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Oil dispersible polymethylsilsesquioxane (PMSQ) microspheres improve the flow behavior of waxy crude oil through spacial hindrance effect

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HIGHLIGHTS

- The synthesized PMSQ microspheres disperse well in oil phase as single spheres.
- PMSQ microspheres can inhibit the development of wax crystal network structure.
- PMSQ microspheres greatly improve the rheology of the oil samples at temperatures ≤WAT.
- Adding PMSQ microspheres in the oil samples also inhibits asphaltenes precipitation.
- PMSQ microspheres impede the interactions of wax crystals through spacial hindrance effect.

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ABSTRACT

Application of nanocomposite pour point depressants to improve the rheology of waxy crude oil is a novel and efficient technique and receives much attention. However, the effects of nano and microparticles alone on the rheology of waxy crude oil are unclear up to now. In this paper, monodispersed PMSQ microspheres with different sizes (200 nm–10 μm) were successfully synthesized through a two-step sol-gel route. Then the effect of the PMSQ microspheres on the flow behavior of two typical waxy crude oils was studied. The results showed that the PMSQ microspheres disperse well in oil phase as single spheres. A small dosage of the PMSQ microspheres significantly decreases the gelation point, elastic modulus G', viscous modulus G'', apparent viscosity and yield stress of the two oil samples, indicating that the PMSQ microspheres improve the flow behavior of waxy crude oil at temperatures below the wax appearance temperature. The flow improving efficiency of the PMSQ microspheres is greatly influenced by the size and dosage of the microspheres. Moreover, adding PMSQ microspheres in the oil samples also inhibits asphaltenes precipitation because the PMSQ microspheres are capable of adsorbing part of the asphaltenes. However, the PMSQ microspheres have little influence on the exothermic character and microstructure of the two oil samples. Similar tests on a model waxy oil further confirmed that the PMSQ microspheres cannot participate in wax precipitation process and change the morphology of precipitated wax crystals, but can impede the interactions of the precipitated wax crystals through *spacial hindrance effect*, which inhibits the development of wax crystal network structure and thus improves the flow behavior of the oil. This mechanism brings a new way to improve the flow behavior of waxy crude oil and favors the development of new-generation flow improvers based on nano or microparticles.

1. Introduction

Waxy crude oil, which contains a substantial amount of paraffin waxes, is an important fossil fuel distributed in many oilfields of the world. Paraffin waxes are normally *n*-alkanes with the carbon number ranging from C_{16} to C_{38}. The dissolved paraffin waxes start to crystallize into solid wax crystals when the temperature of waxy crude oil is lower than its wax appearance temperature (WAT) [1,2]. With the further decrease of oil temperature, the continuous precipitation of wax crystals from waxy crude oil seriously aggravates the rheology of the oil and thus brings huge challenges in exploitation and pipeline transportation of the oil [3,4].

It is well known that the rheology of waxy crude oil could be dramatically improved by a small dosage of polymeric pour point

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depressants (PPDs) [5]. The polymeric PPDs, such as the EVA-type [6,7] and the comb-like copolymer type [8–10], often contain nonpolar long alkyl chains ($\geq C_{18}$) and polar groups [5]. The long alkyl chains can take part in the precipitation process of paraffin waxes through nucleation and co-crystallization effects, while the polar groups control the dispersion state of PPD molecules in oil phase and interfere the growth of wax crystals. Therefore, the morphology of precipitated wax crystals is greatly modified by the PPDs' addition, which favors the flow improvement of waxy crude oil.

Nowadays, inorganic nanomaterials have been widely used in polymer science to prepare high performance polymer/inorganic nanocomposites [11,12]. Inspired by the advantages of the polymer/inorganic nanocomposites, some kinds of inorganic nanoparticles such as silica [13,14], clay [15,16] and graphene oxide [17], have been introduced into the polymeric PPDs' matrix to improve the performance of the PPDs. The results showed that the prepared nanocomposite PPDs could act as nucleation templates of wax crystals and then further modify the morphology of precipitated wax crystals. [13–16] Therefore, the rheology of waxy crude oil is further improved after the addition of nanocomposite PPDs. Organic modification of the inorganic nanoparticles facilitates the dispersion of the particles in polymeric PPDs' matrix and favors the performance improvement of the nanocomposite PPDs [13–16]. Meanwhile, the nanocomposite PPDs prepared by melt blending method are superior than those prepared by solvent blending method [16].

However, the effects of nano and microparticles alone on the rheology of waxy crude oil are unclear and studies on this aspect are limited. Could the nano or microparticles improve the rheology of waxy crude oil alone? And if so, what is the improving mechanism of the rheology? To initiate this study, it is crucial to prepare oil dispersible nano or microparticles with regular morphology.

Recently, polysilsesquioxane (PSQ) microspheres have received much attention in chemistry and physic fields because of their special chemical composition and regular morphology [18–20]: on the one hand, the PSQ microspheres belong to organic-inorganic hybrid materials and thus have specific properties such as excellent thermo stability, weather resistance, lubricity, solvent resistance, and dispersibility in organic phases (e.g., polymers and nonpolar solvents); on the other, the prepared PSQ microspheres are normally monodispersed spheres with the size ranging from nano to micrometer. In addition, the PSQ microspheres have diverse functional groups such as methyl, phenyl, mercapto, vinyl, amine, epoxy acrylic and isocyanate [20], which impart the PSQ microspheres potential applications in a wide variety of fields. Much work has been done on the synthesis of monodispersed PSQ microspheres, and the commonly used synthesis methods include the hydrolytic sol-gel route [21,22] and the reverse emulsion polymerization approach [23,24]. The potential applications of the PSQ microspheres in such fields as sunscreen [25], core-shell materials [26,27], pollution treatment [28,29], CO_2 capture [30], plastic and polymers [31,32], catalyst [33], drug carriers [34,35], and luminescence [36] have also been widely studied.

Based on the excellent oil dispersibility and regular morphology of PSQ microspheres, in this paper, oil dispersible polymethylsilsesquioxane (PMSQ) microspheres with different sizes (200 nm–10 μm) were first synthesized and then the effect of the PMSQ microspheres on the flow behavior of two typical waxy crude oils was studied. The results showed that a small dosage of the PMSQ microspheres dramatically improves the flow behavior of the waxy crude oils, and the flow improving efficiency is greatly influenced by the size and dosage of the PMSQ microspheres. The flow improving mechanism of the PMSQ microspheres on waxy crude oil was also discussed and put forward here.

2. Experimental

2.1. Materials

Deionized water purified by reverse osmosis was used throughout the synthesis of PMSQ microspheres. Methyltrimethoxysilane (MTMS), hydrochloric acid (37 wt%), ammonia (25 wt%), ethanol, *n*-heptane and *n*-dodecane were all purchased from Sigma-Aldrich and used as received. The two waxy crude oil samples were kindly provided by PetroChina Co., Ltd. As shown in Table S1 of the support information file, the resins and asphaltenes contents of the two oil samples are relatively small, but the wax contents are relatively high. The wax content of oil sample A (25.2 wt%) is higher than that of oil sample B (16.5 wt%), resulting in the higher pour point (29 °C) and WAT (43.1 °C) of oil sample A. The pour point and WAT of oil sample B are 21 °C and 34.2 °C, respectively. The carbon number distributions of *n*-alkanes in the two oil samples are demonstrated in Fig. S1 of the support information file. Compared with oil sample B, oil sample A has much more high carbon number *n*-alkanes.

The PMSQ microspheres used here were synthesized through a two-step sol-gel route. Firstly, under a fixed stirring speed, MTMS was added dropwise to hydrochloric acid aqueous solution (pH = 4) at 25 °C and the mixed solution was stirred for 4 h; secondly, the pH value of the mixed solution was adjusted to 8.5 by ammonia and the mixed solution was stirred for another 4 h; finally, the sediments in the mixed solution were filtered, washed with excess ethanol, and dried under vacuum at 80 °C, with the final state of the PMSQ microspheres being white powders. The size of the synthesized PMSQ microspheres can be controlled by adjusting the stirring speed. The PMSQ microspheres synthesized at 900, 700, 500, 300 and 100 r/min were labeled as PMSQ-1 ~ PMSQ-5, respectively. The FT-IR curve, TGA curve and SEM images of the synthesized PMSQ microspheres are exhibited in the supporting information file (see Figs. S2 and S3 of the support information file), which confirm the successful synthesis of monodispersed PMSQ microspheres.

2.2. Methods

2.2.1. Morphology and size distribution tests of the PMSQ microspheres dispersed in oil phase

The stability of the PMSQ microspheres dispersed in water and *n*-dodecane (0.2 wt%) was first evaluated through direct observation. Then, the morphology and size distribution of the PMSQ microspheres dispersed in *n*-dodecane were obtained through JEM-100CX TEM (JEOL Co., Japan) and Mastersizer 2000 (Marlvern Co., UK), respectively.

2.2.2. Flow behavior tests of the undoped/doped waxy crude oils

An AR-G2 rheometer (TA Instruments, USA) equipped with a coaxial cylinder system (a standard cup having a diameter of 30 mm, configured with a DIN Rotor having a diameter of 28 mm) was used to evaluate the effect of the PMSQ microspheres on the flow behavior of the two waxy crude oils. The undoped/doped oil samples sealed in glass bottles were first preheated at 60 °C for 20 min and then cooled slowly to 50 °C at a cooling rate of 0.5 °C/min; after that, the oil samples were loaded into the rheometer for testing.

2.2.2.1. Viscoelastic test. The viscoelastic parameters (the elastic modulus G', the viscous modulus G'' and the loss angle δ) of the undoped/doped oil samples were measured by temperature sweeping test under oscillatory mode. The cooling rate, oscillation frequency and shear strain amplitude were fixed at 0.5 °C/min,