

Cationic and Hydrophobically Modified Chitosans as Additives for Water-Based Drilling Fluids

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ABSTRACT: Water-soluble chitosan derivatives are synthesized via a two-step procedure that includes the hydrophobization of chitosan using different acyl chlorides, and then the alkylation of some of the amine groups. Rheology, conventional rolling, and filtration tests are performed to evaluate the effect of the modified polysaccharides on the rheological behavior of the fluid, as well as on the clays cuttings integrity and on the control of fluid loss for the geological formations. The results indicate that the product with C16 segments, 2% (wt/vol) concentration and high molar weight led to aqueous solutions with a pseudoplastic behavior equivalent to the one presented by the commercial rheology modifier used in water-based drilling fluids. In addition, the hydrophobically modified cationic chitosan shows an excellent capacity for inhibiting the clays reactivity and for keeping the cuttings integrity. The results also show that this product can significantly decrease the volume of filtrate, leading to values comparable to the ones obtained with commercial additives, and therefore suggesting that it could be considered to replace some of the drilling fluid additives commonly used.

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INTRODUCTION

Drilling fluids are circulating fluids used in rotary drilling to perform several duties during the drilling of a well.^{1,2} Among the most important functions of drilling fluids, are their duties to drive drilled cuttings to the surface and to keep these cuttings in suspension, stabilize pressures in the wellbore, lubricate and cool the drill bit, prevent hydration reactions of water sensitive shales, and avoid flooding of the wellbore walls and geological formation reservoir. Therefore, an efficient drilling fluid formulation must contain a variety of additives, such as viscosifiers and rheology modifiers to suspend rock cuttings, filtrate control agents to avoid flooding of geological formations, reactive clays inhibitors to prevent wellbore walls and rock cuttings degradation, and lubricants, among others. Each one of these additives has a specific function, and the total formulation of the fluid is extremely important in the design of drilling operations, both from a technical and an economic point of view.²

Drilling fluids can be classified according to their continuous phase as water-based, oil-based, and gas-based fluids. At the moment, some of the drilling fluids used in offshore operations are either oil

or synthetic oil based. These fluids must be used mainly during directional drilling for lubricity purposes and also while drilling through extremely reactive shales. Unfortunately, most of the continuous phases used in these fluids are not completely biodegradable and may be considered toxic to the environment. Due to an increase of the environmental restrictions, the demand for the more ecologically friendly water-based drilling fluids has increased in the last decade. However, the use of these water-based fluids may lead to wellbore instability while drilling through formations containing smectite rich reactive clays that may swell and disintegrate in contact with water, leading to serious borehole problems. To prevent wellbore instability and dispersion of the drilled cuttings, different polymeric additives have been used, such as the synthetic cationic polymer polydiallyldimethylammonium chloride (PDADMAC), which can be very efficient. In a previous work, it was shown through adsorption isotherms that a series of cationic polymers had high affinity for reactive clays, and their efficiency as clay inhibitors depended on the amount of adsorbed polymer, which also depended on the length of the macromolecular chain.³ However, these synthetic cationic polymers are also extremely toxic, with low biodegradability, and are expensive to be produced

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in large quantities. On the other hand, many water-soluble polysaccharides are biodegradable and non-toxic, and several have been used in the formulation of drilling fluids.^{4–7} Several investigations in the latter area have focused on the development of environmentally friendly additives for water-based fluids with capacity for acting as rheology modifiers and filtrate loss control, i.e. present low viscosity at high shear rates and high viscosity at low shear rates, and to favor the formation of a thin layer of filter cake in order to reduce the filtrate loss into the geological formation, such as xanthan gum and modified starch.^{8–10}

Hydrophobically modified polymers have become the subject of extensive research due to their unique characteristics and applications such as in enhanced oil recovery and drilling fluids.^{11,12} These polymers are tailored on the basis of a hydrophilic macromolecular chain where a relatively small number of hydrophobic segments is introduced, forming the so-called associative polymers where these hydrophobic segments interact forming aggregates at low shear rates, increasing viscosity.^{13,14} The introduction of hydrophobic alkyl side segments on the backbone of chitosan has been performed by several authors,^{15,16} obtaining a chemically modified chitosan that is water-soluble only at low pH (<6.5) through the protonation of the amine group of the polymer. Although the use of this type of chemical structure could have a potential use as a rheology modifier for water-based drilling fluids, the necessity of a low pH would prevent its application in the field, since drilling fluids must present a high pH (>8.5) for several reasons, mainly to avoid corrosion.²

In the present work, hydrophobically modified truly cationic chitosans were synthesized via a two-step procedure that includes the hydrophobization of chitosan using different acyl chlorides, and then the quaternization of amine groups to yield the final genuine cationic products. FTIR and ¹³C-NMR spectroscopies were used to characterize the modified polymers, which were also evaluated as reactive clays inhibitors, rheological modifiers and filtrate loss reducers for water-based drilling fluids. The use of one single biodegradable product to replace several additives, some of them toxic as the synthetic cationic polymer, should drastically reduce the final cost of the water-based drilling fluids and bring important environmental advantages.

EXPERIMENTAL

Materials and Methods

The three commercial chitosan products with different molecular weights and deacetylation degrees of 75–85% used in this study were purchased from Sigma-Aldrich, Brazil. According to the manufacturer, these products are referred as low molecular weight (LMW, 50–190 kDa), medium molecular weight (MMW, 190–310 kDa), and high molecular weight (HMW, 310–375 kDa) chitosans. Mean molecular weights were determined in the lab using gel permeation chromatography (GPC) and dynamic light scattering (DLS), and the results showed a wide MW distribution (LMW = 117 ± 27 kDa, MMW = 190 ± 45 kDa, HMW = 270 ± 115 kDa), as expected for technical grade products, such as those used in the petroleum industry.

Acid chlorides (octanoyl, myristoyl, and palmitoyl chlorides), and PDADMAC were also purchased from Sigma-Aldrich. Hydroxypropyl starch (HPA) and xanthan gum were a gift from Petrobras

S.A. *N*-methyl-2-pyrrolidone (NMP), acetic acid, sodium iodide, methyl iodide, potassium chloride, and sodium hydroxide were obtained from Vetec-Brazil (Table SI). The lubricant DP400 was from Dhaymers Ltda. Brazil. All chemicals used were of analytical grade and were used as received. Deionized distilled water was used throughout the experiments. The clay used in the cuttings rolling tests and adsorption experiments was a bentonite supplied by Bentonorte Company (Paraíba, Brazil).

Synthesis of Modified Chitosans

The method for the synthesis of trimethylated cationic chitosan was based on a quaternization reaction, following the protocol described in Ref. 17 (Figure 1): 20 g of chitosan were first dispersed in 510 mL of *N*-methyl pyrrolidone; then after 24 h, 90 mL of 30% NaOH solution, 33 g of NaI, and 90 mL of CH₃I were added to the reaction medium.¹⁷ After 26 h, the trimethylated cationic chitosan (TC) was precipitated with acetone, and then re-solubilized in 1 mol L⁻¹ HCl solution. The product was re-precipitated three times with acetone, and the material obtained was dissolved in distilled water. This final solution containing the cationic product was placed in Petri plates and dried in an oven at 60°C for 4 days until solid films were formed.

The synthesis route used to obtain hydrophobically modified cationic chitosans consisted of two stages: first, the hydrophobization reaction of chitosan using different acyl chlorides (Figure 2), as described by Le Tien et al.,¹⁸ and second, the cationization of the obtained hydrophobically modified derivative (Figure 3). As a result, it was obtained a series of hydrophobically modified cationic chitosans, with varied lengths of the hydrophobic alkyl chain which in turn determines the degree of hydrophobicity of the derivative product.

In the first step, a mixture of chitosan and aqueous acetic acid (0.12 mol L⁻¹) was stirred at room temperature for 24 h to ensure total solubility. The pH was adjusted to 7.0 by slow addition of 1 mol L⁻¹ NaOH under strong agitation to yield a slurry gel. The acid chloride (containing 8, 14, or 16 carbon atoms in the hydrocarbon chains) was added and the reaction volume adjusted to 2 L with distilled water. After magnetic stirring at room temperature for 5 h, each preparation was neutralized (pH 7.0), and the product was precipitated with acetone. The precipitate was collected by filtration and washed three times with an excess of methanol at 60°C, to remove the residual acid. Finally, the hydrophobically modified chitosans (R-HMC) were dried in an oven at 60°C for 1 week, to obtain the corresponding derivative powders.

The second step was a quaternization reaction similar to the procedure described above for the synthesis of the cationically modified chitosan, but using the hydrophobically modified chitosans as starting reagent (Figure 3). All the derivative products (hydrophobically modified cationic chitosans, R-HMTC) were characterized by solid state ¹³C-NMR and FTIR. The abbreviations of chitosan derivatives used in this work are summarized in Table S1, in Supporting Information.

Structural Analysis

Solid state ¹³C-NMR analysis was performed on a Bruker spectrometer (DRX300 model, 7.05 Tesla magnetic field) operating

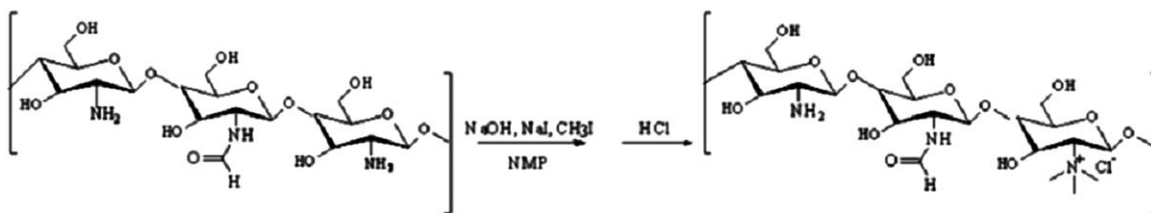


Figure 1. Scheme of the synthesis of cationic chitosan (TC).

at 75.4 MHz using the CPMAS probe. The spectra obtained were analyzed using the dmfit software to obtain an approximation of the spectrum using a model with a mixed Gaussian/Lorentzian function, which allowed the integration of the signals assigned to the functional groups in the macromolecules under study. The NMR spectra were used to calculate the mean degree of hydrophobization degree (nucleophilic substitution degree at the amines nitrogens) and the mean degree of cationization degree (trimethylation degree at the amines nitrogens), using eqs. (1) and (2), respectively. Peaks labeled as *m*, *d* and *t* were assigned to carbons from methyl groups that were introduced by the quaternization reaction to obtain hydrophobically modified cationic chitosan (C16 HMTc). The *m*, *d*, and *t* labels refer to the peaks corresponding to the methyl groups from N-monomethylation, N,N-dimethylation, and N,N,N-trimethylation, respectively. The peak labeled as *a* refers to the alkyl chain of the acyl group (*n* = no. carbon atoms in the alkyl chain).

$$\text{HD (\%)} = \frac{a/n}{(A_{C1} + A_{C2} + A_{C3} + A_{C4} + A_{C5} + A_{C6})/6} \times 100 \quad (1)$$

$$\text{CD (\%)} = \frac{t/3}{(A_{C1} + A_{C2} + A_{C3} + A_{C4} + A_{C5} + A_{C6})/6} \times 100 \quad (2)$$

Infrared spectra were obtained by using an absorption spectrometer with Fourier transform in the region of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans per sample. The spectrometer used was a Nicolet 740 FTIR with DTGS KBr detector and KBr beamsplitter.

Rheological Tests

The rheological tests were carried out using a Haake RS1 rheometer, with cylindrical type rotors DGH-41-Ti or cone-plate type C60/1°, depending on the viscosity of the system under consideration. Aqueous solutions of hydrophobically modified cationic chitosans with different molecular weights and alkyl chain lengths were prepared at concentrations of 1.0, 2.0, and 3.0% wt/vol. All rheological tests were conducted at 25°C. The

results were compared with those obtained using xanthan gum at a standard concentration of 0.57% wt/vol, where it shows the appropriate pseudoplastic behavior. Xanthan gum is a commercial additive commonly used as rheological modifier in water-based drilling fluids.

Inhibition of Reactive Clays

The inhibition assay consists in testing the capacity of the additive to inhibit clay reactivity, and it is performed by evaluating the size and quantity of cuttings before and after the contact with the additive solution, under controlled temperature, agitation, and time, following the procedure by Beihoffer et al.¹⁹ In this test, the clay sample is broken into small bits, which are previously passed through mesh sieves of 4 and 8 size to standardize the size of gravel. A mass of 15 g of gravel was placed in a Baroid cell, followed by the addition of 100 mL of solution containing the high MW hydrophobically modified cationic chitosans (C16 HMTc) in the concentration range of 1.0–3.0% (wt/vol). The cells were closed and transferred to a Baroid roller oven, and remained for 16 h at 60°C. After that time, the cells were cooled, opened and their contents poured into a second sieve (mesh 30). The gravels were then carefully washed with water, transferred to a Petri dish, and dried in an oven at 100°C during 16 h. The dry material was weighed and then it was passed through a sieve (mesh 8), weighing the material retained on the sieve. Blank samples (water) were prepared without the addition of modified chitosans (C16-HMTc) or PDADMAC, and also a standard sample with the commercial synthetic cationic polymer PDADMAC was used for comparison. The percentage of recovered clay is calculated as the ratio between the recovered clay weight and the initial weight.

Filtrate Loss Reduction

When evaluating the filtrate loss reduction performance of the new additives, HPA was replaced by the modified chitosans in the standard formulation. Evaluation of filtrate volume reduction by the developed modified chitosans in the fluids under study was

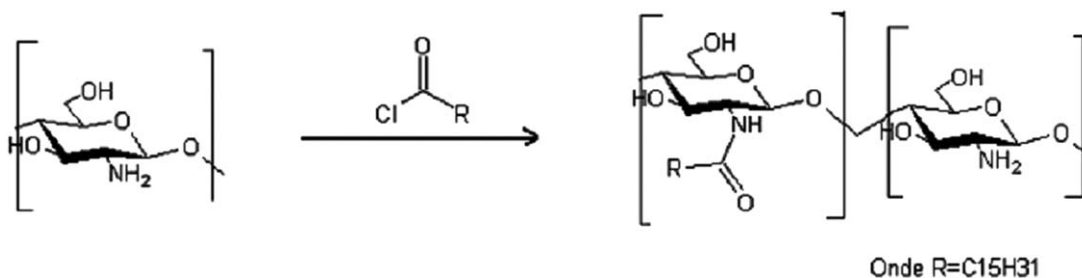


Figure 2. Scheme of the synthesis of hydrophobically modified chitosan (R-HMC), where R represents a saturated hydrocarbon chain of 8, 14, or 16 carbon atoms.

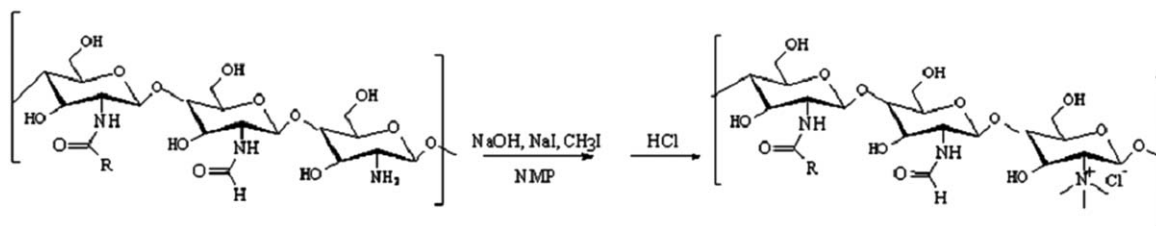


Figure 3. Scheme of the synthesis of hydrophobically modified cationic chitosan (R-HMTC), where R represents a saturated hydrocarbon chain of 8, 14, or 16 carbon atoms.

done by adding the different compounds under constant agitation at 13,000 rpm in a Hamilton Beach Mixer (Model 936), following the order described in Table S2 (Supporting Information). Once all the fluid components were added, the speed of the agitator was increased to 17,000 rpm, for 10 min. The formulated fluid was transferred to a Baroid cell, and placed in a roller oven for 16 h, at 60°C. After this period, the fluid was cooled to perform the corresponding American Petroleum Institute (API) test, which provides standard procedures for determining the filtration characteristics of water-based drilling fluid.²⁰ When evaluating the filtrate loss performance of the new additives, HPA was replaced by the modified chitosans in the standard formulation.

American Petroleum Institute (API) tests to evaluate the fluids capacity of reducing the filtrate volume were performed in a filter press (Fann Instruments, series 387) at high temperature and high pressure. The fluid was poured into a 150-mL filtration cell with a filter paper, and tightly closed. The cell was then placed in the filter press with a heating blanket. A 100 psi pressure was injected into the cell, and filtration started when the bottom valve of the cell was opened. After 30 min, the valve was closed and the filtrate was collected in a graduate cylinder. The filtrate volume is calculated as twice the amount collected in the graduate cylinder, in mL.

RESULTS AND DISCUSSION

Synthesis and Characterization of Chitosan Derivatives

The introduction of a permanent positive charge by trimethylation of amine groups in the chitosan molecules leads to derivative products that are soluble in water in a wide pH range. Other chitosan derivatives were obtained by nucleophilic substitution reaction between the amino groups of chitosan, and the carbon of the acyl chloride acid, forming a hydrophobic amide with a variable length of the hydrophobic segment. The hydrophobically modified cationic derivatives are not only water-soluble, but also became amphiphiles.

The ¹³C-NMR spectra of chitosan, before and after modifications, and the corresponding assignments, are presented in the Supporting Information (Figures S1 and S2, Tables S3 and S4). The hydrophobically modified cationic chitosan (HMTC) products used in this work showed hydrophobization degrees of 2.0–2.6% and degrees of cationization of 22–25%, calculated using eqs. (1) and (2), and by deconvolution of ¹³C-NMR spectra in the program Dmfit. In the FTIR spectra (see Supporting Information, Figure S3), the chitosan spectrum shows OH bands, primary amines (NH₂) in 3420 cm⁻¹, and C=O bands corresponding to the acetyl groups from chitosan, since chitin is usually incompletely de-

acetylated. The trimethylated chitosan (TC) spectrum shows the cationization of the amine group, which can be identified by the 1474 cm⁻¹ band, from the CH₃ groups, confirming the formation of the quaternary ammonium group. The more important bands in the FTIR spectrum of the cationic and hydrophobically modified chitosan (HMTC) are assigned to the carbonyl group from secondary amide (1560 cm⁻¹) and to alkyl CH₂ group (2924 and 2853 cm⁻¹). Other band assignments are shown in Supporting Information Tables S5–S7.

Rheological Properties of Chitosan Derivatives

Effect of Hydrophobization and Alkyl Chain Length. To evaluate the effect of hydrophobization on rheological properties of water-soluble high molecular weight chitosan derivatives, the curves of the dependence of viscosity on shear rate for hydrophobically modified cationic chitosans (HMTC, 2% wt/vol) of different alkyl chain lengths and for trimethylated cationic chitosan (TC) were obtained (Figure 4). Results for xanthan gum were also included for comparison.

The rheology curve for the non-hydrophobized trimethylated cationic chitosan shows a Newtonian behavior, with almost no change in viscosity with shear rate. In contrast, hydrophobically modified derivatives show a pseudoplastic behavior, i.e. high viscosity at low shear rates and low viscosity at high shear rates, similar to that of xanthan gum, being the C16-derivative the one with the closest behavior to the one from the standard modifier xanthan gum. The pseudoplastic behavior was observed for all the hydrophobically modified polymer solutions, confirming that the presence and size of hydrophobic segments in the macromolecules are the most important aspects to be considered in the design of a polysaccharide molecule that could be used as rheological modifier. Bataille et al. observed a similar rheological behavior in aqueous solutions of hydrophobically modified carboxymethylpullulan at different concentrations.¹⁴ The authors also found a behavior typical of pseudoplastic fluids containing polysaccharides, and attributed this result to the interactions between hydrophobic segments present in the modified polysaccharide chain.

Although the variation in the hydrophobic chain length did not compromise the pseudoplastic behavior of the polymer solutions, there was a higher increase in solution viscosity at low shear rates for the polymers with the larger hydrophobic segment (16 carbon atoms), which can be related to an increase in the strength of the associative networks derived from hydrophobic interactions. It has been reported that the hydrophobic groups present in hydrophobically modified chitosans are associated through intermolecular hydrophobic interactions, which increase the viscosity of the systems

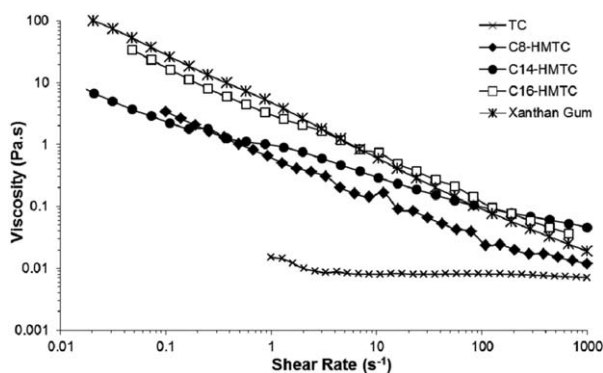


Figure 4. Rheological behavior of high molecular weight chitosan derivatives (2% wt/vol), compared with the one from xanthan gum (used as standard at 0.57% wt/vol).

at low shear rates.²¹ In that work, the authors concluded that the larger the size of the hydrophobic chain, the greater would be the viscosity of the fluid. These hydrophobic interactions can be observed when the hydrophobic segment has at least six carbon atoms. Since this rheological behavior is one of the requirements for hole cleaning by water-based drilling fluids, it is possible to consider the hydrophobically modified cationic chitosans synthesized in this work as promising rheological modifiers for this type of formulations. Hole cleaning is one of the most important functions of a drilling fluid. The cuttings that are produced by the drilling bit must be carried by the fluid to the surface. If the hole cleaning process is not efficient, serious problems can occur such as getting the pipe stuck at the well's bottom, excessive torque or too slow drilling rates. The drilling fluids capacity to transport the cuttings is given mainly by its rheological behavior. For this reason, the fluid must present high viscosities at low shear rates, in order to maintain the cuttings in suspension when the drilling process is interrupted, and low viscosities at high shear rates, in order to allow for the fluids pumping during drilling. This is the pseudoplastic behavior that must be obtained with the addition of rheology modifiers such as xanthan gum.² It is important to notice that in this case, one of the most relevant features of the obtained rheological curve is the high viscosity presented at very low shear rates.

Effect of Polymer Concentration. The rheological behavior of the solutions from the best product, i.e. the C16-modified high MW cationic chitosan was also studied at different polymer concentrations. As expected, the results shown in Figure 5 indicate that the higher the concentration of the hydrophobically modified cationic chitosan solutions, the higher the viscosity, at all shear rates. There have been some studies on the effect of polysaccharide concentration in the viscosity of the aqueous system. For example, Desbrieres and Babak reported that hydrophobic interactions may exist even in solutions with very low concentrations of hydrophobically modified polysaccharides.²¹ However, there is a limiting concentration of the solution at which the viscosity drastically increases compared to the unmodified polysaccharide. On the other hand, Esquenet et al. confirmed the formation of these associative networks, demonstrating the extent at which the concentration of polysaccharide in solution increases, favoring the formation of inter- and intramolecular hydrophobic interactions, leading to networks of flower-type

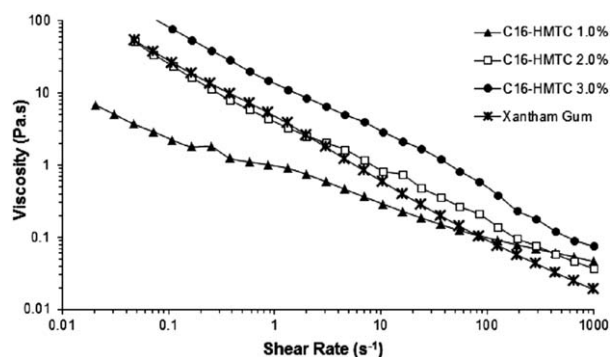


Figure 5. Rheological behavior of high molecular weight chitosan derivatives at different polymer concentrations (wt/vol), compared with xanthan gum (used as standard at 0.57% wt/vol).

aggregates, which are responsible for the significant increase in solution viscosity.²² At low shear rates, the C16-HMTC 2% wt/vol concentration solution presented the same viscosity as xanthan gum at 0.57% wt/vol, indicating that it would be necessary to use a higher concentration of C16-HMTC in order to obtain the necessary low shear rate high viscosity normally achieved with xanthan gum. However, 2% is also the concentration that did lead to good inhibition and filtrate loss results, as will be shown in the next sections, therefore justifying a fluid formulation with a higher concentration of C16-HMTC.

Effect of Molecular Weight of Polymer. The rheological behavior of C16-hydrophobically modified cationic chitosan derivatives with different molecular weights are shown in Figure 6. The obtained curves show that both chitosan derivatives of high and medium molecular weight present a rheological curve similar to the one from xanthan gum (pseudoplastic behavior), suggesting that chitosans of both molecular weights could be used as rheological modifiers for drilling fluids. Apparently the low molecular weight chitosan derivatives would produce much lower viscosities at low shear rates.

Inhibition of Reactive Clays

Chitosan, which is a polysaccharide obtained from the alkaline deacetylation of chitin, is a natural water insoluble polymer. In contrast, the trimethylated cationic chitosan derivative (TC) is

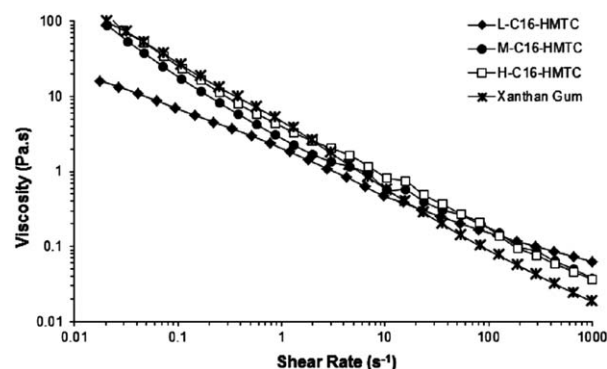


Figure 6. Rheological behavior of C16-hydrophobically modified cationic chitosan derivatives (C16-HMTC at 2% wt/vol) at 25°C, of different molecular weights, compared with xanthan gum (used as standard at 0.57% wt/vol).

Table I. Recovered Clay (in %) When Using TC, C16-HMTC, or PDADMAC as Additives

% wt/vol	Blank (water)		TC		C16-HMTC		PDADMAC	
	Mesh 30	Mesh 8	Mesh 30	Mesh 8	Mesh 30	Mesh 8	Mesh 30	Mesh 8
1.0	36 ± 6	14 ± 1	89 ± 1	86 ± 3	85 ± 3	68 ± 4	98 ± 1	84 ± 1
2.0	36 ± 6	14 ± 1	90 ± 1	85 ± 7	92 ± 1	80 ± 2	99 ± 1	90 ± 1
3.0	36 ± 6	14 ± 1	93 ± 1	88 ± 1	99 ± 1	93 ± 1	100 ± 1	93 ± 2

water-soluble over the whole pH range. This high solubility in water is an essential requirement for application of polymers as inhibitors of reactive clays in water-based drilling fluids. In that case, the polymer will penetrate into the clays gallery and the positive charges in the polymer chain of the cationic chitosan will interact with the negative charges present on interlayer surfaces, turning the interlayer space hydrophobic and avoiding the typical expansion of the clays basal spacing that occurs when the water enters the interlayer space.²³

Aqueous solutions containing trimethylated chitosan and hydrophobically modified high MW cationic chitosan were used in the cuttings rolling test for clay inhibition, to assess the influence of the hydrophobic segment of the molecules on their performance as reactive clays inhibitors (Table I).

These results showed that the hydrophobically modified cationic chitosans are better inhibitors of reactive clays when compared to the cationic chitosan (TC), at 3.0% wt/vol concentrations. Compared with the synthetic cationic polymer PDADMAC, the hydrophobically modified derivative showed a similar capacity for inhibition at the highest concentration studied here (3%), being its performance as good as that of the commercial additive, at the same concentration value. The clay inhibition tests give a quantitative estimation of the extent of intergranular cohesion, and also resistance to hydration and to mechanical stresses of the cuttings after contact with the inhibition additive in the fluid. The material collected in Mesh 30 is called dispersed material and the one collected in Mesh 8 is called the intact material. Therefore, C16-HMTC at 2.0 and 3.0% has shown to be a highly inhibitive additive, producing a low level of cuttings dispersion and a high final recovery, therefore able to replace the toxic PDADMAC in water-based drilling fluids.

Filtrate Loss Performance

The results obtained from this API test showed that the presence of hydrophobically modified cationic high MW chitosan (C16-HMTC) in the formulated drilling fluid significantly decreased the volume of filtrate obtained at the concentrations studied in this work. Filtrate loss volumes were 6.0 mL, 4.8 mL, and 4.2 mL when using 1, 2, and 3% (wt/vol) of modified polymer, respectively. All the values were below the blank filtrate loss (10 mL), and comparable to that obtained with the commercial additive HPA (at 4% w/v, filtrate loss volume = 4.8 mL), commonly used in the formulation of drilling fluids.

CONCLUSIONS

The results showed that the hydrophobically modified chitosan derivatives obtained in this work are promising substitutes for

several additives used in commercial formulations of water-based drilling fluids. These derivatives of chitosan showed pseudoplastic behavior in the concentration range studied. The results indicated that a product with C16 segments, 2% (wt/vol) concentration and high molar weight led to aqueous solutions with a pseudoplastic behavior equivalent to the one presented by a xanthan gum solution, that is the commercial rheology modifier regularly used in water-based drilling fluids. Therefore, the results show that there is a good potential for cationic and hydrophobically modified chitosans to be used as rheology modifiers for water-based drilling fluids. When compared with the toxic commercial cationic polymer polydiallyldimethylammonium chloride (PDADMAC), the high MW hydrophobically modified cationic chitosan (C16-HMTC) showed the same excellent capacity for inhibiting the clays reactivity and for keeping the cuttings integrity, at the same concentration. The results obtained from the fluid loss control test showed that this hydrophobically modified cationic chitosan also significantly decreased the volume of filtrate of the formulated drilling fluid, leading to values comparable to the ones obtained with the commercial additive HPA, commonly used in those formulations. Therefore, the obtained modified polysaccharides are promising candidates for replacing commonly used additives, in a more environmentally benign approach for water-based drilling fluids.

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