

Finally, some preliminary measurements have been made at high temperature and high pressure for bentonite alone and a bentonite/polyethylene oxide system. This allows us to verify the direct influence of the polymer on the rheological properties of bentonite suspensions under HPHT conditions.

1 EXPERIMENTAL PROCEDURE

1.1 Materials

A commercially available bentonite clay sold under the trade name Gelwhite H-NF was supplied by *Laporte Absorbents*. Details of the chemical composition are referred to in a previous publication [6].

The polymers used were supplied by *ICI (Imperial Chemical Industries)* and termed the Synperonic NPE and Pluronic series. The Synperonic NPE series (NPE1800; NPEA; NPEB; NPEC) is composed of a nonylphenol (polypropylene oxide)(polyethylene oxide) chain, where the polypropylene oxide part is fixed and the number of ethylene oxide units in the chain varies from approximately 27 to 150 EOU. The Synperonic PE series (PE/103; PE/105; PE/108) consists of an ABA block copolymer of (polyethylene oxide)(polypropylene oxide)(polyethylene oxide) chain where the polypropylene oxide part is fixed and the polyethylene oxide chain varies from 16 to 150 EOU. Table 1 shows the name, chemical composition, molecular weight, number and distribution of the ethylene oxide units of the two series of polymers. The ethoxy part has a Poisson distribution. For the high pressure high temperature studies, bentonite suspensions with polyethylene oxide (PEO) of molecular weight 4000 g/mol was used. This last polymer was obtained from *Aldrich Chemical Co.*

1.2 Determination of Surface Area

The dry surface area of the clay was first determined by BET nitrogen adsorption, giving an area of 71 m²/g. It was possible to estimate the "wet surface area" of the

clay by methylene blue adsorption [7] and [8]. The surface area for bentonite was found to be ~1100 m²/g, which shows that all the platelets in the clay are available for methylene blue adsorption. We used the latter area for all calculations.

1.3 Adsorption Measurements

Solutions of different concentration of each polymer were prepared and placed in contact with fixed volume of clay suspension, giving a final clay content of 0.2% (w/w). The suspensions were placed into glass tubes and left to rotate for 24 hours to ensure maximum adsorption at each concentration. After this period, the samples were centrifuged until a clear supernatant was left. The equilibrium concentration was then analysed using UV spectroscopy for the Synperonic NPE series and a calorimetric method described by Baleux [9] and Tadros and Vincent [10] for the Synperonic PE series. For the PEO series, TOC (total organic carbon) analysis was carried out to determine the equilibrium concentration. The adsorbed amount Γ (mmol/m²) was calculated from the ratio of the adsorbed amount Γ (mmol/g) and the surface area of bentonite.

1.4 Rheological measurements

The preparation of concentrated bentonite suspensions (3-6% w/w) with added polymer consisted of two stages: a concentrated suspension of bentonite was prepared with a high shear Silverson mixer and addition of the polymer solution to the suspension using a low shear blade mixer and allowing sufficient time to

TABLE I
Physical characteristics of the polymers and maximum amount adsorbed

Polymer	Number of PPO units (η_{PPO})	Number of EO units (η_{PEO})	Molecular weight (g/mol)	Maximum amount adsorbed onto clay Γ_{max} ($\mu\text{mol}/\text{m}^2$)
NPE 1800	12.9	27.5	2180	0.340
NPE A	12.9	48.0	3080	0.190
NPE B	12.9	79.4	4460	0.115
PE/103	56	2 x 16	4700	0.026
PE/105	56	2 x 37	6500	0.016
PE/108	56	2 x 148	16200	0.011
PEO 600	—	14	600	> 0.08
PEO 1500	—	34	1500	0.085
PEO 4000	—	91	4000	0.043

ensure uniform mixing. The suspension was then left to stand for up to 24 hours before the measurements were made, allowing buildup of the gel-like structure. The pH of the resulting suspensions were ~ 9 -9.5 and measurements were made at room $25, \pm 0.1^\circ\text{C}$. A Bohlin VOR rheometer (*Bohlin Reologie*, Lund, Sweden) was used for both steady state and oscillatory measurements. A shear stress(τ)-shear rate($\dot{\gamma}$) sweep was applied to each suspension varying the shear rate over a wide range between 0.1 and 1160 s^{-1} . The flow curves were analysed and fitted to the Bingham model and the Herschel-Bulkley model. For the Bingham model:

$$\tau = \tau_B + \eta_{pl}\dot{\gamma} \quad (1)$$

one can obtain the Bingham yield stress τ_B and the plastic viscosity η_{pl} .

The Herschel-Bulkley equation is given by:

$$\tau = \tau_y + K\dot{\gamma}^n \quad (2)$$

where n is the flow behaviour index, K the consistency factor and η_{HB} the high shear viscosity.

A Bohlin VOR rheometer is a constant-strain instrument which performs oscillatory tests by turning the cup back and forth in a sinusoidal movement. From the phase shift and the magnitude of the stress and strain, the elastic G' and loss G'' modulus may be calculated [6]. Values were reported at 1 Hz.

1.5 High Temperature - High Pressure Rheological Studies

A Haake searle type HTHP viscometer was used to study the effects of high temperature and pressure on bentonite suspensions. A detailed description of this viscometer has been recently published, along with some fundamental improvements of the equipment and working experiences [11]. The shear-rate is continuously variable and is ramped up and down at rates between 0 and 1130 s^{-1} . It is possible to measure pressures up to 1000 bar and temperatures up to 150°C .

We compare a pure bentonite suspension of 5% (w/w) and a bentonite suspension of the same concentration with PEO 4000 g/mol at different temperatures (25 - 150°C) and pressures (1-1000 bar). Sufficient PEO was added to the clay suspension to ensure maximum coverage of the clay particle by the polymer. The flow curves for the bentonite suspensions were obtained by ramping the shear rate up to 600 s^{-1} and back down again. Each sample was subjected to the same

pre-shearing conditions and a fixed waiting time was required before each measurement. By using this procedure it was possible to achieve reproducible and comparable measurements. The flow curves obtained by ramping down the shear rate were fitted to the Herschel-Bulkley models.

2 RESULTS AND DISCUSSION

2.1 Adsorption of Polymers onto Bentonite

Table 1 shows the maximum amount (Γ_{max}) of polymer adsorbed onto bentonite for each series. Various conclusions can be drawn from these values. For the three series (NPE, PE and PEO) the amount adsorbed decreases as the number of ethylene oxide units in the polyethylene oxide chain is increased. A similar behaviour has been observed for these polymers (NPE, PE) adsorbed on other substrates [12, 13, 14]. This suggests that the area occupied on the surface by the polymer molecule increases with the number of ethylene oxide units. However, the amount adsorbed is significantly higher for the NPE series than for the other two, indicating that a closer packed polymer layer is formed when the hydrophobic nonylphenol portion is present. PEO polymers have been found to interact strongly with the hydroxyl groups on the surface of bentonite clay through hydrogen bonding [15] and [16], and similar values were obtained compared to these previous studies. The PEO series adsorb to a greater extent than the PE series, since in this last case the molecular weight is higher and less molecules adsorb on the surface. It can thus be concluded that the preferential adsorption of the polymers onto bentonite (in mmol/m^2) occurs in the order $\text{NPE} > \text{PEO} > \text{PE}$.

2.2 Rheological Studies

Figure 1 shows the Bingham yield stress and plastic viscosity for a 5% bentonite suspension as a function of NPEB polymer content. It can be seen that with increasing NPEB content the yield stress reaches a maximum at approximately 50% surface coverage of bentonite (twice the initial value). After this point, the yield stress decreases again and a steady value is reached after 100% of surface coverage. The Bingham

yield stress values for the high polymer contents were found to be higher than the suspension without polymer. The plastic viscosity increases at this point, after which it remains fairly constant. Figure 2 shows the values of the elastic (G') and storage (G'') moduli as a function of polymer concentration. G' is significantly higher than G'' indicating that the suspension is highly elastic. This plot shows the same trend as in Figure 1, namely a peak of G' at 50-60% surface coverage and then a decrease of the value.

Figure 3 shows the rheological behaviour of the suspension containing the PE/103 polymer. The Bingham yield stress increases slightly with polymer concentration, whereas the yield stress estimated by the HB model decreases gradually to approximately 60% of the initial value. We consider the value estimated by the latter model to be more accurate, since the stresses corresponding to shear rates in the order of 0.5 to 1000 s^{-1} were taken into account. The gradual stabilisation of the suspension can be more clearly seen in Figure 4, which shows a continuous decrease of G' with PE/103 concentration. This trend was the same for all other suspensions containing PE polymers. From Figures 2 and 4 we may conclude that the oscillatory shear measurements are more sensitive to the polymer concentration and can give a clearer understanding of the interactions taking place between clay particles.

The difference in behaviour between the suspension containing the NPE polymer and the the PE polymer may be ascribed to the polymer structure. In a previous study regarding the adsorption of nonylphenol

ethoxylated polymers onto hydrophilic silica [17], it was suggested that below the maximum surface coverage of the clay particles the polymer adsorbs via the ethylene oxide chain. This was concluded from adsorption isotherms, where a greater affinity for the surface was detected with increasing ethylene oxide units. It is therefore probable that for hydrophilic bentonite suspensions, which contain silanol groups on the surface, this form of polymer attachment occurs. In this case, the observed increase of G' (Fig. 2) could be attributed to hydrophobic interactions between nonylphenol groups of neighboring particles causing aggregation of the suspension. As the surface becomes more saturated, a more close-packed layer is formed which prevents the suspension from flocculating. In the case where the nonylphenol group is absent (PE/103), gradual deflocculation takes place (Fig. 4).

Significant information regarding the interactions of concentrated suspensions can be obtained from scaling concepts [18]. In particular, the elastic modulus G' can be related to the volume or weight fraction of the suspension according to the power law equation:

$$G' = k\phi^n \quad (3)$$

The value of n is of importance, since it can qualitatively determine the degree of flocculation of a dispersion. Values of n in the order of 2-4 have been related to flocculated suspensions for other systems, whereas those whose magnitude is considerably higher are regarded as stable [19]. For bentonite suspensions, a value of the order of 8 has been associated to a stable suspension [20] and studies involving the use of

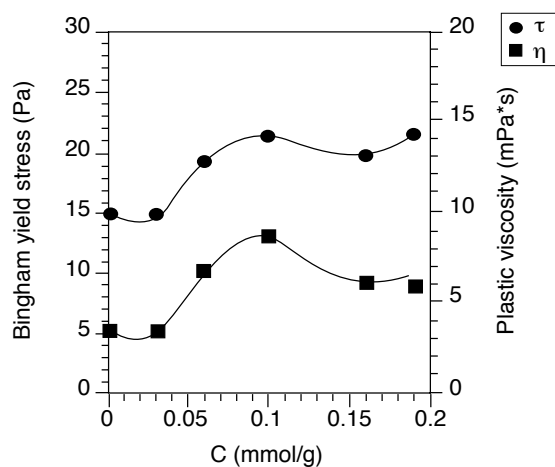


Figure 1

Bingham yield stress and plastic viscosity as a function of NPEB concentration for a 5% Bentonite suspension.

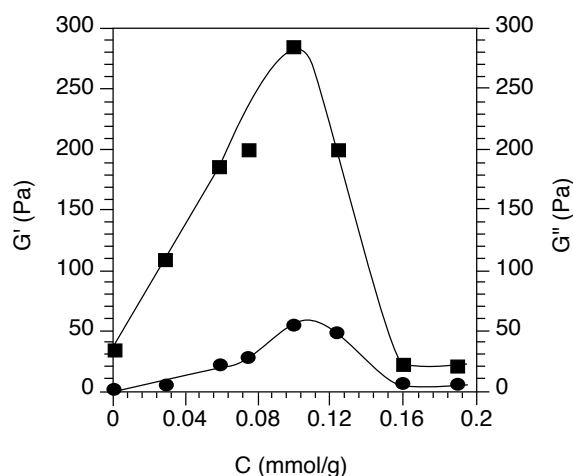


Figure 2

Elastic and loss modulus as a function of NPEB concentration for a 5% Bentonite suspension.

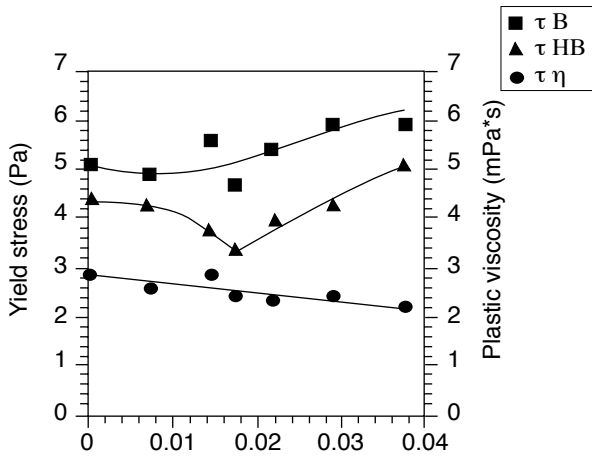


Figure 3

Bingham and HB yield stress, plastic viscosity as a function of PE/103 for a 5% bentonite suspension.

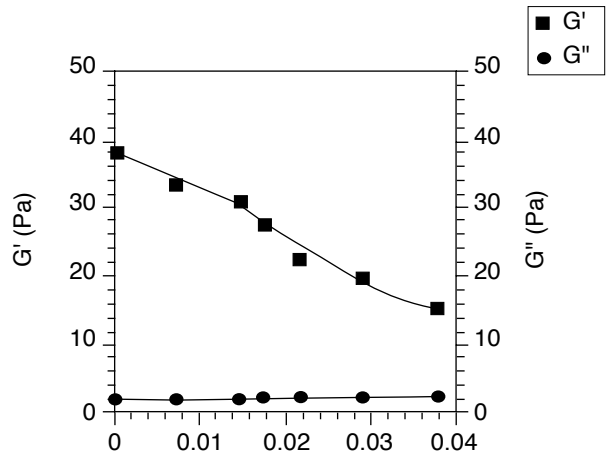


Figure 4

Elastic and loss modulus viscosity as a function of PE/103 content for a 5% bentonite suspension.

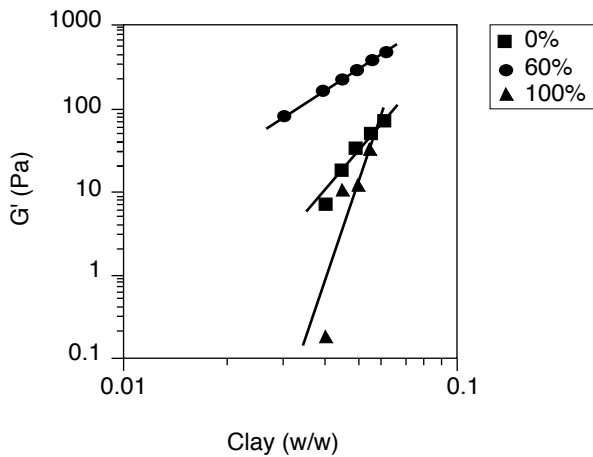


Figure 5

Elastic modulus as a function of bentonite content for different surface coverages of NPEB.

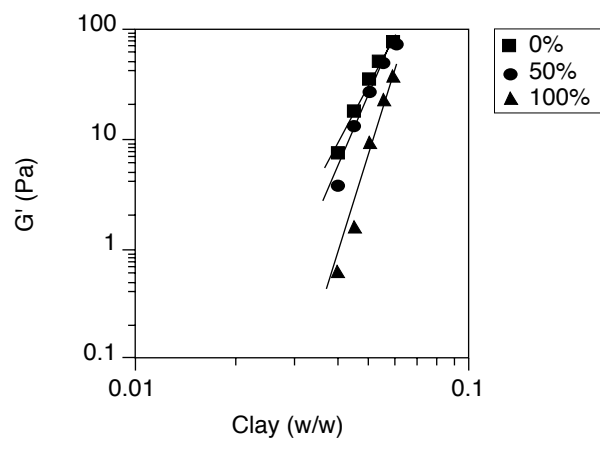


Figure 6

Elastic modulus as a function of bentonite content for different surface coverages of PE/103.

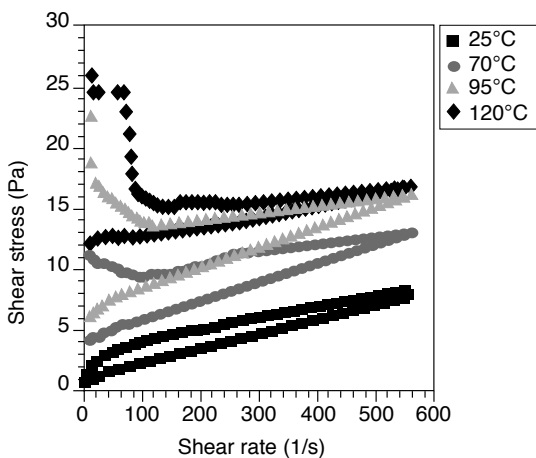


Figure 7

Shear stress shear rate curves for bentonite suspensions stabilised by PEO 4000 at various temperatures ($P = 1000$ bar).

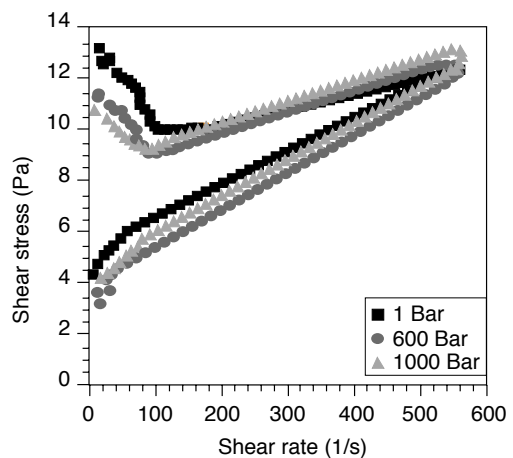


Figure 8

Shear stress shear rate curves for bentonite suspensions with PEO 4000 at different pressures ($T = 70^\circ\text{C}$).

charged polymers and different salts have determined values of n between 2-4 [21]. The power n can be obtained from a log-log plot of G' vs ϕ .

Figure 5 shows the trend of G' against clay weight fraction for suspensions containing different degrees of coverage of NPEB. In the absence of polymer, $G' \sim \phi^{8.1}$. With approximately 50% of surface coverage the value of n is 2.5, reflecting a strongly aggregated suspension. For maximum coverage this value increases to 12.7, indicating that the degree of dispersion of the suspension is higher. Since these values are higher than 8.1, the suspension in the absence of polymer is most likely weakly flocculated. Clay systems with PE/103 show a different behaviour (Fig. 6), where $n = 9.1$ for 50% surface coverage of the particle and $n = 11.2$ for maximum surface coverage. This confirms that the suspension is gradually stabilised by the adsorbing polymer.

2.3 High Temperature-High Pressure Dependency

The effect of temperature on the flow curve for a bentonite suspension stabilised by PEO 4000 and at 1000 bar is illustrated in Figure 7. The stress values obtained for the corresponding shear rates increase with temperature. High temperature gelation of clay suspensions arises through a combination of clay dispersion and flocculation [2]. The Herschel-Bulkley parameters for the bentonite suspension alone and with added polymer at 70°C and different pressures are presented in Table 2 (Fig. 8). For both systems, one may observe a decrease of the yield stress with increasing pressure. This behaviour is different from an essentially pressure-independent yield stress for bentonite suspensions in a previous study [5]. The suspension does not seem to have recovered fully after the pressure is applied. For the clay suspension alone the yield stress decreases 35%, whereas with the polymer the decrease is of 20%. The high shear viscosity η_{HB} increases with pressure, due to fluid compressibility. A 30% increase of the viscosity from 1 to 1000 bar is obtained for the suspension alone, whereas it is 20% with the suspension containing polymer. Therefore it seems that the rheological properties of bentonite suspension with PEO are less sensitive to pressure variations. However, more studies need to be conducted to verify this effect.

TABLE 2

Herschel-Bulkley parameters for 5% bentonite suspensions under different pressures at 70°C

P (Bar)	Bentonite			Bentonite + PEO 4000		
	1	600	1000	1	600	1000
τ (Pa)	3.65	2.70	2.41	3.12	2.45	2.65
η_{HB} (mPa*s)	9.02	11.29	12.53	8.50	10.26	10.93
n	0.72	0.77	0.79	0.74	0.78	0.79
K	0.087	0.069	0.065	0.072	0.061	0.061

Overall, the yield stress and high shear viscosity values are a bit lower for the suspension stabilised with PEO as is expected. The flow behaviour index n increases with pressure and the contrary is observed for the consistency factor, showing that the suspensions become more Newtonian.

CONCLUSIONS

Low molecular weight nonionic polymers affect the rheological behaviour of bentonite suspensions depending on the extent of surface coverage of the polymer on the surface. For polymers containing the nonylphenol group, significant aggregation takes place at 50% surface coverage. This is attributed to hydrophobic interactions between the semi-covered clay particles. Gradual stabilisation of the bentonite suspension occurs when using polymers where this group was absent. The oscillatory shear measurements are more sensitive to the interactions between clay particles containing polymer, than the steady-state shear stress shear rate measurements. It is possible to qualitatively describe the degree of dispersion through scaling analysis of the elastic modulus. The Herschel-Bulkley model gives better estimates of the yield stress than the Bingham model, and can be applied to HTHP rheological data. Bentonite suspensions in the presence and in the absence of PEO are very sensitive to temperature, and a smaller pressure effect is obtained.

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