

Article

Influence of Chemical Grafting Method on the Performance of SiO₂ Nanocomposite Pour Point Depressant

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Abstract: Differences in the synthesis methods can affect the performance of nanocomposite materials. The synthesis methods of SiO₂-based nanocomposite pour point depressants synthesized by chemical hybrid are mostly in situ polymerization and chemical grafting. However, there are still some gaps in the synthesis of nanocomposites using chemical grafting. In this paper, the amino-modified Nano-SiO₂ and octamethyl methacrylate-maleic anhydride copolymer was used to prepare PM18-g-NSiO₂ by an amidation reaction, and the product was compared with PM18/SiO₂ prepared by the solution blending method. The characterization results of FT-IR and SEM showed that the chemical bond formed between PM18 and NSiO₂ and PM18-g-NSiO₂ showed a more regular morphology structure. The results of rheological tests showed that the optimal concentration of PM18-g-NSiO₂ and PM18/SiO₂ is 300 mg·kg⁻¹, but the decrease of PM18-g-NSiO₂ is 19 °C, while the decrease of PM18/SiO₂ is only 13 °C. The lowest viscosity of model oil added PM18-g-NSiO₂ was only 214 mPa·s while PM18/SiO₂ reached 453 mPa·s. The wax crystal structure after adding PM18-g-NSiO₂ is also more regular and smaller compared to PM18/SiO₂. We concluded that differences in the synthesis methods may lead to the different coverage of the polymer on the surface of the nanoparticle.

Keywords: nano-SiO₂; polymethacrylate; nanocomposite pour point depressant; flow properties; wax crystal



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1. Introduction

Unconventional crude oil occupies an important proportion of crude oil production. As a kind of unconventional crude oil, the significance of waxy crude oil in production and life is also obvious [1]. In order to solve the problem that wax crystals are easy to precipitate, connect and deposit at low temperatures due to the high paraffin content of waxy crude oil, which leads to economic losses and serious safety risks [2,3], the chemical reagent method has gradually become the focus of research due to its advantages of low cost and high efficiency. Pour point depressant (PPD) is a commonly used chemical reagent [4,5]. Polymethacrylate [6,7] is a typical comb-like polymer PPD. Because of its long side chain alkyl structure, it is easy to crystallize with wax and has an excellent effect of pour point reduction and the function of shear resistance. However, the complexity of crude oil composition leads to the selectivity of polymer PPDs for crude oil, which means single polymer PPDs cannot satisfy the needs of various types of crude oil [8]. For this problem, the common modification method is to introduce new monomers [9–11] or perform nanohybridization [12–14].

Because it is cheap and easy to obtain and has stable properties as well, Nano-SiO₂ is widely used to modify polymer PPDs. The synthesis methods of nanocomposite pour point depressants (NPPDs) can be divided into the physical blending method (solvent blending method [15], melt blending method [16]) and chemical hybrid method (chemical grafting method [17], in-situ polymerization method [18]). Yao et al. [19,20] found that different physical mixing methods can lead to different sizes of modified nanoclay/POA

nanocomposites, which affects the dispersity in crude oil. Yang's research group [21,22] also found that the melt blending method enhanced the interaction between polymer and nanoparticles, thus promoting the adsorption of polymer and further enhancing the nucleation of EVA. These results all indicate that the different synthesis methods of the nanocomposite particles can affect the properties of the nanocomposite materials.

The nanocomposites synthesized by SiO₂ are mainly prepared by the physical blending method [23–25], but the physical blending method is faced with the problem of poor compatibility between the nanoparticles and polymer. Norrman [26] and Yang [27] et al. showed that when the POA/SiO₂ NPPD was formed by solution blending, POA was adsorbed to the surface of nanosilica by mono-layer adsorption, and the coverage of POA was an important factor affecting the performance of NPPDs. However, for long-distance pipeline transportation, POA is easy to desorb from the nanosilica surface, thus reducing the properties of nanocomposites. In order to improve dispersion and stability, NPPDs synthesized by the chemical hybridization method mainly use carbon-carbon double bonds for in-situ polymerization [28]. However, there are still some problems with complex processes, requiring additional reagents and low yield. Compared with in-situ polymerization, the chemical grafting method provides a new approach for the industrialized production of high-performance nanocomposite pour point depressants due to its mild synthesis conditions and simple operation. Liu [17] used the esterification reaction to branch GO with EVAL. The results showed that EVAL-GO had good oil dispersion and compatibility with organic solvents. EVAL-GO has a better effect than EVAL on the waxy crude oil and significantly improves the low-temperature fluidity of Daqing waxy crude oil. Due to the low price of nano-silica, it has potential market value to study the preparation of high-performance silica nanocomposite pour point depressants by the chemical grafting method.

So, in order to obtain a simpler and more rapid method of preparing polymethacrylate/nano-SiO₂ NPPDs, polymethacrylate/nanosilica NPPDs were prepared by an amidation reaction for chemical grafting. By co-polymerizing MAH and methacrylate high carbon alcohol esters, a certain amount of anhydride group is introduced in the methacrylate polymer and then reacted with amino-modified nano-silica to obtain the desired product. At the same time, this paper compared the nanoparticles synthesized by the solution blending method with the chemical grafting method. By comparing with the NPPDs prepared by the traditional solution blending method, we found that the nanocomposite particles synthesized by the grafting method show better oil dispersion and stability, and their effect is also more excellent, which further proves that the different synthesis methods of NPPDs will affect the performance of NPPDs.

2. Materials and Methods

2.1. Materials

Nanosilica (average particle size 30 nm), Octadecyl methacrylate (AR), 3-Aminopropyl triethoxysilane (KH550) (AR), dodecane (AR), maleic anhydride (AR) and Dibenzoyl peroxide (BPO) (CP) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Ethanol (AR) was purchased from Shenyang Huadong Reagent Factory (Shenyang, China). Toluene (AR) was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). -35# diesel was obtained by PetroChina Co., Ltd. (Beijing, China). 59# paraffin was supplied by Daqing Petrochemical Company (Daqing, China).

2.2. Sample Preparation

2.2.1. Preparation of Octadecyl Methacrylate/Maleic Anhydride Copolymer (PM18)

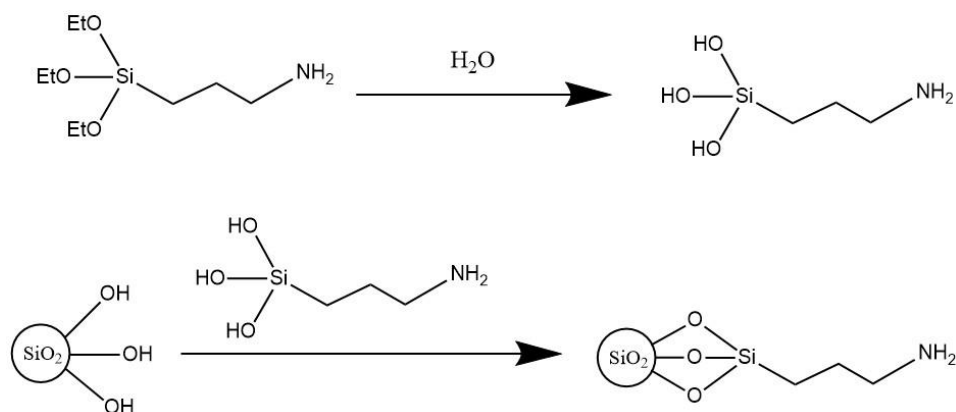
The reaction used toluene as a solvent, and BPO as an initiator. PM18 was prepared from Octadecyl methacrylate and maleic anhydride (where the molar ratio between Octadecyl methacrylate and maleic anhydride is 6:1) in a three-neck flask. The reaction continued for 6 h at 80 °C. Finally, the products were washed several times with cold methanol solution. PM18 was obtained after the solid was vacuum-dried [29].

2.2.2. Preparation of PM18/SiO₂ Nanocomposite Pour Point Depressant

PM18 was added into toluene, stirring with ultrasound at 60 °C until PM18 was completely dissolved. SiO₂ whose mass is equaled to PM18 was added into the solution, stirring with ultrasound for 3 h at 80 °C. Finally, PM18/SiO₂ NPPDs were separated by vacuum distillation.

2.2.3. Preparation of Amino Modified Nanosilica

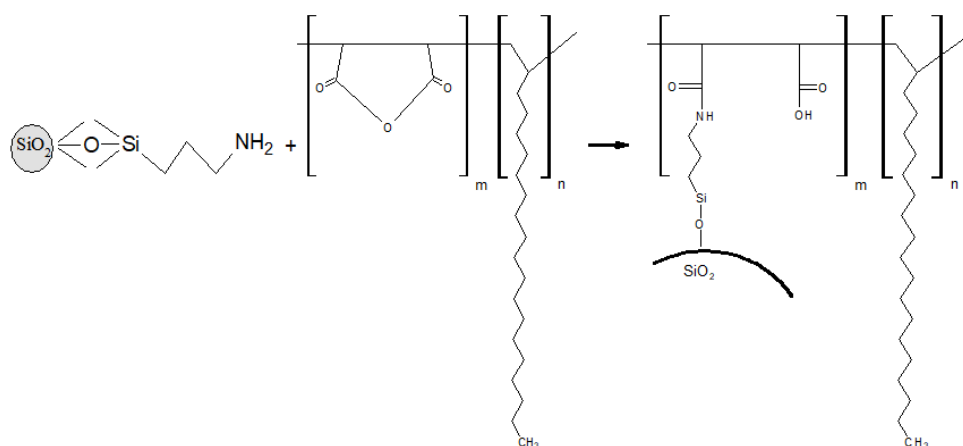
Aminated NanoSilica was modified with silane coupling agent KH550 via grafting the amino group onto the surface of Nano-SiO₂. The reaction steps are as follows: KH550 whose weight is 5 wt% of Nano-SiO₂ was added into a three port flask containing ethanol aqueous solution (where the mass ratio between ethanol and water is 9:1), and stirred at 30 °C for 1.5 h. Then nano-SiO₂ was added to the above solution. After ultrasonic stirring for 0.5 h, the mixture was heated to 75 °C and then refluxed for 3 h. The finished solution was separated by centrifugation to obtain the product. The solid was washed using ethanol and deionized water 2~3 times, respectively, and then dried in a vacuum at 50 °C for 12 h to obtain amino modified SiO₂. After grinding, the amino modified nano SiO₂ was labeled as NSiO₂. The modification mechanism is shown in Scheme 1.



Scheme 1. Synthesis Mechanism of NSiO₂.

2.2.4. Preparation of PM18-g-NSiO₂ Nanocomposite Pour Point Depressant

PM18 was weighed and added into toluene, stirring it with ultrasound at 60 °C until PM18 was completely dissolved, then NSiO₂ whose mass is the same as PM18 was added into the solution, stirring it with ultrasound for 3 h at 90 °C. The product was separated by vacuum distillation and washed several times with a methanol solution to obtain PM18-g-NSiO₂ NPPD. The specific synthesis mechanism is shown in Scheme 2.



Scheme 2. Synthesis Mechanism of PM18-g-NSiO₂.

2.2.5. Preparation of Waxy Model Oil

-35# diesel oil was used as solvent oil. A certain amount of 58# paraffin section was added to -35# diesel oil (the mass ratio between 58# paraffin and -35# diesel oil is 3:17), then stirred at 70 °C for 2 h to mix paraffin components and diesel oil. After that, the mixture was cool to room temperature.

2.3. Characterization

2.3.1. Nanocomposite Pour Point Depressant Properties Characterization

The NPPDs were analyzed by Fourier transform infrared (FT-IR) spectrometry (TENSOR27, Bruker, Germany), Scanning Electron microscopy (SEM) analysis (Σ IGMA scanning electron microscope, Zeiss, Jena, Germany).

2.3.2. Model Oil Properties Characterization

Pour Point Test

The pour point of the model oil before and after dosing was measured using the Chinese petroleum and natural gas industry standard SY/T 0541-94 [30]. First, the model oil is kept constant for 1 h in a water bath at 60 °C. Then a certain quality of model oil and PPD were mixed and stirred evenly at 60 °C for 0.5 h. The sample was put into the pour point measuring device and was cooled at the cooling rate of 0.5 °C/min. When the temperature reached 50 °C, the measuring tube was taken out and tilted 45° after each 2 °C temperature drop. When the sample temperature was close to the estimated pour point, the above steps were repeated after each 1 °C temperature drop. When the measuring tube is tilted for 5 s, and the oil sample remains stationary, the temperature can be recorded as the pour point of the sample. For each sample, the test was repeated three times.

Viscosity Curves Test

The rheological properties of model oil without and after the addition of the agent were measured by Brookfield rotational viscometer (DV-II+Pro) equipped with a heating/cooling system. First, the model oil was kept for 1 h in a water bath at 60 °C. Model oil and PPD were mixed and stirred evenly at 60 °C for 0.5 h. The sample was put into the measuring device while cutting for 5 min at a constant shear rate of 20 S⁻¹. The apparent viscosity was measured from 60 °C to 20 °C at a cooling rate of 0.5 °C/min.

Polarized Optical Microscopy (POM)

The results of POM can effectively observe the morphological changes of wax crystals before and after adding PPDs [31]. A polarizing microscope fitted with an IMc5 camera (Zeiss, Germany) was used to test the model oil. The model oil which had been heated for 1 h at 60 °C was stirred for 0.5 h at 60 °C each time after adding agents. The sample was put into the sample table and cooled to 15 °C at a cooling rate of 0.5 °C/min for observation. The same steps were finished after treating PPDs.

3. Results

3.1. Characterization Analysis

3.1.1. FT-IR Analysis

The FT-IR spectra of PM18, PM18/SiO₂ and PM18-g-NSiO₂ are shown in Figure 1. According to the FT-IR spectrum of PM18, the stretching vibration peaks of C-H provided by octadecyl methacrylate are at 2847 cm⁻¹ and 2924 cm⁻¹. The C=O stretching vibration peak of octadecyl methacrylate is at 1730 cm⁻¹, and the C=O and C-O-C stretching vibration peaks of maleic anhydride are at 950 cm⁻¹ and 1780 cm⁻¹. The above absorption peaks show that the product is the target product. As shown in Figure 1b–d, SiO₂, PM18/SiO₂ and PM18-g-NSiO₂ display Si-O-Si bending and stretching vibration peaks at 800 cm⁻¹ and 1096 cm⁻¹. Both PM18/SiO₂ and PM18-g-NSiO₂ have the characteristic absorption peaks of PM18 at 1730 cm⁻¹, 2847 cm⁻¹ and 2924 cm⁻¹ [32]. These

results combined with the results of SEM indicated that PM18 had been successfully covered on the surface of nano silica. Compared with Figure 1c,d, PM18-g-NSiO₂ displays a new characteristic absorption peak belonging to amide N-C=O that appeared at 1640 cm⁻¹, indicating that the NSiO₂ surface formed a chemical bond with PM18 in PM18-g-NSiO₂ [33].

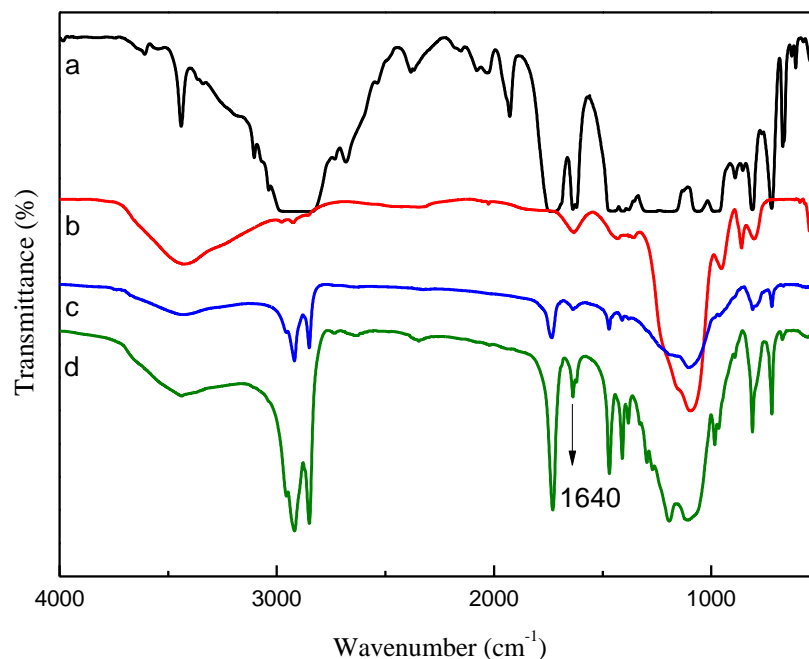


Figure 1. FT-IR spectra of (a) PM18; (b) SiO₂; (c) PM18/SiO₂; (d) PM18-g-NSiO₂.

3.1.2. SEM Analysis

The SEM picture of the NPPD dispersed in dodecane solvent after 48 h is shown in Figure 2. It can be seen from Figure 2A that the unmodified nano silica agglomerated seriously because the surface energy of nano silica is large, and the surface of nano silica is rich in active hydroxyl groups, which can be bonded to each other through hydrogen bonding. As shown in Figure 2B,C, when a certain amount of PM18 is coated on the surface of nanosilica, the size of nanosilica increases while the surface energy decreases, and the agglomeration of nanoparticles is improved [34]. It is worth noting that comparing the morphology of PM18/SiO₂ and PM18-g-NSiO₂, the morphology of PM18-g-NSiO₂ is more regular, and the particle size is larger and the dispersion is more uniform. Combined with the result of FT-IR that PM18 did not form a chemical bond with unmodified SiO₂ and the conclusion of monolayer adsorption by Jing [23] and Norrman [26], we may suppose that the nanosilica in PM18/SiO₂ prepared by physical adsorption alone has poor compatibility with PM18. When PM18/SiO₂ is dispersed in dodecane solvent for a period of time, part of PM18 will be desorbed from the surface of the nanosilica, reducing the stability of PM18/SiO₂ in organic solvents and causing the agglomeration of nanocomposites; In PM18-g-NSiO₂, because of the stable chemical bond formed between the surface of nano silica and PM18, PM18 is firmly wrapped on the surface of the nanosilica, which improves the stability of PM18-g-NSiO₂ in organic solvents.

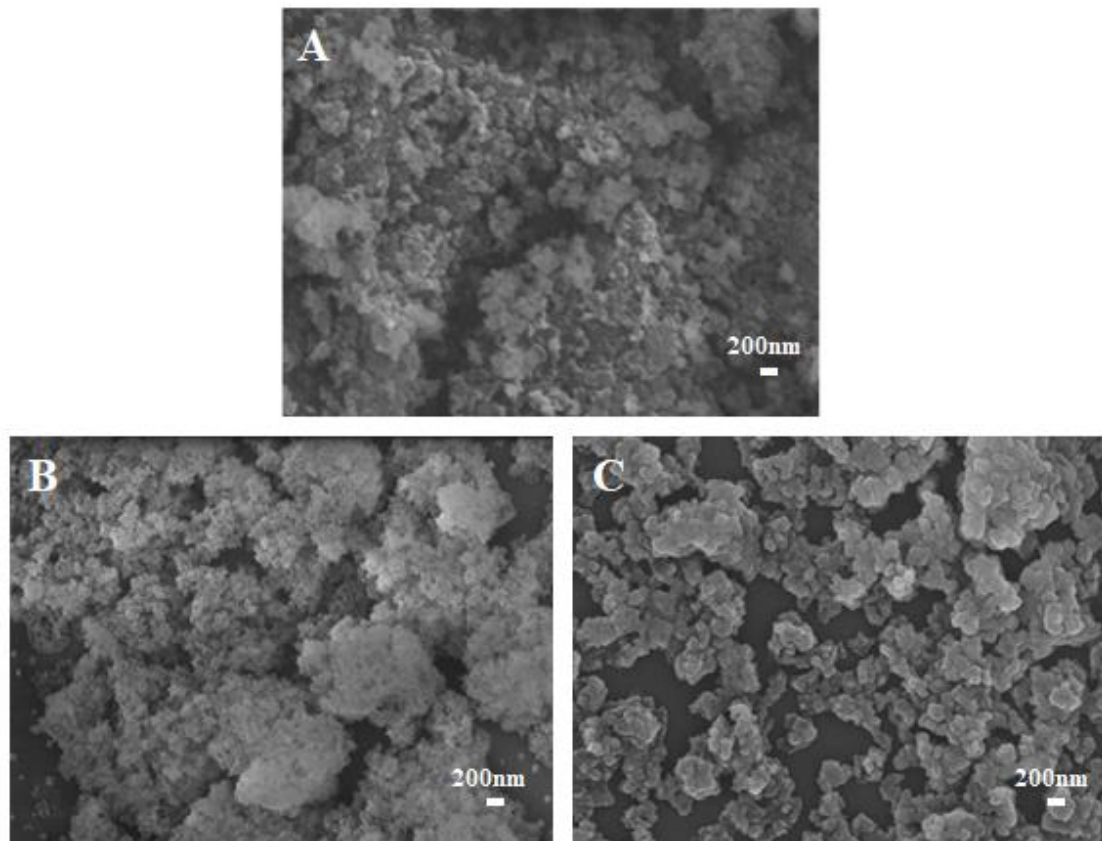


Figure 2. SEM images of SiO₂ and NPPDs dispersed in dodecane after 48 h: (A) SiO₂; (B) PM18/SiO₂; (C) PM18-g-NSiO₂.

3.2. Effect Evaluation of Nano-SiO₂ PPD Synthesized by Different Method on Model Oil

3.2.1. Pour Point

The pour point change of 15 wt% wax-containing model oil after adding different kinds and doses of PPDs is shown in Figure 3. With the increase in PPD dose, the pour point of model oil shows a trend of decreasing first and then increasing. At the same time, compared with the traditional methacrylate PPD PM18, the optimal dosage of NPPD is significantly reduced, and all NPPDs show a better effect on decreasing the pour point. The best pour point depressing performance is obtained with a 300 mg·kg⁻¹ dosage of PM18/SiO₂ and PM18-g-NSiO₂, in which the pour point drops from 30 °C to 17 °C and 11 °C, respectively. At the same time, compared with the same dosage of PM18/SiO₂, PM18-g-NSiO₂ can further improve the low-temperature fluidity of oil. This is because the coverage of polymer on the surface of nanoparticles is the key factor to determine the effect of NPPD. Compared with simple physical adsorption, making the surface of nanoparticles form a stable chemical bond with polymer through grafting can effectively improve the stability of polymer on the surface of nanoparticles, prevent polymer shedding from the surface of nanoparticles, and effectively improve the effect of NPPD.

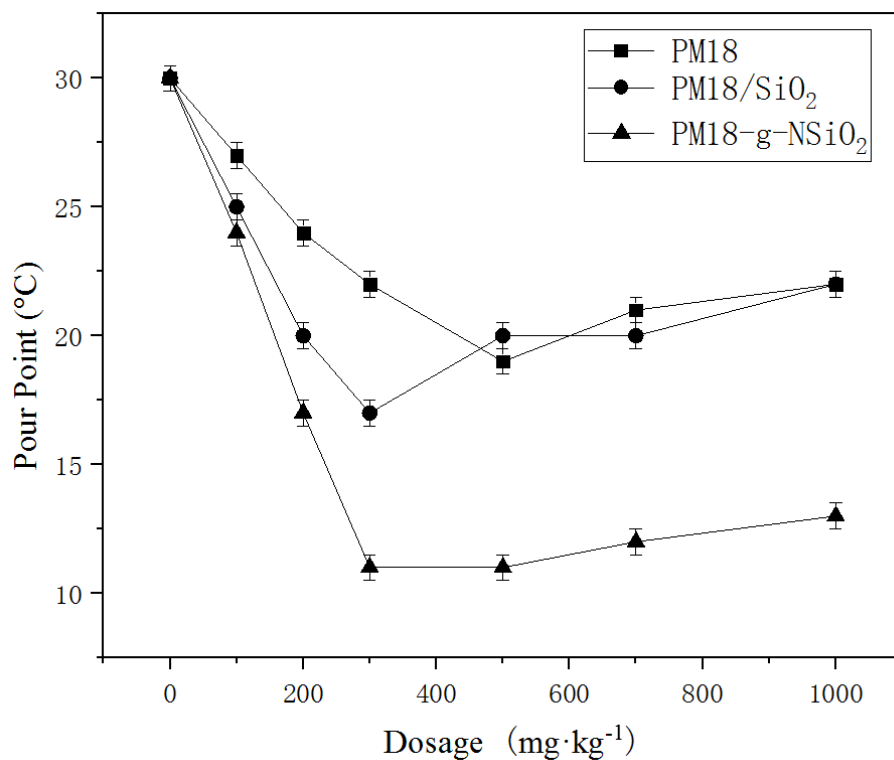


Figure 3. Pour point of 15 wt% model oil adding different kinds of NPPD.

3.2.2. Rheology Properties

The viscosity curves of the model oil before and after adding different doses of PM18-g-NSiO₂ are presented in Figure 4 while the viscosity of model oil with different additives is presented in Figure 5.

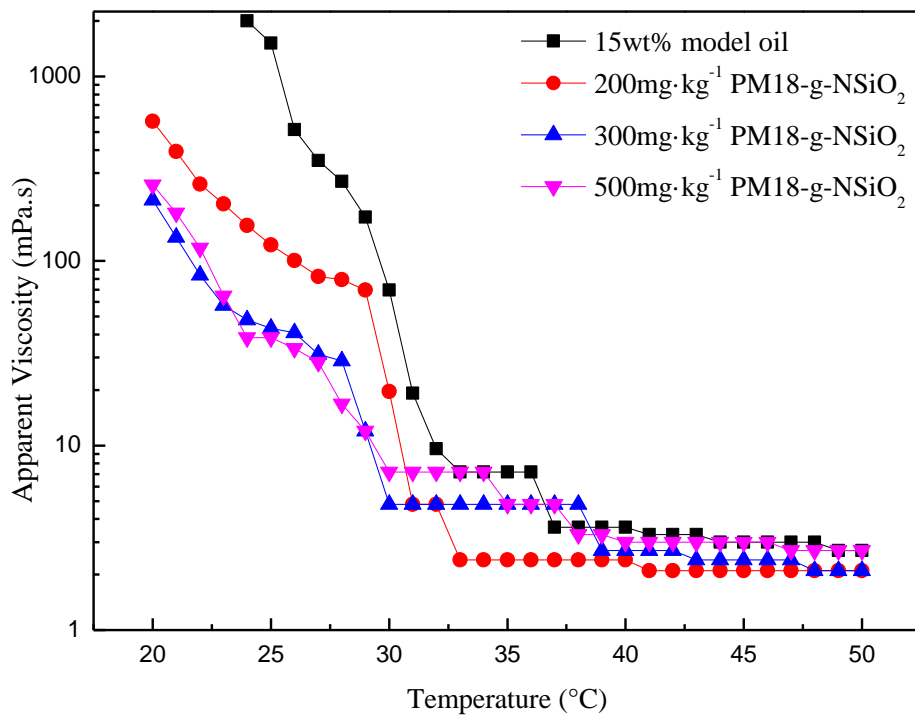


Figure 4. Semi-logarithmic curves of the viscosity versus temperature for the 15% wax model oil untreated and treated with PM18-NSiO₂.

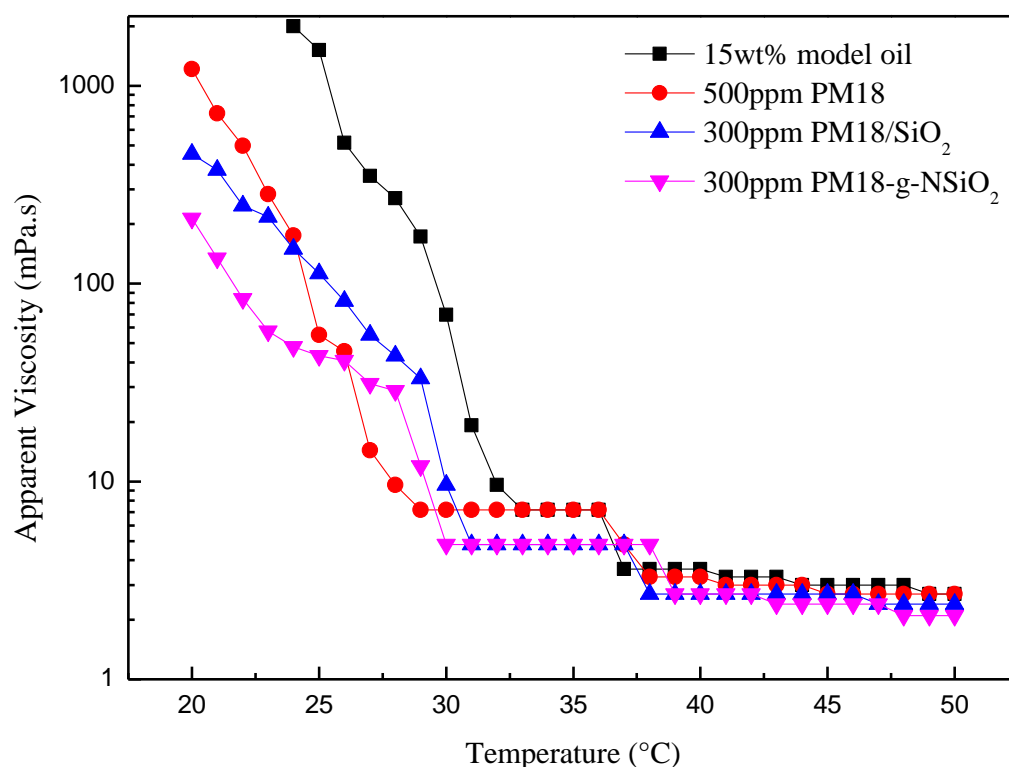


Figure 5. Semi-logarithmic curves of the viscosity versus temperature for the 15% wax model oil untreated and treated with different individual PPDs.

In Figure 4, adding a spot of PM18-g-NSiO₂ can significantly reduce the low-temperature viscosity of model oil. With the increase in PM18-g-NSiO₂ dosages, the trend of the viscosity of the model oil system first decreases and then increases. When adding 200 mg·kg⁻¹, 300 mg·kg⁻¹, and 500 mg·kg⁻¹, the viscosity of the model oil at 20 °C is 573 MPa·s, 214 MPa·s and 259 MPa·s, respectively. The above results may be related to the fact that PM18-g-NSiO₂ can provide the nucleation site, and will promote wax crystallization and change the wax crystal structure [35]. With the increase in the dose of PM18-g-NSiO₂, the NPPD will induce the formation of more and smaller wax crystals. Although the smaller size has weaker structural strength at lower temperatures and is easier to be destroyed, with a further decrease in temperature the excessive wax crystals form a three-dimensional network structure with a stronger structure, resulting in the viscosity of the oil increasing and the fluidity becoming poor.

In Figure 5, it is shown that the viscosity of the model oil adding PM18 is lower in a certain temperature range below WAT, compared with the model oil containing any NPPD. However, compared with PM18, the overall viscosity of the system with NPPDs changed gently, and NPPDs can effectively promote the flow of oil samples at low temperatures. At 20 °C, the model oil viscosity of the three kinds of PPD are 1217 mPa·s, 453 mPa·s, 214 mPa·s, respectively. This result is consistent with the experimental result in Figure 3 to a certain extent. This is because NPPDs dispersed in the model oil system are more likely to interact with wax crystals and act as crystal nuclei to promote wax crystallization resulting in more small wax crystals being formed in the model oil [36]. The smaller wax crystals are more likely to inhibit the flow of the model oil, exhibiting a higher viscosity than the model oil with PM18. At the same time, it would be easier to destroy at lower temperatures. Therefore, the model oil system with NPPDs added has better fluidity at low temperatures.

It is worth noting that PM18-g-NSiO₂ can further improve the low-temperature fluidity of oil samples compared with PM18/SiO₂ prepared by conventional physical adsorption. Compared with the model oil system with PM18/SiO₂ at 20 °C, the viscosity of model oil with PM18-g-NSiO₂ is further reduced by 52.8%. These results show that the grafting

method can effectively improve the stability of polymer on the surface of nanosilica, inhibit the desorption of polymer from the surface of silicon dioxide to maintain stable polymer coverage and improve the effect of the nanocomposite pour-point depressant.

3.2.3. Microscopic Study

In order to further analyze the action mechanism between NPPD and model oil, the changes in wax crystal morphology and structure in model oil before and after adding agents were studied using a polarizing microscope [37,38]. The results are shown in Figure 6. It can be seen that the shape, size and quantity of wax crystals are different in the model oil before and after adding different kinds of PPDs. Wax crystal morphology in pure model oil shows large flake growth, and the NPPD can change the wax crystal morphology, reduce the size of the wax crystal and disperse the wax crystal by interacting with the wax crystal through heterogeneous nucleation. As shown in Figure 6c,d, after adding PM18/SiO₂ and PM18-g-NSiO₂, the wax crystal morphology in the model oil changed from a large irregular crystal shape to an irregular small block structure and regular elliptical structure, indicating that the heterogeneous nucleation effect of PM18-g-NSiO₂ is significantly enhanced compared with PM18/SiO₂. This is because, in the PM18/SiO₂ NPPDs, there is no chemical bond between PM18 and the SiO₂, and only physical adsorption in action, which lead to the poor compatibility between PM18 and SiO₂. As a result, PM18 is easy to desorb from the surface of nano SiO₂, and the stability of PM18/SiO₂ in the waxy oil is poor. At the same time, the desorbed PM18 and PM18/SiO₂ have crystallization competition for wax crystals, resulting in the formation of irregular small block structures in the system. Compared with simple physical adsorption, the stable chemical bond formed between the surface of nanoparticles and polymer by the grafting method can effectively improve the stability of polymer on the surface of nanoparticles and prevent the polymer from desorbing from the surface of nanoparticles, so as to effectively improve the heterogeneous nucleation of NPPD and form the regular elliptical structure. At the same time, compared with the irregular small block structure, the regular oval structure releases more originally wrapped liquid oil, greatly reducing the wax oil interface area, and thus further improving the low-temperature fluidity of the wax-containing model oil [39].

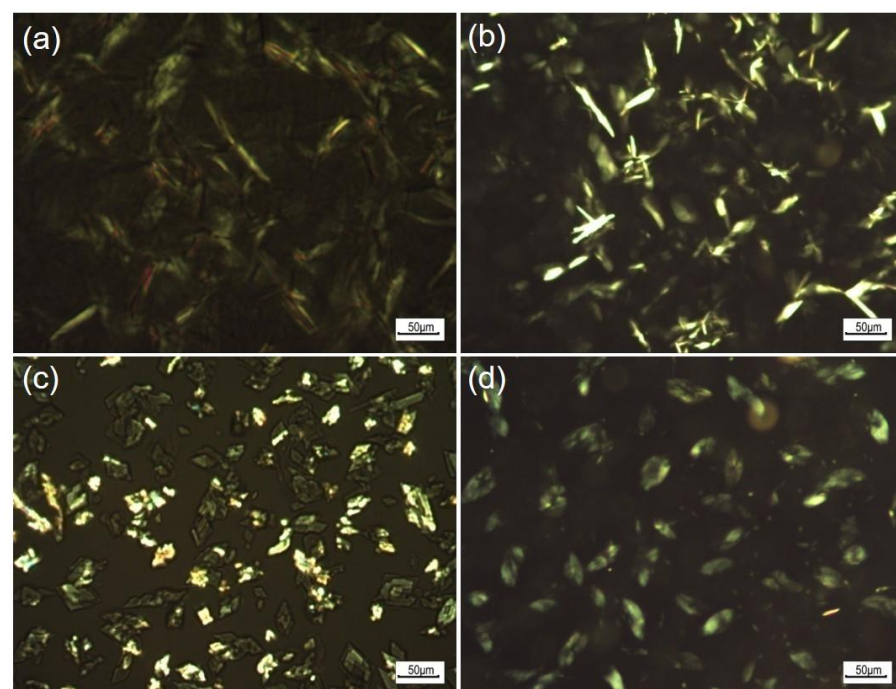


Figure 6. The polarized optical microscope images of the 15 wt% model oil in the (a) untreated (b) 500 mg·kg⁻¹ PM18; (c) 300 mg·kg⁻¹ PM18/SiO₂; (d) 300 mg·kg⁻¹ PM18-g-NSiO₂.

3.3. Proposed Mechanism

Based on the above experimental results, we analyzed the mechanism of PM18-g-NSiO₂ NPPD on model oil (shown in Figure 7). As shown in Figure 7, compared with simple physical adsorption, the grafting method can form a stable chemical bond between the surface of nanoparticles and polymers, and prevent the polymer from desorbing from the surface of nanoparticles, so as to effectively improve the stability of polymers on the surface of nanoparticles and enhance the dispersion of NPPDs in the oil phase. Furthermore, due to the NPPDs can provide the nucleation site of wax crystal, the guiding effect on the nucleation of wax crystal is enhanced through the long-chain molecular structure of polymer on the surface of nanoparticles and the eutectic of wax crystal [40,41]. On the other side, nanomaterials have high surface energy. In order to maintain the energy stability of the system, wax crystals in the model oil with added NPPDs tend to be more compact than those in the model oil with the same amount of pure polymer PPDs [42], so as to reduce the interface area and reduce the surface energy. In addition, the precipitated wax crystals grow evenly on the surface of the nanoparticles to form a regular morphology and structure. The compact wax crystal aggregate makes more liquid oil originally wrapped to be released [43], greatly reducing the wax oil interface area, reducing the friction dissipation energy between wax crystal and liquid crude oil when crude oil flows, further reducing the viscosity of crude oil at low temperature and further improving the fluidity.

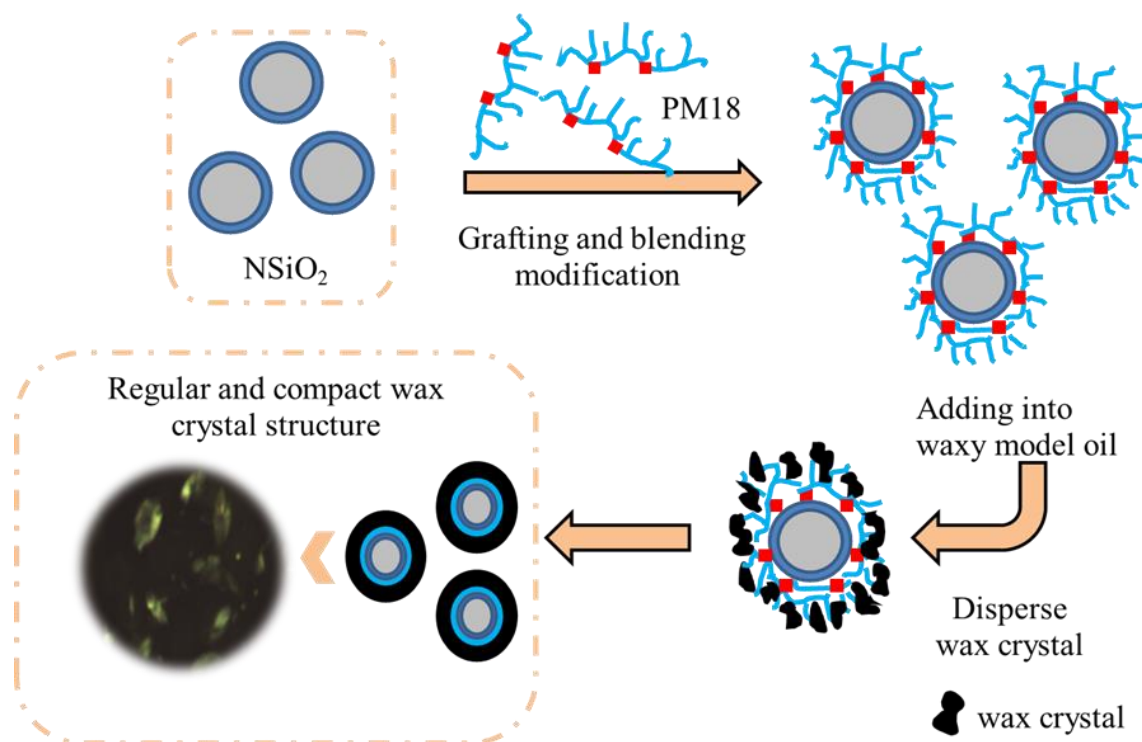


Figure 7. Schematic diagram of the flow improving mechanism of PM18-g-NSiO₂ on waxy model oil.

4. Discussion

In this work, PM18-g-NSiO₂ was synthesized simply and efficiently by the amidation reaction. The results of the rheological tests showed that when adding 300 mg·kg⁻¹ PM18-g-NSiO₂ and PM18/SiO₂, and the pour points were reduced by 19 °C and 13 °C, respectively. The viscosity of model oil after adding PM18-g-NSiO₂ at the optimal dose was only 214 mPa·s while that of added PM18/SiO₂ reached 453 mPa·s. Compared with PM18/SiO₂, PM18-g-NSiO₂ has the best flow modification effect on the model oil, which can effectively change the wax crystal into smaller irregular block structures and regular ellipses, and the heterogeneous nucleation effect is significantly increased [44]. We

concluded that different synthesis methods of nanocomposite pour-point depressant can effectively affect the coverage of polymer on the surface of nanoparticles and thus affect the effect of pour-point depressant.

Author Contributions: Conceptualization, Z.S. and G.J.; methodology, Z.S.; validation, Z.S., Y.Y. and H.L.; formal analysis, Z.S. and F.Z.; investigation, F.Z. and B.Y.; resources, G.J.; data curation, Z.S.; writing—original draft preparation, Z.S. and B.Y.; writing—review and editing, Z.S. and B.Y.; visualization, Z.S., Y.Y. and H.L.; supervision, G.J.; project administration, Z.S. and G.J.; funding acquisition, Z.S. and G.J. All authors have read and agreed to the published version of the manuscript.

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