Introduction

Hydraulic fracturing has proven to be most significant technological advancement in the Oil and Gas industry. This technique has opened the way to produce from unconventional reservoirs in a scenario when the easily recoverable petroleum reserves are declining faster, there is increased demand coupled with strong geopolitics. The fluid involved in this technology has been under investigation since the inception of the technology. The researcher has worked on different types on fracturing fluid from oil-based fluids to water-based fluids using natural polymer, synthetic polymer, surfactants, hybrid polymer-surfactant, foam base etc [Barati and Liang, 2014], depending on the reservoir characteristics. Polymer based fluid in slick, linear and crosslinked formed has been widely used till now due to efficient fracture propagation and economic considerations. However, since the industry is moving towards the unconventional reservoirs and there is a strong transition in the trend from crosslinked gels back towards linear and slick fluids due to high applications in the low permeability reservoirs like shale and CBM where crosslinked fluids are not efficient and have problems in fluid breaking and permeability impairment of the conductive proppant path [Smith and Montgomery 2014].

Synthetic polymers are exceptionally clean and are designed for high-temperature reservoirs (more than 200°F) but their toxicity and carcinogenicity limit their usage in applications where biocompatibility and ecological issues are primary [Jennings, 1996]. However, there is still meager of available polymers which can sustain a temperature beyond 130°C, and with low formation damage. Guar is preferred owing to its favorable biological, chemical and physical properties like bio-compatibility, renewability, non-toxicity, biodegradability, equilibrium swelling, low cost and high solution viscosity. The limitations with guar gum is the high insoluble residues on breaking and the temperature limits to 94°C, which can cause a reduction in the generated conductive channels thereby decreasing the production rate. The limited supply of guar over high demand, low thermal stability and high residue after fracturing necessitate to look for the alternative of guar-based fracturing fluid, which can solve one or more problems associated with guar-based fracturing fluid. In addition, for the recovery from high-temperature tight reservoirs (at the temperature as high as 205°C) where most of the conventional fracking fluids decompose, new fluids need to be developed. Though a significant amount of work has been carried out on synthetic polymers and surfactant based fracturing fluid, but no research is going on new natural polymers that can be used as an alternative for Guar [Sun et al., 2014].

Nano composites formed with biodegradable polymers have high rewards and opportunities in the future for the application in the design of environmentally friendly materials and therefore, in last two decades, strong emphasis has been paid towards the development of polymeric nanocomposite, having at least one reinforcing material with nanometer range dimensions [Chauhan and Ojha, 2016]. In petroleum industry, nanotechnology is being used to improve oil and gas productivity, downhole separation processes and for non-corrosive material development. But its application in the development of developing smart drilling and fracturing fluids for HTHP applications is still not well explored. The present study proposes novel biopolymer nanocomposite fluid as a solution to the challenges of HTHP which is synthesized using novel anionic polymer Gum Tragacanth and Nano sized silicon di oxide particle. Gum Tragacanth is also a natural polymer like Guar gum but its molecular weight is less which

Figure 1: a) Schematic showing polymer residue (green) clogging the proppant pack (yellow) pack conductivity, 1.b) Nanoparticles binding with SiO$_2$ nanoparticles leading to the formation of biopolymer nanocomposite.
will generate less insoluble polymeric residues as compared to guar but will also result in low viscosity at higher temperatures. To solve this issue nanoparticles has been utilized to increase the thermal stability of the novel nanofluid synthesized.

**Methods and Procedures**

Biopolymer nanocomposites were prepared at different polymer and nanoparticle concentrations and were optimized for their properties and cost. The nanocomposite gels were studies for structure (FTIR analysis), morphology (AFM using Bruker AXS, Santa Barbara, CA, USA), and Cryo-TEM JEM-2100F Transmission Electron Microscope (JEOL, Japan) analysis), HTHP rheological studies using Bohlini rheometer, breaking studies (using Ammonium PerSulfate breaker) and sand pack regained permeability using sand pack flooding experiment. The rheology was studied under field simulated conditions of pressure 900 psia and in the temperature range between 30-150°C at 100s⁻¹ shear rate for 1 hour. The viscosity measurements above 10s⁻¹ shear rates provide no direct indication of proppant suspension rather one uses the choice of minimum viscosity (90cP at 100s⁻¹ shear rate) on the basis of field experience to infer proppant suspension [Harris et al., 2009]. Therefore, the fluids which maintained viscosity above 100cp for 1 hr under studied conditions were considered efficient for proppant suspension.

![Figure 2. A Cryo-TEM image (a) and AFM image (b) of TG-SiO2 showing uniform distribution of nanoparticles over TG (polymer) matrix.](image)

**Results and Discussion**

Nanoparticles generally have a high tendency to form aggregate and therefore while forming a nanocomposites the foremost important consideration is to separate nanoparticles from each other and form a uniform packing density of nanoparticles in the polymer matrix so that homogeneous mechanical properties are resulted. Ultra-sonification technique used to formed nanocomposite resulted in almost uniform distribution of nanoparticles over biopolymer matrix which is confirmed by the FE-SEM and Cryo-TEM results. The results showed sufficient contrast to differentiate between nanoparticles and polymer matrix [Guo et al., 2010]. The FTIR analysis confirmed that silicon di oxide particles offer active acid and base sites on hydrolysis for the mechanochemical reactions helpful for synthesis of bio-polymer nanocomposite.

Rheological measurements are crucial for the selection of a suitable fluid for fracturing operation. in the laboratory to ensure the fulfillment of the required criteria to create fracture as well as proppant transportation [Chauhan et al., 2017]. In the present study, KCl (2wt%) and ethanol (20wt%) have been added to the base fluid as an anti-clay swelling agent and temperature stabilizer, respectively to fulfill the field requirements of the fluids. As could be seen from the Figure 3 and 4, 1 wt.% TG is able to sustain its viscosity much higher than the minimum required viscosity of 90cP at 100 s⁻¹ at 120°C and
2 wt.% TG and their nanocomposite were found to maintain viscosity much higher than the required value at pressurized condition. The addition of alcohol and nanoparticles was found to improve the stability. The time variable does not affect significantly the apparent viscosity under applied pressure and it was found to be sufficient for the fracturing fluid application. Enhancement in thermal stability at higher pressure may be explained by the compressibility effect of fluids and favorable alignment of molecules under applied pressure. The nanocomposite offered almost similar polymeric resides upon breaking on using same polymer concentration, whereas synthesis of nanocomposite was helpful in reducing the polymer concentration to achieve desired rheological properties with less polymeric residues and higher regained sandpack permeability.

Figure 3. Variation of viscosity with time (3600 sec) for 1 wt.% TG and its composite and CMHPG at 900 psi and 120°C.

Figure 4. Variation of viscosity with time (3600 sec) for 2 wt.% TG and its composite and CMHPG at 900 psi and 150°C.
Table 1: Comparison of Percentage regained permeability of the sand pack for various fracturing fluid samples

<table>
<thead>
<tr>
<th>Gel Treatment</th>
<th>Sand Pack Porosity, %</th>
<th>Water Permeability, Before Fluid Treatment, Darcy</th>
<th>Water Permeability, After Treatment, Darcy</th>
<th>Regained Permeability, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% TG</td>
<td>29.6</td>
<td>3.690</td>
<td>3.211</td>
<td>87</td>
</tr>
<tr>
<td>1% Guar</td>
<td>30.1</td>
<td>3.7205</td>
<td>2.5299</td>
<td>68</td>
</tr>
<tr>
<td>1% CMHPG</td>
<td>31.3</td>
<td>3.7791</td>
<td>2.7209</td>
<td>72</td>
</tr>
<tr>
<td>1% TG-0.50% SiO2</td>
<td>29.4</td>
<td>3.6848</td>
<td>3.132</td>
<td>85</td>
</tr>
</tbody>
</table>

Conclusions

The biopolymer nanocomposite synthesized using novel polymer has not been used in oil industry as fracturing fluid before and it can solve the breaking residue problem associated with guar (as polymer molecular weight is low here) and can give viscosities similar to guar with benefits of biodegradability. The improved properties of nano-composites over the linear polymer gels are due to the development of “pseudocrosslinking” between nanoparticles and polymer chains that reduce the mobility and increases the residence time of the structure.

References: