

## POTENTIALS OF POLYACRYLAMIDE-SODIUM CARBOXYMETHYL CELLULOSE GRAFT POLYMER AS FLOODING MATERIAL IN ENHANCED CRUDE OIL RECOVERY

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Cellulose-based derivatives have been used in drilling fluids as viscosifiers and fluid loss reducers for many years. But more recently due to evident advantages, such as technology and relative ease of large-scale production of cellulose derivatives as powders or granules and the generally non-toxic nature of cellulose ethers, research efforts have been intensified to optimize their possible applications as polymer flooding materials in enhanced oil recovery. Consequently, this paper addresses the synthesis and characterization of polyacrylamide-sodium carboxymethyl cellulose graft polymer produced from locally available cellulose material.

Notable improvement was achieved in the specific viscosity of the graft polymer when compared with the unmodified sodium carboxymethyl cellulose (NaCMC). For a 1% (wt%) solution at 25°C and a shear rate of 200s<sup>-1</sup>, NaCMC has a viscosity of 74.6 centipose while the graft polymer recorded a viscosity of 154 centipose. The influence of mono and multivalent cations such as sodium, calcium and aluminium ions on the viscosity of the graft polymer solution was relatively minimal, suggesting improvement in the so-called salt tolerance or cation compatibility.

**Key words:** Polyacrylamide, Crude oil, Visocifiers

### Introduction

Crude oil is an important energy source and a vital chemical raw material. It occurs within the pore spaces of underground reservoir and the amount of crude oil that can be recovered is dependent on a number of factors including the nature of crude, reservoir properties, existing technology and prevailing economic climate. The total amount of crude oil that exists in a reservoir prior to production is referred to as the original oil-in-place (OOIP) and recovery rate can range from less than 5% of OOIP to as high as 80%. However, a reasonable global average is presently estimated at about 35% (Leckie 1998).

Nigeria's crude oil reserve is estimated at about 25 billion barrels at an average production rate of 200 million barrels per day. It can be assumed that local crude oil resources will be exhausted in 30 years time except when new oil discoveries are made. It has been shown that for each 1% increase in production yield, an increase in supply for an additional one be applied successfully to highly saline reservoirs and are capable of recovering of additional 10%-20% OOIP (Maitin and Volz 1981).

A few types of polymers have been found to satisfy the technical and commercial demands of polymer flooding, which broadly requires properties such as:

- 1) Viscosity builder at low concentration
- 2) Good injectivity
- 3) Temperature resistance
- 4) Good tolerance to cation
- 5) Price/effectiveness.

Polymers that have been found suitable for enhanced crude

oil recovery with the desirable properties include: Xanthan, Scleroglucan, Polyacrylamide and cellulose derivatives. Though no optimal polymer flooding material currently exists, Xanthan gum has remained relatively the best on all round requirements. Xanthan is known to exhibit such desirable properties as stability at elevated temperature and high viscosity level, but it is prone to microbial degradation (Kulicke and Makromd 1986).

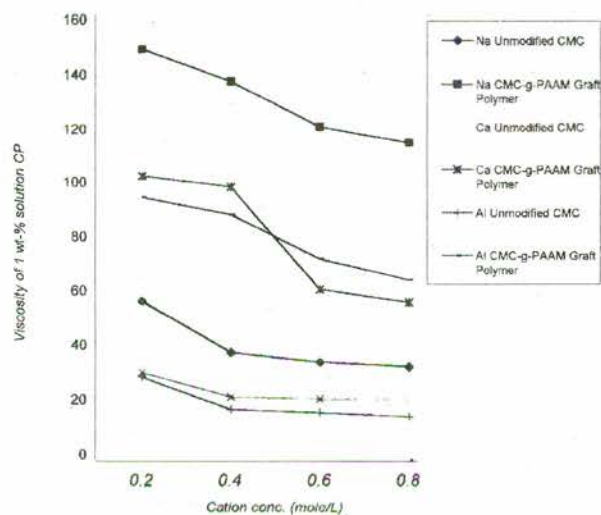
The use of poly (styrene-sulphonate) as a polymer-flooding agent has also been studied, (Kulicke and Lehmann 1986) but its sensitivity to brine its viscosity loss with aging and the possibility of side-reactions tend to limit its application in enhanced oil recovery. Although, polyacrylamide sulphonate is reported to attain high viscosity level due to steric hindrance and restricted rotation about the backbone, it suffers the disadvantage of non-compatibility with bivalent cations (Kulicke and Lehmann 1986).

Cationic polymers have also been employed in polymer flooding. However, they exhibit strong adsorption on the surface of silicate materials and rocks thereby giving rise to problem of pore blockage in the crude oil reservoirs. Another attractive polymer type is the class of polyvinylsaccharides; these polymers display a resistance to microbial degradation because of an all carbon backbone. They also exhibit a stable solution structure in the presence of salt (Klein *et al* 1985), but their viscosification efficiency is low. Concerning cellulose derivatives, hydroethyl cellulose is characterized by an excellent salt and temperature resistance, but has unsatisfactory injectivity behaviour. Whereas, carboxymethyl cellulose

**Table 1**

Effect of graft copolymerization system on the molecular weight (Mw) of grafted polyacrylamide chain and frequency of grafting acrylamide onto carboxymethyl cellulose by semi-continuous process.

Graft copolymerization system	% Graft-on level	Mv of grafted chain $\times 10^{-4}$	Frequency of grafting Ng $\times 10^4/100$
100% aqueous medium without catalyst	315.62	23.09	13.67
Ceric ion in 0.1M HNO <sub>3</sub> plus catalyst through substrate	527.21	14.92	35.37
100% aqueous medium plus catalyst added ceric ion in 0.01M HNO <sub>3</sub> and catalyst through monomer	469.90	17.30	27.16
Ceric ion in 0.01 HNO <sub>3</sub> without catalyst.	438.71	20.11	21.82
20% ethanol medium plus catalyst.	377.16	13.08	28.83
20% ethanol medium without catalyst.	305.07	14.24	21.42



**Fig 1.** Effect of mono and multivalent cations on the viscosity of carboxymethyl cellulose-polyacrylamide graft polymer and unmodified carboxymethyl cellulose

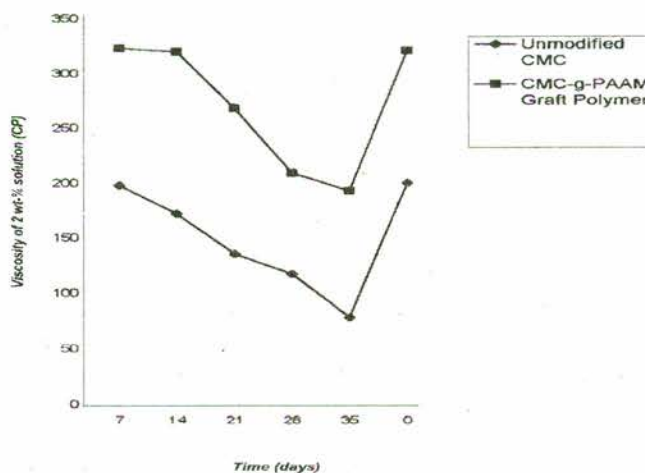
which exhibits good injectivity properties often exhibits low salt tolerance.

Since the injectivity of the polymer solution into the crude oil reservoir without any plugging effect is one of the most important criteria for polymer flooding materials, it is therefore of great interest to develop novel or improved cellulose derivatives with this characteristic as well as other advantages.

**Table 2**

Effects of mono and multivalent cations on the viscosity of carboxymethyl cellulose polyacrylamide graft polymer and unmodified carboxymethyl cellulose.

Sample 1 wt- (%/vol)	Viscosity in distilled water 25°C (Share rate of 200s <sup>-1</sup> )cP			
	0.2M	0.4M	0.6M	0.8M
Sodium ion conc. (M)				
Unmodified CMC	56.3	37.4	33.8	32.0
CMC-PAAM graft polymer	149.5	137.8	121.2	115.0
Calcium ion conc				
Unmodified CMC	30.0	21.2	20.4	20.0
CMC-PAAM graft polymer	102.6	98.6	60.7	56.0
Aluminium ion conc				
Unmodified CMC	28.4	16.7	15.4	14.0
CMC-PAAM graft polymer	94.8	88.5	71.9	64.0



**Fig 2.** Effect of time on the specific viscosity of CMC-g-PAAM graft polymer and unmodified carboxymethyl cellulose using 2 wt% polymer solution at 50°C

These advantages include: 1) Ease of large scale production, 2) The technology of cellulose derivatives production as powder or granules is well established and relatively easy to handle, 3). Cellulose ethers are generally non-toxic.

Thus, this paper addresses the optimization of the viscosification efficiency and metal cations compatibility of carboxymethyl cellulose through graft copolymerization of acrylamide monomer unto the cellulose backbone.

## Material and Methods

Holocellulose from *Terminalis superba* (white afara) wood meal was obtained by the chlorite pulping method by Jayme (1942) and Wise *et al* (1946) (DP = 287). Acrylamide monomer (Cambrian chemicals, England) was purified by recrystallization from Chloroform. Ceric ammonium nitrate (BDH Ltd, England) was used without further purification.

**Carboxymethylation.** The cellulose was carboxymethylated by the use of standard method. In a typical procedure Heinze *et al* (1994) 10g of air-dried cellulose in 400ml of isopropanol were vigorously stirred, while 20ml of 4% aqueous sodium hydroxide was added dropwise over 30 min at 29°C. stirring was continued for another hour and 18g of monochloroacetic acid was then added during a 30-min period. The mixture was placed on a water bath for 3 hours at 55°C with stirring, suspended in 1 litre of 80% aqueous methanol and neutralized with acetic acid. The product was collected after filtration, washed three times with 80% aqueous methanol and dried at 55°C in vacuum. The degree of substitution of carboxymethyl cellulose was determined by the ASTM acid wash procedure. (ASTMD, 1967).

**Graft copolymerization.** Graft copolymerization of acrylamide on caroxymethyl cellulose was carried out at 29°C using a semi-continuous polymerization procedure. 1 g of carboxymethyl cellulose was dissolved in 50ml of alcoholic medium and initiated with 5ml of 10.00 moles of ceric ammonium nitrate solution for 15 min. After the initiation, 15 ml of the initiator and 20ml of various monomer concentrations were introduced in a drop-wise manner simultaneously into the reaction flask with stirring continuously for 1 h.

The polymerization was stopped by addition of 1ml 2% (w/v) quinol solution in acetone to the reaction mixture. The reaction mixture was poured into a large excess of methanol. The product was filtered and the residue air-dried and weighed. The ungrafted polyacrylamide homopolymer was then extracted with excess warm water. The CMC graft copolymer was then air-dried and weighed. The percentage graft level is reported as the weight of the graft polymer, divided by the weight used, multiplied by hundred.

**Isolation of polyacrylamide grafted chains and molecular weight determination.** The grafted polymer chain were isolated from the carboxymethyl cellulose substrate using the method of Ogiwar and Kubota (1967). In the procedure 2g of the graft copolymer was used with 20ml of 70% (v/v) aqueous solution of sulphuric acid for 24 h at 20°C. The mixture was filtered on sintered glass funnel and the filtrate poured into excess of methanol. The recovered polyacrylamide was redissolved in distilled water and reprecipitated with methanol. The molecular weight of pure polyacrylamide extracted was determined from viscosity measurement of dilute polymer solutions in aqueous 1M NaNO<sub>3</sub> at 30°C using Ubbelohde viscometer. The molecular weight was then computed graphically from the value of intrinsic viscosity, using Mark-Houwink Equation (Suen *et al* 1958).

$$[\eta] = 3.73 \times 10^{-4} Mv^{0.56}$$

The number of grafted polyacrylamide chains (Ng) is reported as the ratio of percent graft level and molecular weight expressed in m moles per 100g of substrate.

**Determination of viscosity and effects of cations on the viscosity of sodium carboxymethyl cellulose and nacme-g-PAAM copolymer.** The viscosities of sodium carboxymethyl cellulose and the graft copolymer were determined by the standard ASTM procedure ASTM D (1967) using the Bariod Hank Crank type rotary viscometer at a shear rate of 200s<sup>-1</sup>.

While the effects of cations on viscosity ascertained by the introduction of 10ml of aqueous solution of sodium chloride, calcium chloride and aluminium sulphate (0.2m to 0.6m) respectively into 1wt-% solution of test materials and stirred thoroughly, and the viscosity determined again by the ASTM procedure.

## Results and Discussion

**Effect of graft copolymerization system on the molecular weight (Mw) of grafted polyacrylamide chain and frequency of grafting acrylamide onto carboxymethyl cellulose.** The variation of average molecular weight (Mv) of grafted polyacrylamide chains and frequency of grafting acrylamide into cellulose using varying copolymerization system is shown in Table 1. The results show that the molecular weight of grafted PAAM chains ranged generally from  $1.31 \times 10^5$  for the (20/80) 10% vol. ethanol copolymerization medium without the sodium hydroxide catalyst to a peak  $2.31 \times 10^5$  for the 10% aqueous medium without catalyst. The molecular weight of grafted PAAM chains was relatively lower in copolymerization system containing alcohol. Although carboxymethyl cellulose and alpha cellulose as substrate, do not seem to affect the overall average molecular weight of the grafted chain as the values obtained are comparable (Idehen 1998), however, significant improvements were recorded in the frequency of grafting for all the copolymerization systems using carboxymethyl cellulose as compared with alpha cellulose. The values for the former substrate ranged from  $13.67 \text{ Ng} \times 10^4/100\text{g}$  to  $35.37 \text{ Ng} \times 10^4/100\text{g}$  while the highest value obtained for cellulose is  $5.72 \text{ Ng} \times 10^4/100\text{g}$ . The specific effects of the sodium hydroxide catalyst and ceric initiator in acidic medium on the molecular weight of grafted PAAM chains are uncertain, since no trend was observed from the results.

The variations of the frequency of grafted with monomer concentration seem to suggest that reactions other than propagation by radicals on the substrate may be responsible for graft polymer formation.

**Characterization of carboxymethyl cellulose-polyacrylamide graft polymer (CMC-g-PAAM).** The characterization of carboxymethyl cellulose-polyacrylamide graft polymer produced (575.21% graft-on level) was carried out using specific viscosity, effects of temperature and time on viscosity, and stability against salts as outlined in the experiment. These parameters were chosen because; the principle of

displacing crude oil from its deposit in polymer enhanced crude oil recovery is strongly connected to the above properties of the polymer.

The specific viscosity of CMC-PAAM graft polymer and unmodified carboxymethyl cellulose at 25°C and 50°C using 1 wt% solution showed a significant enhancement in the specific viscosity of the modified carboxymethyl cellulose-polyacrylamide graft polymer as compared with the unmodified. The observed increase in specific viscosity due to modification was about 58.16% at 15°C and 51.68% at 25°C using 1 wt-% polymer solution. The loss in specific viscosity in changing from a test temperature of 25°C to 50°C was about 29.89% for the unmodified carboxymethyl cellulose and 19.04% for the CMC-g-PAAM graft polymer suggesting polymer, suggesting also some improvement in viscosity stability to temperature of the graft polymer.

The effects of mono and multivalent cations on the viscosity of carboxymethyl cellulose polyacrylamide graft polymer and unmodified carboxymethyl cellulose is shown in Table 2 and plotted in Fig 1.

The results show a gradual decrease in viscosity with increase in cation concentration. The loss of viscosity with cation concentration was generally higher for the unmodified carboxymethyl cellulose than for the CMC-PAAM graft polymer, and the magnitude of the effect was in the order  $\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$  in the case of unmodified carboxymethyl cellulose.

The above trend is also applicable to the graft polymer except for  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  at concentration of about 0.48 M and above when the effects of  $\text{Ca}^{2+}$  are relatively greater than for  $\text{Al}^{3+}$  (see Fig. 1). The introduction of  $\text{Na}^+$  from a concentration of 0.2M to 0.8M into test solutions accounted for about 43.16% loss in viscosity of the unmodified carboxymethyl cellulose while the graft polymer recorded about 23.1% loss in viscosity under the same conditions. The viscosity losses at 0.8M  $\text{Ca}^{2+}$  in the  $\text{Al}^{3+}$  concentrations corresponded to 73.19% for  $\text{Ca}^{2+}$  and 81.23% for  $\text{Al}^{3+}$  in the case of unmodified carboxymethyl cellulose and 63.66% for  $\text{Ca}^{2+}$  and 58.54% for  $\text{Al}^{3+}$  in the case of CMC-PAAM graft polymer.

These observations seem to suggest some improvement in the compatibility of the graft polymer with mono and multivalent cation a desirable property for viscosity builders in flooding media in enhanced crude oil recovery.

*Changes in the specific viscosity of carboxymethyl cellulose-polyacrylamide graft polymer and unmodified carboxymethyl cellulose solutions with time.* The variation of specific viscosity of CMC-PAAM graft polymer and carboxymethyl cellulose solutions with time using 2 wt% polymer solution at 50°C is plotted in Fig. 2. The results showed that the graft polymer maintained a stable viscosity for up to about two weeks of storage, while the unmodified carboxymethyl cellulose recorded about 14% loss in specific viscosity as at two weeks of storage.

Three regimes are identified in the time Vs viscosity graph of the polymer solution namely. i) A relatively stable period (1-14 days), ii) A period of pronounced viscosity loss (14-28 days) and iii) A period of moderate loss in viscosity (28-35 days)

The unmodified carboxymethyl cellulose was relatively stable for the first 7 days, after which viscosity loss proceeded markedly. The viscosity loss 50°C after 35 days was 61.07% for the unmodified NaCMC and 39.87% for the CMC-g-PAAM polymer, indicating an improvement in the long-term temperature stability of the graft polymer.

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