Influence of the chemical structure of different carboxymethylcelluloses on the performance of clay dispersions

(Influência da estrutura química de diferentes carboximetilceluloses no desempenho de dispersões de argila)

K. C. Nóbrega1*, S. S. S. Silva2, L. V. Amorim2, H. L. Lira1, W. R. P. Costa1

1Universidade Federal de Campina Grande, Programa de Pós-Graduação em Ciência e Engenharia de Materiais, R. Aprígio Veloso 882, 58429-970, Campina Grande, PB, Brazil
2Universidade Federal de Campina Grande, Unidade Acadêmica de Engenharia de Petróleo, Campina Grande, PB, Brazil
3Universidade Federal de Campina Grande, Programa de Pós-Graduação em Exploração Petrolífera e Mineral, Campina Grande, PB, Brazil

*karine.nobrega@hotmail.com

Abstract

The aim of this work was to evaluate the influence of the chemical structure of carboxymethylcellulose (CMC) on the rheological performance and fluid loss of clay dispersions. The dispersions were prepared with a fixed content of bentonite clay (15 g/350 mL of water) and different concentrations of CMCs (0.5, 1.0, 2.0 g/350 mL of water). After aging for 24 h in ambient and static conditions, the dispersions were tested in a viscometer. Apparent and plastic viscosities, yield point and gel strength were obtained using the viscometer, according to Petrobras’ standard (EP-1EP-00011-A). The filtrate volume was determined using the API filter press. The results showed that the addition of long chain, low degree of substitution and lower substitution uniformity of CMC contribute to the flocculation phenomenon. In addition, the different chemical characteristics of CMC only influence fluid loss when the ionic strength of the dispersion is set to any other value than zero.

Keywords: carboxymethylcellulose, performance, bentonite clay, chemical characteristics.

INTRODUCTION

During overbalance drilling operations, the hydrostatic pressure of the drilling fluid is higher than the pore pressure of the rock formation. This differential pressure results in the filtration process, which consists of the influx of the liquid phase of the fluid, the filtrate, into the formation, followed by the formation and consolidation of the mudcake, a layer of wet solid particles deposited on the walls of the wellbore [1, 2]. The fluid loss additives are in charge of the filtration control on drilling fluids. The most common additives are colloidal clays, dispersing and deflocculating agents, modified polymers and natural polymers [3, 4]. Among the modified polymers is carboxymethylcellulose (CMC), a water-soluble compound, derived from the slurry process of cellulose, sodium hydroxide and monochloroacetic acid [5]. The ability of CMC to disperse clays and prevent fluid loss to the porous and permeable formation is greater than any other chemical additives used in fluids or dispersions. This ability resulted in increasing use of CMC in the oil well drilling [6]. The various properties and applications of CMC depend on four factors: average degree of polymerization (DP), average degree of substitution (DS), substitution uniformity (UN), and purity of the product [7-9]. The DP refers to the number of monomer units present in the polymer molecule.
The viscosity of carboxymethylcellulose dispersions is used as a measurement of the degree of polymerization, since it increases with the increase of molecular weight [11]. The DS is defined as the average number of hydroxyl groups substituted by the D-glucopyranosyl unit of the polymer chain [7]. Commercial CMCs presents DS usually in the range from 0.5 to 0.85, but it may vary from 0.4 to 1.5 [12]. The UN refers to the regularity of distribution of the carboxylic substituents along the polymer chains [9]. Finally, purity refers to the percentage of active raw matter present in the carboxymethylcellulose [13]. The degree of solubility is recognized as a function of the degree of substitution. The thixotropic carboxymethylcellulose (less uniformly substituted and more hydrophobic) has a higher fraction of aggregates, thus exhibiting a lower solubility in water when compared to a non-thixotropic CMC [14].

The current literature offers many studies focused on the use of carboxymethylcellulose in aqueous drilling fluids and subsequent evaluation of the physical properties of the fluid after polymeric additivation [15-19]. However, the effects of CMC’s chemical characteristics, specifically viscosity, average degree of substitution, and substitution uniformity on filtration and rheological properties of clay dispersions have not yet been fully explored.  Heinle et al. [20] studied the adsorption of several polysaccharides in peptized montmorillonite and their influence on the filtration properties of clay drilling fluids modified with these soluble polymers as a function of increasing salinity of the solution. The authors observed that increasing the degree of substitution (from 0.99 to 1.46), CMC become more effective in controlling filtrate loss, probably because of the extended loops of anionically charged polymeric segments and to the increased hydrophilicity provided by these segments. According to [21], when CMC is added to the calcium montmorillonite suspensions, it promotes the covering of clay particles by the polymer and avoids the reorganization of the agglomerates by face-to-face association. In this case, the rheological behavior of the bentonite-CMC suspensions depends on the structural state (flexible) of this polymer. Amorim et al. [22] carried out a study to evaluate the influence of ionic strength on apparent viscosity (AV), plastic viscosity (PV) and filtrate volume (FV) of sodium bentonite suspensions treated with polymers [low viscosity carboxymethylcellulose (CMC LV), polyanionic cellulose (PAC) and partially hydrolyzed polyacrylamide (HPAM)]. The authors concluded the following: the polymeric treatment alters the viscosities and filtrate volume of the bentonite suspensions, leading to the development of structures with different degrees of flocculation; the HPAM acts as a flocculant and the CMC LV and PAC as deflocculants. In addition, the authors observed that the apparent and plastic viscosities and the filtrate volume of the bentonite suspensions treated with CMC LV were only slightly affected by the increase in salinity. Benchebaine and Benyounes [23] studied the effect of the addition of an anionic polymer (CMCs with different molecular weights) on the rheological characteristics of aqueous suspensions of bentonite. The results showed that the rheological behavior of the suspensions was notably affected by the increase in molecular weight and concentration of the polymer in the water-bentonite-CMC system. According to [24], the advantage of the use of carboxymethylcellulose is that the desired rheological properties can be achieved in dispersions with less bentonite, thus the undesirable effects of high concentrations of clay can be avoided. In these studies, the viscosity of 8.0 wt% pure bentonite dispersions was achieved by adding 0.10 wt% carboxymethylcellulose to 4.0 wt% bentonite dispersion, but with a higher degree of thixotropy.

The control of the filtration and rheological properties of water systems and clay is one of the most important elements in the drilling of oil wells. Depending on the type of interaction between the clay particles, flocculated and deflocculated structures are produced and can be modified by additives such as electrolytes, polymers and surfactants. Since CMC has been routinely used in drilling fluids to increase viscosity and control the fluid loss to the rock formation, the knowledge of the chemical characteristics of this polymer combined with the knowledge of the properties of the drilling fluid should highlight the functions performed by this polymer, as well as help to define, more precisely, the concentrations for its application [25]. In this context, the aim of this work is to evaluate the influence of the chemical structure of carboxymethylcellulose on the rheological performance and fluid loss of clay dispersions.

**MATERIALS AND METHODS**

For the preparation of the dispersions, the following additives were used: a sample of industrialized bentonite clay, commercially known as Volclay, supplied by Bentonit União Nordeste - BUN/PB and five samples of carboxymethylcellulose with different chemical structures (viscosity, degree of substitution and substitution uniformity) provided by the Denver Especial. Quím./SP. The differences between the chemical characteristics of the CMC samples are given in Table I. The determination of purity, viscosity (in the Brookfield LVF viscometer at 30 rpm, spindle 1 - aqueous solution 2 wt% on a dry basis), degree of substitution and substitution uniformity of the carboxymethylcellulose samples were carried out based on the ASTM standard test D1439-03 and internal procedures of laboratory adopted by the Denver Especial. Quím., which carried out these assays [13].

| Table I - Chemical characteristics of the CMC samples used. [Tabela I - Características químicas das amostras de CMC utilizadas.] |
|---|---|---|---|---|
| CMC sample | Purity (%) | Viscosity (cP) | DS | UN |
| CMC 1 | 99.87 | 138.00 | 0.87 | Thixotropic |
| CMC 2 | 99.87 | 30.00 | 0.87 | Non-thixotropic |
| CMC 3 | 99.87 | 30.00 | 0.73 | Non-thixotropic |
| CMC 4 | 99.87 | 120.00 | 0.73 | Thixotropic |
| CMC 5 | 99.87 | 30.00 | 0.72 | Thixotropic |

DS - degree of substitution; UN - substitution uniformity.
in cP, the yield point (YP) in N/m² and the gel strength (GS) readings obtained in the viscometer were used to calculate was repeated with a longer waiting time of 10 min. The
toward, to obtain the final gel strength, the procedure
was increased to 17000 rpm, remaining for 5 min under mixing at 17000 rpm. While
the clay dispersion was under mixing, the polymeric solution was prepared, using 150 mL of deionized water and varying concentrations of CMC, according to Table II. For the preparation of the CMC solution, the polymeric additive was added to water under stirring at 13000 rpm using the Hamilton Beach mixer. Then, the stirring speed was increased to 17000 rpm, remaining for 5 min in order to guarantee the hydration of the polymer chains. Finally, the polymeric solution was added to the clay dispersion, remaining for 5 min under mixing at 17000 rpm.

**Formulation of clay dispersions:** 16 dispersion formulations with the fixed content of bentonite clay (15 g/350 mL deionized water) and different concentrations of CMC (0.5, 1.0, 2.0 g/350 mL deionized water) were prepared (Table II). **Preparation of clay dispersions:** the content of clay was added to 200 mL of deionized water with constant stirring at 13000 rpm using a Hamilton Beach (mod. 936) mixer. After the addition of the clay, the speed was increased to 17000 rpm, remaining at this speed for 15 min. While the clay dispersion was under mixing, the polymeric solution was prepared, using 150 mL of deionized water and varying concentrations of CMC, according to Table II. For the preparation of the CMC solution, the polymeric additive was added to water under stirring at 13000 rpm using the Hamilton Beach mixer. Then, the stirring speed was increased to 17000 rpm, remaining for 5 min in order to guarantee the hydration of the polymer chains. Finally, the polymeric solution was added to the clay dispersion, remaining for 5 min under mixing at 17000 rpm.

**Determination of rheological properties:** for the study of rheological properties, after a 24 h aging, at room temperature and static condition, the dispersion was mixed for 5 min using the Hamilton Beach mixer at 17000 rpm. Then, the dispersion was transferred to the cup of the Fann 35A viscometer. The viscometer was switched on at 600 rpm for 2 min and the dial was read. Then the speed was changed for 300 rpm and a new reading was taken after 15 s. The initial gel strength was obtained as follows: the dispersion was stirred at 600 rpm for 15 s, then the speed was changed to 3 rpm and the dispersion was rested for 10 s; then the reading was taken obtaining the initial gel strength value. Afterward, to obtain the final gel strength, the procedure was repeated with a longer waiting time of 10 min. The readings obtained in the viscometer were used to calculate the apparent viscosity (AV) in cP, the plastic viscosity (PV) in cP, the yield point (YP) in N/m² and the gel strength (GS) in N/m², using Eqs. A, B, C and D, respectively, following the standard EP-1EP-00011-A [26]:

\[
AV = \frac{R_{600}}{2} \quad (A)
\]

\[
PV = R_{600} - R_{300} \quad (B)
\]

\[
YP = R_{300} - PV \quad (C)
\]

\[
GS = G_f - G_o \quad (D)
\]

where \(R_{600}\) is the reading at 600 rpm, \(R_{300}\) is the reading at 300 rpm, \(G_f\) is the value obtained for the final gel strength and \(G_o\) is the value obtained for the initial gel strength.

**Determination of filtrate volume:** the filtrate volume (FV) was determined according to ANSI/API 13I standard [27]. The dispersion was stirred for 1 min under constant speed (17000 rpm) on a Hamilton Beach mixer, and then it was transferred to the API filter-press cup, at a pressure of 100 psi (690 kPa) for 30 min. At the end of 30 min, the filtrate was collected in a graduated beaker and the corresponding value in mL was recorded for each dispersion tested.

**RESULTS AND DISCUSSION**

Fig. 1 shows the data obtained after measurements of rheological properties [apparent viscosity (AV), plastic viscosity (PV), yield point (YP) and gel strength (GS)] and filtrate volume (FV) of the samples analyzed. The dispersion 1 presented the lowest values of AV (12.25 cP), PV (7.0 cP) and GS (10.5 N/m²). These results can be justified by the dispersed and deflocculated state of the system formed by water and clay. In this state, there were few electrical and mass interactions between the clay particles. According to the literature [28, 29], Volc clay is a natural sodium bentonite from Wyoming/USA, which has a large amount of fine fraction (with an average particle size <2 μm), high cation exchange capacity and high specific area. These physicochemical characteristics, together with the low clay content (15 g/350 mL of water) used, promoted a greater dispersion of the colloidal particles, resulting in a low viscosity for dispersion 1. When the polymeric additives are added to the dispersions, they are dispersed in the liquid phase (water) and their functional groups become more or less dissociated. In this way, the flexible polymer chain assumes an elongate configuration. This configuration is responsible for increasing the viscosity of the system. The polymer chains are then adsorbed to the surfaces of the clay particles and neutralize them, i.e. an adsorption occurs between the negative charges of the polymer and the positive charges present on the edges of the clay particles. With this neutralization, the particles acquire an electrically negative character and mutual repulsion occurs between them, avoiding the phenomenon of flocculation [30]. According to [31], the polyelectrolyte-surface interaction of clay occurs mainly at the edges of the clay minerals. Miano and Rabaioli [32] added that the edges of the clay

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC 1</td>
<td>-</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMC 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMC 3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMC 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMC 5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

**Tabela II - Teor de CMC (g) usado para 350 mL de água nas dispersões de argila com 15.0 g de bentonita.**
particles maintain a lower negative charge in relation to the faces and, therefore, the electrostatic repulsion between the clay and the polymer is low. The dispersion 6, prepared with average concentration (1 g/350 mL of water) of CMC 2, presented the lowest value of gel strength, probably due to the occurrence of few electrostatic interactions among the dispersed particles [33].

Improvements in rheological properties were observed for the dispersions prepared with different CMCs, compared to the dispersion 1, which was formulated with clay only. The best results were obtained for dispersions 4 and 13 prepared with maximum concentration (2 g/350 mL of water) of CMC 1 and CMC 4, being 48.25 and 54.0 cP for AV, 31.0 cP for PV, 34.5 and 46.0 N/m² for YP, and 27.5 and 34.5 N/m² for GS, respectively. These results were related to the chemical characteristics of the respective CMCs, which presented high viscosity (138 and 120 cP) and thixotropic behavior. Debutts et al. [34] studied the flow properties of sodium carboxymethylcellulose aqueous solutions and classified the rheological behavior as pseudoplastic flow, time-independent, and as thixotropic flow, time-dependent, both means of non-Newtonian flow. The CMC solutions exhibit pseudoplasticity because the polymer molecules tend to assume the direction of flow as the applied force (shear stress) increases, thereby the flow resistance (viscosity) decreases. When a smaller force is applied, the apparent viscosity is

![Figure 1: Rheological properties and filtrate volume of the clay dispersions studied.](image-url)
Thixotropy is characterized by an increase in viscosity when the solution remains at rest for a period. In some cases, the solution may develop a gel strength or even a nearly solid gel structure. If a sufficient shear stress is exerted on the solution, the structure is broken and the viscosity is reduced [6]. The relationship between the molecular weight (M) of the polymer and the intrinsic viscosity ($\mu_{int}$) is given by the Mark-Houwink equation [35]:

$$\mu_{int} = KM^a$$ (E)

where $K$ and $a$ are the Mark-Houwink constants. These constants are characteristic of a particular polymer in a particular solvent. The viscosity of the carboxymethylcellulose dispersions increases as the molecular weight increases and so it is used as a measure of the degree of polymerization [36]. Therefore, according to Eq. E, it can be inferred that CMC 1 and CMC 4 presented high molecular weight or high molar mass in relation to the other CMCs studied. The addition of polymers with a high molar mass decreases the distance between the clay particles, since the polymer chains are adsorbed to the surfaces of the clay particles. The longer these chains, the more easily the flocculation phenomenon is obtained, since several particles are adsorbed in the same polymer chain generating the encapsulation phenomenon (formation of large flakes or agglomerates of clay particles). In addition, flocculation occurs due to the formation of bridges, which are lateral interactions between hydrophobic groups of the polymer that make the clay particles approach each other [30, 37]. Although the CMC 1 and CMC 4 had long polymer chains and less uniformity of substitution of the carboxylate groups along the chain, CMC 1 had higher DS (0.87) than CMC 4 (0.73). The higher DS gives the CMC a better solubility and, consequently, greater homogenization with the clay particles. It justifies the lower values of $AV$, $YP$ and $GS$ presented by dispersion 4 when compared to dispersion 13 [30].

Although the samples CMC 2, CMC 3 and CMC 5 had been added to the clay dispersions in different concentrations (0.5, 1.0, 2.0 g/350 mL of water), all of them presented better rheological properties in relation to dispersion 1. This is because these CMCs were short chain polymers, whose main function was the reduction of the filtrate. Short-chain polymers generally act as deflocculants because they neutralize some of the positive charges of the clay particles, coating their ends and increasing the distance between them [38]. Moreover, the higher degree of substitution (DS=0.87) of CMC 2 and the greater regularity with which the carboxymethyl groups are distributed in the chain of CMC 2 and CMC 3 tend to avoid the flocculation phenomenon. The increase in CMC concentration from 0.5 to 1 g/350 mL of water, and from 0.5 to 2 g/350 mL of water, suggested its contribution to the improvement of rheological properties. It can be seen in Fig. 1 and also in Fig. 2, which illustrates the relationship between the increase in CMC concentration in the clay dispersions and the apparent viscosity increase. According to the analysis of Fig. 2, it can be stated that the viscosity of the dispersions depended on the number of CMC particles present in the clay dispersion, due to the formation of complex chains (CMC-clay, for example), which increased the viscosity of the dispersion. This increase was more visible with increasing polymer concentration, which increased the number of particles in the dispersion [39]. CMC is a water-soluble organic colloid. As observed in Fig. 1, small amounts of CMC dissolved in the clay dispersions significantly improved the viscosity, which contributed to the reduction of filtrate volume [40]. Anionic polymers such as carboxymethylcellulose may be active, as the polymer chain with negative ions adheres to the positive sites in the clay particles or to the surface of the hydrated clay by means of hydrogen bonds [2]. This process of interaction between the clay surface and the polymer chain of the CMC reduces the inflow of the liquid phase from the dispersion to the permeable rock formation.

Table III shows the rate of filtrate volume reduction of clay dispersions prepared with maximum concentration (2 g/350 mL of water) of carboxymethylcellulose in relation to the dispersion formulated only with clay (15 g/350 mL of water). The CMCs studied promoted a significant average reduction of the filtrate volume, equivalent to 52.35%, in relation to the filtrate volume of the dispersion 1. In all formulated clay dispersions, both increasing the CMC concentration from 0.5 to 1.0 g and from 0.5 to 2.0 g resulted in a reduction in the filtrate volume, which can be attributed to the increasing values of viscosities shown in Fig. 1. According to [40], the effect of CMC’s physicochemical characteristics (viscosity, degree of substitution and substitution uniformity) on the filtrate volume is related to the hydrodynamic volume of the polymer. By analyzing the Fig. 1 it can be observed that there is no evidence of the influence of the different physicochemical characteristics of CMCs on the fluid loss of the clay dispersions studied. The observed behavior can be attributed to the dynamics of the interactions between the clay and the polymer chain of the CMC, which is the result of the considerable contribution of
the electrostatic interactions and hydrogen bonds between the carboxylate and hydroxyl groups located along the chain of this polymer and the ionic sites and polar regions of the clay surface [41]. According to [35], fluid loss in bentonite/polymer dispersions, in which the ionic strength is equal to zero, is independent of the average molecular weight or degree of substitution of the polymer in the ranges from 5 to 25x10^4 g/mol and from 0.7 to 1.0, respectively. However, the fluid loss depends on the polymer concentration, which suggests that the dependence of this property on the molecular weight would be observed for molecular weights <50000 g/mol. Thus, the experimental results obtained from the filtrate volume in this work were in agreement with the literature [35]. Based on the above considerations, when using CMCs with different physicochemical characteristics in clay dispersions, these polymers reduce the fluid loss indirectly acting on the clayey solids present in the dispersion or directly acting as a thickener. In most cases, they affect the flow properties as well as the fluid loss for the formation [3].

Table III - Rate of filtrate volume reduction (%) of clay dispersions prepared with maximum content of polymer in relation to dispersion 1 (no polymeric addition).

<table>
<thead>
<tr>
<th>CMC 1</th>
<th>CMC 2</th>
<th>CMC 3</th>
<th>CMC 4</th>
<th>CMC 5</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.01</td>
<td>52.30</td>
<td>51.43</td>
<td>52.30</td>
<td>53.73</td>
<td>52.35</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Aiming to evaluate the influence of the chemical structure of carboxymethylcellulose (CMC) on the rheological performance and fluid loss of clay dispersions, it was concluded that: i) the dispersion 13, with maximum concentration (2 g/350 mL of water) of CMC with high molar mass, low degree of substitution and lower uniformity of substitution provided better rheological properties in relation to the other dispersions studied; ii) the addition of increasing concentrations of CMC contributed to the increase in viscosities and a considerable reduction in the filtrate volume of the clay dispersions when compared to the dispersion formulated only with clay; iii) the clay dispersions added with different CMCs showed better rheological behavior and less fluid loss, however, the influence of their physicochemical characteristics were only evident in the rheological properties of the dispersions. In summary, it can be concluded that the optimization of the rheological properties of the clay dispersions studied can be achieved by the addition of CMC with high molar mass, low degree of substitution and low substitution uniformity. In addition, it is also concluded that the fluid loss in dispersions with ionic strength equal to any other value different of zero can be achieved using CMC with variable chain length (short or long), high degree of substitution and greater uniformity of substitution.

ACKNOWLEDGMENTS

The present work was carried out with financial support from the National Council for Scientific and Technological Development (CNPq)/Process 140295/2015-1. The authors are grateful to the Laboratório de Pesquisa em Fluidos de Perfuração (PeFLab) installed on Laboratório de Referência em Dessalinação (LABDES) for the use of its facilities and research support, and to the Bentonit União Nordeste Ltda/PB (BUN) and Denver Especialidades Químicas/SP companies by supplying the samples of clay and carboxymethylcelluloses.

REFERENCES


(Rec. 29/03/2018, Rev. 12/06/2018, Ac. 23/07/2018)