Insights into Flow Improving for Waxy Crude Oil Doped with EVA/SiO₂ Nanohybrids

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ABSTRACT: Nanohybrid materials can significantly inhibit wax deposition and improve the fluidity of crude oil. However, the mechanisms behind wax resolving, crystal modification, and flow improving are still unclear owing to the complexity of crude oil. Here, we compared the effect of ethylene vinyl acetate (EVA) and nanohybrids composed of EVA and SiO₂ nanoparticles on wax crystallization and rheological behavior of Shengli waxy oil. Differential scanning calorimetry results indicate that SiO₂ nanoparticles boost the efficiency of EVA for reducing the wax appearance temperature of waxy crude oil. Thermo X-ray diffraction characterization demonstrates that EVA/SiO₂ nanohybrids cut down the crystal index of waxes, with the grain size of crystal cells decreased in (006) and (200) but increased in (110) cross sections. Polarized optical microscopy imaging reveals that EVA can modify the morphology of wax crystals to suppress the formation of wax gel, and nanohybrids serve as nucleuses to adsorb asphaltenes and resins, restraining the appearance of wax crystals. The rheological test shows that nanohybrids outperform EVA in decreasing the viscosity, viscosity index, and yield stress of waxy crude oil. These findings help the understanding of flow improving by nanohybrid materials and offer guidelines for designing the new generation of wax inhibitors for safe transportation and flow assurance of waxy crude oil.

1. INTRODUCTION

As the latest statistics¹ shows, crude oil still retains its dominant position in the global primary energy map; in addition, petroleum distillate also serves as an important chemical feed stock.² Among the crude oil stored in reservoirs, heavy oil, especially waxy heavy oil, accounts for a considerable proportion. For example, about two-thirds of the crude oil reserves in China is waxy heavy oil, causing great trouble to the extraction and transportation of crude oil due to the deposition of wax paraffins.³ Specifically, the long-chain paraffins interlocking with each other, forming a percolated and thickened network, entrapping light hydrocarbons inside, and causing poor mobility of the waxy crude oil.⁴,⁵ Recently, it has been found that nanohybrid doping is a promising strategy to suppress paraffin interlocking and improve the fluidity of waxy crude oil. Our group has previously studied the effect of SiO₂ nanoparticles on the rheological behavior of model oil, which was formulated according to the composition of Shengli crude oil, and verified the adsorption effect of SiO₂ on asphaltenes and resins.⁶ Although several research studies⁷,⁸ have engaged in various nanohybrid systems aiming to interpret the underlying mechanism in the crystallization behavior of the waxes, universal opinion has not yet emerged out ascribing to complex composition of crude oil. Therefore, it is of great significance to understand the interaction between nanohybrids and waxes in crude oil for proper development of high-efficiency flow improvers.

A variety of means have been developed for flow assurance of crude oil, which can be classified into physical and chemical modes. As for the former, the temperature of crude oil remains above the pour point through thermal treatment during pipeline transportation to ensure its smooth conveyance,⁹,¹⁰ but a large demand for power pushes up the costs dramatically. On the contrary, chemical means, especially for the addition of pour point depressants (PPDs), are generally cost-effective and convenient because the chemical additives may transform the structure and morphology of wax crystals and prevent the crystals from formation of a compact three-dimensional network at ambient or even lower temperatures.¹¹–¹³ Up to date, diversified PPDs have been prepared to improve the fluidity of waxy crude oil, evolving from conventional, block, comb-like polymers to nanohybrid materials. The polymeric
PPDs, such as polymethacrylate and ethylene/vinyl acetate (EVA) copolymers, usually consist of polar and nonpolar groups. Nonpolar segments tend to co-crystallize with wax in crude oil to regulate the orientation of crystals, and the polar fractions of PPDs repel each other to impede interactions between wax crystals. Such an amphiphilic architecture furnishes PPDs to suppress the formation of a thick three-dimensional network. However, application of those polymeric PPDs in oil field is limited sometimes due to their high selectivity of crude oil. For example, the Aburto team and the Kuzmić laboratory respectively reported that EVA was disabled for some crude oil and even caused an opposite effect in the fluidity of oil. Recently, several studies have indicated that addition of nanoparticles into polymeric PPDs can lower the pour point and viscosity of crude oil. Such nanohybrid PPDs can improve the fluidity of crude oil owing to the large specific surface area, high adsorption capacity, and unique surface activity of the nanoparticles added. Song et al. examined the effect of SiO₂ nanoparticles on wax crystallization and flowability of model crude oil, and they concluded that these particles could adsorb and disperse asphaltenes to prevent their aggregation, thus restraining the nucleation effect of asphaltenes on wax crystallization. Yang’s team surveyed the influence of organic montmorillonite on the yield stress of the model waxy oil, and they found that the addition of montmorillonite nanosheets can result in a great reduction of the yield stress, which attributed to the suppression of montmorillonite nanosheets on the wax gelation. Normann and co-workers developed another class of nanohybrid PPDs via coating poly(octadecyl acrylate) (POA) on the surface of silica nanoparticles. It is indicated that nanoparticles with full coverage of POA significantly lowered the wax gel strength, and the presence of the nanoparticles changes the nature of the wax crystallization. Although EVA copolymers and SiO₂ nanoparticles are frequently used to prepare nanohybrid flow improvers, the comparison between SiO₂/EVA nanohybrids and pure EVA copolymers was rarely reported. More importantly, crude oil has much more complex composition than model oil that is often adopted for better visualization in the research of nanohybrid materials, but the crystallization and rheological behaviors of real crude oil are still unclear. Therefore, it is necessary to gain insights into the mechanisms how nanohybrids improve the fluidity of crude oil other than model ones. Using crude oil tends to provide oilfield workers with more realistic data and facilitates the development of more practical flow improvers.

Herein, we aim to reveal the effect of EVA/SiO₂ nanohybrids on the crystallization and rheological behavior of Shengli waxy crude oil, which is also the reference formulation for the model oil used in our previous study of SiO₂ nanoparticles. To this end, differential scanning calorimetry was applied to examine the wax appearance temperature (WAT) of waxy oil doped with EVA and nanohybrids. Thermo X-ray diffraction (XRD) was utilized to understand the influence of nanohybrids on wax crystal parameters. A polarized optical microscope was employed for gaining better insights into the modification of wax crystal morphology by EVA and nanohybrids. Finally, the rheological test was carried out to evaluate the flow improving ability of nanohybrids on Shengli waxy crude oil.

Figure 1. TEM images of (a) SiO₂ and (b) EVA/SiO₂ nanohybrids, scale bar: 50 nm; SEM micrographs and element analysis results of (c) SiO₂ and (d) EVA/SiO₂ nanohybrids. Scale bar: 300 nm. (at. % means the percentage of atoms).
2. RESULTS AND DISCUSSION

EVA/SiO₂ nanohybrids were prepared by mixing SiO₂ nanoparticles with the EVA copolymer in different mass ratios. The morphology and dispersibility of nanohybrids were first studied by TEM and optical microscope imaging. Then, the wax crystallization behavior of crude oil doped with EVA or nanohybrids was investigated to explore the flow improving mechanism of nanohybrids. Finally, the rheological test was performed to check the effect of nanohybrids on the flow behavior of crude oil, and the optimized dosage of SiO₂ was acquired.

2.1. Morphology and Dispersibility of SiO₂ and EVA/SiO₂ Nanohybrids. In order to observe the morphology of SiO₂ nanoparticles or EVA/SiO₂ nanohybrids, both TEM and SEM were employed to visualize their structure. As shown in Figure 1a, SiO₂ nanoparticles present a smooth surface with a distinguishable outline. In contrast, the surface of EVA/SiO₂ nanohybrids (Figure 1b) is blurry, suggesting that the surface of SiO₂ particles was coated with EVA copolymers.

To verify that EVA copolymers were attached on the surface of SiO₂ nanoparticles, SEM−energy dispersive X-ray spectroscopy (EDS) was employed to analyze the elemental composition of the nanoparticle surface. As shown in Figure 1c, no carbon element is detected on the surface of SiO₂ nanoparticles, with atomic contents of Si and O approximately to be 2:1, attributed to a pure SiO₂ system. Figure 1d shows that a large amount of carbon element (75.35 wt %) resides on the surface of nanohybrids, due to EVA copolymers coated on the SiO₂ surface. These EDS results further demonstrate that EVA copolymers are anchored on the surface of SiO₂ nanoparticles in EVA/SiO₂ nanohybrids.

The large specific surface area endows nanoparticles with superior performance, but it also leads to high surface energy and aggregation tendency. Aggregation and coagulation of nanoparticles are unfavorable for the flowability of crude oil, and so, the dispersibility of nanoparticles is a prerequisite for practical use. To better simulate the dispersing state of nanoparticles in crude oil, we formulated a mixed solvent based on the ratio of saturated and aromatic hydrocarbons. The weighted average carbon number of aliphatic hydrocarbons was calculated to be 18, and so, we prepared the oil phase with the mass ratio of n-octadecane and xylene at 7:5 according to the ratio of aliphatic and aromatic fractions in crude oil to evaluate the dispersibility of nanoparticles and nanohybrids. As displayed in Figure 2a, SiO₂ nanoparticles cannot be seen under a microscope on account of their nanoscale size, while the nanohybrid dispersion (Figure 2b) shows amorphous submicron aggregates, indicating that SiO₂ nanoparticles are wrapped with EVA copolymers. As exhibited in the insets of Figure 2a,b, the dispersion of SiO₂ nanoparticles is transparent and homogeneous, while that of nanohybrids turns to be semitransparent. As the transparency of the dispersion depends on the particle size, the size of nanohybrids must be larger than that of SiO₂ particles.

To evaluate the dispersion stability of SiO₂ nanoparticles and EVA/SiO₂ nanohybrids, their dispersions were left at room temperature until agglomeration appeared in the system, as stated in previously reported work. Figure 2c,d shows the dispersion state of SiO₂ nanoparticles and EVA/SiO₂ nanohybrids after a week of standing. It can be seen that

![Figure 2](https://example.com/figure2.jpg)
SiO$_2$ nanoparticles agglomerate together in the dispersion, and a mass of floccule appears in the microscopic image. While the EVA/SiO$_2$ suspension retains a semitransparent and homogeneous state, no coagulation is observed under microscope observation. SiO$_2$ nanoparticles tend to aggregate because of high surface energy and density, while the kinetics is delayed due to the adsorption of EVA on the SiO$_2$ nanoparticle surface in nanohybrid suspension. The dispersion stability results indicate that SiO$_2$ nanoparticles are not likely to be used as PPDs due to their poor dispersibility, while EVA/SiO$_2$ nanohybrids show the potential to improve fluidity of crude oil.

2.2. Effect of EVA and EVA/SiO$_2$ Nanohybrids on Wax Crystallization of Crude Oil. To comprehend the effect of EVA and EVA/SiO$_2$ nanohybrids on wax crystallization, DSC was used to examine WAT of crude oil samples. WAT is a crucial parameter to evaluate wax crystallization, which is defined as the temperature at which wax crystals begin to precipitate during cooling of crude oil.$^{36}$ As can be seen in Figure 3, the WAT of crude oil decreases gradually with the increase of EVA loading, achieving a reduction of 0.5 °C at 0.04 wt % EVA.

![Figure 3](image)

**Figure 3.** WAT of crude oil treated with EVA and EVA/SiO$_2$ nanohybrids (EVA is fixed at 0.02 wt % in the nanohybrid case).

It is supposed that the nonpolar groups of EVA copolymers co-crystallize with waxes, and then, the subsequent wax molecules cannot align in the same manner with the crystal lattice, yielding an overall distorted morphology. This underlying behavior theoretically suppresses the interaction between wax crystals, postponing the trace of wax crystals in crude oil.$^{37−40}$ Interestingly, the WAT of samples doped with EVA/SiO$_2$ nanohybrids decreases by 0.5−1.5 °C, implying that the introduction of SiO$_2$ nanoparticles into EVA copolymers further restrains the deposition of waxes. In our previous report, we found that SiO$_2$ nanoparticles tend to adsorb asphaltaltenes in model oil.$^6$ It is hypothesized that SiO$_2$ nanoparticles in the EVA/SiO$_2$ nanohybrids can also adsorb asphaltaltenes in crude oil, thus inhibiting the formation of wax crystals. In addition, EVA has been adsorbed onto the nanoparticles first, and so, it is in a well-dispersed state with an extremely high specific surface area. Therefore, the introduction of SiO$_2$ nanoparticles greatly boosts the efficiency of EVA.

As an efficient means to characterize the crystallization behavior of wax with a temperature variation, thermo XRD was used to monitor the crystallization of wax during temperature changes. Figure 4a,b shows the XRD pattern of undoped crude oil and crude oil doped with EVA with the change in temperature, and the diffraction peaks 6.04, 21.19, and 23.55° that appeared at 45 °C suggest that both start to crystallize between 55 and 45 °C.

However, crude oil doped with EVA/SiO$_2$ nanohybrids (Figure 4c) does not show these diffraction peaks until 35 °C, implying that crude oil doped with nanohybrids begins to crystallize between 45 and 35 °C. These results demonstrate that nanohybrids inhibit the appearance of wax crystals, so that the crystallization peaks appear at a lower temperature, which is in line with DSC findings. The diffraction peaks at 6.1° (006), 21.3° (110), and 23.5° (200) imply that the wax crystals of these samples belong to the orthorhombic system.$^{22,43}$ Further comparison of the intensity of crude oil doped with EVA and EVA/SiO$_2$ nanohybrids at 25 °C is shown in Figure 4d, and the effect of EVA and EVA/SiO$_2$ nanohybrids on the crystallization parameters of crude oil is analyzed below.

Table 1 shows the crystallization parameters of crude oil samples doped with EVA and nanohybrids at 25 °C, with the initial value acquired from Figure 4d. These parameters provide the information of interplanar spacing, crystallinity index, and grain size of wax crystal cells and can be calculated by the following eqs 1−7.$^{19,42−44}$

\[
\lambda = 2d_{hkl} \sin \theta_{hkl} \tag{1}
\]
\[
a = h \times d_{000} \tag{2}
\]
\[
c = l \times d_{000} \tag{3}
\]
\[
\frac{1}{d_{hkl}^2} = \frac{k^2}{a^2} + \frac{l^2}{b^2} + \frac{l^2}{c^2} \tag{4}
\]
\[
CI = \frac{\sum_{i=1}^{n} S_{hkl}}{S_{total}} \times 100\% \tag{5}
\]
\[
\Phi_{hkl} = \frac{Kl}{fwhm_{hkl}} \times \cos \theta_{hkl} \tag{6}
\]
\[ \Phi_{\text{average}} = \sum_{i=1}^{n} \Phi_{hkl} \times \frac{S_{hkl}}{\sum_{i=1}^{n} S_{hkl}} \]  

(7)

where \( d \) is interplanar spacing; parameters \( a, b, \) and \( c \) refer to the lattice arguments of wax crystals in \( x, y, \) and \( z \)-axis, respectively; \( h, k, \) and \( l \) stand for the Miller index of wax crystals; \( CI \) denotes the crystal index, that is, fraction of crystallization wax in oil; \( S \) represents the area of each diffraction peak; \( m \) represents the count of diffraction peaks; \( \Phi \) indicates the grain size of unit cell in wax crystals; \( K \) is a constant of 0.89; \( 2 \) full width at half-maximum (fwhm) means full width at half maxima; and \( \theta \) and \( \lambda \) are the diffraction angle and wavelength of X-ray (1.54056 Å), respectively.

It can be seen from Table 1 that the EVA copolymer enhances, while EVA/SiO₂ nanohybrids decrease the CI, demonstrating that only nanohybrids reduce the number of crystal cells. Clearly, the lattice parameter \( c \) is significantly larger than \( a \) and \( b \), indicating that the crystal cell in crude oil is needle-like. The lattice parameters \( a \) and \( b \) decrease slightly, while \( c \) drops significantly, which reveals that EVA copolymers and EVA/SiO₂ nanohybrids mainly decrease the size of crystal cells by inhibiting their extension along \( z \)-axis.

The effect of nanohybrids is more profound than that of the EVA copolymer. Compared with undoped crude oil, the grain size of crystal cells in (006) decreases obviously but rises a little in (110) with the addition of EVA/SiO₂ nanohybrids, whereas the addition of EVA decreases the grain size slightly in all three sections. From these results, it can be concluded that the mechanism of EVA differs from that of EVA/SiO₂ nanohybrids. For the EVA copolymer, the crystal index is increased and the grain size of the crystal cell is decreased in all three cross sections; for EVA/SiO₂ nanohybrids, the crystal index is decreased and the grain size of the crystal cell is decreased in (006) and (200) but increased in (110). Therefore, both EVA copolymers and EVA/SiO₂ nanohybrids modify the morphology of crystal cells, but the mechanism differs as discussed above.

To visualize the microstructures of crystal aggregates, POM was adopted to study the crystallizing behavior of crude oil. As depicted in Figure 5a,b, the wax crystal aggregates of crude oil without any additive are diminutive and concentrated, and a continuous three-dimensional network arises due to the aggregation of crystal cells, leading to the poor fluidity and high viscosity of crude oil.

After the addition of the EVA copolymer, the crystal aggregates increase in size, as depicted in Figure 5c,d. Meanwhile, the morphology of these crystals becomes more regular, inhibiting the formation of 3D networks accordingly. Interestingly, it is observed in Figure 5e,f that the crystal aggregates become sparser and more discrete in crude oil samples mixed with EVA/SiO₂ nanohybrids. Figure 5g exhibits the crystal size distribution in crude oil doped with EVA. The number of crystals is about 242 per square millimeter, with the mean diameter around 22.69 μm. While the crystal distribution of crude oil doped with nanohybrids (Figure 5h) is approximately 126/mm², almost half of crude oil doped with EVA, indicating that EVA/SiO₂ nanohybrids indeed reduce the number of wax crystals. In addition, the standard deviation (\( \sigma \)) of crystal size in crude oil doped with nanohybrids is higher than that of crude oil doped with EVA. It is speculated that the
The morphology of the wax crystal aggregates is affected by the structure of crystal cells. As verified in XRD characterization, the growth of crystal cells in the z-axis direction is significantly inhibited after adding EVA and nanohybrids, which changes the orientation of the wax crystal aggregates. Simultaneously, the distribution of wax crystal aggregates in crude oil added with nanohybrids is sparser, which is consistent with its lower CI. The morphology of crystal aggregates is also deeply affected by the interaction between additives and crude oil components. Our previous studies have shown that SiO₂ nanoparticles can serve as nucleuses to adsorb asphaltenes and resins, restraining appearance of wax crystals. Meanwhile, the specific surface area of EVA adsorbed on SiO₂ nanoparticles is enlarged, providing more sites for co-crystallization with the waxes, so that the size of the wax aggregates becomes larger and the number thereof is reduced accordingly. Besides, there are many studies demonstrating that nanoparticles provide heterogeneous nucleation sites for the crystalline precipitation of wax molecules. Therefore, EVA/SiO₂ nanohybrids make wax crystals more dispersed, so that the flowability of crude oil will be improved.

Compared with studies of nanohybrids applying model oil, the crystallization behavior in crude oil is different in many ways. In this study, WAT of crude oil drops first and then rises slowly with the increasing concentration of nanohybrids, while a previous study using model oil gained a persisting declination in WAT with the addition of nanohybrids. SiO₂ nanoparticles can adsorb asphaltenes and resins in crude oil as crystal nucleus, so that the deposition of wax crystals is inhibited; meanwhile, nanoparticles can also serve as nucleation sites for the crystallization of wax molecules. Due to the complexity of crude oil, the interaction among nanoparticles and other components is sophisticated and unpredictable, such as the agglomeration of nanoparticles and the formation of large aggregates, and an increase in the concentration of nanoparticles will foment these intricacies, and so, there is an effective saturation concentration of nanoparticles. In addition, the wax crystals are needle-like in model oil, but the POM imaging shows the crystals assemble to be spherical particles in crude oil. The reason is that the asphaltenes in crude oil will adsorb wax crystals, so that the self-assembly of wax crystals tends to be isotropic. While asphaltenes are usually absent in model oil to better visualize wax crystals, which keeps them in their original crystal shape. This part demonstrates that the complex composition of crude oil, especially the existence of asphaltenes and resins,
makes the crystallization behavior of wax different from that of model oil. Combined with our previous findings employing model oil,\textsuperscript{6} the interaction mechanism is outlined in Scheme 1.

2.3. Effect of EVA and EVA/SiO\textsubscript{2} Nanohybrids on Rheological Behavior of Crude Oil. To simulate the shear flow of crude oils, rheological tests for both EVA- and nanohybrid-doped samples were carried out. First, we investigated the effect of EVA concentration on the rheological response of crude oil. The temperature scanning in viscosity of crude oil mixed with various amounts of EVA is presented in Figure 6a, and viscosity data ranging from 20 to 80 °C are selected in the results, in order to eliminate the hysteresis effect at the beginning and end of the heating process. One can find that the viscosity of crude oil increases with the drop of temperature, implying the crystallization process of wax. At the temperature lower than the inflection point of 32.7 °C, a rapid viscosity growth is observed. The occurrence of inflection point indicates that the wax crystals have begun to interact with each other, forming a stable three-dimensional network structure, and the flow behavior of crude oil transits from Newtonian to non-Newtonian nature. The inflection point decreases from to 32.7 to 27.4 °C when the amount of EVA increases from 0 to 0.02 wt %, as shown in Figure 6b.

In addition, the viscosity reduction rate of samples at 25 °C with different EVA contents is also shown in Figure 6b. A slump of 86.9% at 0.02 wt % is observed, but the viscosity reduction begins to decline slowly with the further addition of EVA. When EVA concentration is lower, the nonpolar polyethylene backbone of EVA crystallizes with paraffin wax in crude oil, changing the orientation of wax crystals.\textsuperscript{21} As a consequence, the wax crystals are less likely to form a three-dimensional network, resulting in a decrease in viscosity and inflection point. However, the high molecular weight EVA copolymers tend to increase the viscosity of crude oil with the increase in EVA concentration, as no excess wax crystals co-crystallize with EVA. Therefore, there is a competition between the viscosity reduction caused by the co-crystallization effect of EVA and the viscosity enhancement caused by the excess EVA copolymers. It can be seen from Figure 6 that the co-crystallization effect of EVA is dominant when the EVA concentration is below 0.02 wt %, while the viscosification caused by EVA comes into play when the EVA concentration is above 0.02 wt %. Consequently, EVA concentration is fixed at 0.02 wt % in the following study of nanohybrids.

Next, the effect of nanohybrids with varied SiO\textsubscript{2} content on rheological behavior of crude oil was studied, and the concentration of EVA was fixed at 0.02 wt %. The viscosity−temperature relationship for crude oil mixed with nanohybrids is depicted in Figure 7a, and the viscosity reduction at 25 °C of samples and inflection point are plotted in Figure 7b. It can be observed that the viscosity and inflection point reduce significantly after adding nanohybrids into crude oil. The sample treated with 0.04 wt % SiO\textsubscript{2} outperforms others, whose inflection point decreases from 32.7 to 24.1 °C and viscosity at 25 °C drops by 92.7%. However, when SiO\textsubscript{2} content exceeds 0.04 wt %, the viscosity and inflection point of crude oil begin to rise slowly, indicating that there is an optimal concentration of nanoparticles. Consequently, the higher feed ratio (>0.04 wt %) of SiO\textsubscript{2} nanoparticles will decrease the fluidity of crude oil. Interestingly, the reduction ratio of crude oil doped with EVA/SiO\textsubscript{2} nanohybrids in the inflection point and viscosity is larger than that of EVA,
indicating that the introduction of SiO2 nanoparticles slows down the viscosity decay of the EVA system. Then, we studied the effect of EVA/SiO2 nanohybrids on the dynamic yield stress ($\tau_d$) of crude oil. $\tau_d$ is defined as the minimum shear stress required to keep the crude oil flowing, which is a key parameter in pipeline transportation. 35,46 The test temperature in our study was 17 °C, at which the crude oil is doubtlessly nonflowable. For crude oil doped with EVA, the yield stress shown in Figure 8a reduces from 98.03 to 29.77 Pa and achieves a maximum reduction of 69.67% at 0.03 wt % EVA, as shown in Figure 8b.

After introducing EVA/SiO2 nanohybrids to crude oil, the yield stress drops from 98.03 to 22.67 Pa, giving a maximum reduction of 76.89% when SiO2 content is 0.04 wt %, as exhibited in Figure 9a,b. It is well recognized that EVA is able to reduce the yield stress of crude oil through weakening the interaction among wax crystals.20 The introduction of SiO2 particles into the EVA system can further prevent the three-dimensional network structure formation of wax crystals, so that the EVA/SiO2 nanohybrids perform better in yield stress reduction than EVA copolymers.

Finally, the effect of EVA/SiO2 nanohybrids on the pour point of crude oil was studied, as shown in Figure 8b. It is observed that the pour point reduces from 24 to 18 °C with the addition of EVA increasing from 0 to 0.02 wt %. However, the pour point rises again when the EVA concentration exceeds 0.02 wt %. EVA can co-crystallize with wax in crude oil and inhibit wax crystals, forming a three-dimensional network. When the concentration of EVA is above 0.02 wt %, the excess EVA copolymers will precipitate from crude oil to increase the viscosity of the system, thus increasing the pour point of crude oil. The pour point of crude oil mixed with nanohybrids drops from 24 to 17 °C with the SiO2 content increasing from 0 to 0.04 wt %. However, the pour point rises again when the SiO2 feed ratio exceeds 0.04 wt %. When the SiO2 feed ratio is above 0.04 wt %, SiO2 nanoparticles can adsorb asphaltenes and resins to suppress wax depositing from crude oil, thus decreasing the pour point of oil samples.6 When the SiO2 feed ratio is above 0.04 wt %, the excess of nanohybrids tend to interact with each other, so that the PPD effect of nanohybrids is weakened. It seemed that the pour point depressing effect of EVA and nanohybrids is not much different, indicating that nanohybrids are not superior to EVA in every aspect.

The rheological behavior of crude oil doped with nanohybrids is also inconsistent with that of model oil in previous research. It was reported that the rheological parameters of the model oil, including viscosity, yield stress, and pour point, were gradually improved with the concentration increase of nanoparticles. While an optimized dosage of SiO2 nanoparticles is gained in this work, above which the flowability of crude oil would be weakened. The nanoparticles in crude oil can adsorb asphaltenes and suppress the formation of wax crystals, but nanohybrids tend to aggregate and precipitate with the increasing concentration, due to no excess asphaltenes co-crystallizing with SiO2 when the nanohybrid content exceeds its saturation concentration, and therefore, the adsorption of asphaltenes is restricted. Besides, we investigate the effect of nanohybrids on dynamic yield stress rather than static yield stress in other literature.20,26 The dynamic yield stress is the minimum shear stress required to keep the crude oil flowing, while the static yield stress is defined as the minimum shear stress required for the crude oil to flow again under quiescent conditions. It is clear that the time of crude oil to keep flowing during pipeline transportation is longer than that of crude oil to restart under static conditions, so that the dynamic yield stress is an important factor in crude oil transportation. Also, the results of the controlled stress test proved that nanohybrids are beneficial to keep the crude oil flowing, bringing an inspiration for pipeline transportation of crude oil.

3. CONCLUSIONS

In this work, the crystallization behavior of crude oil doped with EVA and EVA/SiO2 nanohybrids was studied by DSC, POM, and thermo XRD. It was found that nanohybrids outperformed EVA in reducing the WAT of crude oil, and the crystal modification mechanism of EVA differed from that of EVA/SiO2 nanohybrids. POM results revealed that EVA could adjust the morphology of wax crystals to be more regular, so that wax crystals became sparser and more discrete. Consequently, the introduction of SiO2 nanoparticles greatly boosts the co-crystallization efficiency of EVA.

EVA/SiO2 nanohybrids decreased the viscosity, inflection point, and yield stress of crude oil, and it behaved better than EVA copolymers. The results showed that there is an optimal dosage of EVA for Shengli crude oil at about 0.02 wt %, and nanohybrids performed the best at the SiO2 content of 0.04 wt %. Viscosity tests and pour point measurements indicated that SiO2 nanoparticles and EVA copolymers can work synergistically in improving crude oil fluidity. The controlled stress tests
demonstrated that nanohybrids are beneficial for the crude oil to keep flowing, which provided an inspiration for the transportation of crude oil in pipelines.

Compared to previous literature of nanohybrid flow improvers, it is found that the flow assurance mechanism of nanohybrids in crude oil is different from that of model oil, due to the complexity of crude oil composition. The asphaltenes and resins in crude oil are easily adsorbed onto waxes, so that the needle-like wax crystals in model oil are adjusted to be sphere-like in crude oil. The nanoparticles in crude oil can adsorb asphaltenes and suppress the formation of wax crystals, but nanohybrids tend to aggregate and precipitate with the increasing concentration. Therefore, an optimized amount of SiO$_2$ is acquired. This work provides oilfield workers with more field-appropriate rheological data and helps to develop more practical flow improvers.

4. EXPERIMENTAL SECTION

4.1. Materials. Xylene (AR), n-octadecane (99%) and EVA (VA = 32%) were acquired from Aladdin (Shanghai, China). The hydrophobic fumed SiO$_2$ nanoparticles with a specific surface area 170–230 m$^2$g$^{-1}$ and average primary particle size $\sim$12 nm were procured from Waker Chemie AG (München, Germany) under the trade name HDK H18. The waxy crude oil was provided by Shengli Oilfield Branch Company of Sinopec (Dongying, China).

4.2. Sample Preparation. 4.2.1. Preparation of EVA/SiO$_2$ Nanohybrids. To prepare the nanohybrids, a designed amount of SiO$_2$ nanoparticles were added into 19 g of xylene, followed by 3 h of stirring and 1 h of sonication at 25 °C. Then, a specified mass of EVA was put into the dispersion and agitated for 3 h. The total concentration of SiO$_2$ and EVA was fixed at 5 wt % in xylene, with the SiO$_2$/EVA mass ratio increasing from 1:10 to 1:2.

4.2.2. Doping Crude Oil with EVA or Nanohybrids. The crude oil samples were first heated in an oven to 80 °C and kept for 1 h. Then, the samples were taken out, cooled to room temperature, and finally put in a dark place at room temperature for 24 h. Then, different amounts of EVA or nanohybrids were added into the treated crude oil to prepare a series of test samples. The concentration of EVA varied from 0.01 to 0.05 wt % in crude oil. For crude oil doped with nanohybrids, the EVA content was fixed at 0.02 wt %, with SiO$_2$ varied from 0.02 to 0.1 wt %. In addition, SiO$_2$ nanoparticles did not separate out in the dispersion before doping crude oil with nanohybrids.

4.3. Characterization. 4.3.1. Composition Analysis of Crude Oil. The carbon number distribution of Shengli crude oil was analyzed on an Agilent 7890A gas chromatograph (Agilent Technology, USA), and the family composition analysis of crude oil was conducted according to the China Petroleum and Natural Gas Industry Standard SY/T 5119-2016. One can find that the hydrocarbon is widely dispersed inside the crude from C$_5$ to C$_{40}$ (Figure 10). In addition, the wax in this type crude oil is 34.35 wt %, and the amount of asphaltenes and resins reaches 15.91 wt %.

4.3.2. Microscope imaging. The morphology of SiO$_2$ nanoparticles and EVA/SiO$_2$ nanohybrids was observed using a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI, USA) and an Apreo 2C scanning electron microscope coupled with EDS (FEI, USA). The latter was also employed to analyze the elemental composition of the nanoparticle surface. The specimens were prepared by dropping and dispersing SiO$_2$ nanoparticles or EVA/SiO$_2$ nanohybrids onto the aluminum foil, followed by irradiation with X-ray to obtain the elemental distribution. The accelerating voltages of TEM and SEM adopted in this work are 200 kV and 20 kV, respectively. The dispersion state of SiO$_2$ nanoparticles and nanohybrids in xylene was visualized via a digital microscope system KEYENCE VHX-1000C (Keyence Co., Japan).

4.3.3. Characterization of Wax Crystals. The crystallization behavior of wax was recorded on an Empyrean Thermo X-ray diffractometer (PANalytical, Netherlands) using Cu Kα radiation ($\lambda = 1.54056$ Å) with a tube voltage of 40 kV. Concretely, the samples were heated to 55 °C and then cooled to 25 °C at a rate of 0.5 °C·min$^{-1}$, and XRD patterns were registered during the cooling process.

Differential scanning calorimetry (DSC) analysis was conducted on a TA-Q200 differential scanning calorimeter (TA Instruments, USA) in the temperature range from 85 to −20 °C at a cooling rate of 5 °C·min$^{-1}$. The size and shape of wax crystals in different crude oil samples were observed at 25 °C on a LECICA DM2500P polarized optical microscope equipped with a Pixelink CCD/C莫斯 camera. Samples spread on slides were initially heated to 80 °C for 5 min to remove thermal history and then were cooled to 25 °C at a rate of 5 °C·min$^{-1}$.

4.3.4. Determination of Pour Point. The pour point of the crude oil doped with EVA or nanohybrids was determined according to the China Petroleum and Natural Gas Industry Standard SY/T 0541-2009. Before the test, the crude oil was preheated to 80 °C and kept for 1 h to eliminate the thermal history. During the test, the crude oil sample was first kept in a test tube at 60 °C for at least 1 h. Then, the sample was cooled at a constant rate of 1 °C·min$^{-1}$. When the temperature was close to 50 °C, the test tube was taken out to observe the flowability of the system for each 2 °C drop. As the sample was cooled near the expected pour point, observations were taken at each 1 °C interval. The temperature at which the sample did not flow (even when the test tube was placed horizontally for 5 s) was recorded as the pour point.

4.3.5. Rheological Test. The rheological flow of samples was performed on a rotational rheometer MCR 302 (Anton Paar, Austria) equipped with a CC27 (ISO3219) concentric cylinder system and a thermostat for temperature control. Before performing the test, the crude oil samples were preheated for at least 1 h at 80 °C to remove their thermal history and then loaded in the rheometer cell to start the test. Afterward, the samples were sheared for 5 min at 90 °C with a constant shear rate 30 s$^{-1}$, followed by the decreasing temperature from 90 to
14 °C with a cooling rate of 0.5 °C·min⁻¹ for temperature scanning. During the rheological test, there is a sealing cover on the rheometer cell to prevent the volatilization of the samples.

The yield stress of crude oil was obtained by a curve extension procedure as reported previously. In detail, the yield stress of oil samples was detected with controlled stress mode by gradually increasing the shear rate on the same rotational rheometer mentioned above. Following the heating process, the samples were preheated to 80 °C at a rate of 0.5 °C·min⁻¹ and remained at 17 °C for 10 min. Finally, the corresponding shear stress with the shear rate increasing from 0.02 to 100 s⁻¹ was recorded at 17 °C.

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