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Structural properties of gelled Changqing waxy crude oil benefitted with nanocomposite pour point depressant

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HIGHLIGHTS

- Nanocomposite PPD prepared by melt blending method shows much better performance.
- Nanocomposite PPD cannot change the precipitated wax crystal amount at low temperature.
- Adding nanocomposite PPD further weakens the structure of gelled waxy crude oil.
- Controlling the dispersed state of polymeric PPD in oil phase can control its performance.
- Nanocomposite PPD particles controls the dispersed state of POA PPD in oil phase.

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ABSTRACT

The novel and effective nanocomposite PPD has garnered attention for its potential application in pipelines transporting waxy crude oil. In this paper, melt blending method was used here to prepare the poly (octadecyl acrylate) (POA)/clay nanocomposite PPD, which shows much better performance on waxy crude oil. The effects of the POA and POA/clay nanocomposite PPDs on the structural properties of gelled Changqing waxy crude oil were well studied through rheological tests, DSC analyses and microscopic observation. The precipitated wax crystal amount of the crude oil at low temperatures does not change with the addition of POA and nanocomposite PPDs, but the addition greatly weakens the structure of the gelled crude oil. Compared with the same dosage of POA, the addition of nanocomposite PPD further inhibits the formation of wax crystal's network and further weakens the structural strength and viscoelasticity of the gelled crude oil. Increasing the dosage of nanocomposite PPD favors the weakening of the gelled crude oil structure. The nanocomposite PPD particles can act as nucleation templates of wax crystals and further weaken the gelled structure of waxy crude oil. In addition, we deduce that controlling the dispersed state of polymeric PPDs in oil phase could control the performance of the polymeric PPDs. The decrease of the mean nanocomposite PPD particle size from 6 μm (prepared by solvent blending) to 2 μm (prepared by melt blending) changes the dispersed state of POA molecules in oil phase and thus greatly enhances the performance of nanocomposite PPD.

1. Introduction

Transportation of waxy crude oil through pipelines is a major problem for the oil industry. When the temperature of waxy crude oil drops below its wax appearance temperature (WAT), supersaturation causes the wax molecules to precipitate continuously from the oil phase [1]. These precipitated wax crystals are platelet-like or needle-like and are liable to overlap and interlock. Therefore, a small amount of the precipitated wax crystals (as little as 0.5 wt%) can form a continuous network in the oil phase, causing the transition of the crude oil from a sol to a gel [2,3]. The sol-gel transition of the waxy crude oil induced by the temperature drop is responsible for restart problems in pipelines. Pipelines transporting warm waxy crude oil might shut down for normal operating reasons or emergent reasons [4]. In these cases, the warm waxy crude oil in the pipelines might cool statically below its gelation point (GP) or pour point (PP), leading to the transition of the oil from sol to gel. In many theoretical studies, GP is widely used to denote the sol-gel transition point of waxy crude oil. The GP, at which the elastic modulus G′ of the oil begins to become larger than the vis-

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cous modulus G″ of the oil, can be tested by a cooling rheological test under oscillatory mode [5,6]. In the crude oil industry, PP is often used to denote the sol-gel transition point of waxy crude oil, which can be tested by the methods listed in the Petroleum & Natural Gas Industrial Standard of China or the ASTM Standards [6,7].

The structure of gelled waxy crude oil is in direct relation to the restart of pipelines transporting waxy crude oil. Many works have focused on the structural properties of gelled waxy crude oil to guide the processes for restarting pipelines [5–7]. The macrostructure of gelled waxy crude oil is normally measured by rheological tests and is characterized by dynamic viscoelasticity, yield behavior, and creep-recovery behavior. The dynamic viscoelasticity, through which the development of the wax crystal network with the decrease of temperature could be supervised, can be measured by a cooling rheological test under oscillatory mode [2,5,8–10]. The yield behavior of gelled waxy crude oil, which is important for successfully restarting pipelines, undergoes an initial elastic deformation, followed by creep deformation and final fracture [2,6,11,12]. The creep-recovery behavior of gelled waxy crude oil is divided into two stages (an elastic and creep deformation stage followed by a deformation recovery stage), which can further exhibit the structural property of gelled waxy crude oil [9,13]. In addition, microscopic observation techniques, such as polarized-microscopy and electronic microscopy, are also used to discover the microstructure of gelled waxy crude oil. The relationships between the macrostructure (rheology) and the microstructure (wax crystal network) of gelled waxy crude oil were established by several works [10,14,15].

Some solutions have been developed to make the pipeline transportation of waxy crude oil safer and more economical. A well-recognized and efficient solution is to use polymeric pour point depressant (PPD) [3]. Conventional polymeric PPDs are homo- and co-polymers of different monomers, which can interact with the wax crystals through nucleation, adsorption and co-crystallization effects, thus greatly modifying the growth habits and morphology of the wax crystals [3,16–18]. Therefore, the rheology of waxy crude oil improves substantially after a small dosage of PPDs. Comb-like polymeric PPDs are widely used in pipeline industry because of their excellent performance and versatile structure. Poly(octadecyl acrylate) (POA), which co-precipitates with wax molecules and forms island defects on the wax crystals' surface, is an effective comb-like PPD for waxy crude oil, weakening the wax crystals' interactions and blocking their growth [19,20]. To improve the performance of POA PPD, some types of polar groups or aromatic groups are introduced into the molecular structure of the POA [7,21–23]. The structural property of gelled waxy crude oil doped with POA PPD was also investigated in several works [16–24]. However, studies on this particular aspect were incomplete.

Polymer/inorganic nanocomposites or nano-hybrid materials have become the research hotspot of the 21st century [25,26]. After inorganic nanoparticles were dispersed into the polymer matrix, resultant properties (such as mechanical, thermal, and electrical) of polymer are improved greatly and the improving efficiency is in direction to the dispersion degree of the nanoparticles in polymer matrix [27–30]. The dispersion degree can be greatly enhanced by increasing the compatibility of nanoparticles in polymer matrix or by improving the preparation method [27–33]. Compared with solvent blending method, melt blending method with the aid of an extruder is a more efficient method in terms of dispersing nanoparticles in the polymer matrix [31–33]. Therefore, the melt blending method has been widely used to prepare polymer/inorganic nanocomposites.

Informed of the advantages of polymer/inorganic nanocomposites, some researchers have developed several nanocomposite PPDs by dispersing inorganic nanoparticles into polymeric PPD matrix. Wang et al. [34] prepared a nano-hybrid PPD and found that the PP depressing performance of the nano-hybrid PPD for a waxy crude oil is better than that of the traditional ethylene-vinyl acetate (EVA) bipolymer PPD. He et al. [35] studied the influence of a patented nano-hybrid PPD on the rheology of a waxy crude oil and found that adding the nano-hybrid PPD decreases the amount of precipitated wax crystals at low temperatures, which favors the further improvement of the crude oil rheology. However, the result obtained by He et al. [35] differs from the traditional understanding that polymeric PPDs can delay wax precipitation but cannot noticeably reduce the amount of precipitated wax crystals at low temperatures [3]. Yang et al. [36] prepared a nano-hybrid PPD by dispersing a hydrophilic nano-silica directly into POA matrix. The nano-hybrid PPD shows a better GP, viscosity and yield stress depressing performance for the synthetic waxy oils. However, because of the poor compatibility of hydrophilic nano-silica in POA PPD, the rheological improving performance of the nano-hybrid PPD decreases with rest time, comparable to the performance of pure POA in the end. To enhance the compatibility of nanoparticles in polymeric PPD matrix, a hydrophilic nano-clay was first modified organically through intercalation with cationic surfactants, and then the organically modified nano-clays (abbreviated as organic nano-clays) were dispersed into the POA matrix by solvent blending [37]. The prepared POA/clay nanocomposite PPD acts as nucleation templates of wax crystals and results in the formation of larger and more compact wax crystal flocs, so the rheology of waxy crude oil is further improved [37]. In addition, the rheological improving performance of the nanocomposite PPD does not aggravate with rest time, meaning that the organic nano-clays have good compatibility in the POA matrix and can be well dispersed in POA.

In this paper, the POA/clay nanocomposite PPD was successfully prepared by melt blending method. The effects of the POA and POA/clay nanocomposite PPDs on the structural properties of Changqing gelled waxy crude oil were well studied through rheological tests, DSC analyses and microscopic observation. The improving mechanism of different PPDs on the structure of gelled waxy crude oil was also summarized and discussed here. This work has important guiding significance for the restart process of pipelines transporting waxy crude oil.

2. Experimental section

2.1. Materials

A waxy crude oil sample obtained from the Changqing oilfield of China was used here. As shown in Table 1, the crude oil is rich in saturates (69.3 wt%) and aromatics (22.2 wt%), whereas the resins and asphaltene contents are relatively small (7.5 wt% and 1.0 wt%). The high wax content (16.5 wt%) results in a high PP (19 °C) of the crude oil. The carbon number distribution of alkanes in the crude oil was measured by gas chromatograph (Agilent 6820 SN, America) and shown in Fig. 1. The n-alkane content in the total alkanes is 41.22 wt%, while the non n-alkane content in the total alkanes is 57.20 wt%. The n-alkane mainly distributes from C_9 to

Table 1
Physical properties of the Changqing waxy crude oil.

Parameter			
Density at 20 °C (kg/m^3)	0.87	Initial boiling point (°C)	62
Wax content (wt%)	16.5	Saturates (wt%)	69.3
WAT (°C)	30.3	Aromatics (wt%)	22.2
Pour point (°C)	19	Resins (wt%)	7.5
Gelation point (°C)	24.3	Asphaltenes (wt%)	1.0