Thixotropic properties and thermal stability of Xanthan Gum biopolymer solutions for Enhanced Oil Recovery

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Abstract

This study investigated the potential applications of Xanthan gum (XG) at different salinities and temperatures as a biopolymer-flooding agent for an enhanced oil recovery process. Rheological and thixotropical measurements were performed to realize the shear viscosity alteration when the polymer solutios applied under a variation of salinities and temperatures. The results showed that XG biopolymer solutions have non-Newtonian fluid characteristics like pseudoplasticity at each concentrations in any temperatures of 25, 40, 55 or 70 °C. Consequently, due to the beneficial and practical achieved results XG biopolymer flooding is a suitable and proper option under oil reservoir conditions.

Keywords: Rheology, Thixotropic properties, Xanthan gum, Enhanced oil recovery.

Introduction

To have the maximum production from an oil reservoir, primary recovery methods are not enough, and concerning Enhanced oil recovery (EOR) methods is inevitable. One of the main parameters which should be modified through an EOR process is the mobility ratio that is directly related to the rheological behavior of oil and flooding fluids in reservoirs. Rheology attempts to detect the inherent flow behavior of materials by studying the interrelationship between force, deformation, and time. The most serious rheological parameters are shear stress, shear rate, and the viscosity [1]. To have a better illustration relationship between rheological parameters, shear rate and, shear stress are usually plotted against each other in a graph. The resulting curve is called the flow curve that is very important to analyze the rheological properties of materials. Using flow curve and relationship between rheological parameters and time, materials can be classified into two groups; Newtonian fluids and non-Newtonian fluids (time-independent and time-dependent) [2].

Newtonian fluids follow Newton laws of flow, which consider a linear relationship between shear rate and shear stress, i.e. linear flow curve. In other words, viscosity in a Newtonian fluid is independent of flow conditions (shear stress, shear rate, and time) and Newtonian fluids are usually liquids with simple molecular formula and light molecular weight [3].

Non-Newtonian fluids do not show a linear relationship between shear rate and shear stress which goes through the origin. Also, non-Newtonian fluid does not necessarily show a constant viscosity at different shear rates. Non-Newtonian fluids can also be divided into two different groups; time-independent and time-dependent. It means at any given shear rate these materials

display a single viscosity and this viscosity does not change with time. For a time-dependent fluid, if a constant shear rate is applied on time-dependent materials, the value of shear stress and consequently viscosity will change by the time [4].

Shear thinning fluids show a decline in viscosity by an increase in shear rate. On the other hand, shear thickening fluids show higher viscosity by an increase in shear rate. For these types of materials, viscosity needs to be measured at each specific shear rate. In this case, viscosity at a specific shear rate is the slope of the line that passes through the corresponding point on the flow curve and the origin, and it is called apparent viscosity [5].

Thixotropy is defined as the continuous decrease of viscosity with time when the flow is applied to a sample that has been previously at rest and the subsequent recovery of viscosity in time when the flow is discontinued [6]. There are two general definitions which the first one says that thixotropic materials are non-Newtonian (time-independent) which exhibits shear thinning behavior and therefore, their shear history impacts their thixotropic behavior, and the second one affirms that thixotropy is a reversible process. Thixotropic materials, due to their microstructure, show complex rheological behavior [7].

Thixotropy is seen in many fluids like paints, resins, clays, personal products, chemical products, and some home cleaning supplies. Thixotropy was originally referred to as reversible changes from a fluid to solid-like elastic gel. A simple physical explanation for thixotropic behavior mentions the particle interaction forces determine potential energy well for each particle [8].

According to the author's latest review of recent articles, very little researches have been done on the thixotropy properties of Xanthan gum (XG) biopolymer and its thermal stability in EOR. This work, in a view of the above points, concentrated on the rheological and thixotropic behavior and XG biopolymer performance in reservoir temperature.

Experimental
Material
The XG biopolymer was purchased from Fufeng Co., Shandong Province, P.R. China with a molecular weight of about 2.0×10^6 g.mol^{-1} ($\geq$ 99.5%) and salts including NaCl and CaCl$_2$ (Merck Co., Ltd. Germany) dissolved in distilled water (DW) for making ready two common concentrations of low salinity solution (42000 ppm NaCl) and high salinity solution (42000 ppm NaCl + 18000 ppm CaCl$_2$) for simulation of the Persian Gulf water [9].

The initial routine range of polymer concentration for the rheology test was settled on the XG biopolymer and then the optimum and more efficient concentration of XG was used to study the effect of temperature.

Method
The rheological behavior of the aqueous XG solution was investigated by using a rotational rheometer RST-CC Brookfield (USA) and the device was connected to a constant temperature water bath which was adjusted to 25 °C for general thixotropy behavior tests and 40 °C, 50 °C, and 70 °C to simulate oil reservoir temperature conditions. Firstly, the XG biopolymer was slowly added to DW for making a stock solution of the 6000 ppm XG biopolymer under the API RP 63 standard approach. At the next step, it was stirred and prepared by a digital integrated wise overhead stirrer HS-30D Witeg (Germany) at 1200 rpm. After a few minutes, the stirring speed was decreased and a gentle mixing was maintained overnight to ensure full hydration, homogenous solution at minimum agitation rates, avoid any mechanical degradation, and finished dissolution of the XG stock solution. The ultimate obtained solution was stored in closed polyethylene containers to minimize oxygen uptake.

Results and discussion

For a better and more complete description of the main relations and parameters of rheology, a simple two-plate model can be expressed. As can be seen in Figure 1, it is assumed that the material is confined between two parallel plates. The gap between the two plates is Y. The bottom plate is stationary and the top plate is moving with a constant velocity of V. Thus, the flow velocity of material changes linearly from zero at the bottom plate to maximum velocity of V at the top plate, and shear rate (velocity gradient) can be mathematically shown as [10]:

$$\text{Shear rate } (\Upsilon) = \frac{\text{Velocity difference between two plates (V)}}{\text{Distance between two plates (Y)}} \qquad \text{Eq.1}$$

which unit of shear rate is 1/S or S^{-1}.

Shear stress (τ) is shown as the applied force (F) on the top plate over its area (A):

$$\text{Shear stress } (\tau) = F/A \qquad \text{Eq.2}$$

which unit of shear stress is N/m^2 or Pa.

Viscosity (μ) is defined as the resistance of the material to flow and demonstrates the relationship between shear stress and shear rate. Based on Newton laws of flow, viscosity is simply shown as shear stress over shear rate:

$$\text{Viscosity } (\mu) = \tau / \Upsilon \qquad \text{Eq.3}$$
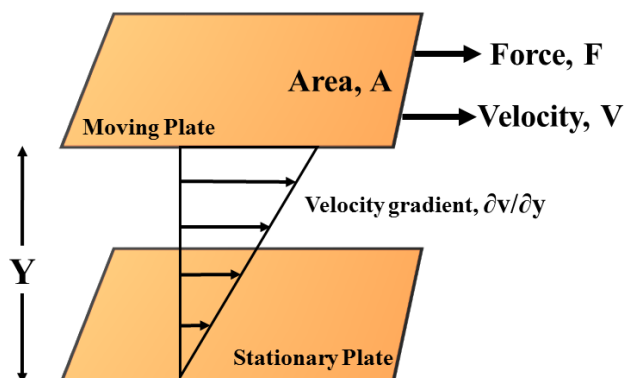
and its unit is Pa.s [11].

Figure 1: Relationship between rheological parameters in a two-plate model

Hysteresis loop has been the most common method of measuring thixotropy of fluids and materials in the last few decades. In this method, the area between two subsequent flow curves, an up-curve followed by a down-curve, is measured and linked to the thixotropic characterization of fluid or material. During the up-curve, the shear rate is gradually increased from zero to a maximum value which breaks down part of the already formed structure. Then, in the down curve, the shear rate is gradually reduced from the maximum value back to zero, which lets the sample rebuild part of its breakdown structure. The idea is, the area between these two curves represents the work done per unit time and unit volume of the sample to break some of the initially present linkages [12].

Some problems are associated with the hysteresis loop method. Firstly, the shear history of the sample resulted from mixing, transporting, and even placing samples in equipment. Secondly, the sample does not reach an equilibrium condition. Thus, test results are very dependent on experimental conditions such as maximum shear rate value and rate of increase and decrease in shear rate [13].

In addition to the factors affecting the hysteresis loop method, there are many different factors that may influence rheological properties. Some of the main factors are mix proportions, shape and texture of aggregates, chemical and mineral admixtures, mixing, transportation, placing and pumping procedure, ambient condition, elapsed time, etc. For a proper and complete response to these negative influencing factors, the API RP 63 standard approach and the process described in the previous section were applied to minimize the impact of these factors [14].

As it can be seen in Figure 2, all possible fluids in 1000, 2000, and 3000 ppm concentrations have been prepared and thixotropic curves were obtained. These hysteresis loops are at their best state and complete position when they complete the path of build-up and break-down and, as mentioned, start from zero and end there. Although it does not give an intrinsic value of any physical rheological parameters but hysteresis loop is a quick quantitative method that easily and with acceptable accuracy indicates which fluids or materials have thixotropic properties [15]. After completing rheology experiments, it was inferred that adding divalent ions to the solutions (high salinity in comparison to low salinity) did not have a meaningful effect on the viscosity. It can be concluded that from one side the viscosity of 3000 ppm polymer solution is so high, therefore due to the injectivity problem is not appropriate for flooding, and on the other side, the viscosity of 1000 ppm polymer solution is too low and cannot improve the poor mobility ratio of the water/oil system, hence an average concentration of 2000 ppm at high salinity was selected for sweep temperature test to understand the biopolymer function at the oil reservoir condition.
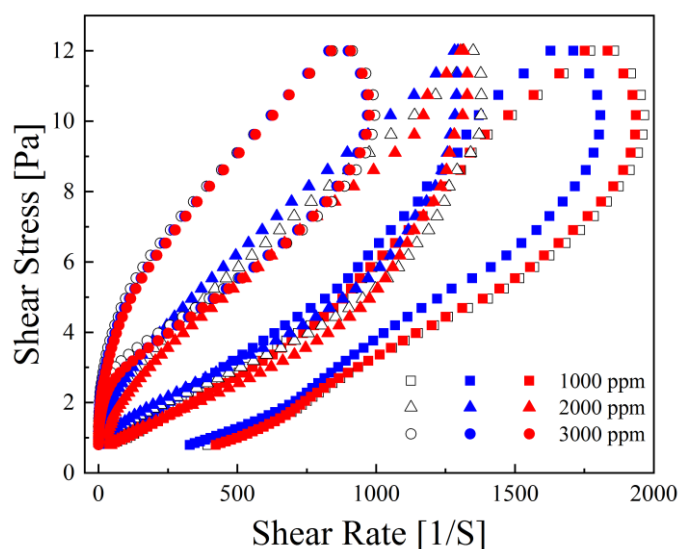

Figure 2: Thixotropic curves of XG biopolymer solutions at 1000, 2000 and 3000 ppm concentrations, without salt (open), low salinity (blue), and high salinity (red)

As Figure 3(a) points out, the viscosity of the biopolymer solutions decreased with increasing shear rate, which indicates shear thinning or pseudoplastic behavior. Shear Thinning mechanism here are alignment of rod-like particles in flow direction, loss of junctions in polymeric solution and rearrangement of microstructure so due to the thixotropy definition of microstructure responding to flow, it can infered that thixotropy is always expected from shear-thinning mechanisms [16, 17]. As shown in Figure 3 (b), when the temperature rises from 25 °C to 70 °C step by step, the thixotropic properties of the polymeric fluid are still preserved, which as mentioned above, from completion the path of build-up and break-down, inception from zero and end to zero, and having enough area between the hysteresis loops can be seen.
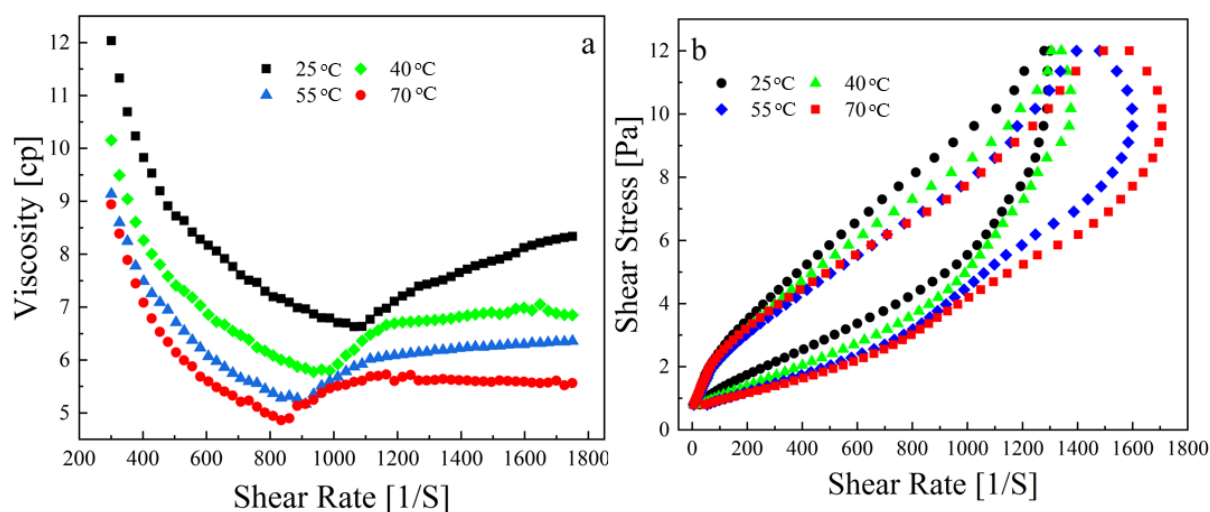
Figure 3: Viscosity (a) and shear stress (b) vs. shear rate of XG biopolymer solution at 2000 ppm and high salinity in different temperatures

Conclusions

This study examined the applicability of XG biopolymer at different salinities and temperatures for a EOR process. The rheological and thixotropical characteristics of XG biopolymer at various salinities, concentrations and temperatures were analysed and compared in terms of the viscosity. The steady shear viscosity of XG biopolymer solutions clarified non-Newtonian fluid characteristics like pseudoplasticity at each concentrations at 25 °C. The rheological and also thixotropical test results demonstrated that XG biopolymer solutions are not particularly sensitive to high temperatures and salinity. These consequences will be effective and applicable in the studies investigating the practicability of employing XG biopolymer flooding under oil reservoir conditions.

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