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SHORT COMMUNICATION

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# Application of a new family of amphoteric cellulose-based graft copolymers as drilling-mud additives

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**Abstract** A new family of amphoteric cellulose-based graft copolymers (CGADs), which were prepared by grafting acrylamide and dimethylaminoethyl methacrylate onto sodium carboxymethyl cellulose, have been investigated for their properties as multifunctional drilling-mud additives with respect to shale inhibition, rheological control and filtrate-loss control. For the CGADs investigated, the shale-inhibition ability improves but the filtration-control ability weakens with increasing content of cationic groups. An increase in the concentration of CGADs results in better inhibition and viscosity-building as well as lower fluid loss. The pH of the medium has an effect on the inhibitive property. A comparative study among CGADs and some commercial polymeric drilling-mud additives was also carried out.

**Key words** Amphoteric graft copolymer · Water-soluble cellulose derivative · Drilling-fluid additive · Water-based mud · Oilfield drilling

## Introduction

Growing concerns over the environmental impact of oil-based drilling fluids in oilfields have lead to an increasing reliance on water-based systems [1–3]. An important aspect of water-based muds is the design and testing of water-soluble polymers to control the main functions of the muds: shale stabilization, rheological characteristics and fluid loss [4, 5]. To date, naturally occurring and synthetic polymers have found extensive applications in water-based muds. Among these additives, conventional anionic polymers and recently developed cationic polymers are most widely used [6–21]. Anionic polymers such as sodium carboxymethyl cellulose (CMC), polyanionic cellulose and partially hydrolyzed polyacrylamide have good viscosity-building and filtration-control properties but weak shale inhibition. Cationic polymers such as cationic polyacrylamide and quarternary polyamine exhibit effective shale inhibition but weak mud performance and bad compatibility with the other drilling fluid components. Thus, it is expected that amphoteric polymers containing both cationic and anionic groups along the polymer chain may overcome these problems and combine cationic and anionic polymer behavior advantageously. In this study, a new family of amphoteric cellulose-based graft copolymers (CGADs), which were prepared by grafting acrylamide (AM) and dimethylaminoethyl methacrylate (DMAEMA) onto CMC, have been investigated for their properties as multifunctional drilling-mud additives with respect to shale inhibition, viscosity-building and filtration control.

## Experimental

### Materials

CGADs were prepared by grafting DMAEMA and AM onto CMC in aqueous solution using ammonium persulfate and *N*,*N*,*N*′,*N*′-tetramethylethylene as the redox initiator. Details of the synthesis, purification, structural characterization and composition analysis of CGADs have been reported in a previous paper [22]. Three CGADs with different composition and intrinsic viscosity ([$\eta$]) were used (Table 1). Commercial CMC, a shale sample and Anqiu bentonite were provided by the Drilling Mud

**Table 1** Amphoteric cellulose-based graft copolymer (*CGAD*) samples used in this study. The percentages of acrylamide (*AM*) units ($\% W_{AM}$), dimethylaminoethyl methacrylate (*DMAEMA*) units ($\% W_{DMAEMA}$) and sodium carboxymethyl cellulose (*CMC*) units ($\% W_{CMC}$), and the intrinsic viscosity ($[\eta]$), measured using a Ubbelohde viscometer at pH 8.0 and 30 ± 0.02 °C in 0.6 M NaCl aqueous solutions, are given

| No. | $\% W_{AM}$ | $\% W_{DMAEMA}$ | $\% W_{CMC}$ | $[\eta]$ (dl/g) |
|---|---|---|---|---|
| CGAD-1 | 58.77 | 8.84 | 32.46 | 1.74 |
| CGAD-2 | 55.70 | 17.54 | 26.76 | 1.60 |
| CGAD-3 | 53.60 | 22.15 | 24.25 | 1.54 |

Company of Shengli Petroleum Administration, China. Commercial FA367 was provided by the Southwest Petroleum Institute, China.

### Shale hot-rolling tests

The weathered shale was ground and sieved to retain a suitable mesh fraction for the hot-rolling tests. A 5.0-g portion of this shale was added to the test fluid in a stainless steel aging jar and the system was rolled for 12 h at 120 °C. After the rolling, the contents of the jar were passed over an 80-mesh screen. The retained shale was then dried to constant weight at 100 °C. The shale recovery ($\% R$) was calculated for each sieve on a dry-mass basis as follows:

$$\% R = W/W_0 \times 100 \quad (1)$$

where $W$ and $W_0$ denote the weight after hot-rolling and the weight before hot-rolling, respectively. Based on these tests, the effects of polymer composition, concentration and pH medium on the shale recovery were investigated.

### Mud property tests

Mud property tests were performed according to American Petroleum Institute (API) specifications. Two kinds of muds, a fresh-water-based mud (4% prehydrated Anqiu bentonite), which was made up by maintaining the ratio of the clay to $Na_2CO_3$ to $H_2O$ at 4:0.2:100 by weight, and a saline-based mud (4% prehydrated Anqiu bentonite +4% NaCl ), were made. Prior to use, these saline- and fresh-water-based muds were aged for 24 h at room temperature to hydrate the bentonite. The required quantity of polymer was added to the saline- and fresh-water-based muds and stirred at high speed for 10 min. Then the rheological properties of the treated mud as well as those of the saline- and fresh-water-based muds were measured using a DNN-$Z_6$ type rotating viscometer. The rheological parameters such as apparent viscosity ($\eta_a$), plastic viscosity ($\eta_b$) and yield point ($\tau_0$) can be determined as follows [23]:

$$\eta_a = \Phi_{600}/2 \text{ (mPa s)} \quad (2)$$

$$\eta_p = \Phi_{600} - \Phi_{300} \text{ (mPa s)} \quad (3)$$

$$\tau_0 = 0.511(\Phi_{300} - \eta_p) \text{ (Pa)} , \quad (4)$$

where $\Phi_{600}$ is the viscosity at a rotation rate of 600 rpm and $\Phi_{300}$ is the viscosity at a rotation rate of 300 rpm. API filtrate volumes were measured using a ZNS-III-type medium-pressure filtration apparatus made by the Lanzhou Oil Refinery, China.

## Results and discussion

The values of shale recovery in pure water and in aqueous solutions containing different polymers at pH 8.0 are given in Table 2. The values of shale recovery in the polymer solutions are greater than the value of the shale recovery in pure water, especially in CGAD-2 and CGAD-3 solutions, showing the inhibition of these polymers on the disintegration or dispersion of the shale. The three CGADs suppress the dispersion of the shale more effectively than unmodified CMC, demonstrating the contribution of the cationic groups to the inhibition. According to Shen and Perricone [15], high molecular weight and large hydrodynamic volume of a polymer are favorable for its inhibition on the shale. Of the three CGADs, however, CGAD-1, with the greatest $[\eta]$, does not demonstrate improved inhibition. This shows that the inhibitive property of the CGADs investigated is not controlled by $[\eta]$. In contrast, the shale recovery increases with increasing content of dimethylaminoethyl groups ($\% W_{DMAEMA}$), suggesting that the high content of the cationic groups favors the inhibitive property. This may be attributed to two causes. First, the cationic groups can neutralize the negative charges on the shale surfaces and decrease the shale's zeta potential, thus reducing the hydration ability of the shale. Second, the cationic groups can reinforce the adsorption of the polymer and form a film on the shale, thus hindering water from entering the shale. Compared with amphoteric FA367, a commercial hydration inhibitor applied successfully in drilling fluids [24–26], CGAD-2 and CGAD-3 have better inhibitive properties. Besides, it is seen from Table 2 that an increase in the concentration of CGAD-2 results in an increase in shale recovery.

The effect of the pH of the medium on the inhibition of CGAD-2 is shown in Fig. 1. As the pH decreases, the shale recovery increases. This phenomenon may be ascribed to the gradual conversions of dimethylaminoethyl groups along the CGAD-2 chain from the non-protonated state to the protonated state and carboxymethyl groups along the CGAD-2 chain from the dissociated state to the associated state. In other words, in an acidic solution the CGAD-2 molecule

**Table 2** Shale-recovery performance ($\% R$)

| Test fluid | pH | $\% R$ |
|---|---|---|
| Pure water | 8.0 | 30.7 |
| 0.2% CGAD-1 | 8.0 | 54.3 |
| 0.2% CGAD-2 | 8.0 | 85.1 |
| 0.4% CGAD-2 | 8.0 | 87.6 |
| 0.6% CGAD-2 | 8.0 | 91.5 |
| 0.2% CGAD-3 | 8.0 | 91.7 |
| 0.2% CMC | 8.0 | 46.5 |
| 0.2% FA367 | 8.0 | 60.5 |

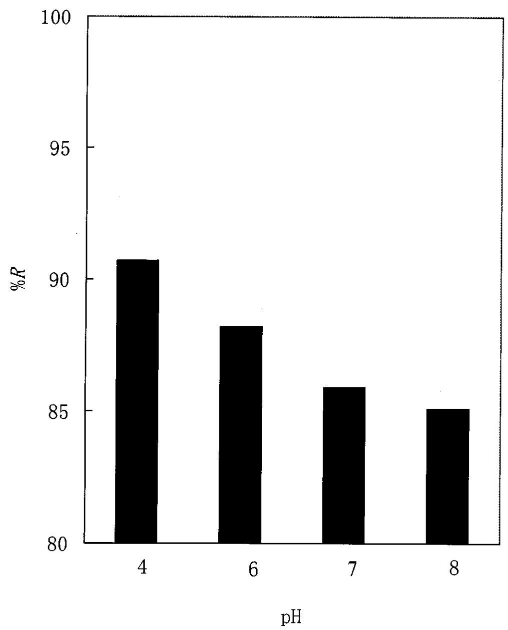


**Fig. 1** Effect of pH of the CGAD-2 solution on the shale recovery (%$R$). Polymer concentration: 0.2 wt%

is primarily positive (the charge being centered at the nitrogen atom), which improves the interactions of CGAD-2 with the shale due to the corresponding increase in the Coulombic attraction between them.

In contrast to the dispersed or high-solid mud formulated with bentonite, the rheological behavior of the inhibitive polymer mud with low bentonite content is largely controlled by the viscosifying effect of the dissolved high-molecular-weigh polymer [27]. The rheological properties of the fresh-water-based muds and the saline-based muds before and after treatment with different polymers (CGAD-1,CGAD-2,CGAD-3, CMC, FA367) are given in Table 3. The treated muds have higher $\eta_a$, $\eta_b$ and $\tau_0$ than the untreated mud regardless of mud type. This shows that these polymers produce a viscosity-building property. Despite the variation in $\%W_{AM}$, $\%W_{DMAEMA}$, $\%W_{CMC}$ and $[\eta]$ (see Table 1), there is little dependence of the rheological property on composition for the CGADs investigated. There is, however, a marked dependence of the rheological property on the polymer concentration. An increase in the concentration results in stronger viscosity-building properties. It seems that a high polymer concentration is favorable for the formation of a mud network structure. Like commonly used CMC, CGADs have a good viscosifying effect both in the fresh-water-based mud and in the saline-based mud. In spite of the good properties in the fresh-water-based mud, commercial FA367 demonstrates weaker viscosity-building ability in the saline-based mud when compared with CGADs.

Filtration control is an important property of any drilling fluid. High fluid loss will result in bad mud performance and troublesome drilling [28]. API filtration volumes of the bentonite mud and the bentonite–polymer muds are shown in Fig. 2. For the muds treated with CGAD-1, CGAD-2, CGAD-3, CMC and FA367, API filtration volumes decrease in contrast to the based muds, indicating the filtration-control ability of these polymers. Compared with commercial CMC and FA367, the three CGADs show control ability matched to the fluid loss. For the CGADs investigated, the filtration-control property improves with the increase in

**Table 3** Rheological properties in fresh-water-based muds and saline-based muds

| Formulation of mud | Rheological property | | | pH |
|---|---|---|---|---|
| | $\eta_a$ [mPa s] | $\eta_b$ [mPa s] | $\tau_0$ [Pa] | |
| Fresh-water-based mud (I) | 6.0 | 4.0 | 2.0 | 8.5 |
| (I) +0.2% CGAD-1 | 11.3 | 8.5 | 2.8 | 8.5 |
| (I) +0.1% CGAD-2 | 6.5 | 3.0 | 3.5 | 8.5 |
| (I) +0.2% CGAD-2 | 9.0 | 7.0 | 2.0 | 8.5 |
| (I) +0.3% CGAD-2 | 16.5 | 8.0 | 8.5 | 8.5 |
| (I) +0.2% CGAD-3 | 11.5 | 7.0 | 4.0 | 8.5 |
| (I) +0.2% CMC | 9.3 | 7.0 | 2.3 | 8.5 |
| (I) +0.2% FA367 | 16.3 | 13.0 | 3.3 | 8.5 |
| Saline-based-mud (II) | 2.0 | 1.5 | 0.5 | 8.0 |
| (II) +1.0% CGAD-1 | 25.5 | 13.0 | 12.5 | 8.0 |
| (II) +1.0% CGAD-2 | 23.0 | 13.0 | 10.0 | 8.0 |
| (II) +1.0% CGAD-3 | 24.5 | 13.0 | 11.5 | 8.0 |
| (II) +1.0% CMC | 22.0 | 19.0 | 3.0 | 8.0 |
| (II) +1.0% FA367 | 10.3 | 9.0 | 1.5 | 8.0 |

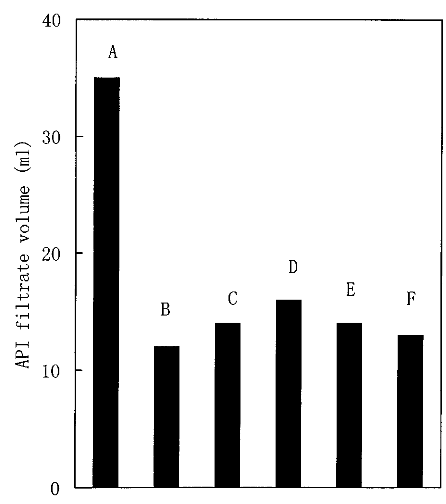


**Fig. 2** American Petroleum Institute (*API*) filtrate volumes of the bentonite mud and the bentonite–polymer muds. *A*: 4% prehydrated Anqiu bentonite; *B*: (*A*) +0.2% CGAD-1; *C*: (*A*) +0.2% CGAD-2; *D*: (*A*) +0.2% CGAD-3; *E*: (*A*) +0.2% CMC; *F*: (*A*) +0.2% FA367. pH = 8.5

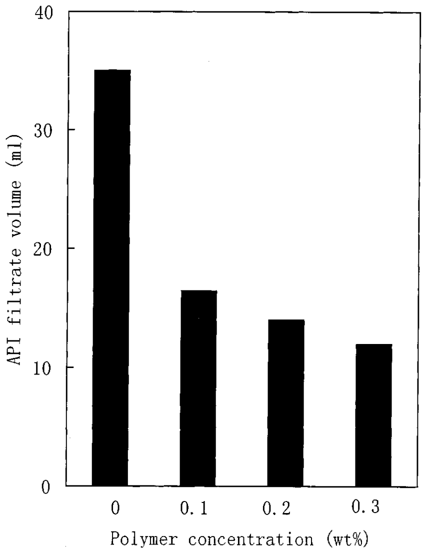


**Fig. 3** Effect of CGAD-2 concentration on API filtrate volume. Based mud: 4% prehydrated Anqiu bentonite. pH = 8.5

[$\eta$] and the decrease in $\% W_{\mathrm{DMAEMA}}$. There is, therefore, a conflict in introducing the cationic groups of CGADs since a high value of $\% W_{\mathrm{DMAEMA}}$ is desired for shale inhibition but is unfavorable to the filtration control. The mechanism for the reduction of the fluid loss of bentonite muds by polymers is not clearly understood. Heinle et al. [29] suggested that the control of fluid loss was achieved by the polymers adsorbing on bentonite and preventing flocculation of the bentonite.

The effect of CGAD-2 concentration on API filtration volume of the mud is shown in Fig. 3. An increase in the concentration improves the filtration-control property.

## Conclusions

New CGADs of CMC with AM and DMAEMA have been investigated for their properties as multifunctional drilling-mud additives. Increasing the cationic groups of CGADs results in good shale-inhibition ability but weak filtration-control properties. An increase in the concentration of CGADs favors inhibition, viscosity-building and fluid-loss control, and the pH of the medium has an effect on the inhibitive properties. It is shown that amphoteric CGAD with suitable structural parameters can be expected to be a drilling-fluid additive with both good inhibitive and mud properties.

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