A NOVEL PROMISING, HIGH VISCOSIFIER, CHEAP, AVAILABLE AND ENVIRONMENTAL FRIENDLEY BIOPOLYMER (POLYMTEA) FOR DIFFERENT APPLICATIONS AT RESERVOIR CONDITIONS UNDER INVESTIGATION. PART A: POLYMER PROPERTIES

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1. ABSTRACT

Polymer solutions are used to improve waterflood performance and to maintain favorable mobility ratios for microemulsion flooding. Increasing the oil recovery or reducing the residual oil after the primary recovery is the challenge for both the petroleum engineers and the petroleum companies. Polymers are used successfully in many reservoirs all over the world, but the problem is the finding the suitable economical polymer for the harsh reservoir conditions of high temperatures and high salinity.

The target of this study is to find a new polymer (POLYMTEA). This new advent is cheap, available and could be a new revolution on the polymer applications in the oil fields. It can be applied under the harsh reservoir conditions. The work is divided into three parts:

PART A: Will be discussed her and it concerns with POLYMTEA properties such as viscosity yield, the effect of temperature and salt on the polymer viscosity, p-H, surface tension and the cost. POLYMTEA shows that high temperatures have no effect on its viscosity. The investigations have been done for different temperatures and different shear rates. The new polymer has salinity resistant since salt has no effect till 30% salt content (300,000 ppm) with the applied polymer concentration. The cost estimation shows that it will be cheap compared with other types.

PART B from this work concerns with POLYMTEA applications in the oil fields.

PART C will study its use for permeability modification.

Key Words: Chemical enhanced oil recovery, Polymer types, Polymer properties, Water shut-off.
2. INTRODUCTION

The first attempts to improve sweep efficiency in water flooding by polymers (Chemical Enhanced Oil Recovery; EOR) were made by Detling (1944). Polymer flooding became as a method to enhance the oil recovery after 1964 by the laboratory and field test development results by (Sandiford and Pye, 1964)\(^5\).

Primary recovery from oil reservoirs is known to be low, and the attempts to increase this recovery by both secondary and tertiary methods are well known. The challenge for both the petroleum engineers and the petroleum companies is to increase the oil recovery by reducing the residual oil after the primary recovery. There are two common methods for that, the first is to decrease the oil viscosity by injecting steam or hot water and the second is to increase the water viscosity.

Water soluble polymers are common agents used in enhanced oil recovery processes to reduce the mobility of water in porous media by increasing its viscosity and hence to improve the sweep efficiency. Polymer solutions are used to improve waterflood performance and to maintain favorable mobility ratios\(^4,14,16,17\).

Polymers are used successfully in many reservoirs all over the world, but the problem is to find the suitable and economical polymer for the harsh reservoir conditions of high temperatures and high salinity.

There are two main types of polymers which can be applied in the reservoir application; these are synthetic polymers and biopolymers. Synthetic
polymers are not stable at high temperatures and salinity while, the biopolymers are stable but are expensive and suffer from bacterial attack.

Successful polymer projects are used in many reservoirs all over the world during the past few years and attractive statistical data have been published which clearly prove the superiority of polymer treatment even in the next future all over the world. The first two polymer flood projects, Hankensbuettel field and Oerrel-Süd field, Germany are considered successful and polymer application was used with larger parts of both fields \(^{(6)}\).

Littmann et al. (1992)\(^{(7)}\) has reported that, the polymer flooding is the only chemical method, that is technically and also economically feasible for a polymer pilot project which was started in 1984 in the small oil field Eddessee-Nord sandstone reservoir (Germany). The polymer project can be regarded as successful and the incremental oil production was somewhat higher than the predicted 6% of the original oil in place.

Also, Moawad and Pusch (2004)\(^{(1-2)}\), also Push\(^{(8)}\), and Rivenq et. al.\(^{(9)}\), published many articles representing intensive practical experimental and simulation work in this area with Egyptian, German and international fields, including the development of the polymer flooding process through the evaluation and contribution of the enhanced oil recovery to crude oil reserves.

This work will investigate a new polymer which has many advantages which enable it to overcome the above deficiency. These benefits include, (a) cheap (b) has high viscosity yield at high temperatures and high salinity and (c) environmental friendly.

### 3. LABORATORY MEASUREMENTS FOR NEW POLYMER PROPERTIES

In this section the laboratory measurements for the most important polymer properties such as preparation, determination of molecular weight, measuring polymer viscosity, pH-value, surface tension etc., have been measured as shown below:

#### 3.1 Polymer preparation as polymer solution or as powder

#### 3.1.1 Polymer preparation as a solution

Sometimes preparing many polymer solutions from chemicals, such as polyacrylamides, causes many problems such as fish-eyes, precipitation and
other accompanied problems. Therefore certain chemicals in addition to complicated mixing and agitation systems are needed for preparing such polymers.

However, the POLYMTEA polymer is different because it does not have such problems. The best method for the preparation and filtration the POLYMTEA polymer to cause no formation damage or plugging has been studied in the laboratory and the following points have been observed:

- Preparing the new product solution is easy and cheap.
- During the POLYMTEA preparation, the product forms no fish-eyes and no chemicals are needed.
- The new polymer needs no complicated systems for mixing, agitating and other preparation processes.
- The POLYMTEA needs no harmful chemicals for stabilization which can cause corrosion or formation damage.
- The new POLYMTEA can be prepared with fresh water or brine.
- The solution should be filtrated to separate the small solid particles (if present) by a suitable filter (between 0.45 µm and 45 µm) depending on the formation permeability.
- The filtrated solution can be injected at any temperature from the room temperature even up to 100 °C.
- The POLYMTEA can be injected directly after its preparation or after certain times (24-48 hrs.) without any viscosity loss depending on the temperature and environmental conditions. However, for long time, preservation chemicals such as formaldehyde should be used. Using the formaldehyde with very small percent can keep the new polymer and its original viscosity for long times (3 months and still has no problems)

3.1.2 Polymer preparation as a powder

The new polymer can also be produced as a powder to be easy in transportation and handling. A test has been done to investigate this possibility where 100 ml polymer solution with concentration of 240 Kg (raw material)/m$^3$ was dried in an oven at 80 °C for sufficient time and the solid
material was found to be 0.4 gram. This means that, the material concentration is 4g/litre or 4000 ppm.

3.2. Is this new polymer is economically effective or not?

To answer such question, the results of the above section (3.1.1) where a polymer sample of 100 ml polymer solution with concentration of 240 Kg (raw material)/m$^3$ gives solid material (powder) of 0.4 gram.

The cost of 1 kg of the raw material is about 0.1 - 0.2 LE/Kg$^{(10)}$ (0.06 - 0.13 SR/kg or about 0.015 - 0.03 $/Kg). By calculating the price of 1 kg powder of this new polymer, it is found that; the price is in the range of 3.6 - 7.2 $/kg which is less than one-third of the world price for such biopolymer classes (Scleroglucan biopolymer and sulfonated polymers)$^{(1,11)}$.

Comparing the price of this new biopolymer with the Scleroglucan and sulfonated biopolymers which are considered to be the best one in the world field applications$^{(1, 9, 11)}$, for high salinity and high temperature, the new biopolymer can be considered as an economically attractive polymer.

Note: LE = Egyptian pound, SR = Saudi Riyal, $ = American Dollar.

3.3 Viscosity yield measurements

Most polymers proposed for enhanced oil recovery are mainly characterized by their high viscosity yield. The higher the polymer viscosity yield, is the more desirable polymer used for enhanced oil recovery. The idea of using polymer is to increase the water viscosity which improves the sweep efficiency and hence increasing the oil recovery. In polymer flooding, a water-soluble polymer is added into the flood water which increases the water viscosity.

For comparing such effect, the water viscosity is shown in Table (1). Therefore increasing the water viscosity by adding the polymer is very important to increase the sweep efficiency by decreasing mobility ratio and then to increase the oil recovery.

There are three potential ways in which a polymer flooding makes the oil recovery process more efficient: (1) through the effects of
polymers on fractional flow, (2) by decreasing the water/oil mobility ratio, and (3) by diverting injected water from zones that have been swept.

Table 1: Water viscosity as a function temperature \(^{(15)}\):

<table>
<thead>
<tr>
<th>Temperature (°F)</th>
<th>Absolute Viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>1.794</td>
</tr>
<tr>
<td>40</td>
<td>1.546</td>
</tr>
<tr>
<td>50</td>
<td>1.310</td>
</tr>
<tr>
<td>60</td>
<td>1.129</td>
</tr>
<tr>
<td>70</td>
<td>0.982</td>
</tr>
<tr>
<td>80</td>
<td>0.862</td>
</tr>
<tr>
<td>90</td>
<td>0.764</td>
</tr>
<tr>
<td>100</td>
<td>0.682</td>
</tr>
<tr>
<td>120</td>
<td>0.559</td>
</tr>
<tr>
<td>140</td>
<td>0.470</td>
</tr>
<tr>
<td>160</td>
<td>0.401</td>
</tr>
<tr>
<td>180</td>
<td>0.347</td>
</tr>
<tr>
<td>200</td>
<td>0.305</td>
</tr>
</tbody>
</table>

3.3.1 Viscosity of the polymers at different shear rates

Polymer solutions are Non-Newtonian fluids; therefore the polymer viscosity must be measured at different shear rates.

Polymer solutions are classified as "Pseudo plastic fluids" which exhibits a smaller resistance to flow as the shearing rate increases. **Measuring the POLYMTEA polymer viscosity at different shear rates**

The viscosity of the POLYMTEA solution was determined at different concentrations and at different shear rates. Figure (1) shows the effect of the shear rate on the viscosity of the studied polymer solution at a concentration of 4000 ppm at the room temperature. As the shear rate increases the polymer viscosity decreases.

From Figure 1, the viscosity yield of this new polymer can be recognized compared with that published one by Revinq et al. \(^{(9)}\), in Figure 3, which used in high temperature and high salinity oil field applications. This new polymer solution shows high viscosity yield.
Figure 1: POLYMTEA viscosity at different shear rates at room temperature.

3.3.2 Effect of temperature on the viscosity yield measurements

Usually petroleum (oil and gas) reservoirs are characterized by their high temperatures. Also, all polymers used for enhanced oil applications suffer from thermal degradation. The viscosity of the most used polymers decreases with temperature. High temperatures which cause thermal degradation are also sources of polymer instability. In the present study, the effect of the temperature on the polymer viscosity was investigated at different shear rates.

Figure 2, shows the followings:
1- The effect of the temperature from the room temperature to 100 °C at different shear rates.
2- At the same shear rate the polymer viscosity decreases as the temperature increases.
3- The studied polymer viscosity yield is high even at high temperatures compared with that of water.
4- The new polymer can be applied at high temperatures and high shear rates.
Figure 2: Effect of temperature on the viscosity yield of POLYMTEA measurements

Figure 3: Scleroglucan biopolymer viscosity at different temperatures after Rivenq et al.\(^9\)

From Figures 2, 3; by considering the polymer characteristics for the viscosity at infinite shear rate and consider that the viscosity at 100 Sec\(^{-1}\) for
the Scleroglucan can be compared with that at 40 Sec\(^{-1}\) for the POLYMTEA, the following table can be summarized:

Table 2: A Comparison between the viscosities of POLYMTEA and Scleroglucan at different temperatures and at the same concentrations (2000 ppm)

<table>
<thead>
<tr>
<th>Temp. C°</th>
<th>Viscosity of POLYMTEA, cp(^{**})</th>
<th>Viscosity of Scleroglucan, cp(^{+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>10</td>
<td>5.5</td>
</tr>
<tr>
<td>50</td>
<td>8</td>
<td>4.8</td>
</tr>
<tr>
<td>75</td>
<td>4.5</td>
<td>4.1</td>
</tr>
<tr>
<td>90</td>
<td>3.25</td>
<td>4</td>
</tr>
</tbody>
</table>

* The viscosity of the new polymer in this table is the half of the measured in Figure 2.
+ The POLYMTEA price/kg is about 1/3 of that of Scleroglucan.

3.3.3 Effect of time on the viscosity yield measurements

Three categories which represent all used cases have been studied:

a- As stated above the polymer can be injected immediately after its preparation or it can be stored in tanks without adding any chemicals for (24 - 48 hrs) depending on the temperatures and the environmental effects.

b- The solution can be kept at low temperature (8 °C) in the refrigerator with a little considerable change in its viscosity for more than 15 days. Figure 4 shows the effect of time on the polymer viscosity at a temperature of 8 °C.

c- If you need to store the solution for long time, formaldehyde should be added with small percentages. Adding formaldehyde with about 1% concentration, can keep the polymer viscosity without considerable change for more than 3 months

Figure 5 illustrates the effect of time on the new polymer viscosity in the presence of formaldehyde at 23 °C for different time intervals. The measurements were carried out at the time of preparation to be the reference case and at 30, 60, 120 days. It is clear that the viscosity of the new polymer stay almost the same even for very long times (120 days).

As a result from the present studies, the best strategy is to inject the prepared solution as soon as possible.
3.3.4 Effect of salinity on the POLYMTEA viscosity

Usually oil reservoirs have brine as formation waters. One of the most common shortcomings of the polymer solution, to be applied for enhanced oil recovery, is its sensitivity to salts. The sensitivity of the polymer viscosity to
salt is greater for synthetic polymers. Biopolymers have salinity resistance more than the synthetic polymers.

In salt water the polymer minimizes its contact with solvent. Distilled (fresh) water is a good solvent for most polymers. As salt added, the electrolyte neutralizes the charge of the polymer molecule, reducing its contact with water reducing the viscosity of the polymer.

The new polymer has a very important advantage that is its high resistance for salt water. Three salt concentrations 5%, 12% and 30% are used for preparing the studied polymer samples with the used polymer concentration (4000 ppm) and their viscosities were investigated. The salt concentrations have no considerable effects on the polymer viscosity as shown in Figure 6.

![Figure 6: Effect of salt concentrations on POLYMTEA viscosity at 23 °C](image)

3.3.5 Effect of polymer raw material concentration on polymer viscosity

The new solution viscosity must be examined based on the used raw material concentration. Three concentrations were investigated which are 250, 125 and 65 g/liter raw material (4000, 2000 and 1000 ppm, as powder) and the results are shown in Figure 7.
It is found that the measured viscosity is directly related to the used concentration. This means; when the concentration was reduced to the half, the viscosity was also, nearly reduced to the half.

![Effect of polymer concentration on polymer viscosity at 23 °C](image)

Figure 7: Effect of polymer raw material concentration on polymer viscosity at 23 °C.

### 3.4 pH-Value

The pH-value is important for polymer applications in the enhanced oil recovery. Since the acidic solutions can harm the production tools causing corrosion and the alkaline solutions can alter the rock properties such as wettability. Therefore, the effect of pH-value of the solution should be tested.

In the other hand, polymer solutions should not alter the pH-value of solution by more than ± 0.5 pH-units.

The pH-value for the present new polymer is found to be 6.1 and this pH-value is intermediate which can help in permeability stimulation and in the same time not corrosive for the production tools.

### 3.5 POLYMTEA surface tension

Using surfactant is one of the most important methods to increase the oil recovery by reducing the interfacial tension in the oil reservoirs.
One of the most interesting measures for this new polymer is the value of the interfacial tension. The average surface tension is ranged from only (39.46 - 48 mN/m.).

The new product shows low surface tension (nearly half of water) which means that this new polymer is very useful and works as a surfactant in the same time works as a polymer.

3.6 Polymer specific gravity

Specific gravity of the polymer is important because of the induced hydrostatic pressure gradient. If the specific gravity of the polymer is too high, this can cause injection problems which results in formation fracture.

The sp. gr. with the used polymer concentration was measured with different methods. By the pycnometer method, the measured value was ranged from 1.11-1.17 g/cc (it depends on its concentration). This means that this is another advantage which causes no high hydrostatic pressure which can cause problems during polymer injection such as formation fractures.

3.7 POLYMTEA stability against bacterial degradation

Bacterial degradation can be one of the shortcomings of most biopolymers including this new polymer. The degradation decreases polymer viscosity causing loss in the polymer economic values.

As stated above, the polymer can be used for enhanced oil applications just after its preparation or can be kept in a tank for (24-48 hrs) without any degradation, but after this time it can suffer from bacterial degradation. The researchers advise that the best injection time is just after its preparation.

3.8 POLYMTEA is environmental safe

The POLYMTEA is not toxic, has no harmful chemicals and 100% environmental safe.

4. CONCLUSIONS

This work has introduced a new material as a biopolymer which has many attractive properties and from the above discussion, the following conclusions can be observed:
1- The new polymer gives high viscosity yield even at high temperatures which is very desirable for the field applications.

2- The polymer is economical and cheap compared with the applied and published world-wide polymers from the same biopolymer classes.

3- The polymer has been tested for high salinity till 30% salt (300,000 ppm) and it shows low effect with saline content.

4- The polymer shows low surface tension (nearly half of water) which means that it is very useful and works as a surfactant in the same time works as a polymer.

5- One of the most important properties is its safe and environmental friendly, available and cheap since it can be obtained easily.

6- The polymer pH-value is 6.1 which is intermediate and can help in permeability stimulation and in the same time not corrosive for the production tools.

5. RECOMMENDATIONS

1- The oil recovery by flooding the new polymer (POLYMTEA) under the reservoir conditions is now under investigation with Brea-sandstone cores for field applications.

2- This new POLYMTEA should be adopted and applied in a field sector to show the results.

3- Also, the reaction with the crosslinkers to form weak and strong gels for permeability modifications should be studied at the room and different temperatures.

4- The POLYMTEA viscosity must be measured with high temperature-high pressure viscometer.

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10- Personnel communications with Egyptian-Professors in the same area of research


