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Influence of the nano-hybrid pour point depressant on flow properties of waxy crude oil

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HIGHLIGHTS

- Nano-hybrid pour point depressant (NPPD) was prepared and firstly used for waxy crude oil.
- The yield stress and viscosity of waxy crude oil were reduced by 99.3% and 82.1% by NPPD, respectively.
- The high energy barrier inhibited wax crystal aggregation and the formation of gel networks in NPPD doped oil.

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ABSTRACT

The influence of the nano-hybrid pour point depressant (NPPD) on flow properties of waxy crude oil was studied. Rheological results showed that NPPD demonstrated better improvement in viscosity, yield stress and pour point reduction for crude oil than the conventional polymer PPD (N6) did. Moreover, the viscoelastic behavior data showed that the NPPD doped oil had a weaker gel network structure at a low temperature compared with N6 doped oil. Differential scanning calorimetry results revealed that NPPD reduced the wax appearance temperature (WAT) and the wax precipitation amount within the temperature range from WAT to −20 °C. The difference of shape and size of wax crystals in undoped and doped oils was studied by X-ray diffraction and polarized optical microscopy. The total interaction energy between wax particles was calculated according to the Derjaguin–Landau–Verwey–Overbeek theory using ζ potential. It was found that the energy barrier between the wax particles in the NPPD doped oil was higher than that in N6 doped oil. The larger electrostatic repulsion inhibited the aggregation of the wax particles and stabilized the NPPD doped oil system.

1. Introduction

Wax deposition is a serious problem in waxy crude oil storage and transportation. With decreasing temperature, the paraffin precipitates from crude oil and forms wax crystals. Attractive London van der Waals forces among the crystals cause to form a volume-spanning network, which entrap liquid oils in and deteriorate the flow properties of the oil [1–3]. As a result, the waxy crude oil has a high pour point, viscosity and yield stress [4].

A common solution to above problem involves chemical additives known as pour point depressant (PPD). Conventional PPDs are homo- and co-polymers of different monomers [5]. Reducing the transportation cost and improving the oil flowability were still necessary, even if lots of polymer PPDs have been prepared [6,7]. Moreover, exploring the universal explanation of the pour point depression mechanism was still in challenging in this field.

Previous studies [8–10] confirmed that nanoparticles could significantly influence the heat distortion temperature, crystallization temperature, crystallinity and grain size of the polymer nanocomposites. The geometrical shape and dispersion state of nanoparticles in the polymer matrix as well as the interaction between the particles and polymer chains determined the structure and properties of the nanocomposites [11,12]. In addition, crystallization of long-chain *n*-alkanes in nanoscale confined environment were reported in many works [13,14]. Fu et al. [15] reported that the nano-microcapsule enhanced the stability of rotator phase (a metastable intermediate phase between low-temperature crystalline phases and the high-temperature isotropic liquid phases) of the *n*-dodecane and decreased the transition temperature between the rotator phases and crystalline phases. Those results are meaningful for improving the oil flow properties. When doped

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with nanoparticles, the alkanes in crude oil would be in a stable liquid state or a metastable solid state rather than a stable solid state at low temperatures, and the wax gel might have a weak structure. On the other hand, the nucleation and crystallization of the alkanes would also be affected. As a result, the flow properties of the oil would be improved.

On this basis, the nano-hybrid pour point depressant (NPPD) was prepared and successfully applied in Daqing waxy crude oil. It is a nanocomposite of montmorillonite (MMT) and ethylene/vinyl acetate (EVA). Both laboratory experiments [16–18] and the field-applied tests [19] confirmed that NPPD had good efficiency on pour point depression and viscosity reduction even at a small dosage. For example, when the dosage of NPPD was 50 ppm, the apparent viscosity and pour point of Daqing crude oil decreased by about 87.4% and by 14 °C [16], respectively. Yang et al. [20] prepared a kind of poly(octadecyl acrylate)/nanosilica hybrid nanoparticles to improve the flow properties of model waxy oil and found that the nanoparticles modified the size and shape of the wax crystals and reduced the gel point of the oil.

Nucleation, co-crystallization and adsorption have been used to explain the action mechanisms of the PPDs. The PPDs modify the crystal size and shape, and inhibit the aggregation of the wax crystals [21,22]. Wax crystals adsorbed asphaltenes can be considered as colloid particles dispersed in crude oil [23,24]. The zeta (ζ) potential of the wax crystal particles can be used to evaluate the stability of the oil colloid systems. Agaev [25] studied the metal-contained PPD and found that the electrostatic double layer surrounding the wax particle surfaces would produce repulsion effect and inhibit the interaction among the particles.

The aim of this work is to investigate the influence of NPPD on the shape and size of wax crystals and the flow properties of waxy crude oil. Throughout this study, the commercially available polymer PPD N6, having been used for the oil, was selected as comparison. Moreover, the mechanism of NPPD will be studied by considering the electrostatic repulsion effect.

2. Experimental

2.1. Materials

The waxy crude oil was obtained from Jinqiao Pipeline Company, Xuzhou, China. The physical characteristics are listed in Table 1. The waxy crude oil had a relatively high pour point and viscosity as a result of the large wax, resins and asphaltenes contents.

NPPD, a patent protected nanocomposite composed of organically modified montmorillonite (MMT) and ethylene/vinyl acetate copolymers (EVA, VA content 25 wt%), was prepared by melt blending method. The modification of MMT was conducted by ion-exchange with excessive alkylammonium cations. N6, a kind of polymer PPD, which has been used in the transportation of waxy crude oil for many years, was supplied by Jinqiao Pipeline Company. The supplier did not disclose the composition of N6 but pointed out that 100 ppm was the optimal dosage to achieve low transportation cost and good performance for waxy crude oil. Analytical reagent *n*-heptane was commercially available and used without further purification.

The doped waxy crude oils were prepared by dropwise adding the concentrated dispersion of the PPDs and then heated to 70 °C under mechanical stirring at 200 rpm for 30 min. For convenience, the waxy crude oil, N6 doped oil and NPPD doped oil were abbreviated to WCO, WCO-N6 and WCO-NPPD, respectively.

Table 1
Physical characteristics of waxy crude oil.

Parameter	Waxy crude oil	Methods
API gravity	33.5	ASTM D-287
Viscosity (mPa s)	1720[a]	SY/T 0520-2008
Pour point (°C)	30.0	GB/T 510-1983
Wax content (wt%)	30.9	SY/T 7550-2012
Resin content (wt%)	9.57	SY/T 7550-2012
Asphaltenes content (wt%)	0.33	SY/T 7550-2012
Water content (wt%)	<0.5	SY/T 5402-2008

[a] Viscosity was measured at 30 °C and shear rate 30 s^{-1}.

2.2. Characterization of the polymer PPDs

The structure of the polymer N6 was analyzed by Fourier transition infrared (FT-IR) spectrometry (Thermo Nicolet 6700). ^1H NMR spectra were recorded in Bruker Advance-400 equipment using deuterated chloroform as the solvent. Melt Flow Index (MFI) was measured by the Haake Meltflixe Htr according to the ASTM D1238.

2.3. Pour point

The pour point of the oil samples was determined with procedures similar to Chen et al.'s research [26], according to the China National Standard GB/T 510-1983. An oil sample was loaded into the test tube which had been kept in a water bath at 50 °C for 30 min. Then the sample was cooled to 35 ± 5 °C in the room ambient. As soon as the sample reached the specified temperature, the tube was transferred into the pour point tester which was 7–8 °C lower than expected pour point. Then, the sample was cooled close to the expected pour point. After each 2 °C interval the test tube was removed from pour point tester to observe the flowability of the oil. The temperature, at which the oil did not flow even when the test tube was held horizontal for 5 s, was recorded as the pour point. If the oil showed any movement, it should be at once reheated to 50 °C and the experiment was carried out for a second time till it acquired the pour point. For each sample, the measurement was repeated for three times. The uncertainty of the pour point measurements was within 1 °C.

2.4. Rheological measurements

Rheological tests were performed on a rotational concentric cylinder rheometer (AR-2000ex, TA Instrument Company) connected to a heating/cooling system. The oil was initially heated to 70 °C for 3 min and then cooled dynamically to 30 °C at 0.5 °C/min. The apparent viscosity was measured with increasing shear rate from 10 to 50 s^{-1}.

Yield stress was determined by a rotational viscometer method according to SY/T 7547-1996, which was similar to the method reported by Paso et al. [2] and Wardhaugh and Boger [27]. The oil was initially heated to 70 °C for 3 min and then cooled dynamically to 22 °C at 0.5 °C/min. After being held at this temperature for 30 min under quiescent conditions, shear stress versus strain curve was measured at a constant shear rate of 0.02 s^{-1}.

The structure variation of the oil was performed by oscillatory time sweep tests. Before the time sweep test, small amplitude oscillatory stress sweep test was carried out to determine the linear viscoelastic region. The oil was initially heated to 70 °C for 3 min and then cooled dynamically to 22 °C at 0.5 °C/min. The test was carried out at 0.01 Hz and fixed shear stress of 0.1 Pa, which ensured that the measurements were within the linear viscoelastic regime. The storage moduli (G'), loss moduli (G'') and loss tangent ($\tan\delta$) were recorded during the experimental time.