

Preparation and Performance Evaluation of a New Type of Polyethylene-vinyl Acetate/Polystyrene Microsphere Composite Pour Point Depressant for Waxy Crude Oil

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ABSTRACT: Polymer/inorganic nanocomposite pour point depressant (PPD) is a research hotspot in the field of waxy crude oil pipelining. However, the inorganic nanoparticles need to be organically modified to improve their organic compatibility, and the inorganic nanoparticles are harmful to crude oil refining. In this work, organic PSMS with an average size of 1.4 μm was first synthesized by dispersion polymerization. Then, a new type of EVA/PSMS composite PPD was prepared by melt blending. The effects of the PSMS, EVA PPD, and composite PPD on the pour point, rheological properties, and wax precipitating properties of a specific waxy crude oil were investigated. It was found that adding 50–200 ppm of PSMS alone slightly improves the crude oil rheology through a spatial hindrance effect, while adding 20 ppm of EVA PPD greatly improves the crude oil rheology by modifying the wax crystal morphology. Compared with EVA PPD, adding 20 ppm composite PPD improves the crude oil rheology further, and the rheological improving ability first enhances and then weakens with increasing the PSMS content in the composite PPD (0–10 wt %). At the PSMS content in the composite PPD 5 wt %, the EVA/PSMS 5% composite PPD makes the wax crystal aggregates more compact, thus showing the strongest rheological improving ability. The EVA molecules could adsorb on the PSMS and form the composite particles, which further regulate the wax crystal morphology and then improve the crude oil rheology further.



1. INTRODUCTION

Paraffin wax, which is normally denoted as the *n*-alkanes with a carbon atom number range of $\text{C}_{16}\text{C}_{40}$,¹ is an important component in crude oil and has tremendous influence on the crude oil's flowability. The crude oil rich in paraffin wax (≥ 10 wt %) is often called waxy crude oil, which has great reserves and is widely distributed on the earth. As the waxy crude oil temperature is lower than the wax appearance temperature (WAT), paraffin wax continuously precipitates into wax crystal particles with the decrease of oil temperature due to oversaturation.^{1,2} The precipitated wax particles impart the characteristics of high pour point and complicated rheological property to the waxy crude oil, which make the pipeline transportation of waxy crude oil costly and danger.^{1–3} Meanwhile, when the pipe wall temperature is below the WAT, wax particles deposit on the pipe wall and then impede the flow of pipelines transporting waxy crude oil.^{4,5}

In the pipeline industry, a small amount of polymer known as pour point depressant (PPD) or wax inhibitor (WI),^{6,7} is often added in waxy crude oil to alleviate the problems mentioned above. The structure of PPD molecules is composed by two parts:^{6,7} long alkyl chains and polar groups. The long alkyl chains

can interact with wax molecules during the wax precipitating process via nucleation, adsorption, and eutectic effects, while the polar part of the PPD could adjust the aggregation state of the precipitated wax particles. Based on the interactions between the polymer PPD and paraffin wax, the rheology of waxy crude oil is greatly improved and the wax deposition is substantially inhibited, thus dramatically enhancing the operating economics and security of the pipelines.

Polyethylene-vinyl acetate (EVA)^{6–10} and its modified derivatives^{11,12} are by far the most extensively used commercial PPD due to its abundant supply and relatively good pour point depressing efficiency. The effects of vinyl acetate (VA) content, molecular weight of EVA, surfactants, and waxy oil composition on the performance of EVA PPD have been widely studied.^{6–12} The results showed that the EVA PPD with VA content around

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28 wt % shows the best performance;^{6,7} the EVA molecules could cocrystallize with paraffin wax and interfere the wax precipitating process,^{6,7} thus improving the waxy crude oil rheology and inhibiting wax deposition.

The traditional polymer-based PPD still has some limitations, including the high selectivity toward waxy crude oils and the diminished effectiveness under repeated heating/shearing. In the polymer industry, a small amount of inorganic nanomaterial is often hybridized into the polymer matrix to improve the mechanical, thermal, magnetic, electric, and optic properties of the polymers.^{13–15} Enlightened by the polymer/inorganic nanocomposites,^{13–15} during the last one decade, some researchers have incorporated inorganic nanoparticles into the polymer PPD matrix to prepare the nanocomposite PPDs.^{16–25} The related nanoparticles include silica,^{16–18} clay,^{19–21} graphene oxide,^{22,23} carbon nanotube,²⁴ magnetic Fe₃O₄,²⁵ etc. It was found that the nanocomposite PPDs disperse in the oil phase as composite particles, which could act as nucleating templates for paraffin wax to modify the precipitated wax particle morphology.^{16–25} Therefore, the rheology of waxy oils is further improved, and the wax deposition is further inhibited after adding the nanocomposite PPDs. However, inorganic nanoparticles often have poor compatibility with organic polymer PPDs. An initial organic modification of the inorganic nanoparticles is necessary to facilitate the dispersion of nanoparticles in the polymer matrix,^{16–25} which complicates the preparing process of the nanocomposite PPD. In addition, inorganic nanoparticles are nondegradable; the introduction of inorganic nanoparticles into waxy crude oil is harmful for the crude oil refining process.

Polymer microsphere^{26–32} is a kind of organic high molecular weight material with the particle size from nanometer to micrometer. Compared with inorganic nanomaterial, polymer microsphere not only has a very small size and high specific surface area but also has many other advantages such as low skeleton density, good degradability, excellent organic/bio compatibility, and easy synthesis and functionalization.^{26–32} The traditional dispersing polymerization and emulsion polymerization are enough to synthesize the polymer microspheres with different particle sizes and different functional groups.^{26–32} Nowadays, the polymer microsphere has been extensively utilized in such fields as adsorption, catalysis, biomedicine, oil recovery, lubrication, coating, and cosmetics.^{26–32} Because the polystyrene microsphere (PSMS) has relatively good stability and oil dispersibility, low adhesion, and low production cost, it has become one of the most widely used polymer microspheres.^{30–32}

In this paper, PSMS with an average particle size of 1.4 μm was first synthesized and then was used to prepare a new type of EVA/PSMS composite PPD through a simple melt blending method. The effects of the PSMS, the EVA PPD, and the EVA/PSMS composite PPD on the pour point, rheological properties, and wax precipitating properties of a specific waxy crude oil were investigated. The rheological improving mechanisms of the PSMS and the PSMS/EVA composite PPD were also well discovered according to the PSMS-EVA-wax interaction analysis. For the first time, this work utilized the polymer microsphere to prepare the nanocomposite PPD that is easy to prepare and does not harm crude oil refining, which has both theoretical and engineering values.

2. EXPERIMENTAL SECTION

2.1. Reagents and Crude Oil Sample. The reagents include polyvinylpyrrolidone (PVP), styrene (St), 2-methoxyethanol (MOE), azo-isobutyronitrile (AIBN), dodecane, and absolute ethanol. All of the reagents are analytically pure and were purchased from Shanghai McLean Biochemical Technology Co., Ltd. The EVA PPD used in the work has a VA content of 28 and a melt index of 06, which is a gift from ARKEMA of France.

The waxy crude oil used in the work is donated by Changqing Oilfield of China, and its basic physical properties are shown in Table 1. As seen in the table, the crude oil contains large

Table 1. Physical Properties of Waxy Crude Oil

saturates/ wt %	aromatics/ wt %	resins/ wt %	asphaltenes/ wt %	wax/ wt %	ρ_4^{20} / kg m ⁻³
81.67	13.26	4.44	0.63	12.1	846

amounts of saturated hydrocarbons (81.67 wt %) and aromatic hydrocarbons (13.26 wt %), but the contents of resins (4.44 wt %) and asphaltenes (0.63 wt %) are relatively small. The wax content of the crude oil is higher than 10 wt % (12.1 wt %), and the crude oil density is 846 kg·m⁻³ at 20 °C, indicating that the crude oil is a typical light waxy crude oil.

2.2. Preparation and Characterization of PSMS. The PSMS with narrow particle size distribution were synthesized by dispersion polymerization. First, 4 g of PVP is weighed and added into a 250 mL three-necked flask containing 72 g of anhydrous ethanol and 8 g of MOE. Second, 20 g of St were added into the flask and then the nitrogen gas was introduced to remove oxygen from the flask. After that, the reaction temperature was set at 70 °C and 0.4 g of AIBN were added to the flask to initiate the polymerization reaction. The entire reaction time was set to 24 h. After the reaction, the dispersion was centrifuged and the sediment was washed with absolute ethanol 3 times. Finally, PSMS could be obtained after the sediment was dried in a vacuum oven at 45 °C and crushed into pieces.

The chemical structure of the PSMS was analyzed through a Nicolet ISS FT-IR instrument (Thermo Fisher Scientific, USA). The morphology of the PSMS was tested by JSM-6700F SEM (Jeol, Japan). The dispersibility of the PSMS in deionized water and dodecane was directly observed through the bottle tests; the dispersing state and the particle size distribution of the PSMS in dodecane was measured by a BX51 microscope (Olympus, Japan) and a Zetasizer nano ZS90 (Malvern Panalytical, England), respectively.

2.3. Preparation and Characterization of EVA/PSMS Composite PPD. The EVA/PSMS composite PPD was prepared by dispersing a small amount of PSMS into the EVA PPD matrix through a melt blending method. The melt blending temperature was set at 140 °C, at which the EVA shows nice flowability. The melt blending time was set at 20 min. Detailed description of the melt blending process could be seen in the former published papers.^{33,34} The PSMS content in the composite PPD in the prepared EVA/PSMS composite PPD are 2.5, 5, 7.5, and 10 wt %. Therefore, four types of the composite PPD were prepared, which were named EVA/PSMS 2.5%, EVA/PSMS 5%, EVA/PSMS 7.5%, and EVA/PSMS 10% successively.

Both the EVA PPD and EVA/PSMS PPD were dissolved or dispersed in dodecane before they were added to the waxy crude

oil. The concentration of the EVA PPD and EVA/PSMS PPD in dodecane was fixed at 10 wt %. The dosage of the EVA PPD and EVA/PSMS PPD in the waxy crude oil was fixed at 20 ppm; that is, the real dosage of PSMS in the waxy crude oil was only 0.5–2 ppm.

2.4. Gelling Point Test. The gelling point of the waxy crude oil undoped/doped with the EVA/PSMS composite PPD was tested according to the Chinese petroleum and natural gas industry standard SY/T 0541–2009 “Determination of crude oil gelling point”. The thermal treatment temperature of the oil sample was fixed at 60 °C, and the temperature dropping rate was controlled at 0.5–1 °C/min.

2.5. Rheological Test. The DHR-1 stress controlled rotational rheometer (TA, USA) was used to examine the rheological characteristics of the undoped/doped waxy crude oil. The thermal treatment temperature of the waxy crude oil was unchanged at 60 °C, and the temperature dropping rate was controlled at 0.5 °C/min.

Viscoelasticity Test. The oil samples loaded into the rheometer were first kept at 60 °C for 20 min, and then the oil samples were gradually cooled from the initial temperature of 60 °C to the predetermined test temperature of 1 °C. During the cooling process, an oscillation with the frequency of 1 Hz and the amplitude of 0.0005 was applied. The changes of the viscoelastic parameters, including storage modulus G' , loss modulus G'' , and loss angle δ , with the temperature drop were recorded. The gelation point at which the G' begins to equal the G'' was also obtained.

Viscosity–Temperature Curve Test. During the cooling process of the undoped/doped oil samples from 60 to 1 °C, a constant shear rate of 20 s⁻¹ was applied. Then, the variation of the viscosity/apparent viscosity of the oil samples with the temperature drop could be obtained.

Flow Curve Test. The undoped/doped oil samples were first cooled from 60 to 1 °C quiescently and then remained at 1 °C for 20 min. After that, a scanning of shear rate from 1 to 200 s⁻¹ was applied, and the scanning time is 10 min. Finally, the variation of the apparent viscosity of the oil samples with the increase of the shear rate was obtained.

2.6. DSC Test. The DSC-821e differential scanning calorimeter (Mettler Toledo, Switzerland) was used to test the crystallization exothermic characteristics of the undoped/doped waxy crude oil. First, an oil sample with a mass of 6–12 mg was added into an aluminum crucible and placed into the instrument sample cell. Then, under constant nitrogen flow protection, the DSC curves of the oil samples were measured from 85 to 20 °C and at an unchanged cooling rate of 10 °C/min.

2.7. Microscopic Observation. Using the BX51 polarized microscope (OLYMPUS, Japan) fitted with a temperature controlling platform, the wax crystal morphology in the undoped/doped waxy crude oils was directly observed. Each oil sample was placed first on a slide and then was covered with a cover glass. After that, the oil sample was placed into the temperature controlling platform and was statically cooled from 60 to 5 °C at a rate of 0.5 °C/min. Finally, the microstructure of the oil sample was photoed and recorded.

3. RESULTS AND DISCUSSION

3.1. Characterization of the PSMS. **3.1.1. FT-IR and SEM image of the PSMS.** Figure 1a shows the FT-IR of PSMS, and several characteristic absorption peaks can be observed in the figure. The absorption peaks at 3083.71, 3061.58, and 3024.74 cm⁻¹ correspond to the stretching vibrations of the unsaturated

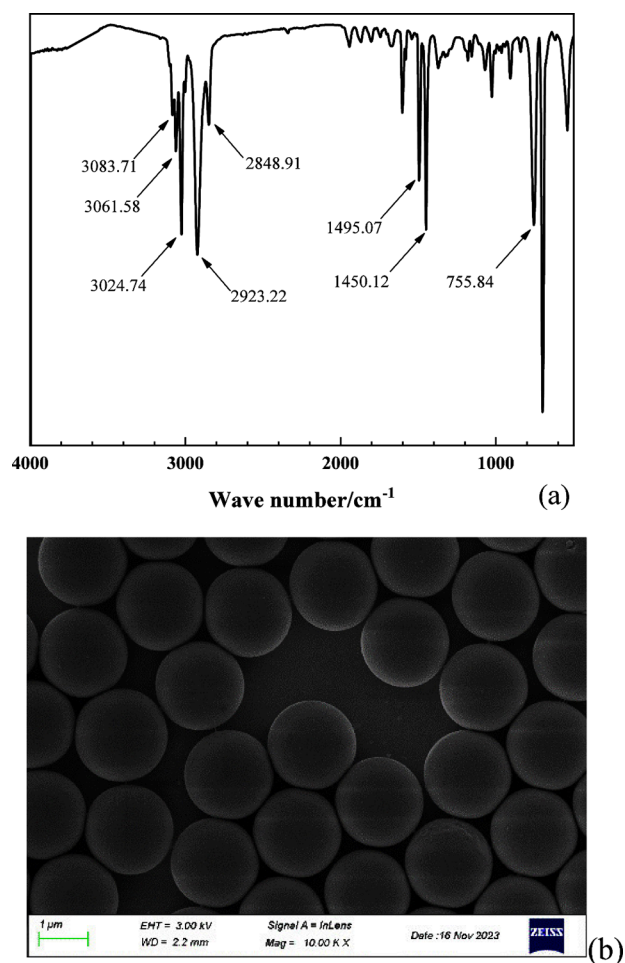


Figure 1. FT-IR spectra (a) and SEM images (b) of the PSMS.

C–H bonds on the benzene ring, indicating the presence of a benzene ring structure. The absorption peaks at 2848.91 and 2923.22 cm⁻¹ are the stretching vibrations of the methyl and methylene groups, which confirm the alkyl side chain structure of the polymer. The adsorption peak at 1495.07 cm⁻¹ belongs to the in-plane bending vibration of the C–H bond on the benzene ring, while the peak at 1450.12 cm⁻¹ is the in-plane bending vibration of the methyl group. The peak at 755.84 cm⁻¹ is a characteristic absorption peak for the monosubstituted benzene rings. In summary, these characteristic absorption peaks mentioned above are in accord with the characteristic peaks of polystyrene. As seen in Figure 1b, the synthesized PSMS exhibits a smooth and complete spherical appearance and the particle size is relatively uniform. The particle size of the PSMS is around 1.4 μm and shows good monodispersity. Based on Figure 1a,b, it could be concluded that the PSMS with good monodispersity is successfully synthesized here.

3.1.2. Dispersion State and Particle Size Distribution of the PSMS in Dodecane. The prepared PSMS were separately dispersed in deionized water and dodecane at a concentration of 0.02 wt % and underwent ultrasonic treatment for 20 min at 60 °C. Then, the two dispersions were placed in two bottles and observed after 2 h. As shown in Figure 2a, the PSMS has poor dispersibility in deionized water and presents an aggregated or flocculated state, thus causing a low transparency. In contrast, the PSMS disperses well in dodecane and the dispersion has a good transparency. Figure 2b demonstrates the morphology of

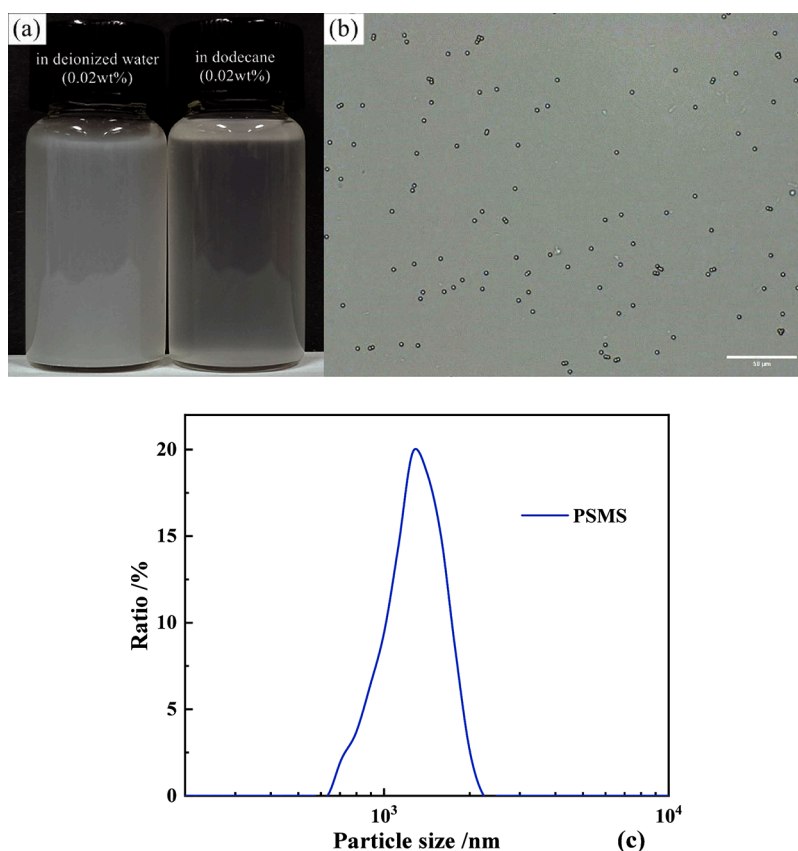


Figure 2. Dispersibility of the PSMS in deionized water and dodecane (a), microstructure (b), and particle size distribution (c) of the PSMS in dodecane.

Table 2. Gelling Point, Gelation Point, and G'/G'' at 15 °C of the Waxy Crude Oil Undoped/Doped with PSMS

	gelling point /°C	gelation point/ °C	G'/Pa	G''/Pa
undoped	15	22.6	1099.45	183.23
20 ppm PSMS	15	22.3	1033.47	165.14
50 ppm PSMS	15	21.5	883.83	114.59
100 ppm PSMS	15	20.1	413.22	74.26
200 ppm PSMS	15	21.2	606.76	124.70
400 ppm PSMS	15	22.5	972.52	150.97

PSMS dispersed in dodecane. It is clear that most of the PSMS are dispersed in dodecane as single particles, but several aggregates also exist. The particle size distribution of the PSMS-in-dodecane dispersion is shown in Figure 2c. Obviously, the PSMS demonstrates good monodispersity in the oil phase, and the average particle size of the PSMS is about 1.4 μm .

The PSMS is composed of polystyrene, which is an oil-soluble polymer. Therefore, the PSMS cannot disperse in deionized water but can disperse well in dodecane.

3.2. Performance Evaluation of the PSMS. **3.2.1. Effect of PSMS on the Rheological Properties of Waxy Crude Oil.** As seen in Table 2, the gelling point of the pure waxy crude oil is 15 °C, and adding 20–400 ppm of PSMS cannot change the gelling point of the crude oil. The viscoelastic properties of the waxy crude oil undoped/doped with PSMS are shown in Figure 3 and Table 2. The gelation point of the pure waxy crude oil is 22.6 °C, while the gelation point decreases to 22.3, 21.5, and 20.1 °C by increasing the dosage of PSMS to 20, 50, and 100 ppm. With the further increase of the PSMS dosage from 200 to 400 ppm, the

gelation point recovers to 21.2 and 22.5 °C, respectively. The variations of G' and G'' at 15 °C with increasing the PSMS dosage show the same trend. The G' and G'' of the pure waxy crude oil are 1099 and 183 Pa, respectively. At the PSMS dosage of 100 ppm, the G' and G'' have the smallest values of 413 and 74 Pa, respectively. Obviously, PSMS can improve the viscoelasticity of the waxy crude oil to some extent, and the best performance is shown at the dosage of 100 ppm.

The effect of the PSMS dosage on the flow curve of waxy crude oil at 1 °C is described in Figure 4. The data from the figure indicate that the PSMS can marginally reduce the apparent viscosity of the waxy crude oil, and the viscosity reducing ability is correlating to the PSMS dosage. For example, at the shear rate of 100 s^{-1} , the apparent viscosity of the pure waxy crude oil is 1988 mPa·s; with the increase of PSMS dosage, the apparent viscosity first decreases from 1910 mPa·s at 50 ppm to 1836 mPa·s at 100 ppm and then recovers from 1866 mPa·s at 200 ppm to 1907 mPa·s at 400 ppm. Obviously, the PSMS shows the strongest viscosity reducing ability at the dosage of 100 ppm. At the PSMS concentration of ≤ 100 ppm, the special hindrance effect is dominant and then the viscosity of the crude oil slightly decreases with increasing the PSMA concentration. At the PSMS concentration of ≥ 200 ppm, the particle interactions among wax crystals and PSMS play a key role and then the viscosity of the crude oil slightly increases with the further increase of PSMS concentration.

3.2.2. Effect of PSMS on the Wax Precipitating Properties of the Waxy Crude Oil. As seen in Figure 5, for the pure waxy crude oil, the WAT and the cumulative precipitated wax amount at -20 °C are 32 °C and 11.9 wt %, respectively. The addition of

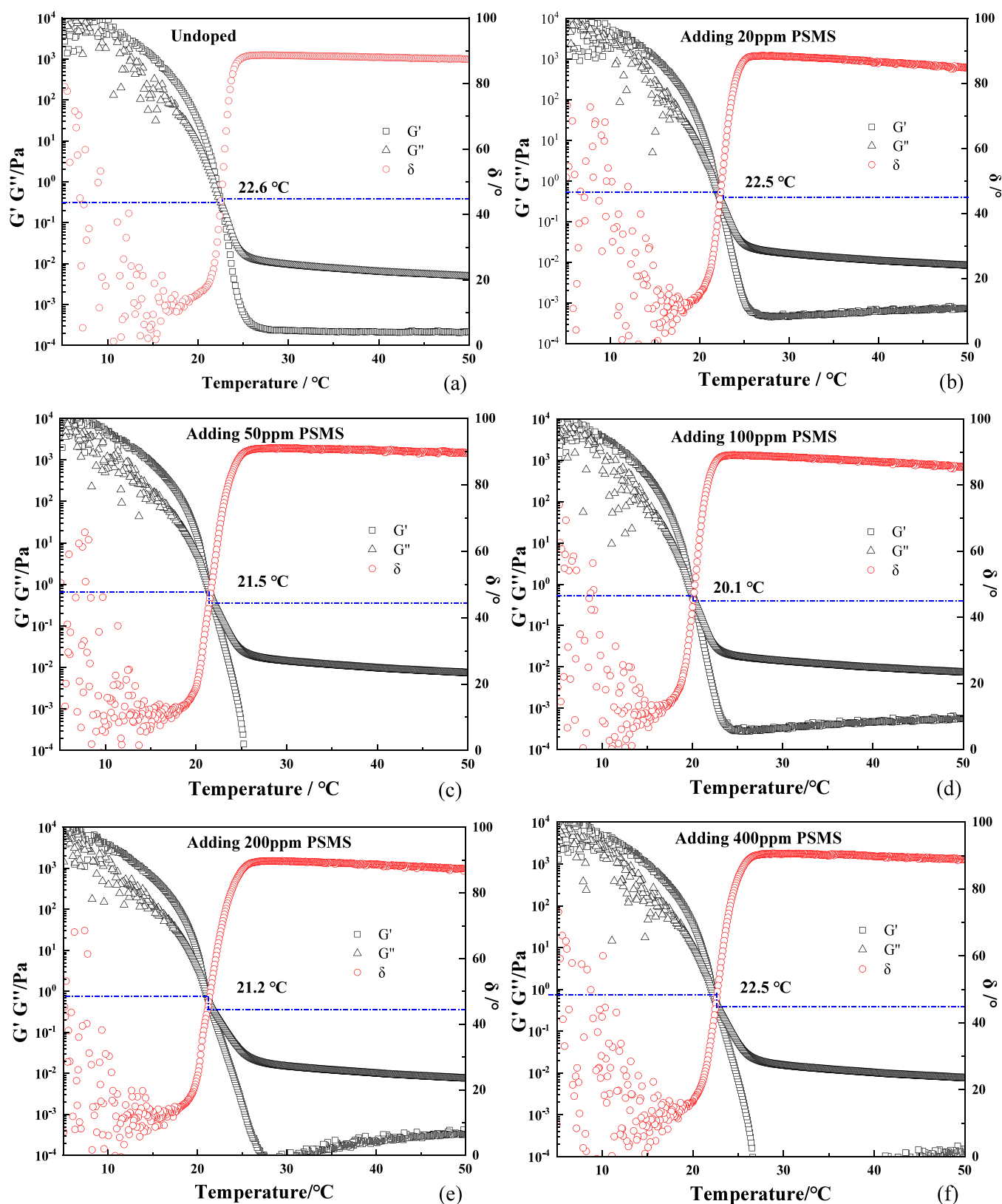


Figure 3. Effect of the PSMS dosage on the viscoelastic development of the waxy crude oil with temperature drop: (a) undoped; (b) 20 ppm; (c) 50 ppm; (d) 100 ppm; (e) 200 ppm; (f) 400 ppm.

100 ppm of PSMS has little influence on the WAT and the cumulative precipitated wax amount. Figure 6 shows the wax crystal morphology in the undoped/doped waxy crude oil at 5 °C. It is also clear that adding 100 ppm of PSMS has little effect

on the morphology of the wax crystals. We deduce that the rheological improving effect of the PSMS on waxy crude oil is not generated by the PSMS-wax interactions.

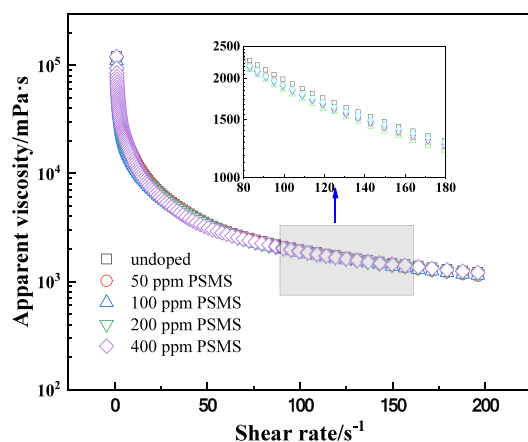


Figure 4. Effect of the PSMS dosage on the flow curve of waxy crude oil at 1 °C.

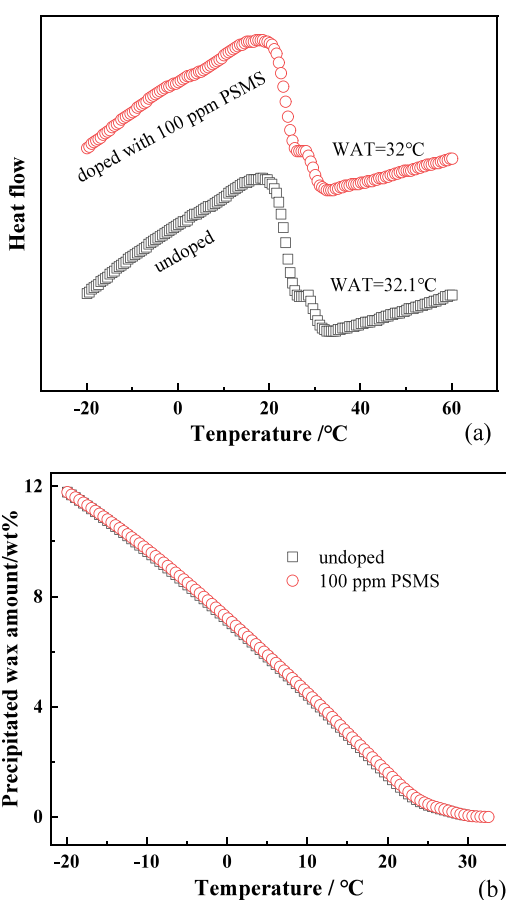


Figure 5. DSC curves (a) and cumulative precipitated wax amount (b) of the waxy crude oil undoped and doped with 100 ppm of PSMS.

3.3. Performance Evaluation of the EVA/PSMS Composite PPD.

3.3.1. Effect of the Composite PPD on the Rheological Properties of Waxy Crude Oil. As seen in Table 3, adding 20 ppm of EVA PPD can greatly reduce the gelling point of the waxy crude oil to 4 °C, while adding 20 ppm of EVA/PSMS composite PPD can further reduce the gelling point. With the increase of the PSMS content in the composite PPD, the gelling point depressing ability of the composite PPD first slightly enhances and then decreases, indicating the existence of an optimal PSMS content in the composite PPD of the composite PPD. When the waxy crude oil

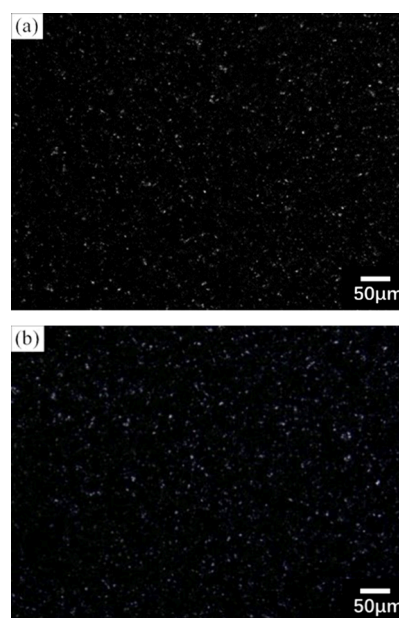


Figure 6. Polarized microscopic images of the waxy crude oil at 5 °C: (a) undoped; (b) doped with 100 ppm of PSMS.

Table 3. Effect of the EVA PPD and EVA/PSMS Composite PPD on the Gelling Point of the Waxy Crude Oil

type of PPD	gelling point /°C
undoped	15
20 ppm EVA	4
20 ppm EVA/PSMS 2.5%	3
20 ppm EVA/PSMS 5%	2
20 ppm EVA/PSMS 7.5%	3
20 ppm EVA/PSMS 10%	3

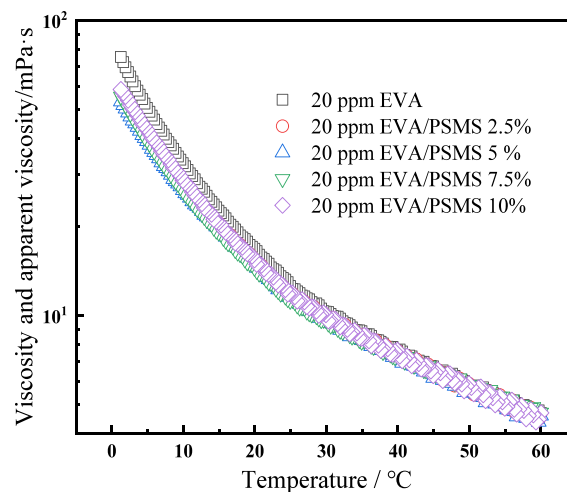


Figure 7. Effects of the EVA PPD and EVA/PSMS composite PPD on the viscosity–temperature curves of waxy crude oil. The shear rate is 20 s⁻¹.

is treated with the EVA/PS 5% (the PSMS content in the composite PPD is 5 wt %), the best gelling point depressing effect is achieved and the gelling point is 2 °C.

Because the gelation point of the waxy crude oil is less than 1 °C after adding 20 ppm of EVA PPD or composite PPD, the viscoelasticity of the doped oil is difficult to effectively measure.

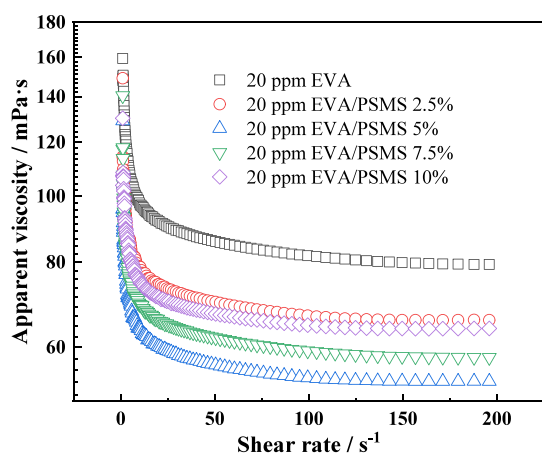


Figure 8. Effects of the EVA PPD and EVA/PSMS composite PPD on the flow curves of waxy crude oil at 1 °C.

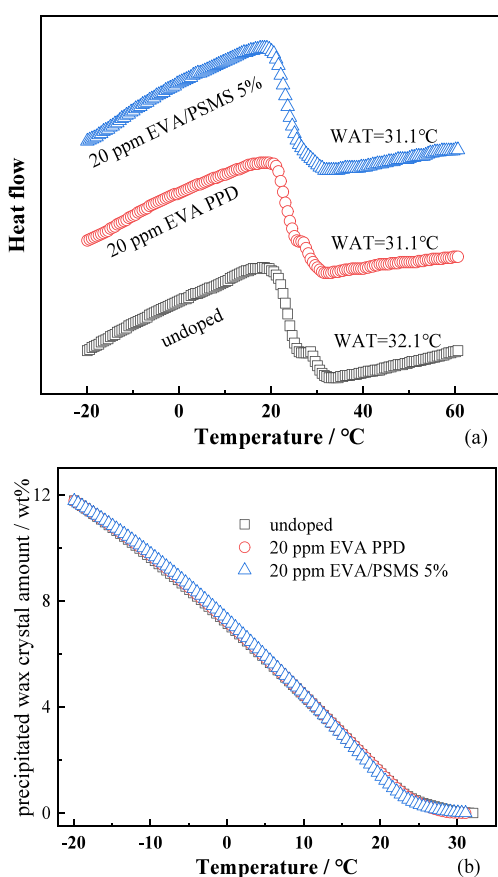


Figure 9. DSC curves (a) and cumulative precipitated wax amount (b) of the waxy crude oil undoped and doped with EVA PPD and EVA/PSMS 5% PPD.

Therefore, the viscosity–temperature curves of the undoped/doped waxy crude oil were tested at the shear rate of 20 s^{-1} . As seen in Figure 7, the composite PPD shows a much stronger viscosity reducing ability than the EVA PPD. For example, at 5 °C, the apparent viscosity of the waxy crude oil after the addition of the pure EVA PPD is 50.2 mPa·s. After adding the EVA/PSMS 2.5%, EVA/PSMS 5%, EVA/PSMS 7.5%, and EVA/PSMS 10%, the corresponding apparent viscosities are 41.2, 38.7, 38.9, and 42.4 mPa·s, respectively. Compared to EVA, the viscosity reduction rates are 17.9, 22.9, 22.5, and 15.5%.

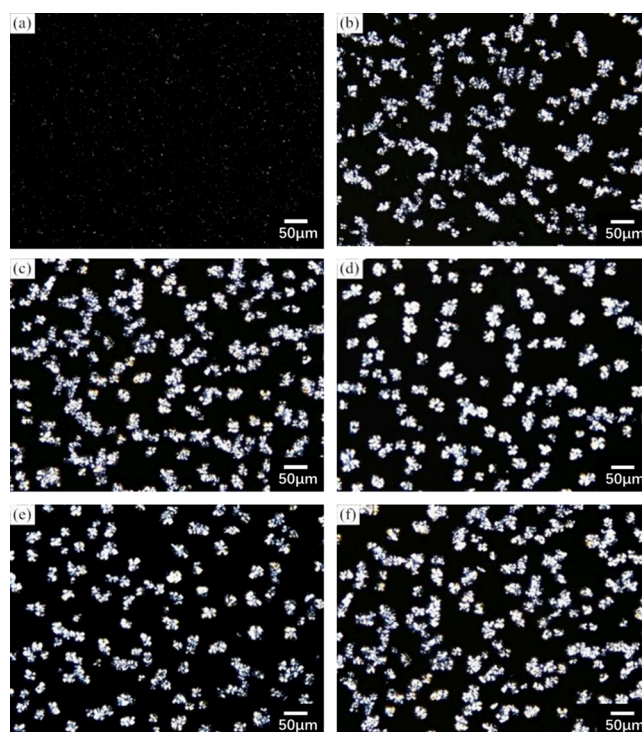


Figure 10. Polarized microscopic images of the waxy crude oil undoped/doped with EVA and EVA/PSMS composite PPD at 5 °C: (a) undoped; (b) EVA; (c) EVA/PSMS 2.5%; (d) EVA/PSMS 5% (e) EVA/PSMS 7.5%; (f) EVA/PSMS 10%.

Obviously, the viscosity reducing ability of the composite PPD first enhances and then weakens with the increase of the PSMS content in the composite PPD. At the PSMS content in the composite PPD of 5 wt %, the composite PPD shows the strongest viscosity reducing ability.

Figure 8 shows the flow curves of the waxy crude oils doped with 20 ppm of EVA and EVA/PSMS composite PPD at 1 °C. With the increase of shear rate from 1 to 200 s^{-1} , the apparent viscosity decreases frequently, showing an obvious shear thinning property. Compared with the EVA PPD, the waxy crude oils doped with the composite PPD exhibits more significant shear thinning property and have much smaller apparent viscosity values. For example, at a shear rate of 100 s^{-1} , the apparent viscosity of the waxy crude oil after the addition of the pure EVA PPD is 81.7 mPa·s. After adding the EVA/PSMS 2.5%, EVA/PSMS 5%, EVA/PSMS 7.5%, and EVA/PSMS 10%, the corresponding apparent viscosities are 67.8, 54.8, 59.7, and 64.2 mPa·s, respectively. Compared to EVA, the viscosity reduction rates are 17.0, 32.9, 26.9, and 21.4%, respectively. With the increase of the PSMS content in the composite PPD, the viscosity reducing ability of the composite PPD first enhances and then weakens, and the composite PPD with 5 wt % PSMS shows the best viscosity reducing ability.

3.3.4. Effect of the Composite PPD on the Wax Precipitating Properties of Waxy Crude Oil. As seen in Figure 9a, adding 20 ppm of EVA could reduce the WAT of the waxy crude oil by 1 °C, meaning that the EVA molecules could cocrystallize with the wax molecules and solubilize some wax. Adding the composite PPD does not further change the WAT of the crude oil. According to Figure 9b, it is obvious that adding the EVA PPD or the composite PPD cannot change the cumulative precipitated wax amount at low temperatures.

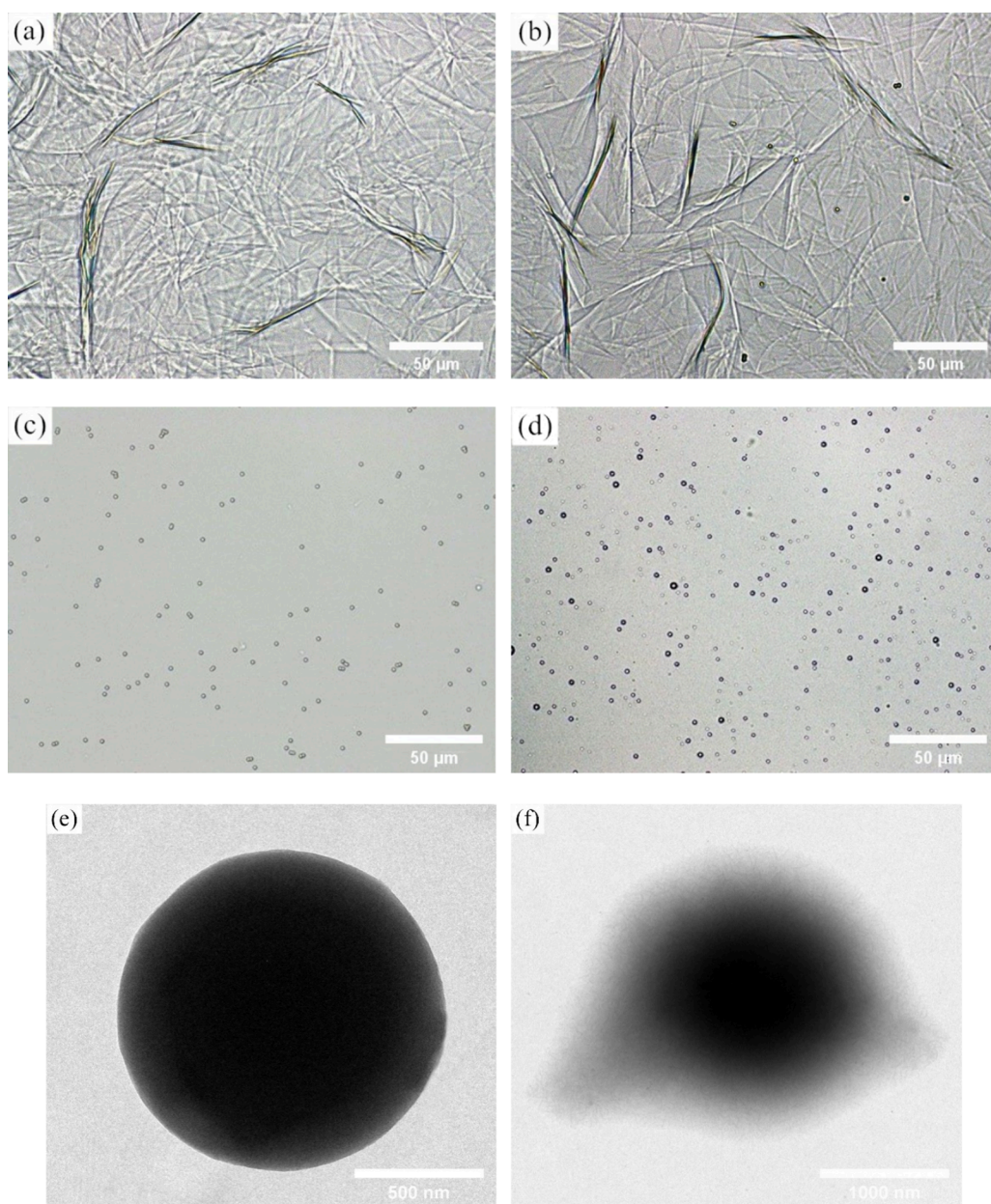


Figure 11. Photographs of wax crystal microstructure of the synthetic waxy oils without (a) and with 0.02 wt % PSMS (b); 0.02 wt % PSMS (c) and EVA/PSMS composite PPD (d) in dodecane; TEM images of the PSMS (e) and EVA/PSMS composite PPD (f).

The wax crystal microstructure of the undoped/doped waxy crude oils at 5 °C are shown in Figure 10. For the pure waxy crude oil, the precipitated wax crystals are very small particles with a large amount (Figure 10a). After adding 20 ppm of EVA, the wax crystals tend to flocculate into big wax aggregates, which favor the improvement of the crude oil rheology, but the structure of the wax aggregates is very loose (see Figure 10b). As seen in Figure 10c–e, the wax crystal morphology does not change obviously after adding 20 ppm of EVA/PSMS 2.5% but changes clearly after adding 20 ppm of EVA/PSMS 5% or EVA/PSMS 7.5%. The structure of the wax aggregates becomes more compact after adding the EVA/PSMS 5% or EVA/PSMS 7.5%, which facilitates the reduction of the gelling point and viscosity. When the EVA/PSMS 10% is added into the waxy crude oil, however, the structure of the wax aggregates becomes loose again, which weakens the performance of the composite PPD.

3.4. Mechanism Discussion. In order to discover the rheological improving mechanisms of the PSMS, a synthetic waxy oil containing 85 wt % dodecane and 15 wt % paraffin wax was prepared. The wax crystal microstructure of the pure waxy oil and the waxy oil doped with 200 ppm of PSMS was observed under a microscope. As seen in Figure 11a,b, the wax crystals in the pure and the doped waxy oil are both long needle-like, and adding the PSMS has little influence on the wax crystal morphology. Yang et al.³⁵ investigated the effect of the oil dispersible polymethylsilsesquioxane (PMSQ) microspheres with the particle size 200 nm–10 μm on the rheology of two waxy crude oils. They found that adding 200 ppm of PMSQ with the particle size 2 μm could improve the crude oil rheology to some extent; the PSMQ does not change the precipitated wax crystal morphology but weakens the wax crystal network structure through the spatial hindrance effect. We consider

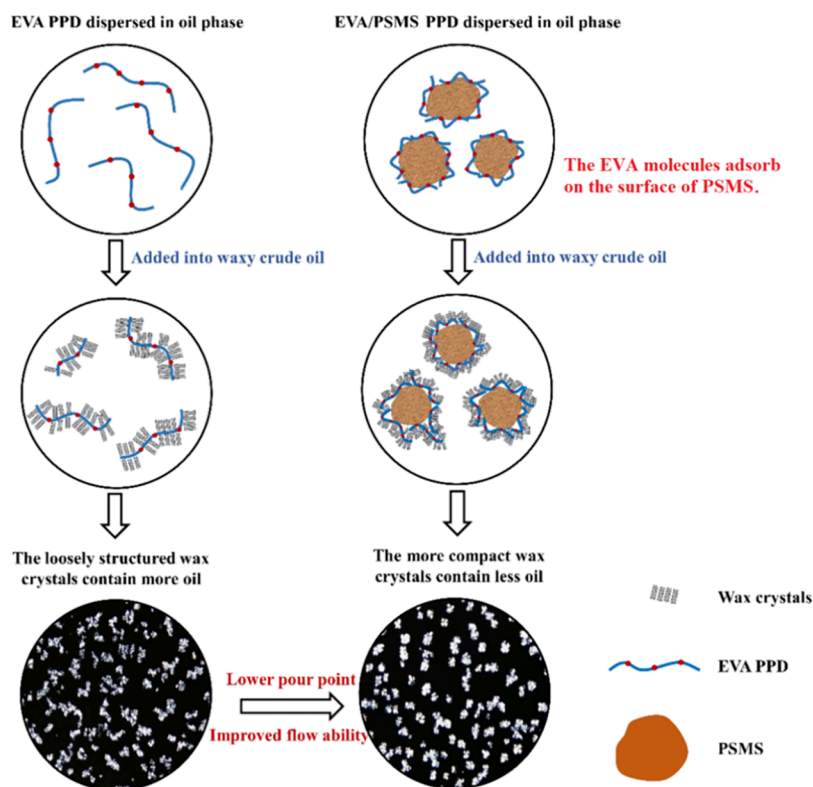


Figure 12. Schematic mechanism diagram of the EVA/PSMS composite PPD.

that the PSMS also improves the rheology of the waxy crude oil by the spatial hindrance effect.

In order to discover the rheological improving mechanisms of the EVA/PSMS composite PPD, the dispersion state of the composite PPD in dodecane was observed by a microscope and was compared with the dispersion state of the PSMS. As shown in Figure 11c,d, the composite PPD also disperses in dodecane as individual spherical particles. However, the contour of the composite PPD particles is much thicker, indicating that some EVA molecules adsorb on the surface of the PSMS. To further support the mechanisms of PSMS alone and the composite PPD, the TEM images of the PSMS and the composite PPD in *n*-dodecane are shown in Figure 11e,f. It is clear that the PSMS exists in the oil phase as regular spherical particle. The composite PPD is also a spherical particle, but the surface is ambiguous, indicating the formation of a thick EVA molecule adsorption layer around the particle surface. The EVA molecules have the ester groups, and the PSMS has the benzene rings; we speculate that the EVA molecules adsorb on the PSMS by the charge transfer interaction. The formed EVA/PSMS composite particles further regulate the wax crystal morphology and then improve the crude oil rheology further (see Figure 12). At the PSMS content in the composite PPD 5 wt %, the interactions between the PSMS and EVA molecules are the strongest, and therefore, the EVA/PSMS 5% composite PPD shows the best ability to improve the wax crystal morphology and the crude oil rheology.

4. CONCLUSIONS

The organic PSMS with an average size of 1.4 μm was successfully synthesized and was applied to prepare a new type of EVA/PSMS composite PPD by melt blending. The effects of the PSMS, the EVA PPD and the composite PPD on the gelling

point, rheological properties, and wax precipitating properties of a specific waxy crude oil were studied in detail. The conclusions are drawn as follows.

1. A small dosage of the PSMS (20–400 ppm) could slightly improve the rheology of the waxy crude oil through spatial hindrance effect, and the rheological improving ability of the PSMS first enhances and then weakens with increasing the PSMS dosage. The strongest rheological improving ability of the PSMS is found at the dosage of 100 ppm.
2. Adding 20 ppm EVA PPD dramatically changes the morphology of wax crystals from the small particles with very large amount to much bigger wax crystal aggregates with small amount, thus greatly improving the waxy crude oil rheology.
3. Compared with EVA PPD, adding 20 ppm composite PPD could improve the crude oil rheology further, and the rheological improving ability first enhances and then weakens with increasing the PSMS content in the composite PPD (0–10 wt %). At the PSMS content in the composite PPD 5 wt %, the EVA/PSMS 5% composite PPD makes the wax crystal aggregates more compact, thus showing the strongest rheological improving ability.
4. The EVA molecules could adsorb on the PSMS and form the composite particles, which further regulates the wax crystal morphology and then improve the crude oil rheology further.

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Notes

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ABBREVIATIONS

PSMS polystyrene microsphere
EVA polyethylene-vinyl acetate
PPD pour point depressant
WAT wax appearance temperature
WI wax inhibitor
VA vinyl acetate
PVP polyvinylpyrrolidone
St styrene
MOE 2-methoxyethanol
AIBN azo-iso-butyronitrile
DSC differential scanning calorimeter

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