

Comparative Studies of Rheological Properties of Jatropha Biopolymer and Xanthan Gum

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ABSTRACT

The present work is concerned with experimental results of rheological characteristic of jatropha biopolymer (polyhydroxybutyrate) and commercial xanthan gum (XG) in NaCl solution with changing experimental conditions such as shear rate, polymer concentrations, salinities and temperatures. In this study, PHB was extracted from cell dry weight of jatropha oil seeds. However, since PHB have low thermal stability, an alternative way to improve PHB properties is to blend with another polymer, Polyethylene oxide (PEO). It has been observed that PHB-PEO and XG exhibited the non-Newtonian behaviour in all condition. The results indicated that the PHB-PEO showed better shear-resistance at high shear rates (100s^{-1}) and temperature-tolerance (90 to 130 °C). The salt-resisting experiment showed that PHB-PEO good anti-salt ability.

KEYWORDS: Jatropha Oil, Polyhydroxybutyrate, Rheological properties, Concentration, Temperature, Salinity.

INTRODUCTION

In many oilfield operations including polymer flooding, water-soluble polymers are used. During water flooding processes, water was injected into reservoir to maintain the reservoir pressure and to displace the oil. However, because of oil typically have higher viscosity than water, unstable displacement was occurred. Unstable displacement during water flooding processes may be improved by increasing the viscosity of injected water through addition of polymer.

Biopolymer xanthan gum (XG) most widely used for enhanced oil recovery (EOR) processes. The application of polymers in EOR processes significantly increased the oil recovery as compared to water flooding. XG as compared to polyacrylamide is a rigid polysaccharide that showed better resistance to shear and salt. Unfortunately, XG have several drawbacks such as susceptible to biodegradation, caused injectivity problem due to remaining cellular debris resulted from manufacturing process and high cost. After long time of water flooded, heterogeneity is getting worse and worse, the demanded of water-soluble polymer which have better shear, temperature and salt resistance mainly for deep oil reservoir became one of the challenge to oil operators [1].

Recently, many research works have indicated new developed and improving water-soluble polymers such as salt of 2-acrylamido-2-methylpropane sulfonic acid (PAMS) [2], Partially Hydrolyzed Polyacrylamide (HPAM) [3], Xanthan Gum through self-association with surfactant [4] and many more. Inspired from previous studies, polyhydroxybutyrate (PHB) extracted from jatropha oil was adopted as new polymer for EOR processes. Polyhydroxybutyrate (PHB) is widely used for medical and packaging application [5]. To optimize the PHB production, selection of suitable carbon source is important as it influence not only PHB content, production cost but also properties of the polymer. To encourage high production of PHB, cheap carbon source was used [6].

Previous studies used jatropha oil as carbon source for PHB production which is generated from jatropha seeds. Jatropha is a non-edible plant and has capability to grow on saline and sandy soils. Since, it is non-edible plant, it does not compete with global food issues [7-9]. However, since PHB have lower thermal stability, it suffers some disadvantages including limit for processing application and low impact strength. One of an alternative ways to improve PHB properties is by blending with another polymer. A number of investigations have been published on the compatibility of PHB blend [10-11]. Among the available polymer, polyethylene oxide (PEO) was selected due to excellent biocompatibility and miscibility with PHB [12-13].

There are limited works studied the rheological properties of blending PHB-PEO. To our knowledge, there is no published report related to rheological properties of PHB extracted from jatropha oil. Understanding the

rheological of polymer is essential for EOR application. The rheological properties of polymers were strongly influenced by shear rate, salinity and temperature [14].

In this present study, the rheological properties of commercial XG and PHB-PEO solutions were made. The effect of shear, salinities and temperatures were investigated.

MATERIALS AND METHOD

Materials

PHB cell dry weight (CDW) used in this study was obtained from School of Biology, University of Science, Malaysia [15]. Polyethylene oxide (PEO) of low molecular weight, $M_w = 1500$ and xanthan gum manufactured from (R & M marketing, United Kingdom) were obtained from chemical laboratory, University of Teknologi MARA (UiTM).

PHB Extraction and Purification

The extraction of PHB from jatropha CDW was performed based on previous study. The CDW of jatropha were dissolved in chloroform solution with ratio of 1:100 for 5 days. The mixture was stirred with magnetic stirrer until homogeneous solution was formed. The solution then was filtered using filter paper to remove cell debris and then concentrated using rotary evaporator (Heidolph) (60 rpm at 27 °C). Approximately, 30 mg of PHB then were subjected to methanolysis with ratio 1:10. The extracted PHB was finally dried and stored in tightly containers under room condition [16].

PHB-PEO Blending Preparation

The PHB was dissolved with PEO in chloroform at room temperature yielding a 2 % of solution. The solutions were mixed and stirred using magnetic stirrer for 8 hours. Since PHB is insoluble in chloroform at room temperature, the solution was prepared using the similar way at 60 °C. In this study, we examined PHB-PEO blend ratio of 80:20. Then, blended solution was cast on a horizontal glass surface followed by slow evaporation. The readily blended film then was placed in sealed bottle for further tests [17].

Polymers Solution Preparation

The PHB-PEO films were then dissolved in an aqueous of acetic acid and sodium chloride (CH_3COOH 0.1 mol/L/ NaCl 0.2 mol/L). The solution then was kept under stirring for 24 hours to ensure complete solubilization of the PHB-PEO [18].

Rheological Measurements

Rheological and temperature measurements were carried out using rotational rheometer Physica, (MCR 301, Austria). Both polymers were dissolved in 3 wt% of NaCl solution. The temperature was controlled by a thermostatic water bath connected to rheometer. The volume of the solution was approximately 30 mL. In addition, the solution was always stirred by the rheometer spindle in the sample cup to ensure temperature throughout the polymers solution were the similar.

The consistency index, k and flow behaviour index, n were calculated by fitting the Ostwald-De-Waele model (Equation (1)):

$$\tau = k\dot{\gamma}^n \quad (1)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), k is the consistency index (Pa.s) and n is the flow behaviour index (dimensionless).

RESULTS AND DISCUSSION

The Concentration and Shearing Resistance Effect

The viscosity curves for solutions of xanthan gum and PHB-PEO in 3 wt% NaCl solution and shear rate changed from 23 to 100 s^{-1} was compared in Figure 1. Both polymer solution used in present investigation behave as non-Newtonian fluids. As can be seen from Figure 1, the viscosity curve for commercial XG and PHB-PEO may be divided into two parts: region below critical shear rate where large shear-thinning effect was observed and region above critical shear rate where shear-thickening behaviour occurs.

In the first region, the reduction of viscosity mainly related to orientation of macromolecules along the streamline of flow and disentanglement of macromolecules with increasing shear rate. The PHB-PEO viscosity curves exhibit shear-thickening region at shear rate ranged from 23 to 100 s^{-1} . The phenomenon of shear-thickening may be related to an entanglement of macromolecules that possibly occurred under flow condition. Large number of polymer chains in the unfolded conformation will participate in the formation of temporary

network thus give rise to increase of viscosity. Once shear forces is removed, the polymer chain spread apart and again form a stable chain. In the case of PHB-PEO solution, the steric interactions participate in shear-thickening phenomenon. The shear forces may disturb the steric interactions and as consequence, the repulsive force reduced thus lead to disordered polymer chain causing increase in viscosity.

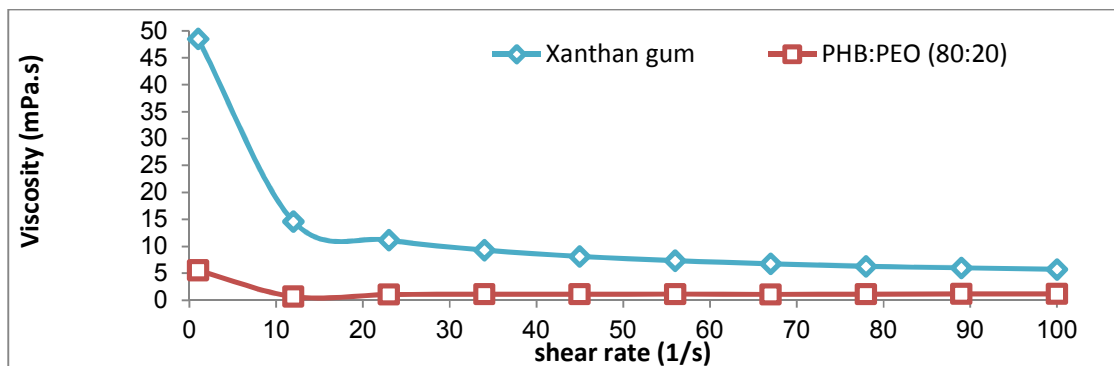


Figure 1: The apparent viscosity of commercial xanthan gum and PHB:PEO (80:20) at 500 ppm in 3 wt% of NaCl solution, T = 27 °C

It can be found that from Figure 1 that the viscosity of PHB-PEO dropped from 5.525 to 0.676 mPa.s. After increasing the shear rate to 100 s⁻¹, no obvious change could be discovered in the value of viscosity and viscosity loss of PHB-PEO could arrive 104.8% (45 s⁻¹) while it was 114.83 % at 100s⁻¹. Meanwhile, XG showed viscosity loss of 72.9% and 51.3 % when measured at similar shear rates. This indicated that copolymer PHB-PEO solution had good viscosity retaining properties by showing better performance in high shear rate.

The values of power law parameter are tabulated in Table 1. Based on tabulated data in Table 1, the consistency index was increased together with concentration due stronger structure development while flow behavior index is decreased resulted from progressive shear-thinning nature. The concentration of XG seem to be more higher than PHB-PEO (Table 1, Figure 1).

Table 1: Calculated power law for PHB-PEO at different concentrations

Concentrations (ppm)	k	n (-)	R ²
PHB-PEO			
500	5.02	0.5726	0.8818
1500	7.582	0.5336	0.9195
2000	7.562	0.455	0.9343
3000	11.6	0.2721	0.9688
Xanthan Gum			
500	6.67	0.7664	0.9935
1500	159	1.443	0.9986
2000	305.6	0.4207	0.9998
3000	1237	0.2755	1

The Influence of Salinity

One of the challenges which imposes a limitation on polymer flooding applications is salinity of formation water. By improving the polymer performance in high salinity reservoir may unlock the oil reserves thus increased the oil recovery [19]. Figure 2 presents the viscosity of the both polymers as function of NaCl concentrations. As can be seen from Figure 2, the viscosity obtained for Figure 2 (b) was higher than Figure 2 (a). The viscosity curves of no salt was higher than with salt addition for both polymers. The plots obtained in no salt and in presence of NaCl concentration showed the reduction of viscosity with increasing NaCl concentration. In presence of salt, the side chain of PHB-PEO would collapsed due to shield ionic repulsion effect and caused disordered transition to take place thus lowered the viscosity (1 and 3 mg/L). Meanwhile, at 5 mg/L of NaCl, the viscosity curves was higher than 1 and 10 mg/L for both polymers. This phenomenon may be due to solvent polarity which enhances the PHB-PEO hydrophobicity prevent polymer molecular chain from being disordered. Then, viscosity is increased.

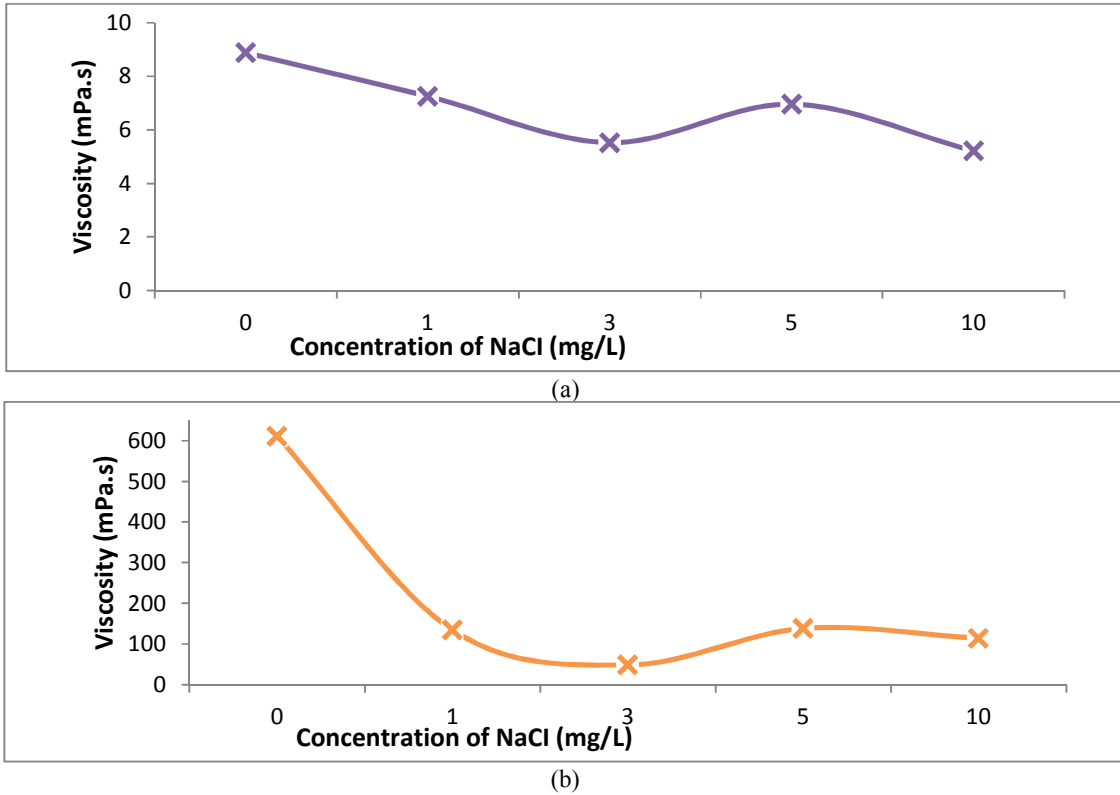


Figure 2: The apparent viscosity of (a) PHB:PEO (80:20) and (b) at 1500 ppm in different NaCl concentrations, $T = 27\text{ }^{\circ}\text{C}$

The Temperature Tolerance

Figure 3 showed the curves obtained on effect of temperatures on commercial XG and PHB-PEO at 500 ppm. Interestingly, it showed that the viscosity of PHB-PEO was gradually increased little by little before $50\text{ }^{\circ}\text{C}$ and kept rose from 90 to $110\text{ }^{\circ}\text{C}$. This may be resulted from dominated fraction of PHB in PHB: PEO blending (80:20) caused the copolymer to have high tolerant to high temperature. General trend however indicated after increased the temperature, apparent viscosity decreased (as displayed by commercial XG curve).

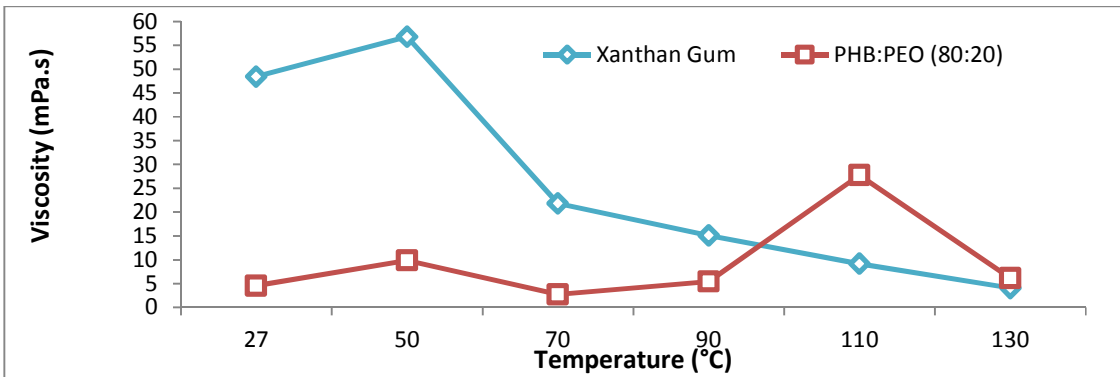


Figure 3: The apparent viscosity of commercial xanthan gum and PHB:PEO (80:20) at 500 ppm in different temperatures at shear rate 1 s^{-1}

At lower temperature, the intramolecular of hydrophobic of PHB-PEO are dominant and with rising the temperature, the intermolecular hydrophobic association slightly strengthened. Thus, increased the apparent viscosity (90 to $110\text{ }^{\circ}\text{C}$). However, large number of associating group would aggregated with each other to form super molecular structure by forming strong Van Der Waal forces. As a result, polymer chain entangled each other by hydrogen bond interaction. At high temperature, the intermolecular interaction became weak and

molecular fracture may be occurred and this may contributed to reduction of viscosity. It demonstrated that the PHB-PEO revealed a good temperature tolerance (90-110 °C).

CONCLUSION

Rheological behaviour of PHB-PEO has been investigated in this paper. The result shows that PHB-PEO had better capability of resisting at high shear rate, high temperature (90 to 110 °C) and different NaCl concentrations. Based on results above, PHB-PEO might be good candidate for polymer flooding for high temperature reservoir.

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