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Original article

Experimental study on the effect of wax inhibitor and nanoparticles on rheology of Malaysian crude oil

Priyatachni A.P. Subramanie, Abhilash Padhi, Norida Ridzuan *, Fatmawati Adam

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Malaysia

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A B S T R A C T

In Malaysia, solid depositions of paraffin wax in the inner walls of production and transportation pipelines, and on the surface of production equipment have been identified as the utmost challenge in production and transportation of crude oil. In order to overcome the wax deposition issue, physical characterization of crude oil is crucial. In this study, the performance of wax inhibitor and nanoparticle, sodium cloisite Na^+ is evaluated to determine their effects on the viscosity of crude oil using Brookfield DV-III viscometer. Nanoparticle was used along with 500, 800, 1000, 2000 and 5000 ppm of Poly (ethylene-co-vinyl acetate) (EVA) and Poly (maleic anhydride-alt-1-octadecene) (MA). Nanoparticle alone was able to lower the viscosity of crude oil to about 92.5%. EVA and MA were able to reduce the viscosity up to 88% and 86.4%, respectively while EVA and MA added to nanoparticle was able to reduce the viscosity up to about 94% and 89.2%. The blend between wax inhibitor and nanoparticle provides significant reduction in viscosity of crude oil.

1. Introduction

Flow assurance is defined as the process of making sure an economical flow of hydrocarbon stream transport from the reservoir to its final storage whereby it comprises of hydrates, wax deposition, asphalthenes, slugging, naphthenates, scales, corrosion, erosion and emulsion (Theyab, 2018). Flow assurance issues in the oil and gas industry reflects the increasing production cost. Looking into the production issues faced by oil industries, the wax deposition obviously falls into the critical category. Wax deposition has been identified as an issue affecting the oil industry as early as 1928 (Huang et al., 2015). Wax formation in crude oil transportation pipeline increases the viscosity of fluid, resulting in an increased pressure. Additional horsepower and an increase in manpower is required in order to increase pressure to mitigate the wax deposition problem (Elsharkawy et al., 2000). The rheology and transportation of crude oil is essential issue to be addressed in the oil and gas industry. Viscosity is identified as a very profound function of wax deposition rate and leads to wax precipitation (Ekaputra et al., 2014). Reduction of viscosity is important through in-situ operation or after production to lower the costs of surface operations (Gudala et al., 2017).

Current solutions that are commonly used to prevent or mitigate the wax deposition includes mechanical (e.g. scrapers, pigs), thermal (e.g. insulation, electrical heating, treatment with hot oil) and chemical methods (e.g. solvents, dispersants, inhibitors), or the combinations of these methods (Jennings & Breitigam, 2010; Towler et al., 2011). Polymer inhibitors such as Poly (ethylene-co-vinyl acetate) (EVA) and Poly (maleic anhydride-alt-1-octadecene) (MA) are made up of polar and non-polar molecules where polar molecules interfere with the crystallization and changes the wax morphology, while non-polar part attach inhibitor and wax molecules to each other (Machado et al., 2001). Polymer inhibitor is able to merge with wax crystals and hinders the agglomeration of wax crystals (Ridzuan et al., 2014). Naturally extracted additives and nanoparticles are two new promising solutions for overcoming the flow assurance issues. Bio additive or bio surfactant such as potato starch (Gudala et al., 2018), Mahua extracted from *Madhuca longifolia* (Kumar et al., 2018a,b) and surfactant extracted from soapnut or *Sapindus mukorossi* (Kumar et al., 2017) successfully reduced the viscosity and improves the flow ability of heavy crude oil.

* Corresponding author.
E-mail addresses: norida@ump.edu.my (N. Ridzuan), fatmawati@ump.edu.my (F. Adam).

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Recent development in nanotechnology gives a promising outcome in overcoming wax issue. This is mainly because nanoparticle technology has been identified to have particles with higher stability, superior adsorption, catalytic behaviour and excellent dispersion ability. Nanohybrid PPD have been proven to lessen the amount of wax crystals formed, reduce the temperature where the first wax crystals starts to form and eliminate the chances of wax aggregation (Wang et al., 2011; Yang et al., 2015). Yao et al (2018) have studied the effect of nanoparticles addition on rheology and successfully proven that nanoparticles improves rheology, thus assisting in slower accumulation of wax molecules. However, the effects of the blend of inhibitor with nanoparticles, and nanoparticles on the viscosity reduction of Malaysian crude oil is unclear, and studies on this particular field is limited. As such, the aim of this work is to evaluate the effect of EVA, MA and nanoparticles and the effect of blend of EVA/nanoparticles and MA/nanoparticles on the viscosity of Malaysian crude oil at different temperature and shear rate.

2. Experimental

2.1. Material

Two wax inhibitors were used in this study: Poly (ethylene-co-vinyl acetate) (EVA) and Poly (maleic anhydride-alt-1-octadecene) (MA). The nanoparticle used was sodium cloisite Na^+. The crude oil sample was provided by PETRONAS Refinery Plant in Kerteh, Terengganu, Malaysia.

2.2. Characterization of crude oil

Physiochemical characteristics of crude oil such as wax appearance temperature (WAT), pour point, viscosity and API were determined. WAT was determined using differential scanning calorimeter (DSC) while pour point was determined using cloud/pour point bath by Koehler. Viscosity and API were determined by Brookfield DV-III viscometer and Micromeritics AccuPyc II 1340 pycnometer, respectively.

2.3. Preparation of polymer and nanoparticles

EVA and MA solutions, each (5000 ppm) were prepared by dissolving 1.25 g of each inhibitor with 500 mL of cyclohexane (solvent) under continuous stirring at 60 °C for 2 h. Nanoparticles are prepared as nanofluid by dissolving sodium cloisite nanoclay in cyclohexane under continuous stirring at 60 °C followed by sonication process in ultrasonic bath (FB15051, Fisherbrand) at 25 °C for 1 h. The wax inhibitor/nanoparticle blend was stirred at 25 °C at the frequency of 20 kHz for 1 h before being used.

2.4. Viscosity measurement

The apparent dynamic viscosity of crude oil was measured using Brookfield DV-III viscometer. Spindle type 31 was chosen to analyse the crude oil viscosity. The procedures comply with ASTM D445-06 and ASTM D5002-99 standards. Prior to the measurement of viscosity, the samples were heated above WAT to make sure that all the wax crystals are dissolved. The samples were then moved into a stainless steel cylinder with a jacket connected to a thermostat circulating water bath in order to study the effect of inhibitor and nanoparticles on the flow behaviour of crude oil.

3. Results

3.1. Characteristics of crude oil

Table 1 represents the characteristics of crude oil sample. The physiochemical properties obtained through different analysis technique and instruments help in identifying and clarifying the causes of wax deposition and guide oil and gas industry to have better prevention techniques in order to overcome the wax deposition issue (Ekaputra et al., 2014).

3.2. Effect of temperature on the viscosity of crude oil

Viscosity is an important aspect in the analysis of wax deposition issue as it plays a crucial role in the flow ability of crude oil. The flow assurance of crude oil affects the wax deposition rate and causes wax precipitation (Ekaputra et al., 2014).

Fig. 1 shows the graph of viscosity of blank crude oil against the temperature. Temperature increase in turn lowers the viscosity essentially which stipulates the alterations in rheological properties of crude oil (Kumar et al., 2018a,b). The WAT of blank crude oil is found to be 28 °C. When the temperature goes down than the WAT, the waxes will part like plate-like crystals and these crystals will interact together to form a three-dimensional network which in turn leads to the oil being trapped. This causes the viscosity of crude oil to increase while decreasing the oil flow assurance and pressure loss in pipelines (Kelland, 2009).

3.3. Effect of nanoparticles on the viscosity of crude oil

The addition of nanoparticles to crude oil results in a viscosity reduction at a very significant level. The viscosity was measured at different temperatures at the fixed shear rate of 61.2 s^{-1} along with the degree of viscosity reduction (DVR) (Hasan et al., 2010). The DVR can be calculated using Eq. (1)

$$DVR\% = \frac{\mu_{ref} - \mu_{treat}}{\mu_{ref}} x100 \quad (1)$$

Table 1
Physical properties of crude oil sample.

Viscosity mPa.s at 35 °C	4.67
WAT, °C	28
Pour point, °C	11
Wax Content at 20 °C, %	9.2
Density, g/cm^3	0.814
°API	42.4

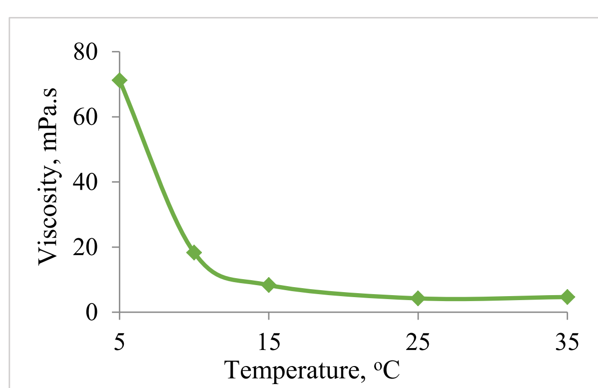

Fig. 1. Viscosity of blank crude oil at different temperature.

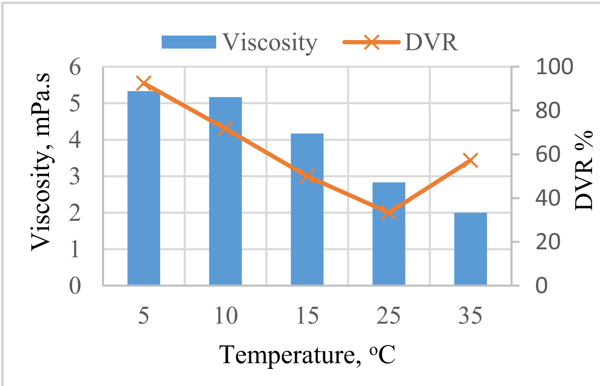

Fig. 2. Viscosity and degree of viscosity reduction (DVR) of crude oil in presence of nanoparticles at different temperature.

where μ_{ref} and μ_{treat} are the reference and the after-treatment incorporation viscosity values.

Fig. 2 shows the viscosity reading of crude oil after the addition of nanoparticles at different temperature. It can be seen that there is a significant reduction of viscosity. From Fig. 2, the DVR is highest at 5 °C at 92.5% and the lowest at 25 °C at 33.4%. At a temperature below the WAT, the nanoparticles reduced the viscosity of crude oil significantly, and as the temperature approaches WAT, there was no much effect on the crude oil viscosity. The wax crystals in blank crude oil are high in density, thus the interspace between the waxes crystals are relatively small, resulting in three-dimensional agglomeration of wax crystals that increases the viscosity. After the inclusion of nanoparticles, the amount of crystals is reduced which leads to the interspace between crystals increasing and resulting in significant decrease in the viscosity of crude oil (Wang et al., 2011).

3.4. Effect of inhibitor with and without the addition of nanoparticles on the viscosity of crude oil

Fig. 3 shows the relationship of crude oil viscosity at different inhibitor concentrations, and these graphs demonstrate that the viscosity of crude oil is controlled by the inhibitor concentration.

Viscosity of crude oil has been reduced with the addition of inhibitors, and further reduced by the addition of nanoparticles.

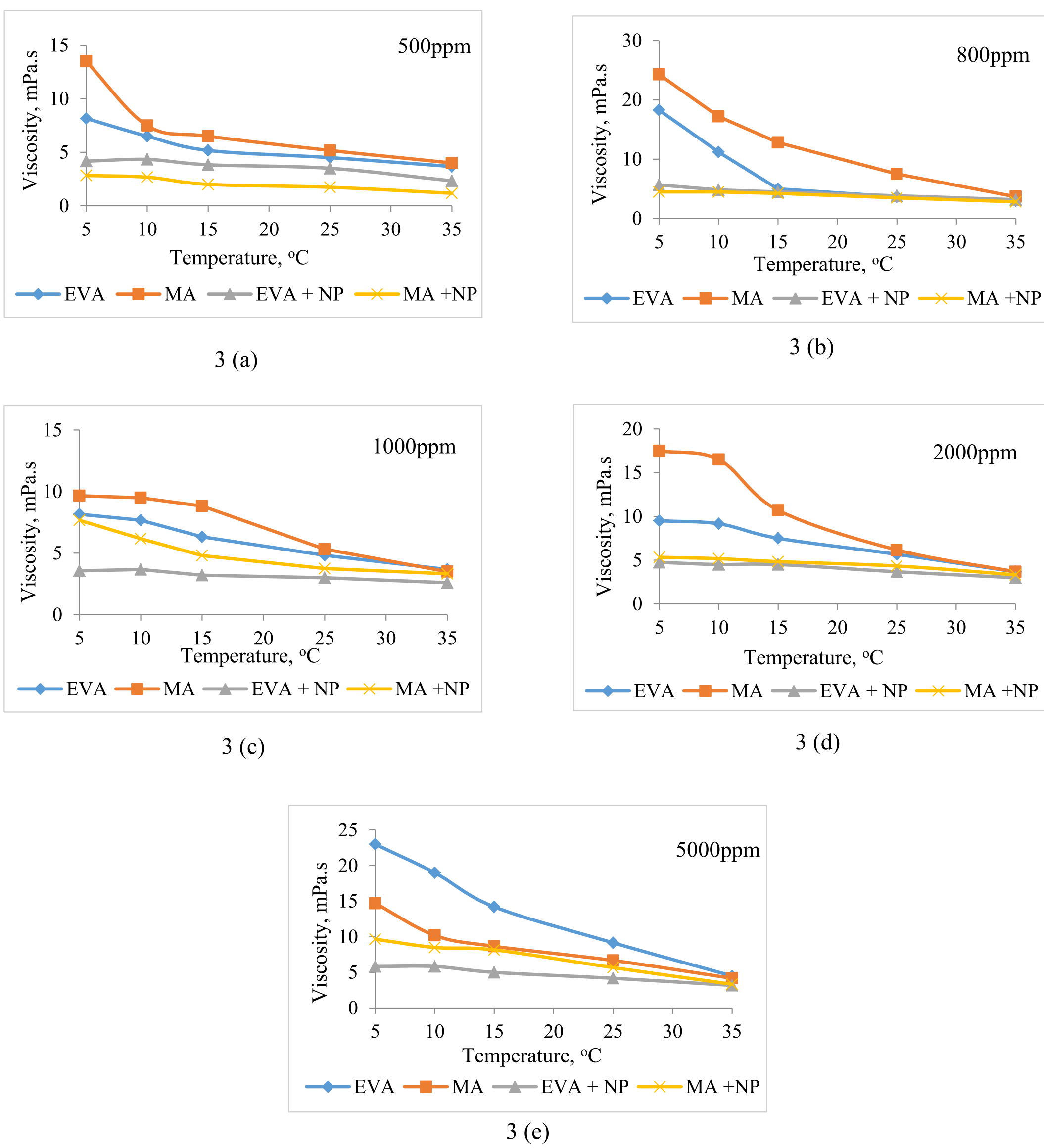

Fig. 3. Comparison of dynamic viscosity of crude oil as a function of concentration against temperature: (a) 500 ppm, (b) 800 ppm, (c) 1000 ppm, (d) 2000 ppm, (e) 5000 ppm.

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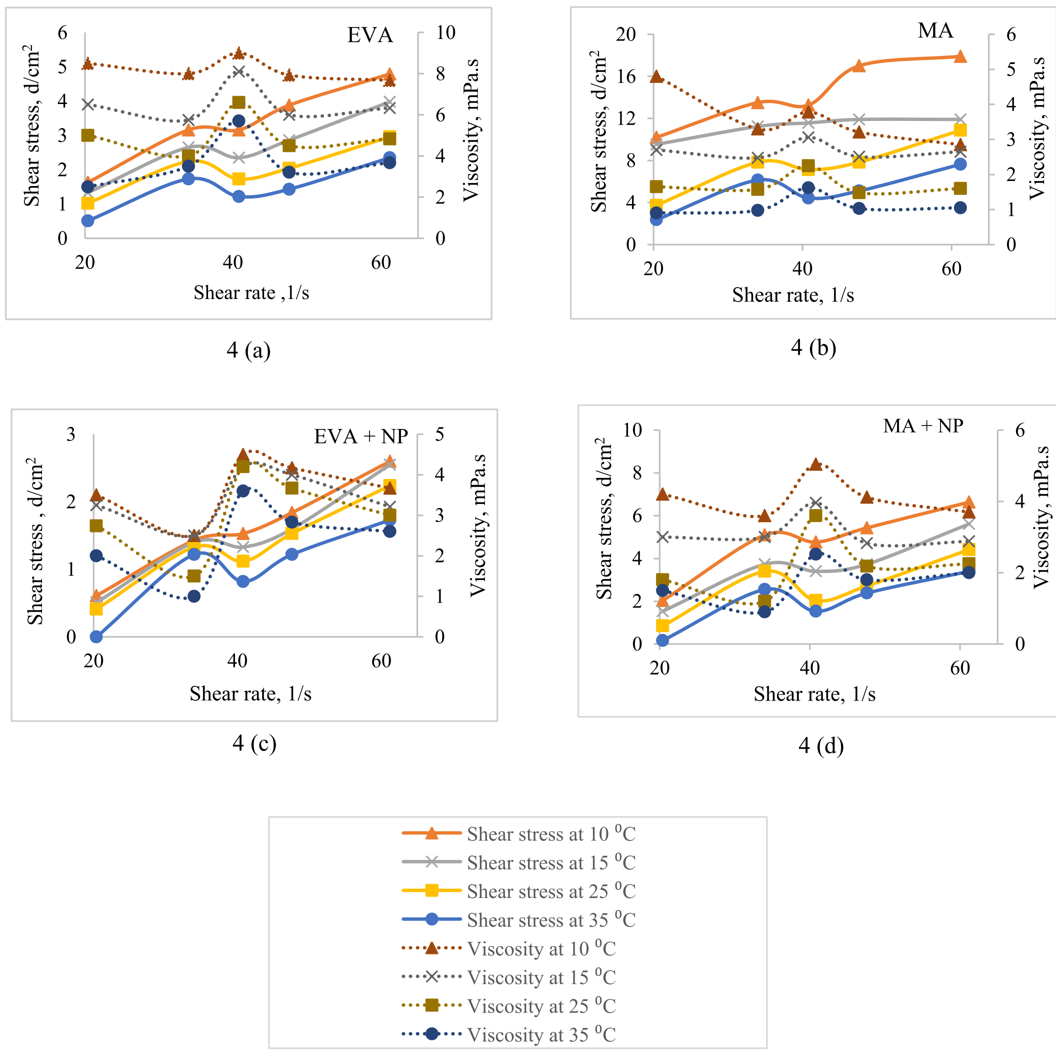

Fig. 4. Comparison of shear stress and viscosity of crude oil as a function of temperature against shear rate: (a) EVA, (b) MA, (c) EVA + NP, (d) MA + NP.

Sodium nanoclay which has been used in this study works well with the wax inhibitors to reduce the viscosity of crude oil. The addition of nanoparticles into the wax inhibitor's polymer matrix alters the properties such as mechanical, thermal, magnetic and electric which results in a smaller and more dispersed wax crystals, bettering the rheology of crude oil (Yang et al., 2015).

As for the concentration of wax inhibitor, 500 and 1000 ppm of inhibitor's concentration shows the most efficient viscosity lessening. The loss of the ability of higher concentrated inhibitors to reduce the viscosity can be associated with the precipitation of the wax inhibitor or wax crystallization through nucleation process caused by the wax inhibitor (Machado et al., 2001).

Below the WAT, the crude oil appears to be thicker as the crude oil changes from liquid phase to amorphous solid phase. Furthermore, below WAT, the rheological behaviour of crude oil is commonly non-Newtonian, which supports the fact that kinematic viscosity of crude oil increases below WAT (Majhi et al., 2015). When the temperature of crude oil drops, the wax molecules start to precipitate and form a complex, three dimensional structure of wax which eventually ties up the lighter components of crude oil, thus lessening the flow ability of crude oil (Majhi et al., 2015).

The viscosity of crude oil reduces as the temperature increases from 15 °C to 35 °C, and this can be explained from the point of molecule movement. When there is an increase in temperature, wax molecules tend to move more rapidly reducing the tendency of interaction (Shigemoto et al., 2006). The order of inhibitor performance based on the rheology method is as follows:

EVA + NP > MA + NP > EVA > MA

The addition of wax inhibitor reduces the viscosity by dissolution of wax particles. Thus, the functional group present in the wax inhibitor plays a significant role in controlling the solubility of wax crystals. From Fig. 3, EVA added with sodium nanoclay is found to be the best combination which improved the values of viscosity when compared to EVA, MA and MA which are added with sodium nanoclay.

Experimentally, it was noticed from Fig. 4, that an increase in shear rate from 20.4 to 34.0 causes an increase in shear stress and it drops at shear rate of 40.8 before showing an increasing trend at shear rates from 40.8 to 61.2. The shear stress causes a break down in microstructures that bind the wax crystals thus the gelling rate reduces when shear stress increases (Ali Theyab and Diaz, 2016). Dwived et al. (2013), Jennings & Weispfennig (2005) and Theyab (2017) have proven that an increase in shear stress causes a drop in wax formation. Thus, a higher shear rate does well in wax mitigation. However, in this study, there is a drop in shear stress at one point, particularly, for all the inhibitor and inhibitor/nanoparticle tested. This drop in shear stress induces an increase in the viscosity of crude oil as it can be seen at Fig. 4. This can be explained as at the shear rate of 40.8 1/s, there is a possibil-

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ity of the wax inhibitor and nanoparticles added not working efficiently as it does in different shear rates. There is a chance that it is resulted from shear thickening of crude oil which causes the wax crystals to form thus increasing the viscosity of crude oil. Ridzuan et al. (2016) has studied the effect of shear rate ranging from 0 to 600 rpm on the wax deposition of Malaysian crude oil using wax inhibitors whereby the minimum wax is produced at 400 rpm instead of at 600 rpm. This can be correlated with the current study whereby at 120 rpm there is a chance that the crude oil thickens due to the presence of wax inhibitor and nanoparticle causing the shear stress to drop and at this particular shear rate the wax deposition may be higher.

It also can be noticed that the shear stress is higher at a lower crude oil temperature. This can be understood as the increase in the temperature of crude oil causes a decrease in the viscosity of crude oil, leading to a drop in the wax deposition force, thus reducing the shear stress (Theyab, 2017).

The addition of nanoparticles to the wax inhibitor improves the flow ability of the crude oil. The nanoparticles added are able to reduce both shear stress and viscosity. EVA and MA were able to reduce the viscosity of the crude oil to 88% and 86.4%, respectively, and these percentage increase with the addition of nanoparticles to 94% and 89.2%, respectively.

Increasing shear rate generally increases the shear stress resulting in a lower viscosity as well as lower amount of wax deposition (Jennings & Weispfennig, 2005). The wax inhibitor and nanoparticles added however contradicts to the current finding, whereby at 40.8 1/s shear rate, the shear rate drops although the shear rate is increased. This proves that the shear rate can alter the efficiency of wax inhibitor.

4. Conclusion

The addition of wax inhibitors improves the flow ability of the crude oil by decreasing the viscosity. The performance of the wax inhibitor, however, depends on certain parameters such as the concentration and shear rate. For the concentration, the highest DVR was obtained at the concentration of 500 ppm. Increment in DVR was obtained when nanoparticles were added. The DVR were increased up to 6% and 2.8%, when nanoparticles was added to EVA and MA, respectively. Nanotechnology can attribute to more efficient, less expensive, and more environmental friendly solutions than those that are readily available. The shear rate plays a crucial role in viscosity reduction. However, in this study there is an apparent disagreement between the reduction in viscosity and increase in shear stress with the increase in shear rate, which can be related to shear thickening behaviour of the crude oil at the particular shear rate of 40.8 1/s. The result shows non-Newtonian behaviour of crude oil at all the parameters tested.

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Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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