

# 1 Formulation of Polymers from Locally Sourced Polysaccharides in 2 Polymer flooding 3

## 4 ABSTRACT

5 The oil industry is experiencing a paradigm shift where the use of green chemicals is been  
6 encourage in order to address environmental issues associated with the use of synthetic  
7 chemicals as well as the fact that most of these synthetic polymers like hydrolysed  
8 polyacrylamide which is used to reduce the mobility of water in enhanced oil recovery; are  
9 imported chemicals. Thus, this brings the need to locally source for polymers that are viable  
10 so as to increase indigenous production for the oil industry.

11 Gum Arabic is a viscosifier mostly found in the northern part of Nigeria. Different  
12 concentrations of the Gum Arabic were analysed as to study their rheology as well as the  
13 effect of salinity on them which will determine their degree of resistance as this is a **crit**  
14 for polymer flooding. However, the stability of Gum Arabic was further enhanced by the  
15 introduction of Carboxymethyl Cellulose (CMC) at varying concentration to determine its  
16 effect on the solution viscosity. From the results, it can be concluded that increased viscosity  
17 was as a result of the modification of Gum Arabic by CMC and this could be related to  
18 increase bonding with CMC.

19  
20 Keywords: Gum Arabic; Carboxymethyl Cellulose (CMC); Polymer; Viscosity; Salinity.

## 21 22 INTRODUCTION

23 Polymer flooding has been carried out for the past 40 years in many marginal oil fields and  
24 its effectiveness has proved to be successful in several fields. The general expectation from  
25 polymer flooding is to obtain about 50% ultimate recovery with averagely 15 to 20%  
26 incremental recovery over secondary water flooding process (Rellegadla, 2017). Both  
27 naturally derived polymers like xanthan gum and synthetic polymers such as the partially  
28 **hydrolysed** polyacrylamide (HPAM) have been used basically for the purpose of viscosifying  
29 water for polymer flooding. Typical synthetic polymers are partially **hydrolysed**  
30 polyacrylamide (HPAM) and its derivatives have been used for most large-scale field  
31 production mostly because it is less costly (Chang, 2011). The commercial bio-polymer used  
32 in oilfield application but not frequently used like the HPAM due to its higher cost is xanthan  
33 gum (Sun, 2012).

34 HPAM in produced water (Back produced water) after polymer flooding in oilfield causes  
35 serious environmental problems such as difficulty in oil - water separation, the treatment of  
36 back produced water from polymer flooding (PWPF) is more difficult to separate than oily  
37 wastewater without HPAM (Zhang, 2010, Bao, 2010, Deng, 2002) because the HPAM  
38 residual component dissolved in water increases the viscosity of wastewater and also HPAM  
39 is equally absorbed onto the oil/water interface, making the separation process much more  
40 difficult to attain (Duan, 2014).

41 Chemical cost of a polymer flooding process is a function of the polymer selected for  
42 flooding. For instance, although chemical cost as well as the treatment cost is said to be  
43 higher for xanthan gum solutions compared to polyacrylamide solutions, Xanthan's cost is  
44 stable when compared to the fluctuating cost of polyacrylamide polymer. The polyacrylamide  
45 is actually synthesised from petroleum products and their costs in the market are very  
46 sensitive to the crude oil prices. (Rellegadla et al, 2017). Thus, there is need to synthesize less  
47 costly environmentally friendly polymers with high degree of stability as this is a sure way of  
48 generating more recovery while reducing cost.

49 Gum Arabic is presently one of the oldest polysaccharides and mostly found in the northern  
50 part of Nigeria also known as *Acacia Senegal*. It is produced as tear-drop-shaped globules  
51 exudates from bark wound of Acacia trees (Glicksman, 1973). Due to the presence of ionic  
52 charges on the backbone of the polymer chain, the viscosity of solution of gum Arabic is  
53 based on changes in pH, viscosity is low at low and also at high pH and reaches a maximum  
54 at about a pH of 6-8. It occurs majorly as a mixture of calcium magnesium and potassium  
55 salts of Arabic-acid and is composed of the following carbohydrates, this include: galactose,  
56 arabino pyranose, arabino furanose, rhamnose, glucuronic acid and 4-0 methyl glucuronic  
57 (Anderson, 1966). The gum is a highly water soluble polysaccharide, it is principally used in  
58 the food and pharmaceutical industries as stabilizer, thickener, suspending and binding agent  
59 in the manufacture of confections, dairy products, beverages and tablets (Nahla, 2000).

60

61 Carboxymethyl cellulose (CMC) is the most popular and cheapest cellulose derivative, it is  
62 an anionic and also a water-soluble natural polymer that is well known as a safe and  
63 biodegradable polymer which is widely used in the food industries as food additives, oil and  
64 gas industries, paper and textile industries e.t.c due to its high viscosity (Ibrahim, 2014).  
65 CMC is **synthesized** by reacting cellulose with sodium hydroxide in the presence of sodium  
66 chloroacetate.

67 In line with Nigerian Oil and Gas Industry Content Development Act, 2010 which seeks to  
68 increase indigenous participation in the oil and gas industry by prescribing minimum  
69 threshold for the use of local services and materials as well as promoting the transfer of  
70 technology and skills to Nigerian staff and labour in the industry, this work investigates the  
71 use of Gum Arabic (locally sourced) as a suitable polymer in enhanced oil recovery while  
72 CMC was added to determine the effect on its stability at increased water salinity.

## 73 MATERIALS AND METHOD

74 In this analysis, different concentrations of Gum Arabic (Figure 1) from 10,000ppm,  
75 30,000ppm to 50,000ppm were dissolved using **500 ml** of water. The solution was stirred  
76 gently to achieved homogeneity, this was then allowed to hydrate for a period of 24hrs.  
77 Rheological characterisation was carried out using Fann Viscometer to determine the  
78 rheology at different Speeds from (600, 300, 200, 100 6) rpm to 3rpm. The stability of the  
79 solutions **was** further analysed using NaCl (1wt%). The concentration of CMC utilized in the  
80 formulation was increased from 1wt% to 1.4wt% to study the effect of CMC on the viscosity  
81 with respect to salinity after another 24hrs. The rheological study equally captured the  
82 investigation of CMC alone as well as when blended with Gum Arabic



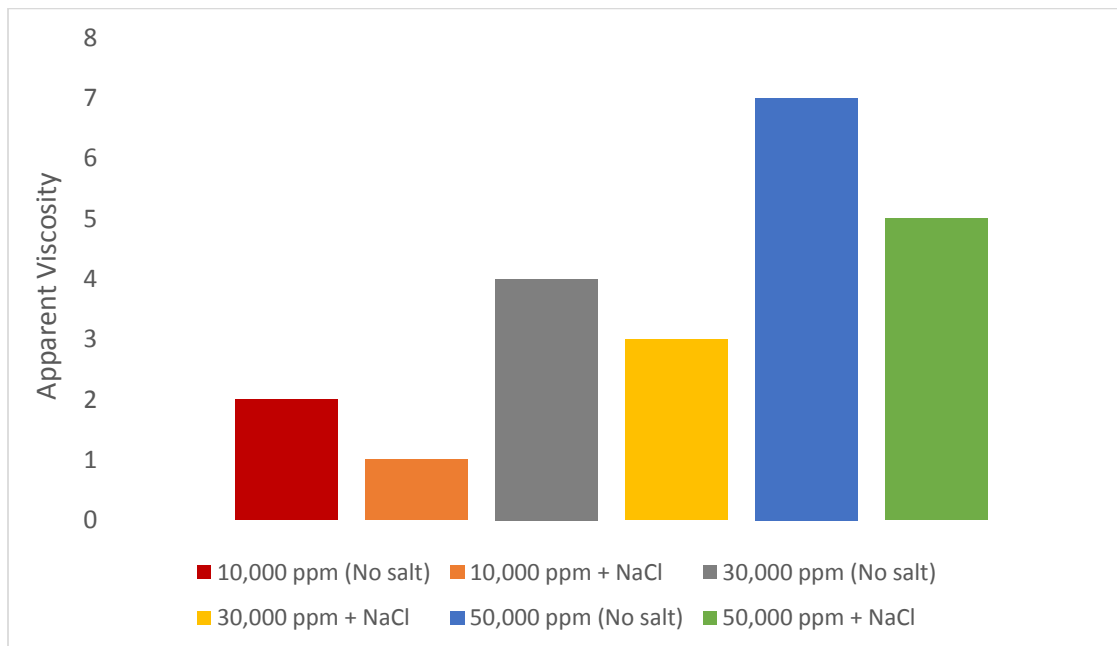
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**FIGURE 1** Gum Arabic

85 RESULTS AND DISCUSSION

86 From Figure 2, it is obvious that increasing the Gum Arabic's concentration improved the  
87 solution's viscosity at higher concentration of 50,000 ppm just like some other  
88 polysaccharides like Xanthan gum, Guar gum e.t.c that show very good rheology at  
89 increasing concentrations (Chatterji 1981, Eiroboyi, 2018). Though, Gum Arabic's viscosity  
90 did not show much appreciable rheology at low concentration of the gum alone, this could be  
91 as a result of the nature of its molecular structure which is in line with the work carried out by  
92 Authur, 2014 where he mentioned that Tragacanth gum and Gum ghatti contain the highest  
93 amount of rhamnose and arabinose, Gum Arabic contains the least amount of these sugars  
94 which makes it less viscous at lower concentrations. Also, the effect of salt affected the  
95 viscosity, this is because of the fact that the gum is polyelectrolyte (Glicksman et al, 1983)  
96 hence its interaction with NaCl.



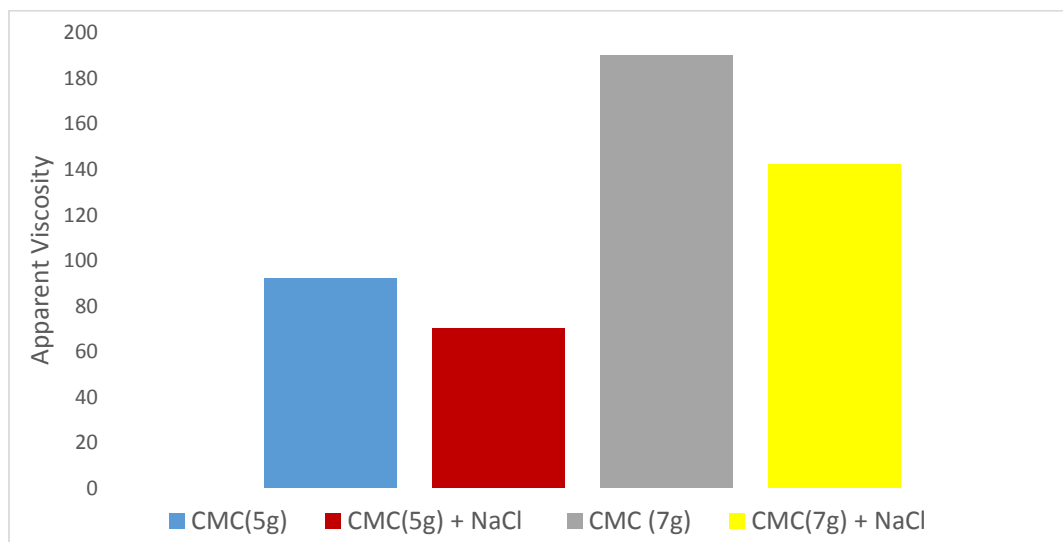
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98 **FIGURE 2** The Effect of salinity on Gum Arabic at increasing concentration

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100 Figure 3 displays the rheological behaviour of Carboxymethyl Cellulose alone at increasing  
101 concentration as well as in the presence of NaCl. However, in this case it was used an  
102 additive in the formulation, the results show that 1wt % of CMC was very viscous even more  
103 viscous at increasing concentration of 1.4wt % which agrees with Chatterji et al, 1981 in  
104 which they stated that CMC has one of the highest viscosifying ability. This particular  
105 analysis was necessary to actually ascertain if there would be synergy between the polymers  
106 after blending based on the viscosity values. Both 1wt% and 1.4wt% reflected reduction in  
107 viscosity in the presence of 1wt% NaCl, this also confirms the analogy given by Chatterji et  
108 al, 1981 in which they mentioned that CMC is anionic making it such that the presence of salt  
yields negative effect on its viscosity.

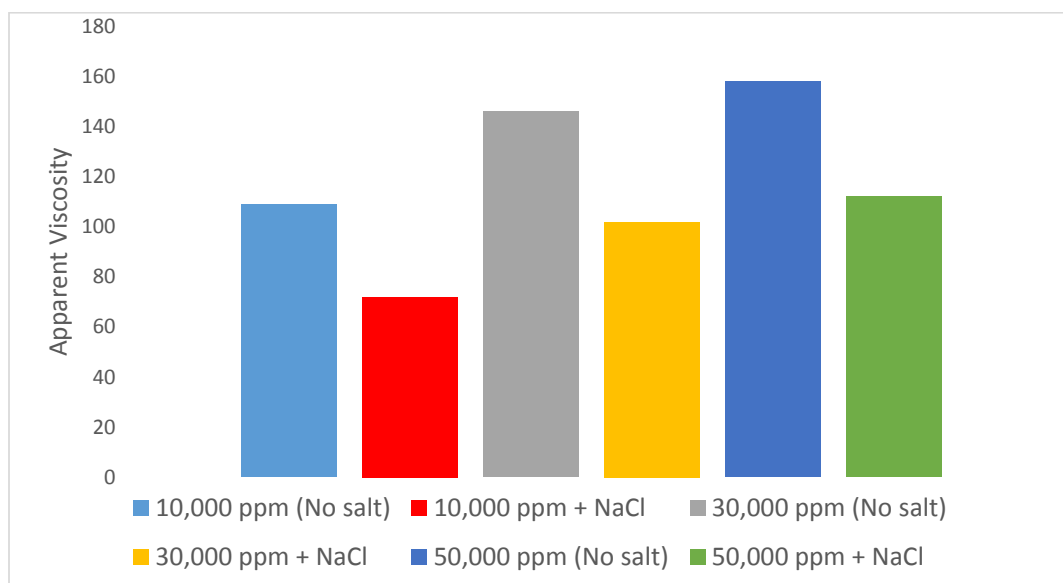
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**FIGURE 3** The effect of salinity on CMC at increasing concentration



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**FIGURE 4** The Effect of salinity on a blend of Gum Arabic at increasing concentration

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and 1wt% of CMC

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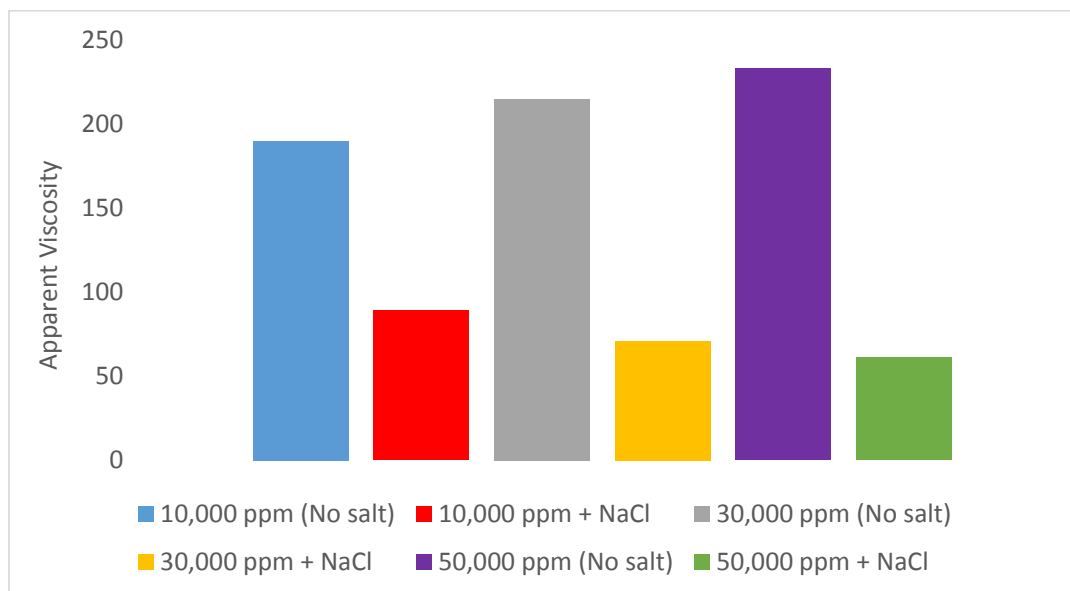
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The presence of CMC in the solution strongly interacts with Gum Arabic solution increasing the viscosity considerably. From Figure 4, 50,000 ppm reflected the highest viscosity than other lower concentrations, this could be as a result of increased intermolecular entanglement from both the molecular chains of Gum Arabic and CMC, **this can equally be related to the interaction that occurs when CMC is added to the cassava starch, the result is increased tensile strength, this behaviour was ascribed to the good interaction between cassava starch and CMC (Ibrahim et al. 2014).** When compared with the viscosity of the gum alone (Figure 2) and the viscosity of CMC alone (Figure 3), the resultant blend in Figure 4 displayed synergy upon blending. Although, the reduction in viscosity based on the effect of salinity was equally obvious, this is because of the nature of the ionic status of both polymer chains (Ibrahim et al. 2014, Chatterji et al, 1981).

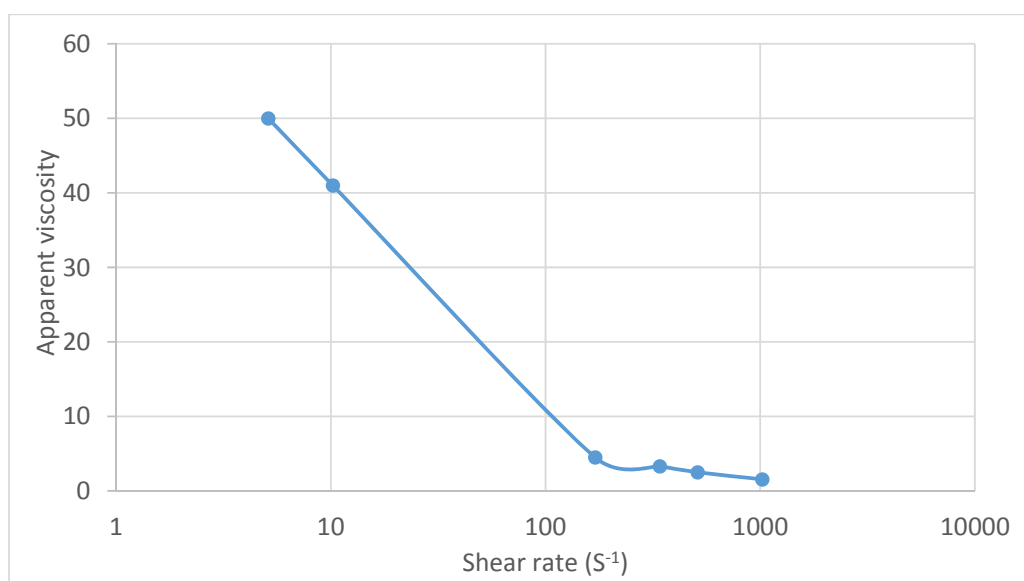


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127 **FIGURE 5** The Effect of salinity on a blend of Gum Arabic at increasing concentration  
 128 and 1.4wt% of CMC

129 The presence of increasing concentration of 1.4wt% of CMC shown in Figure 5 without the  
 130 influence of salinity increased the solution's viscosity more than that of 1wt% CMC.  
 131 However, the resistance provided by Gum Arabic concentration did not improve when the  
 132 concentration increased. This behaviour could be related to the fact that the presence of  
 133 increased CMC concentration increased the anions present within the solution such that in the  
 134 presence of NaCl, there was increased reaction with NaCl, thereby reducing the electrostatic  
 135 repulsion increasingly on the polymer chains which eventually decreased the viscosity.

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137

138 **FIGURE 6** Viscosity-shear rate behaviour

139 Figure 6 depicts that the viscosity reduces with increasing shear rate, this reflects Gum  
140 Arabic's shear thinning behaviour just like other biopolymers used in enhanced oil recovery  
141 which also show shear thinning behaviour when subjected to the effect of shear.

## 142 CONCLUSIONS

143 During polymer flooding, one of the characteristics of a polymer is its ability to remain stable  
144 in the presence of high salinity as such the injected solution must have the ability to maintain  
145 its viscosity for a particular duration. From the experimental analysis,

- 146 • It is obvious that Gum Arabic at increasing concentration with CMC was able to produce  
147 increased viscosity which is a requirement in polymer flooding
- 148 • Blend of Gum Arabic with CMC especially at increasing concentration did not produce  
149 adequately the stability against the effect of salinity for the solution.
- 150 • The experimental analysis proved that attraction and repulsion of molecular charges are  
151 responsible for the resultant solution viscosity especially because both polymers are  
152 ionic.
- 153 • The further reduction in viscosity is related to the increase in anions from the polymers  
154 in solution because both of them are polyelectrolytes and as such would interact strongly  
155 with the cations of NaCl solution thereby decreasing the electrostatic repulsion of the  
156 polymer chains in solution.
- 157 • With respect to the use of Gum Arabic, additives that are non-ionic would suffice better  
158 than ionic additives especially in the face of high salinity.

159

## 160 NOMENCLATURE

161 CMC = Carboxymethyl Cellulose

162 HPAM =Hydrolysed Polyacrylamide

163 NaCl= Sodium Chloride Salt

164 PPM = Pounds per million

165 Cp = Centipoise

166 PWPF= Produced water from polymer flooding

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