Effect of nano pour point depressant on the flow properties of the waxy crude oil from Changqing Oilfield

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Abstract. In this paper, graphene oxide (GO) was modified with alkyl amidopropyl diethanolamine to obtain a nano pour point depressant (GO-PPD), which was used to improve the flowability of the waxy oil extracted from Changqing Oilfield, China. Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and viscometer were employed to evaluate the performance of the GO-PPD. The results showed that compared with traditional pour point depressant (PPD), the GO-PPD exhibited higher performance in promoting the flowability of waxy crude oil. With the presence of 500 mg/kg GO-PPD in the waxy crude oil, the pour point of which could be reduced by 5.5 °C. Also, with the presence of 500 mg/kg GO-PPD, the viscosity reduction rate of the waxy crude oil can reach up to 52% at 30 °C. Through the observation via polarized microscopy, we have also found that with the introduction of GO-PPD in the crude oil, the formation of the wax crystals can be greatly retarded. This confirmed that the graphene oxide derivates could also be served as PPD, which facilitates the flowability of certain crude oil (e.g., waxy crude oil from Changqing Oilfield).

1. Introduction

Paraffin-wax deposition on the walls of wells and pipelines poses a great challenge to oil & gas production [1,2]. Paraffin wax is a major component in some hydrocarbons extracted from special reservoirs (e.g., shale reservoirs), and also is the main component of diesel and other refined products. The main components of the wax are the linear and branched hydrocarbon molecules which usually have more than 16 carbons and less than 40 carbons [3-4]. n-alkanes with higher molecular sizes would converse into the wax at higher temperatures if no wax inhibitor is injected into the production liquids. The formation of wax would reduce the production rate, and also lead to the blockage of the pipelines [5-7].

The traditional methods to mitigate the risk of pipeline blockage caused by the wax deposition including the injection of chemical additives into the flowlines of the extracted hydrocarbons [1,8]. Usually, the chemical additives can be split into two types: crystal modifiers and wax dispersants [9-11]. The crystal modifiers are usually oil-soluble copolymers, which can interact with the nucleus of the wax crystals and inhibit the deposition of the wax crystals [12]. Also, the wax-like segment in the crystal-modifier would participate in the formation of the wax crystal and herein modify the morphology of the wax [12]. Other segments (e.g., branched hydrocarbon chains, amide groups, etc.) in the molecule of modifier do not cocrystallize with the original paraffin waxes in the crude oil. The non-wax-like segments provide steric hindrance on the wax surface that retard the growth and aggregation of the crystals [7]. There are many publishes claiming that the size of the wax crystals can be significantly reduced by the polyaminoamide additives [2, 12]. However, it should be noted that there are many factors that influence the performance and application of the polymers, for example, the high costs of the preparation process, the low performance at high shearing conditions and the unignorable performance loss at reheating conditions. The wax dispersants are usually surface-active molecules that can adsorb on the surfaces of wax and pipeline walls. Due to the adsorption layers on the pipeline inner surface, the wettability of these surfaces are kept in water-philic conditions which would reduce the adhesion force between crystal and the inner surface of the pipeline [13]. The common crystal modifiers are ethylene vinyl copolymers (EVA), poly (ethylene-butene) copolymers (PEB), poly (maleic anhydride amide co-α-olefin) (MAC) and their derivatives. The content of vinyl acetate (VA) in a molecule (polar group content), the molecular weight, the length of the side hydrocarbon chain and the compositions of the crude oil are the main factors that affect the performance of the crystal modifiers [14-17]. The optimum content of VA in a modifier (e.g., EVA) is ~30% [18-19]. The EVA molecules can alter the wax crystals from plates to spheres. It was reported that the MAC was more effect than PEB in crude oils containing a high amount of asphaltenes [10]. Singhal et al.[20]

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summarized two empirical rules for selecting the crystal modifiers: the carbon numbers of the side chain length of the alkyl ester and the wax component should be equal or close to each other, the melting points of the modifier and the wax should be equal or close to each other. Dispersants are different kinds of surfactants, such as sulfonates surfactants [21], alkyl phenol derivatives, polyamides and naphthalene[13]. The water cut may have a significant effect on the performance of the wax dispersants. The crystal modifiers and wax dispersants have attracted much attention from researchers, but their performance still needs to be further improved.

In recent years, the nano pour point depressant has been researched by many researchers to mitigate the risk of pipeline blockage caused by the wax formation and deposition [22-23]. Compared with traditional crystal modifiers and wax dispersants, the nano pour point depressants exhibited higher performance in reducing the pour point and improving the flowability of the waxy oil. However, the working mechanisms of the nano pour point depressant have not been fully understood. In this paper, graphene oxide (GO) was modified with alkyl amido propyl diethanolamine to obtain a nano pour point depressant (GO-PPD), which was used to reduce the pour point and improve the flowability of the waxy oil extracted from Changqing Oilfield, China. Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and viscometer were employed to evaluate the performance of the GO-PPD.

2 Experimental section

2.1 Materials

The waxy crude oil was offered by Chnagqing Oilfield, China. The SARA information of the crude oil is listed in Table 1. The SARA components of the crude oil were separated based on the method described in one of our previous works [2]. The commercial pour point depressant, EVA with a molecular weight of 2000 and vinyl content of 28%, was purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai). The nano material with a purity of 99% was also purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai). N, N-bis-(2-aminoethyl) dodecanamide was prepared in our lab.

Table 1 The basical properties of the waxy oil from Jing'an Block (Changqing Oilfield)

Pour point (°C)	P20 ($g \cdot cm^{-3}$)	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
24	0.88	66.83	10.12	17.70	5.35

2.2 preparation of hybrid pour point depressant GO-PPD

The GO-PPD was prepared by the modification of GO by amine (N, N-bis-(2-aminoethyl) dodecanamide). In this paper, the GO was reacted with an amine at vacuum conditions (10-2 Torr) and 180 °C for 2 hours. After the reaction, the product (GO-PPD) was obtained by removing the amine residues at vacuum conditions and 150 °C for at least 1 hour.

2.3 Viscosity measurement

The viscosity properties of the crude oil with and without the introduction of PPD were evaluated using a Viscometer (Brookfield II, USA) at various temperatures. Each sample was measured three times to increase the quality of the results.

2.4 Pour point measurement

The pour point of each waxy crude oil sample with and without the PPD was measure at a certain temperature range of 5-50°C based on the standard of ASTM D5853 (Standard Test Method for Pour Point of Crude Oils).

2.5 Thermogravimetric analysis (TGA) of the crude oil

The TGA test was performed using a Mettler Toledo A851 TGA/SDTA instrument. During each test, 3-6 mg oil sample was placed on the pans of the instrument. Then the sample was heated from 35 °C to 500 °C at a rate of 10 °C/min under the N2 environment (with a flow rate of 20 mL/min).

2.6 DSC test of waxy crude oil samples

The DSC analysis of the oil samples were carried out using a DSC apparatus (Mettler-Toledo DSC822e, Switzerland). In each measurement, 6-8 mg oil sample was placed in the pans of DSC and then the sample was heated (at a rate of 11°C/min) from room temperature to 50°C in the N2 environment (with a flow rate of 20 mL/min). At 50°C, the sample was kept for 5 min to remove the effect of memory effect of wax formation. Then the sample was cooled from 50 °C to -20 °C at a rate of 8 °C/min. During the cooling stage, the change in the heat was recorded.

2.7 Microscope observation of the morphology of wax crystals

The saturates of the waxy crude oil was extracted[2] and placed on the glass slide of a polarized microscopy (BX41-P OLYMPUS, Japan) to observe the process of formation and morphology of the wax crystals. Before each test, the saturates sample was heated to 50 °C to melt the already formed wax crystals. Then the sample was cooled from 50 °C to 10 °C to facilitate the formation of the wax crystals. During the observation, the temperature of the copper stage placed on the microscopy was kept at 10 °C.

3. Results and discussion

3.1 Thermogravimetric analysis of crude oil sample

Fig 1 shows the TGA curve of the crude oil sample at the temperature range of 35 °C - 500 °C. It can be found that as the temperature ramps to 350 °C, the mass loss of the sample reaches 86.75%, indicating that the main component of the crude oil sample is light hydrocarbons. When the sample was further heated from 350 °C to 450 °C, the mass of the sample was gradually reduced. At the temperature of 500 °C, the mass loss of the sample turned out to be 96.18%, which indicated that there was a little amount of hydrocarbons with carbon numbers higher than 35 in the original crude oil ample.

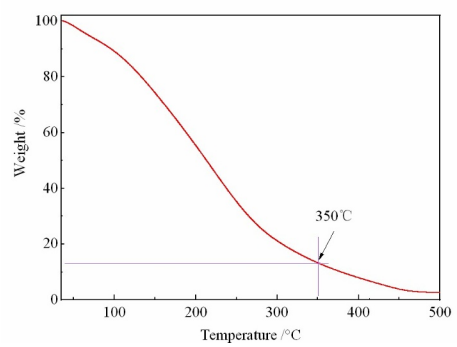

Fig 1. TGA curve of the crude oil sample

3.2 Differential Scanning Calorimetry Analysis of crude oil and saturates samples

The DSC curves of the crude oil and its saturates component were presented in Fig 2. As can be seen from Fig. 2, as crude oil sample (line N0) was cooled from 50 °C to 22.83 °C, the curve encountered an exothermic peak at 22.83 °C, indicating that the wax crystal formed at the temperature of 22.83 °C (wax appearance temperature (WAT)). Based on the area of the exothermic peak, the released heat of wax crystallization was calculated to be 0.53J/g. After the appearance of the peak, the curve gradually decreased till the temperature reduced to -20 °C. The curve of the saturates sample showed a similar trend to that of the crude oil sample. However, the WAT and heat of the wax crystallization were found to be 24.77 °C and 2.90 J/g, respectively. The WAT of the saturates was 2.16 °C lower than that of the crude oil sample, indicating that the polar materials (e.g., resins, asphaltenes, etc.) in the crude oil sample may have inhibition effect on the appearance of the wax crystals.

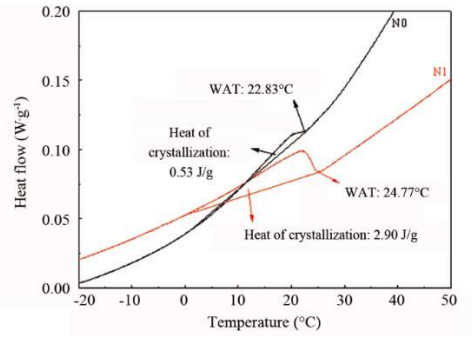

Fig 2. The DSC curves of the crude oil and its saturates component (N0: crude oil sample, N1: saturates sample)

3.3 IR analysis of polar components of crude oil

The component with high polarity was separated using the method described in one of our previous works [2]. The polar component was analyzed using an infrared spectroscopy instrument (Nicolet 5700, USA). The IR results were shown in Fig 3. The peak at the range of 3600-3350 cm^{-1} refers to the hydroxyl stretching vibration. The two peaks at 2600 cm^{-1} and 2550 cm^{-1} may be caused by the stretching vibration absorption of the –SH group. The absorption peaks at 1630 cm^{-1} are exhibited due to the delocalized π bond, the stretching vibration of the C=O bond and amide or bending vibration of the N-N bond. The results show that separated component contains strong polar compounds (e.g., resins, asphaltenes, etc.).

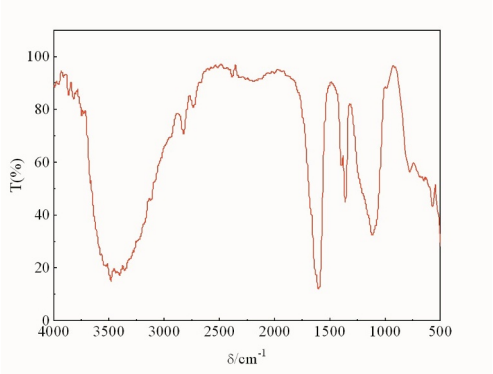

Fig 3. IR spectrum of the adsorption residuals on silica gel

3.4 IR analysis of GO-PPD

The product GO-PPD was analyzed by infrared spectroscopy, the IR curve was shown in Fig 4. The peak at 3340 cm^{-1} refers to the stretching vibration of -OH. The absorption peaks at 1625 cm^{-1} are due to the stretching vibration of -CONH-. The peaks at 3005 cm^{-1}, 2928 cm^{-1} and 2844 cm^{-1} may be caused by the stretching vibrations of $-CH_3$, $-CH_2-$ groups.

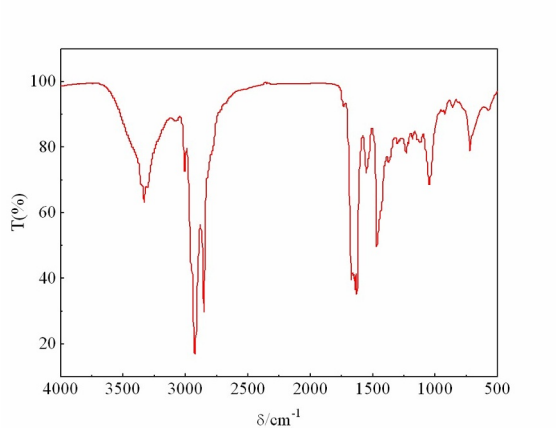

Fig 4. IR analysis of GO-PPD

3.5 Performance of GO-PPD in reducing the viscosity of crude oil

In this section, 500 mg/kg of PPD was introduced into the crude oil sample, and then the viscosity of each mixed oil sample with PPD was measured to see check the PPD's performance. As can be seen in Fig 5, the viscosity of the crude oil sample decreased as the temperature increased. However, at 27 °C, the viscosity of crude oil had a breakpoint. When the sample was further increased from 27 °C, no significant reduction in the viscosity can be found. At 30 °C, the viscosity of the crude oil turned out to be 1855 mPa·s. It should be noted that with the presence of 500 mg/kg GO-PPD (or 500 mg/kg EVA), a similar trend of the viscosity-temperature curve to that of the crude oil sample was observed. With the presence of 500 mg/kg GO-PPD and 500 mg/kg EVA, the viscosity of each mixed oil sample was found to be 146 mPa·s and 126 mPa·s (with a reduction rate of 52%), respectively. Therefore, the performance of GO-PPD in reducing the viscosity of crude oil is higher than EVA.

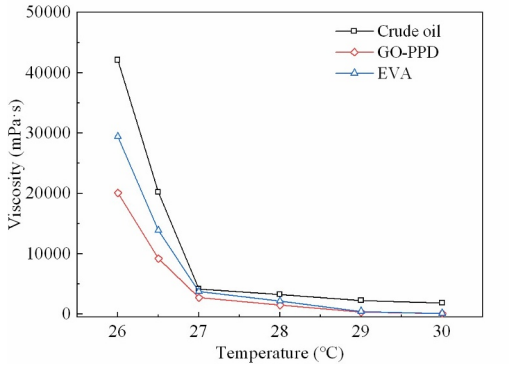

Fig 5 Effect of PPD on the viscosity of the crude oil

3.6 Performance of GO-PPD in reducing the pour point of crude oil

In this section, the effect of GO-PPD on the pour point of the crude oil was measured. As can be seen in Table 2, with the presence of 500 mg/kg GO-PPD in the crude oil sample, the pour point of the oil can be lowered to 18.5 °C, which was lower than the pour point temperature (20.2 °C) of crude oil with 500 mg/kg EVA. This result confirmed the effectiveness of GO-PPD in reducing the pour point temperature of crude oil.

Table 2 The effectiveness of GO-PPD in reducing the pour point temperature of crude oil.

Sample	Crude oil	Crude oil +500 mg/kg EVA	Crude oil +500 mg/kg GO-PPD
Pour point (°C)	24	20.2	18.5

3.7 Wax morphology analysis

In this section, the effects of GO-PPD and EVA on the morphology of the wax crystal were examined, which were present in Fig 6. As can be seen in Fig 6(a), without chemical additive, sword-like wax crystals were observed. As the amount of the crystals increased, a three-dimensional network of wax crystals was observed. However, with the introduction of EVA in the crude oil, the formed wax crystals were effectively dispersed, and also the amount and size of the crystals were significantly reduced (see Fig 6(b)). When GO-PPD was present in the crude oil sample, it was easy to found that the formed wax crystals were further dispersed, and the sizes of each wax crystals were also smaller than that of crystals in the presence of EVA, indicating that the GO-PPD is a promising PPD that can effectively inhibit the formation of wax and promote the flowability of the crude oil (from Changqing Oilfield).

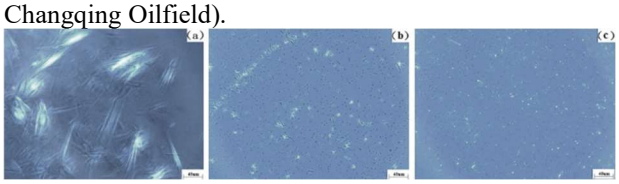

Fig 6. Wax morphologies of sample (a): saturates, sample (b): saturates+500 mg/kg EVA, sample (c): saturates+500 mg/kg GO-PPD

4 Conclusions

In this paper, we have prepared a novel pour point depressant for waxy crude oil in Changqing Oilfield. The performance of GO-PPD was systematically investigated. The results showed that compared with traditional pour point depressant (PPD), the GO-PPD exhibited higher performance in promoting the flowability of waxy crude oil. With the presence of 500 mg/kg GO-PPD in the waxy crude oil, the pour point of which could be reduced by 5.5 °C. Also, with the presence of 500 mg/kg GO-PPD, the viscosity reduction rate of the waxy crude oil can reach 52% at 30 °C. Through the observation via polarized microscopy, we have also found that with the introduction of GO-PPD in the crude oil, the formation of the wax crystals can be greatly retarded. This confirmed that the graphene oxide derivates could also be served as PPD, which facilitates the flowability of certain crude oil (e.g., waxy crude oil from Changqing Oilfield).

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