

Thermal Stability of Bio-Polymers and their Blends



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ABSTRACT: Studies from research have shown that one of the major problems associated with the use of polymers during polymer flooding is polymer degradation. Polymers lose their viscosity as well as their efficiency in the presence of high temperatures. Hence, the need for polymers that are environmentally friendly and can withstand high reservoir temperatures. Therefore, this study was necessary to address this challenge. Three commercial bio-polymers currently being used in the oil and gas industry were used in this study, they are Xanthan gum, Guar gum, and the Imported Locust bean gum (LBG). Also used in this study were, Gum Arabic and Nigerian Locust bean gum (LBG). The thermal stabilities of these polymers were investigated at different temperatures to determine their thermal resistances at high temperatures. Polymer blending was applied to study the impact of blending on the thermal stabilities of the different polymer blends formulated. Rheological analysis was carried out before and after subjecting the polymers and polymer blends using temperatures from 50 °C to 150 °C. The results showed that Guar gum, Imported LBG, and Nigerian LBG displayed improved resistances from 75 °C to 90 °C compared to Xanthan gum, which was thermally stable up to 70 °C. Furthermore, the blends showed higher stable temperatures compared to that of polymers alone and also compared to the thermal stability of Xanthan gum. This study showed that the blends would perform better at high-temperature reservoir conditions.

KEYWORDS: Thermal stability, Xanthan gum, Guar gum, Bio-Polymers, HPAM, Locust bean gum.

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I. INTRODUCTION

Xanthan gum, Guar gum, Carboxymethyl Cellulose, Locust bean gum (LBG) and Partially Hydrolyzed polyacrylamide (HPAM) have been used for various oil field applications. They are applied as viscosifying agents, friction reducers, fluid loss additives, formation damage control additives and flocculants in production, drilling, completion and enhanced oil recovery operations (Sun, 2012). Although, in polymer flooding, synthetic polymers such as HPAM and derivatives of HPAM have been widely used because of their low cost and good viscosifying properties (Chang, 2011). The major challenge with these polymers is that they undergo different forms of degradation; this includes thermal degradation, shear degradation, and chemical degradation (Morel et al. 2008).

In thermal degradation, polymers lose their viscosity under the influence of high temperature, thereby, affecting their overall performance, (Abbas et al., 2013; Morel et al., 2008 and Chatterji et al., 1981). This was further re-emphasized by Martin, (1984) and Rellegadla *et al.*, (2017), where they mentioned that PAM (Polyacrylamide) and HPAM have poor shear and thermal resistance based on results from field applications. Bio-polymers like Xanthan gum and Guar gum have more shear and chemical stability compared to synthetic polymers, but, they are more expensive to use in oilfield operations in comparison to synthetic polymers Changhong, (2014); Sun *et al.* (2012); Chang (1978) and

Rellegadla *et al.* (2017). However, the thermal stabilities of these biopolymers have not been extensively investigated.

Xanthan gum is a commercial biopolymer used in different sectors; food industries, textile industries, pharmaceutical industries, and also in the oil and gas industries. Xanthan gum is a biopolymer released by the micro-organism, *Xanthomonas campestris*, which is manufactured commercially by a fermentation process, (Casas 2000). The molecular weight distribution ranges from 2×10^6 to 20×10^6 Da (Garcia- Ochoa, 2000; Sun 2012). Xanthan gum is a heteropolysaccharide with a structure consisting of repeated pentasaccharide units formed by two glucose, two mannose, and one glucuronic acid (Casas, 2000). Aqueous solutions of Xanthan gum are very viscous owing to the existence of double helix and triple helix structure of the polymer chains with polar side chains that promote extensive hydrogen bonds (Rellegadla *et al.*, 2017; Chatterji, 1981). Xanthan exhibits high viscosity at a low shear force.

According to Guo (1999) and Sun (2012), the major advantages of Xanthan gum over HPAM are excellent viscosifying ability, high tolerance to salinity and temperature, good shear stability, and great ability to thicken at high salinity. Shear-thinning in Xanthan gum is recovered rapidly once the shearing force is removed. However, the disadvantages of this biopolymer are its high cost and difficulty in preparing uniform solutions, so that it does not plug the pores within the reservoir. The occurrence of pore plugging can be avoided by using good quality water and filtration of the polymer solution before injection that is the

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use of microfilters (Rellegadla *et al.*, 2017; Chang, 1978). Micro-filtration, Enzyme clarification, and Diatomaceous earth (DE) are filtration methods, usually employed for the treatment process of polymer solutions before flooding (Rellegadla *et al.*, 2017).

Guar gum is derived as extracts from the seeds of the guar plant (*Cyamopsis tetragonolobus*). Grinding the endosperm of the guar bean produces relatively pure Guar gum. The backbone of the polymer is composed of mannose and galactose units as known as "galactomannan" (Garcia-Ochoa, 2000; Mathur, 2005). There are no ions in the polymer structure; thus, the polymer is termed "non-ionic". Guar solutions have almost a constant viscosity over a pH range of about 1.0-10.5. The chemical stability of Guar gum is believed to be due to the non-ionic, uncharged nature of molecules in its polymer chain. (Casas, 2000, Chatterji, 1981).

Locust bean gum (LBG), also known as Carob bean gum, consists of mainly high molecular weight approximately from 50,000-3,000,000 Daltons. The polysaccharides are composed of galactomannans and are obtained from the endosperm of the seed of the carob (locust) tree also known as *Ceratonia siliqua* (Garcia- Ochoa, 2000; Mathur 2005). The gum is a white to yellowish, nearly odourless gum as powder. Carob bean gum is insoluble in most organic solvents for example ethanol. It is partially soluble in water at ambient temperature and also soluble in hot water. Carob bean gum typically needs heating to above 85°C for complete solubility, (Chatterji, 1981; Gaisford 1986; Mathur 2005). The Carob bean gum is used as thickeners, stabilizers, and emulsifiers in the food, pharmaceutical, cosmetic and agricultural industries, just to mention a few (Chatterji, 1981).

Gum Arabic also called Acacia Senegal, is produced as tear-drop-shaped globules exuding from bark wounds of Acacia trees. The viscosity of solutions of Gum Arabic changes due to the presence of ionic charges, the gum is highly water-soluble. Gum Arabic solution is slightly acidic and it is principally used in the food and pharmaceutical industries as a stabilizer, thickener, suspending, and binding agent. (Glicksman, 1983).

This work, therefore, investigates the thermal stabilities of these biopolymers: Xanthan gum, Guar gum, Imported LBG, Gum Arabic as well as Nigerian LBG and their blends, to enable the formulation of biopolymers with improved properties.

II. MATERIALS AND METHODS

A. Materials

This analysis was done using 1 wt. %- of Xanthan gum, Guar gum, and Imported Locust bean gum (LBG). Xanthan gum and Guar gum were obtained from the Fufeng Group, China. While the Imported LBG was from Amazon.com (United States of America). Also, 1 wt. % and 8 wt. % of Gum Arabic and Nigerian LBG were equally used for this analysis. Gum Arabic was sourced from Kano State, Nigeria while Nigerian LBG was collected from Kaduna State, Nigeria. The gums are displayed in Figures 1 - 5.



Figure 1: Xanthan gum.



Figure 2: Guar gum.



Figure 3: Imported locust bean gum.



Figure 4: Gum Arabic.



Figure 5: Nigerian locust bean gum.

B. Methods

1) Nigerian LBG preparation

El Batal, (2013) and Dakia *et al.*, (2017) employed the use of thermal-mechanical treatment in dehusking seeds of LBG. However, in this research, Nigerian LBG seeds were also manually opened to dehulled the outer covering, this was followed by the removal of the endosperms and then sun drying to eliminate moisture content present within it. A Mesh size of 125 μm was used to screen the gum to the desired particle size.

2) Gum Arabic preparation

Gum Arabic was collected as granules and sorted to remove impurities to improve the quality. The solid form was broken down into smaller pieces before being pulverized to obtain smaller particle sizes and finally sieved using 250 μm to obtain the desired particle size.

3) Rheological characterization

The concentrations of the different polymers were hydrated in water separately at 26 $^{\circ}\text{C}$. The solutions were stirred gently to achieve homogeneity; this was then followed by a hydration period of 24 hrs. Consequently, an initial rheological characterization was carried out using Fann Viscometer at 300 rpm (revolution per minute).

4) Thermal analysis

Thermal analysis was carried out on the hydrated samples using the M1750 Roller Oven (Petroleum Training Institute, Nigeria) at 26 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, 80 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$, 130 $^{\circ}\text{C}$. This temperature study was extended to 150 $^{\circ}\text{C}$ for the imported polymers. Furthermore, a final rheological characterization was carried out at 300 rpm to determine the degree of stability based on the effect of varying temperatures. Figure 6 shows the cells within the Roller Oven with the different samples for thermal analysis. Finally, Xanthan gum was blended with Guar gum, Imported LBG, Gum Arabic, and the Nigerian LBG in the ratio of 3:1, 2:2, and 1:3.



Figure 6: Cells in the roller oven for thermal analysis.

there was a gradual reduction in the viscosity at increasing temperature, which agrees with (Chang, 1978), in which he reported that xanthan gum is thermally stable between 0 $^{\circ}\text{C}$ and 71 $^{\circ}\text{C}$. Guar gum was stable over a wide range of temperatures, it was stable to about 80 $^{\circ}\text{C}$ after which a slight drop in viscosity occurred (Figure 7). Gaisford *et al.* (1986), mentioned that the heating of the gum to 80 $^{\circ}\text{C}$ is needed for a complete dissolution of the gum, which means that the viscosity of the gum will remain stable up to 80 $^{\circ}\text{C}$, so it can attain complete dissolution, its optimum viscosity is at 80 $^{\circ}\text{C}$. The stability displayed by this gum can equally be attributed to the nature of its molecular structure. According to Chatterji *et al.* (1981) and Mathur *et al.* (2005), they stated that the molecular structure of Guar gum has about 60 to 70% solubility in cold water, hence when subjected to the effect of heat, its mannan chains that were initially not soluble in water at room temperature are made available for interaction hence its ability to maintain its viscosity up to 80 $^{\circ}\text{C}$.

The viscosity of the Imported LBG solution increased tremendously with an increase in temperature up to 90 $^{\circ}\text{C}$ before it started to decline (Figure 7). The similarity in high stability between Guar gum and LBG is understood because they are both Galactomannans (Galactose and Mannose polymer chain). However, the increase in viscosity generated by the locust bean gum was much higher compared to the increase produced by Guar gum. These results are in line with the work carried out by Casas, (2000); Gaisford *et al.*, (1986), where they mentioned that “the heating of LBG aqueous dispersions up to about 80 to 90 $^{\circ}\text{C}$ is necessary to obtain a complete dissolution of the gum”. Gaisford *et al.*, (1986), mentioned that LBG should be heated to at least 80 $^{\circ}\text{C}$ for full hydration. LBG has the lowest galactose content and is the least soluble among the other galactomannans such as Fenugreek gum, Guar gum, and Tara gum (Mathur, 2005).

III. RESULTS AND DISCUSSION

The results presented in Figure 7 showed that the viscosity of Xanthan gum solution was stable up to 70 $^{\circ}\text{C}$. Afterward,

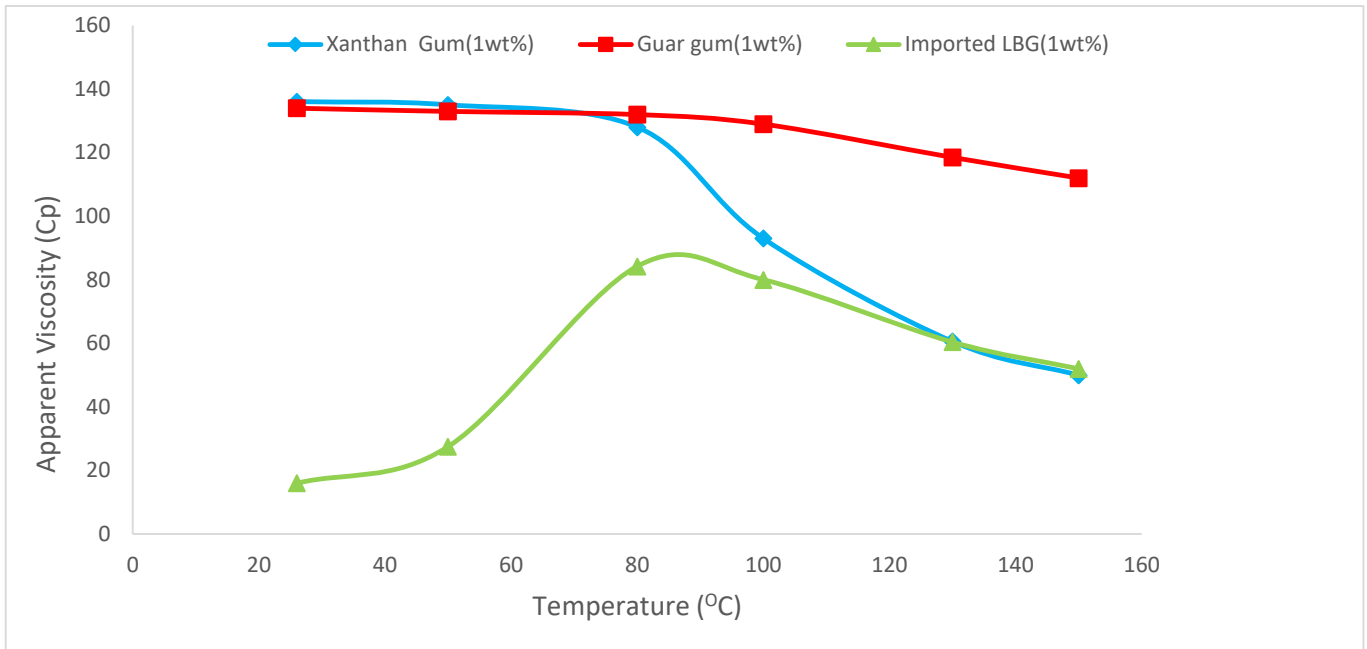


Figure 7: Thermal stability of the imported polymers at 300rpm.

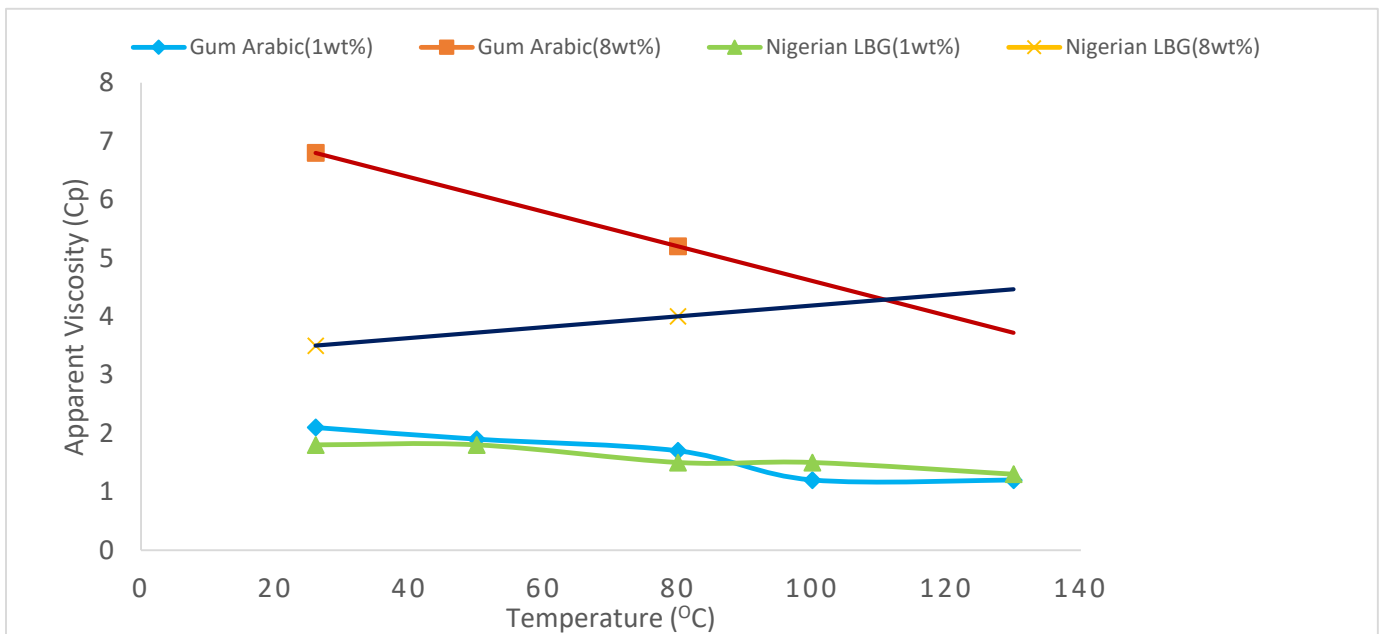


Figure 8: Thermal stability of Gum Arabic and Nigerian LBG at 300rpm.

Figure 8 shows the effect of temperature on Gum Arabic using 1 wt. % and 8 wt. % which resulted in a reduction in viscosity. According to Muller, (1981), the hydrolysis of a polymer solution is the cumulative effect of the pH and the temperature. Based on this, the loss of viscosity can be related to the hydrolysis of the polymer chain which is a function of the pH of the Gum Arabic solution. pH analysis of Gum Arabic from this study ranged from 4 to 5. This implies that the pH of the Gum Arabic solution is strongly responsible for the loss in viscosity encountered. Nigerian LBG (1 wt. %) did not show much increase in viscosity with increasing

temperature. However, the effect of increasing temperature to about 80 °C on a higher concentration of LBG (8 wt. %) was significant, as this led to an increase in viscosity. This improved rheological behaviour is simply based on the fact that LBG has both hot water and cold water soluble components, the cold water soluble regions have more galactose contents than the hot water soluble regions. About 30% of LBG is soluble in cold water, increasing the temperature of the LBG solution will lead to an increase in viscosity because, increasing the temperature will dissolve the

bonds that were initially not soluble in cold water, (Gaisford et al., 1986).

Figure 9 showed that Xanthan/ Guar gum and, Xanthan/ Imported LBG resulted in synergistic blends in the ratios of 3:1, 2:2, and 1:3. However, Xanthan/ Nigerian LBG blend was only able to produce synergism in the ratio of 3:1. The reason behind this synergy is that according to Gaisford et al, (1986), Guar gum and LBG have two types of regions in their molecular structure, they are the smooth regions and the hairy regions. The hairy regions or the substituted regions are regions containing the galactose graft, which determine the apparent viscosity of the polymer. Guar gum has about 33% graft on its mannan chain when compared to LBG that has about 23% galactose graft (Gaisford et al, 1986). Based on this, Guar gum has more viscosifying abilities at room temperature than LBG. Also, the smooth regions also known as the un-substituted regions are the regions without galactose grafts. They are responsible for being able to blend with Xanthan gum because they are the regions that favour interaction with Xanthan gum (Casas et al., 2000).

This observation is in agreement with the works reported by (Kovacs 1973; Tako *et al.* 1984; Dea *et al.* 1986; Kang *et al.* 1993 and Maier *et al.* 1993), where they stated that the viscosity of these polymers is increased synergistically when blended than the viscosity of the gums alone. However, Xanthan/ Gum Arabic blend did not yield synergy because it is a polyelectrolyte (Muller, 1981).

Figure 10 shows the thermal stability of the imported polymer blends. The impact of increasing temperature on the Xanthan/Guar blend using 2:2, displayed a linear drop in viscosity until 80 °C after which the viscosity reduced; apparently due to the influence of Guar gum. Again, Xanthan/ Imported LBG blend at a combination of 2:2 displayed a steady decline in viscosity until 80 °C, after which

there was a gradual rise in the viscosity. This rheological behaviour can be attributed to the impact of the heated LBG in the blend. The gain in viscosity is related to the fact that LBG is only partially soluble in cold water. LBG solutions need heating to at least 90 °C for it to attain full hydration. The heating of LBG aqueous dispersions up to 80 °C is necessary to obtain a complete dissolution of the gum (Casas, 2000).

Analysing Nigerian polymer blends, at increasing temperatures, 3:1 produced a better stability than 2:2, and hence 3:1 was used. Xanthan/Nigerian LBG blend had more stability than Xanthan/Gum Arabic blend, this was because of the thickening behaviour of LBG when subjected to the effect of high temperature (Figure 11). Though, the increase in viscosity produced by Xanthan/ Nigerian LBG was less than Xanthan/ Imported LBG blend, this was due to low viscosity of Nigerian LBG compared to Imported LBG.

This study displays the impact of high temperatures on polymer blends. Xanthan/ Nigerian LBG, Xanthan/ Guar gum and, Xanthan/ Imported LBG showed higher resistance to thermal degradation than Xanthan gum which has been the bio-polymer used in polymer flooding. Therefore, based on the results, these polymer blends can suffice as environmentally friendly polymers for high-temperature reservoirs.

V. CONCLUSION

In summary, based on this study, the following conclusions were drawn:

1. Xanthan gum, Guar gum, Imported LBG, Nigerian LBG, and Gum Arabic used in this study are water-soluble and produce appreciable viscosities at high concentrations.
2. Xanthan gum was thermally stable up to 70 °C, Guar gum showed stronger thermal stability at 80 °C than Xanthan gum, while the Imported LBG displayed the strongest thermal stability at 90 °C compared to Xanthan and Guar gum.

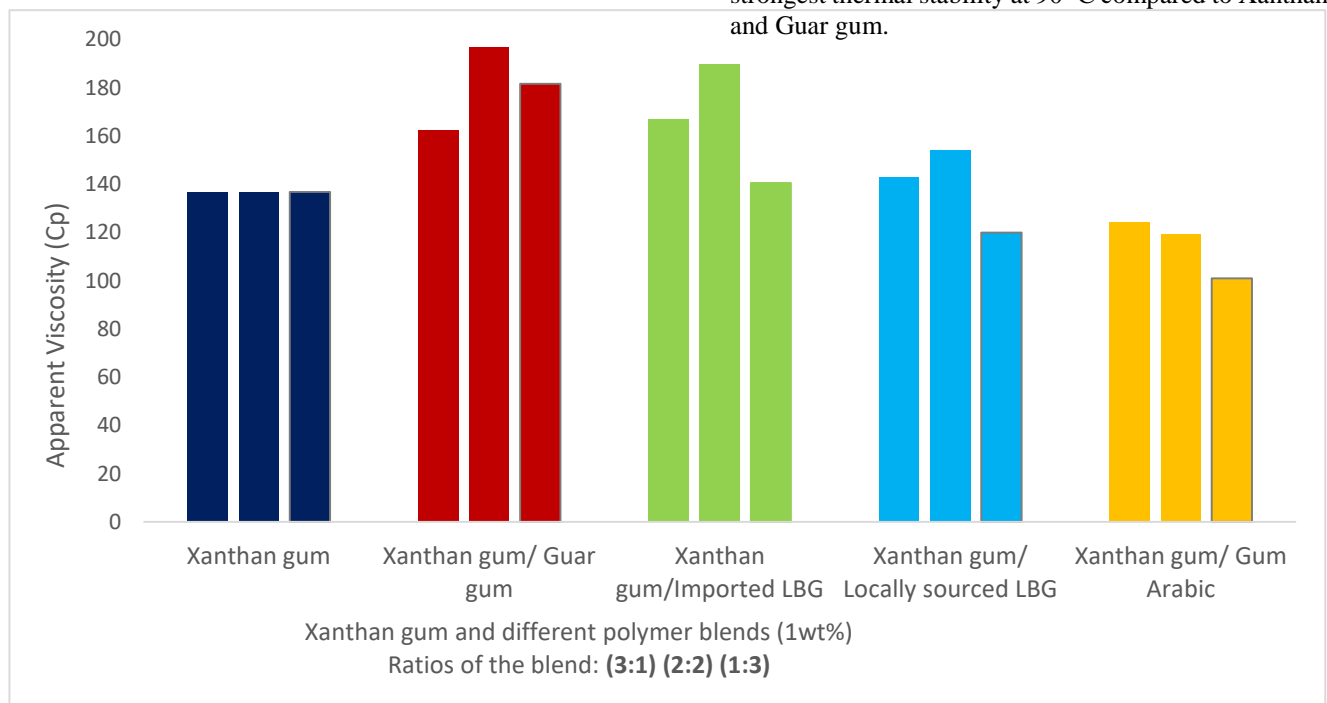


Figure 9: The Effect of Polymer blending (Comparison between Xanthan gum and other ratios of polymer blends).

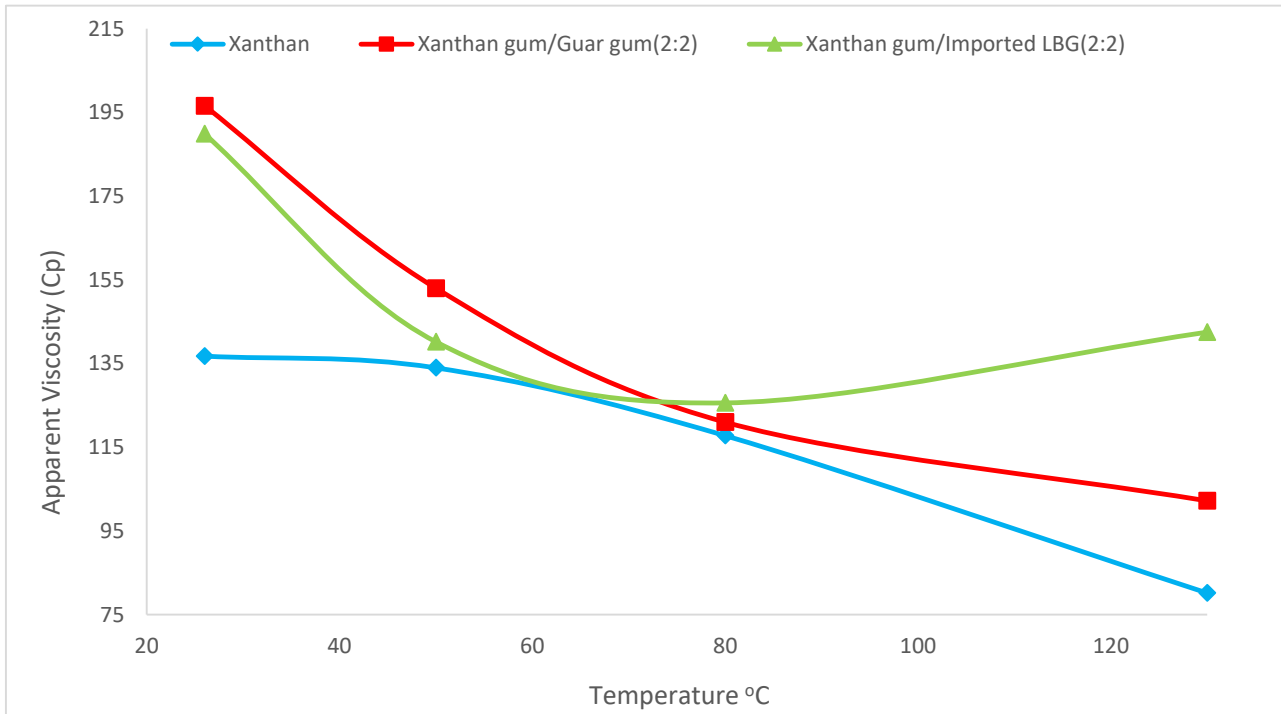


Figure 10: Thermal stability of the imported polymer blends at 300 rpm.

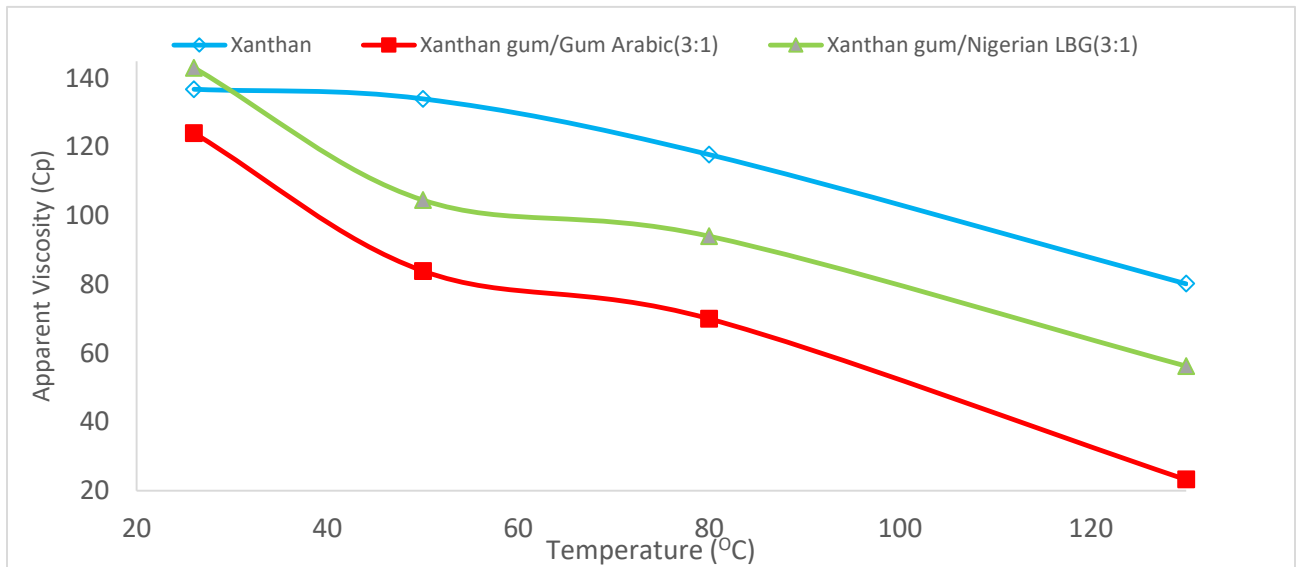


Figure 11: Thermal stability of the Nigerian polymer blends at 300 rpm.

- Gum Arabic did not show any significant stability at varying temperatures. Though Nigerian LBG, at higher concentration displayed similar rheological behaviour to the imported LBG, its viscosity increased with an increase in temperature.
- Gum Arabic did not show any significant stability at varying temperatures. Though Nigerian LBG, at higher concentration displayed similar rheological behaviour to the imported LBG, its viscosity increased with an increase in temperature.

- Polymer blending produced a synergistic effect, Xanthan/ Guar gum, Xanthan/ Imported LBG, Xanthan/ Nigerian LBG produced higher viscosities than the viscosities of the polymers alone.
- The effect of blending improved the thermal stabilities of the blends; Xanthan/ Guar gum, Xanthan/ Imported LBG, and Xanthan/ Nigerian LBG gum.

These improved blends can suffice as Enhanced oil recovery polymers for high-temperature reservoirs.

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