

Multifunctional Characteristics of New Carboxymethylcellulose-Based Graft Copolymers for Oilfield Drilling

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ABSTRACT: New carboxymethylcellulose-based graft copolymers with an amphoteric character were synthesized by grafting 2-(dimethylamino)ethyl methacrylate onto carboxymethylcellulose using a persulfate-initiated solution polymerization technique. Their multifunctional characteristics as an oilfield drilling-mud additive were investigated with respect to shale inhibition, viscosity building, and filtration control. It was shown that the graft copolymer with an appropriate grafting extent is characteristic of both good shale inhibition and mud properties and may overcome the limitations inherent in commonly used anionic and cationic polymeric additives. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 195–201, 2000

Key words: cellulosic copolymer; amphoteric polymers; water-based mud; shale inhibition; rheological control; filtration control; oilfield drilling

INTRODUCTION

Water-based muds for oilfield drilling usually require effective water-soluble polymers to perform such main functions as shale inhibition, viscosity building, and filtration control.^{1,2} Up to now, conventional anionic polymers such as carboxymethylcellulose (CMC), polyanionic cellulose, and partially hydrolyzed polyacrylamide and recently developed cationic polymers such as quarternary polyamine and cationic polyacrylamide have been widely used for these purposes.^{3–18} Both exhibit inherent advantages and disadvantages: The anionic polymers possess good filtration control and viscosity-building properties but weak shale inhibition. The cationic polymers exhibit effective

shale inhibition but suffer from weak mud performance, bad compatibility, as well as high toxicity to aquatic organisms. Therefore, there has been an increasing demand in the oilfield industry to develop environmentally acceptable polymeric additives that can combine cationic and anionic polymer behavior advantageously and overcome the limitations inherent in the above-mentioned additives.^{19–23} In this work, some amphoteric CMC-based graft copolymers were investigated for their multifunctional characteristics as a drilling-mud additive with respect to shale inhibition, viscosity building, and filtration control.

EXPERIMENTAL

Materials

Oilfield-grade CMC, a shale sample, and Anqiu bentonite were provided by the Drilling Mud Co. of the Shengli Petroleum Administration (Shandong, China). The CMC has a degree of substitu-

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Table I Details of Synthesis of New CMC-Based Graft Copolymers

Sample No.	Mol in Reaction Mixture			CMC (g)	Grafting Parameters ^a			$[\eta]^b$ (mL g ⁻¹)
	DMAEMA	APS ($\times 10^{-3}$)	TMEDA ($\times 10^{-3}$)		% <i>G</i>	% <i>E</i>	% <i>C</i>	
CGD-I	0.02	0.44	0.45	4.0	44.2	87.6	56.3	192.9
CGD-II	0.02	0.14	0.45	2.0	65.7	80.7	41.9	181.8
CGD-III	0.02	0.22	0.45	2.0	83.6	81.5	53.2	173.2
CGD-IV	0.03	0.44	0.45	2.0	110.8	78.0	47.2	167.6

The reactions were carried out in a nitrogen atmosphere; 100 mL of distilled water was used as the solvent. Reaction temperature, 35°C; reaction time, 6 h; pH 6.0.

^a The grafting parameters were determined as follows: % *G* (grafting percentage) = $(W_2 - W_0) \times 100/W_0$; % *E* (grafting efficiency) = $(W_2 - W_0) \times 100/(W_1 - W_0)$; % *C* (monomer grafting conversion) = $(W_2 - W_0) \times 100/W_3$, where W_0 , W_1 , W_2 , and W_3 are the weights of CMC, the reaction products, the graft copolymer, and the monomer DMAEMA, respectively.

^b Viscosity measurements were carried out at 30°C using an Ubbelohde viscometer.

tion of 0.732, determined by conductometric titration,²⁴ and an average molecular weight of 1.1×10^5 (25°C, 0.1 mol/L aqueous NaCl solution), determined by the viscosity method.²⁵ Prior to use, the CMC was purified by washing with 85% alcohol. The cationic monomer 2-(dimethylamino)ethyl methacrylate (DMAEMA) was supplied by the Jilu Petroleum Chemical Co. (Shandong, China) and purified by distillation under reduced pressure. Ammonium persulfate (APS; analytical grade) was purified by recrystallization from water and *N,N,N',N'*-tetramethylethylenediamine (TMEDA; biochemical grade) was used without further purification.

Craft Copolymerization

A new CMC-based graft copolymer (CGD) with an amphoteric character was synthesized by grafting DMAEMA onto CMC in an aqueous solution using APS/TMEDA as the initiator system. The following procedure was adopted in carrying out the reaction: A definite amount of the CMC was dissolved in distilled water with stirring and warming, and inert gas (N₂) was bubbled through. After 30 min, the required quantity of the APS solution and the TMEDA solution were added successively to the reaction system. After 10 min, a definite amount of DMAEME was added. The flask content was kept in a thermostatic water bath at 35°C for 6 h. After completion of the reaction, the product was precipitated by pouring the reaction mixture solution into acetone, filtered, and washed with acetone three times, then dried under reduced pressure to a constant weight. To obtain the pure graft copolymers, the reaction product was slurried in aqueous methyl alcohol

followed by filtration and finally dried in a vacuum oven at 40°C. It was found that extracting with a mixture of methyl alcohol and water was quite enough to remove the poly(DMAEM) (homopolymer). The details of the reaction conditions are given in Table I.

Shale Hot-Rolling Tests

The weathered shale was ground and sieved to retain a suitable mesh fraction for the hot-rolling tests. A 5.00-g portion of this shale was added to a stainless-steel aging jar containing the test fluid. The jar was then capped and rolled for 12 h at 120°C. Undispersed shale granules were then collected on a 80-mesh screen, washed gently with distilled water, and dried to a constant weight. The shale recovery (% *R*) was calculated for each sieve on a dry mass basis as follows:

$$\%R = 100 \times W_r/W_i \quad (1)$$

where W_r and W_i denote the weight of the shale recovered and the initial shale weight, respectively.

Mud-Property Tests

Mud-property tests were performed according to the American Petroleum Institute (API) specifications.²⁶ A low-solid base mud, 4% prehydrated Anqu bentonite, was made up by maintaining the ratio of the clay, Na₂CO₃, and H₂O at 4:0.2:100 by weight. Prior to use, the base mud was aged for 24 h at room temperature to hydrate the bentonite. The required quantity of the polymer was added to the base mud and stirred at high speed

for 10 min. Then, the rheological properties of the treated mud as well as that of the base mud were measured using a DNN-Z₆-type rotating viscometer. The rheological parameters such as apparent viscosity (*AV*), plastic viscosity (*PV*), and yield point (*YP*) can be determined as follows²⁶:

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

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

$$YP = 0.511(\Phi_{300} - PV)(\text{Pa}) \quad (4)$$

where Φ_{600} is the viscosity at the rotating rate of 600 rpm and Φ_{300} is the viscosity at the rotating rate of 300 rpm. The API filtrate volume was measured by a ZNS-III-type medium-pressure filtration apparatus made at the Lanzhou Oil Refinery (China).

RESULTS AND DISCUSSION

Preparation of Graft Copolymers

The primary objective of this study was to relate the structural parameters of the CGD to its multifunctional properties as an oilfield drilling–mud additive. In synthesizing this series of graft copolymers, we hope, therefore, to obtain a number of graft copolymers with a varying number and length of poly(DMAEM) chains. For this purpose, four graft copolymers of CMC and DMAEMA were prepared by changing the initiator or CMC concentration and keeping other reaction conditions constant. Table I gives details of the graft copolymerization and the grafting parameters as well as the intrinsic viscosity ($[\eta]$) obtained. Comparing CGD-II with CGD-III in Table I, we see that increase of the APS concentration is accompanied by an increase in the grafting percentage ($\% G$) and a decrease in the $[\eta]$. It seems that by increasing the initiator concentration the number of graft chains per backbone molecule increases but the length of graft chains decreases since a greater number of free-radical sites created by the higher concentration of APS have to compete for the same monomer concentration. Deshmukh et al.²⁷ studied the grafting of CGC and starch with acrylamide using a ceric-ion-initiated solution polymerization technique and found a similar change. These results are also in accordance with the results obtained by Rath and Singh²⁸ on the graft copolymers of starch. Besides, in comparing

Table II Shale Recovery in Different Test Fluids

Test No.	Test Fluid	pH	W_i (g)	W_r (g)	$\% R$
1	Pure water	8.0	5.00	1.5354	30.7
2	0.2% CMC	8.0	5.00	2.3255	46.5
3	0.2% CGD-I	8.0	5.00	2.4802	51.1
4	0.2% CGD-II	8.0	5.00	2.8255	56.5
5	0.2% CGD-III	8.0	5.00	4.2379	84.8
6	0.2% CGD-IV	8.0	5.00	4.6199	92.4

CGD-I with CGD-IV in Table I, we observe that an increase of CMC concentration results in a decrease in the $\% G$ and an increase in the $[\eta]$. Among the CGD samples prepared, CGD-I has the lowest $\% G$ and the greatest $[\eta]$ while CGD-IV has the highest $\% G$ and the smallest $[\eta]$. Thus, these new graft copolymers were used to investigate their multifunctional characteristics.

Shale-Inhibition Characteristics

A large number of static and dynamic methods have been proposed to determine the performance of drilling-fluid additives as shale inhibitors.^{29–35} Among them, the commonly used shale hot-rolling test is confirmed to be an effective method.¹²

Table II lists the values of $\% R$ in pure water and in 0.2% aqueous solutions containing different polymers at pH 8.0, the typical formation equilibrium pH for most shales.² The values of $\% R$ in the polymer solutions are greater than the value of $\% R$ in pure water, especially in the CGD-III and CGD-IV solutions, showing the inhibition of these polymers on the dispersion of the shale. Four CGD samples suppress the dispersion of the shale more effectively than does ungrafted CMC, demonstrating that the grafting modification enhances the shale-inhibition effectiveness.

For the graft copolymers investigated, it is noted that the $\% G$ has a great effect on the $\% R$. As seen in Figure 1, the $\% R$ increases obviously with increasing the grafting extent ($\% G$) of the cationic monomer. Although lower molecular weight and smaller hydrodynamic volume (corresponding to lower $[\eta]$) of a polymer are unfavorable to the enhancement of inhibition,¹² the higher the $\% G$ of the CGD sample with lower $[\eta]$ is, the stronger its inhibitive ability. This indicates that the inhibitive property of the CGD samples depends mainly on the $\% G$. This fact may result from two causes²¹: First, the intro-

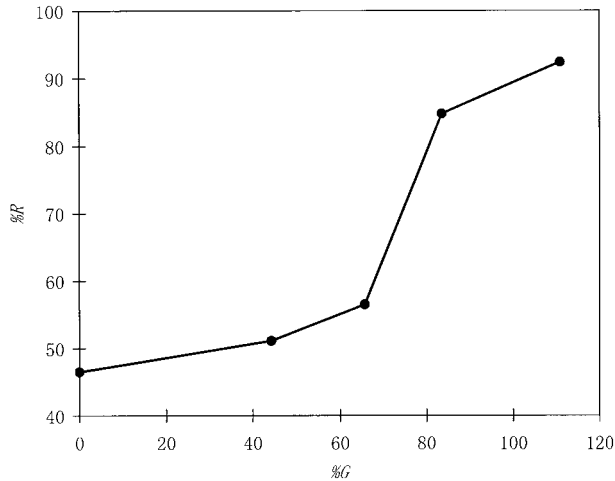


Figure 1 Effect of the grafting percentage (% G) of CGD samples on the shale recovery (% R).

duced cationic groups neutralize the negative charges on the shale surfaces and thus reduce the hydration ability of the shale. Second, the introduced cationic groups reinforce the adsorption of the polymer and form a film on the shale, thus hindering water from entering into the shale.

Figure 2 shows the effect of the pH medium on the inhibitive property of CGD-II. With decrease of the pH, the % R increases. This phenomenon may be ascribed to the gradual conversions of dimethylaminoethyl groups along the CGD-II chain from the nonprotonated state to the protonated state and carboxymethyl groups along the CGD-II chain from the dissociated state to the associated state. In other words, in an acid solu-

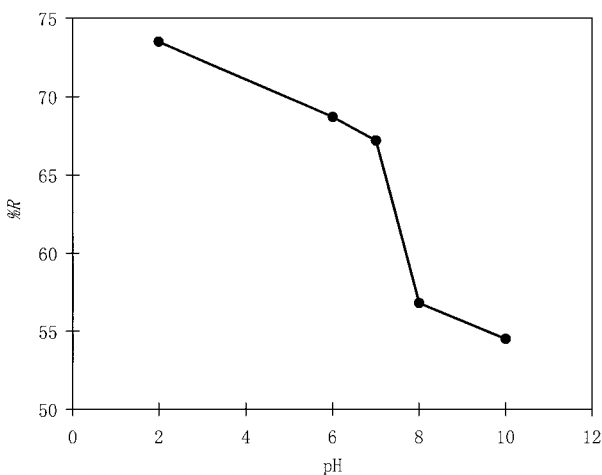


Figure 2 Effect of pH of CGD-II solution on the shale recovery (% R). Polymer concentration: 0.2 wt %.

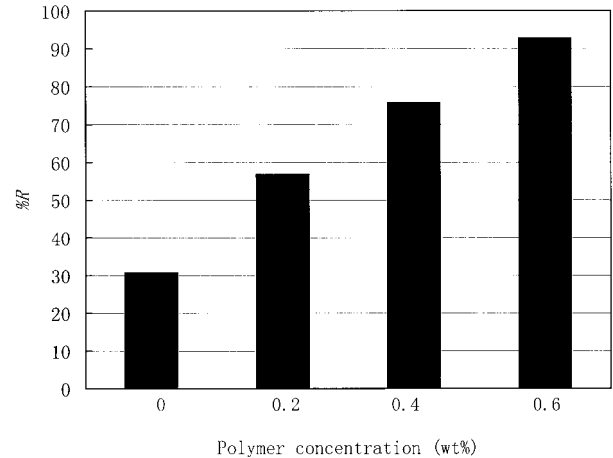


Figure 3 Effect of CGD-II concentration on the shale recovery (% R). pH 8.0.

tion, the CGD-II molecule is primarily positive (the charge being centered at the nitrogen atom), which improves the interactions of CGD-II with negatively charged shale surfaces. Obviously, these will become the advantage when compared with anionic CMC.

Figure 3 illustrates the values of % R as a function of the concentration of CGD-II. As seen, the increase in the concentration results in increase of the inhibitive property.

Viscosity-Building Characteristic

The advantages of low-solid polymer muds with low bentonite content have been known for some time. These advantages include faster penetration rates, fewer bits, and shale inhibition due to lower pH and the adsorption of the polymer on cuttings and on the borehole. Different from the dispersed or high-solid muds formulated with bentonite, their rheological behavior is largely controlled by the viscosifying effect of the dissolved high molecular weight polymer.³⁶

Table III gives the rheological properties of the bentonite base mud and the bentonite-polymer muds. The high values of AV , PV , and YP imply that a network structure is present in the mud, which makes the mud stable and viscous. For the bentonite-polymer muds studied, they have higher AV , PV , and YP than those of the bentonite base mud, showing that the polymers investigated contribute to building up the network structure, resulting in a viscosity-building ability. On the other hand, four CGD samples have a better viscosity-building property than that of the CMC.

Table III Rheological Properties of the Bentonite Mud and the Bentonite–Polymer Muds

Test No.	Mud Formulation ^a	Rheological Parameters			pH
		AV (mPa s)	PV (mPa s)	YP (Pa s)	
1	Base mud	6.0	4.0	2.0	9.0
2	Base mud + 0.2% CMC	9.3	7.0	2.3	8.0
3	Base mud + 0.2% CGD-I	17.0	10.0	7.0	8.0
4	Base mud + 0.2% CGD-II	22.0	12.0	10.0	8.0
5	Base mud + 0.2% CGD-III	25.0	11.0	14.0	8.0
6	Base mud + 0.2% CGD-IV	14.5	8.0	6.5	8.0

^a The base mud is 4% prehydrated Anqiu bentonite with a density of 1.03 g/cm³.

This may result from the fact that the CGD with both anionic and cationic groups can adsorb on negatively charged clay mineral surfaces as well as at the positively charged edges, which favors the clay–polymer interaction and the forming of a mud network structure. Of the CGD samples investigated, CGD-IV, with the greatest % *G* and the smallest $[\eta]$, has the lowest AV, PV, and YP. This may be attributed to the flocculation induced by the high content of the cationic groups and a weak viscosifying effect due to the low molecular weight of the polymer.

Figure 4 shows the effect of the CGD-I concentration on the mud rheological parameters. It was found that there is a marked dependence of the rheological property on the polymer concentration. An increase in the concentration results in an improved viscosity-building property.

Filtration-Control Characteristic

Filtration control is an important property of any drilling fluid, because high fluid loss will

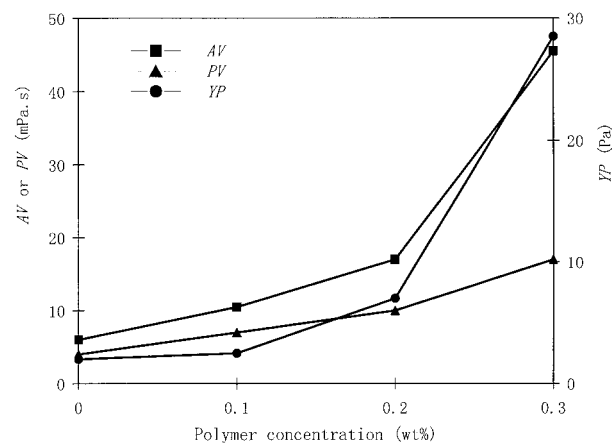


Figure 4 Effect of CGD-I concentration on the rheological parameters of the mud.

result in bad mud performance and a troublesome drilling problem.³⁷ Table IV gives the filtration property of the bentonite base mud and the bentonite–polymer muds. Compared with the base mud, the muds treated with four CGD samples and the CMC have lower API filtration volumes and smaller filter cake thickness, indicating the filtration-control ability of these polymers. For the muds treated with the four CGD samples, API filtration volumes as well as the zeta potentials increased with increase of the % *G* of the CGD, indicating that there is a conflict in introducing the cationic groups of the CGD since a high value of % *G* is desired for the shale inhibition but is unfavorable to the filtration control. According to Heinle et al.,³⁸ reduction of the fluid loss of bentonite muds by polymers is achieved by the polymers adsorbing on bentonite and preventing flocculation of the bentonite. Therefore, an appropriate grafting extent is necessary for the CGD used.

CONCLUSIONS

New amphoteric graft copolymers of CMC with DMAEMA were investigated for their multifunctional characteristics as an oilfield drilling–mud additive with respect to shale inhibition, viscosity building, and filtration control. For the graft copolymers studied, the shale-inhibition ability improves but the filtration-control ability weakens with increasing grafting extent. An increase in the concentration of the graft copolymer results in better inhibition and viscosity-building properties. There is a dependence of the inhibitive property on the pH medium. It is anticipated that the graft copolymer with an appropriate grafting extent has potential appli-

Table IV Filtration Properties of the Bentonite Mud and the Bentonite-Polymer Muds

Test No.	Mud Formulation ^a	API Filtrate Volume (mL/30 min)	Filter Cake Thickness (mm)	Zeta Potential ^b (mV)
1	Base mud	35.0	2.0	-33.4
2	Base mud + 0.2% CMC	14.0	0.5	-42.1
3	Base mud + 0.2% CGD-I	12.0	1.0	-37.8
4	Base mud + 0.2% CGD-II	13.0	1.0	-34.2
5	Base mud + 0.2% CGD-III	17.0	1.0	-28.3
6	Base mud + 0.2% CGD-IV	21.0	1.0	-24.6

^a The base mud is 4% prehydrated Anqiu bentonite with a density of 1.03 g/cm³.

^b The zeta potential was measured using a Model 501 Lazer Zee Meter™ by diluting the mud sample to 0.5 wt % of the solid.

cation as a new multifunctional polymeric additive for oilfield drilling.

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