Review

Research Status and Challenges of Mechanism, Characterization, Performance Evaluation, and Type of Nano-Pour Point Depressants in Waxy Crude Oil

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ABSTRACT: Nano-Pour point depressants have great potential to improve the low-temperature fluidity of waxy crude oil. This Review reviews the recent research progress of nano-pour point depressants in the field of crude oil pour point reduction. The effect and mechanism of nanocomposite pour point depressants are analyzed; the preparation, modification, and microstructure characterization of nanocomposite pour point depressants are introduced; the three main types of nano-pour point depressants, namely, silicon-based, carbon-based, and magnetic metal-based, are introduced; the results of the current research are outlined; and the challenges of the current research and possible directions of future research are also pointed out. The in-depth analysis of nano-pour point depressants and their potential to improve the low-temperature fluidity of waxy crude oil are reviewed in order to thoroughly analyze the mechanism of nano-pour point depressants and to prepare nano-pour point depressants that are more suitable for reducing crude oil coagulation.
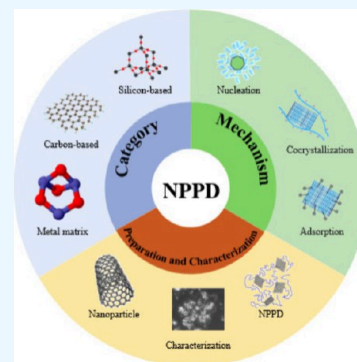
1. INTRODUCTION

In recent years, global oil production, consumption, and trade have been growing steadily. Conventional crude oil production can no longer meet the needs of industrial production and development, and the demand for the extraction of heavy waxy crude oils is increasing day by day. The large-scale development of heavy crude oil has brought new technical problems to the petroleum industry at every level of the process, from extraction to transportation and refining.[1,2]

Paraffin wax in crude oil will be precipitated as the temperature drops, affecting the flowability of crude oil and making it prone to pipeline clogging and other problems, which not only easily cause production loss but also endanger human safety. In order to solve the problems of high wax crude oil condensation and pipeline blockage, the chemical additive method has become the main method and industry consensus to prevent or inhibit wax precipitation and deposition and improve the low-temperature fluidity of crude oil due to its advantages of simple treatment and low cost.[3] Conventional polymeric pour point depressants are commonly used in crude oil pipeline transportation, but they are highly selective to crude oil and have poor thermal stability; additionally, in engineering applications the effect of condensation reduction is significantly reduced as the temperature of the oil stream rises.[4] With the development of nanoscience and technology,[5,6] scientists have found that nano-pour point depressants can improve the fluidity of pipeline crude oil, have good

coagulation and viscosity reduction effects, and have stronger stability than traditional pour point depressants. Therefore, nanoparticle technology can be more widely used in the coagulation reduction of waxy crude oil, and nanocomposite pour point depressants come into being.

Nano-pour point depressants have a wider range of effects on different waxy crude oil fractions, greater shear resistance below the wax precipitation temperature, and a larger reaction surface area and have been widely used in the reduction of crude oil coagulation.[7−9] There is no systematic and complete understanding of how the addition of nanoparticles affects the mechanism of polymeric pour point depressants, whether there is any commonality in the preparation methods of nano-pour point depressants for different substrates, and what factors need to be considered in the selection of nanomaterials for new pour point depressants. This Review presents a summary of the mechanism of nano-pour point depressants, an exploration of the mechanism of nano-pour point depressants on different components of crude oil, and a summary of the research results on the preparation method, performance

characterization, and application effect of nano-pour point depressants. Additionally, the Review puts forward thoughts that can help to guide the design of subsequent experiments and the direction of research in relation to the study of different types of nano-pour point depressants.

2. MECHANISM

Crude oil is a complex mixture of paraffins, aromatics, naphthenes, asphaltenes, and resins.[10−12] During pipeline transport, there is an unavoidable temperature difference between the waxy crude oil and the external environment, and the waxes contained in the crude oil crystallize and precipitate, greatly increasing the risk of pipeline blockage.[13] Misra et al.[14] concluded that petroleum wax deposition is mainly due to the microsoluble components of the petroleum constituents and that the presence of branched chains, despite having less effect on wax deposition, still modifies the trend of paraffin wax crystallization and behavior. Aiyejina et al.[15] found that wax deposition depends on crude oil composition, pressure, temperature, heat and mass transfer, and solid−solid and solid−liquid phase interactions. Lionetto et al.[16] found that a wax content within 1−6% leads to gelling of the waxy crude oil. Wax deposition is influenced by wax composition, molecular weight, shear history, thermal history, paraffin content, asphaltene content, and additives.

Pour point depressants act by one or more postulated mechanisms to prevent or slow the aggregation of wax crystals by altering crystal habit, size, or interactions such as nucleation, adsorption, solubilization, and cocrystallization and improving wax dispersion.[17,18] Nucleation is believed to occur during the interaction between the wax crystal molecules and the pour point depressant molecules, where the pour point depressant molecules are preferentially precipitated to form nuclei, preventing the wax crystals from sticking together to form a reticular structure and thus achieving the purpose of lowering the pour point of the crude oil. The adsorption effect is where the polar groups in the pour point depressant molecules repel each other, increasing the van der Waals force on the surface of the wax crystals so as to change the growth direction of the wax crystals, reduce the contact of the wax crystals with each other, and improve the fluidity of the crude oil. Solubilization is considered to be similar to surfactants, where the interaction of long chain alkyl groups with wax molecules can increase the solubility of wax molecules in crude oil, reduce the amount of wax crystals precipitated, and improve the fluidity of waxy crude oil. Co-crystallization means that the nonpolar parts of the depressant molecules and the wax crystal molecules precipitate together and the polar part changes the growth direction of the wax crystals such that the formed wax crystals have a lower specific surface area and lower surface free energy, making it difficult for the wax crystal network to form and thus achieving the effect of improving crude oil liquidity. Crude oil pour point depressants work through a combination of one or more of these mechanisms.

Li et al.[19] conducted wax deposition experiments using a coldfinger apparatus and found that the pour point depressants reduced the porosity of wax deposits through solubilization and limited the diffusion of asphaltenes and resins in the wax deposits, which significantly weakened the mechanical strength of the wax deposits. Al-Shboul et al.[2] investigated the mechanism of interaction of wax inhibitors with wax molecules as shown in Figure 1, and most of the polymeric inhibitors are able to interact with wax crystals through eutectic interactions;
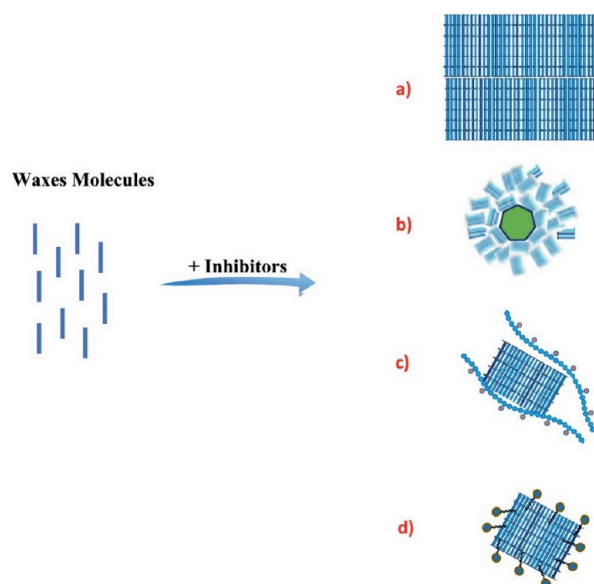

Figure 1. Schematic of inhibitor−wax molecule interaction mechanisms: (a) meshing, (b) nucleation, (c) cocrystallization, and (d) adsorption. Reproduced with permission from ref 2. Copyright 2023 Elsevier.

copolymers with abundant long alkyl chains have higher eutectic efficiencies and thus may be a more preferable choice as wax solubilizers.

Gu[20] investigated the effect of adding cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium bromide (CTAB), or octadecyltrimethylammonium chloride (OTAC) on the improvement of crude oil flowability. The results showed that all surfactants performed well in improving oil flowability, while CTAC was the most effective at reducing viscosity. The authors suggested that this may be due to the adsorbed CTAC alkyl chains on the wax crystals, which create a high electronic repulsion with Cl^- ions. Patel et al.[21] prepared hexyl oleate−hexadecyl maleamide-*co-n*-alkyl oleate copolymers with a range of molecular weights; copolymers with longer side alkyl chains significantly improved oil flow, which the authors attributed to the increase in the chain length of the additives, possibly due to increased cocrystallization with the nonpolar portion of the paraffins, while the polar portion impedes network growth, thus reducing viscosity. Soliman et at.[22] found that comb copolymers of alkyl maleic linoleate significantly reduced the pour point and yield stress of model oils, reduced wax crystal size, inhibited wax crystal formation, and promoted the growth of monoclinic paraffin crystals. The efficacy of these copolymers depended on their interaction with paraffins and asphaltenes and reduced the van der Waals or London dispersion interactions between molecular entities, thus overcoming the energy required for cohesion and adhesion between the oil components and the contacting support material as well as the fluidity of the oil.

Xue et al.[23] synthesized macroporous poly(octadecyl acrylate) (MP-POA), pointing out while the improvement effect of MP-POA on the rheological properties of model wax oils is determined by the joint action of the cocrystallization and nucleation templates, there is a contradiction between the two; that the difference in the amount of divinylbenzene (DVB) added is the main reason for the different impact of the modifying effect of MP-POA on the model oil; and that the degree of polymer cross-linking affects the crystallinity of the
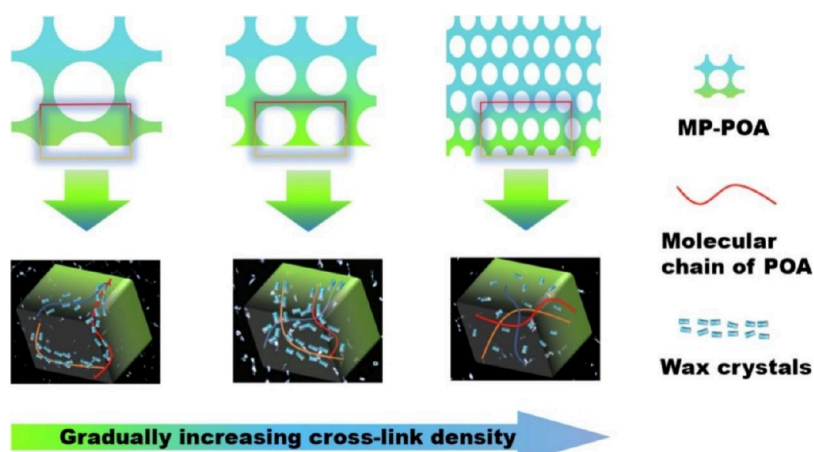
Figure 2. Mechanism of MP-POA to improve the rheology of modeled waxy oils. Reproduced with permission from ref 23. Copyright 2022 Elsevier.

polymer molecules. As shown in Figure 2, the higher the degree of cross-linking, the lower the crystallinity, resulting in a decrease in the material's ability to eutectically precipitate with wax molecules, which is not conducive to the modification of oil samples. Meanwhile, the increase in the cross-linking degree means more porosity, which will favor the nucleation template effect of MP-POA pour point depressants that is conducive to the formation of denser wax crystals and the improvement of rheological properties of oil samples. Many researchers[24−30] conducted wax deposition experiments with different pour point depressants and found that the incorporation of nanoparticles would change some of the depressant mechanisms.

It has been shown that about 2 wt % paraffin is sufficient to cause the gelation of waxy crudes.[4,23,31] This does not mean that the amount of pour point depressant used needs to be increased to cope with crude oils with higher wax contents; it is the interaction between the pour point depressant and the wax molecular structure that is extremely important in determining the amount of pour point depressant required to inhibit wax deposition.

Nanohybrid pour point depressants offer many unique advantages over conventional pour point depressants. Nanoparticles (NPs) are tiny (1−100 nm) particles with excellent penetration and adsorption capabilities, tunable physicochemical properties, and unique thermal properties. In addition, due to their small size, NPs can pass through tiny pores and narrow passages inaccessible to larger materials.[32] In recent decades, nanotechnology has rapidly emerged as a novel and dominant technology capable of competing technologically and economically with conventional methods, and the application of nanotechnology in the oil and gas industry provides an unprecedented opportunity to develop more cost-effective, efficient, and environmentally friendly oil/gas recovery technologies.[31]

Nanomaterials are small in size, with a characteristic quantum size effect and macroscopic quantum tunneling effect, and have a wide range of applications in various industries. In recent years, nanomaterials have been gradually applied in the petrochemical industry and involved in the production of pour point depressants, and nanohybrid materials have become a new field of research to improve the rheological properties of crude oil. These nanomaterials consist of a polymer matrix of inorganic nanoparticles, which

are later organically modified by a polymer pour point depressant coated with nanoclay materials, such as polymethyl acrylate, ethylene−vinyl acetate copolymer, poly α-olefin, etc., to form nano-pour point depressants. The introduction of dispersed nanoparticles significantly improves the mechanical properties and long-term stability of the nanocomposites compared with conventional pour point depressants. The nanocomposites prepared from modified montmorillonite and ethylene−vinyl acetate copolymer showed low transport costs and good performance on waxy crude oil even at a minimum dosage of 100 ppm and were able to inhibit the formation of the wax gel network and enhance the stability of wax crystals, resulting in a significant improvement in the flowability of crude oil.

Although much progress has been made in the research and application of nano-pour point depressants, there is no unified scientific consensus on the interpretation of their pour point depressant mechanism. In particular, the understanding of how nano-pour point depressants affect wax crystal growth and distribution through eutectic and nucleation is still incomplete. Yang's research team[33] incorporated poly(octadecyl acrylate) (POA) into nanoscale silica pores to improve the efficiency of wax deposition inhibition and found that POA worked well at low concentrations (≤200 ppm) because the POA alkyl chains cocrystallized with the waxes and inhibited the homogeneity of the wax crystal network. On the other hand, at higher POA concentrations, the wax crystal network became homogeneous and the deposits became thinner and denser. Sharma et al.[34] mixed 11.9 g of 1-chlorooctane with 8.2 g of 1-methylimidazole in a three-necked round-bottomed flask with a reflux condenser under a nitrogen atmosphere and kept the mixture at 70 °C for 48 h. The unreacted portion of the upper layer was removed by decantation and washed three times with ethyl acetate, and the remaining solvent was evaporated by heating it at 70 °C, followed by vacuum distillation in a vacuum 80 °C. Vacuum distillation in an oven at 80 °C resulted in the ionic liquid [(OMIM)Cl], which was combined with vinyl graphene oxide (VGO) to form a novel nano-pour point depressant, PPDR-GO for short. It was shown that in the presence of PPDR-GO nanocomposites, the VGO flakes provide nucleation sites for the wax to precipitate, and the wax crystals precipitate and grow in a restricted and localized manner and avoid networking, thus leading to the deposition and growth of more dispersed and fragmented wax

crystals. Jia et al.[9] modified a traditional polymer pour point depressant, poly(α-olefin-carbon-acrylate) (PAA-18), by using three carbon-based nanomaterials of different sizes and showed that carbon-based nanohybrids with high surface energy can become the new nucleation sites for wax crystals. The wax molecules adsorbed on the new nuclei to form a relatively narrow and dense morphology that reduced the interfacial area and surface energy, thus forming a larger gap and effectively increasing the mobility of the crude oil. The pour point inhibition properties were investigated using a model wax oil with poly(octadecyl acrylate) (POA) coated on SiO_2 nanoparticles. DSC characterization results showed that the presence of the nanoparticles altered the nature of wax crystallization, most likely through the introduction of multiple nucleation centers. Table 1 shows the pour point depressants and their mechanisms of action.

Table 1. Pour Point Depressants and Their Mechanism of Action

crude oil	pour point depressants	mechanism
China (Jinghe)[20]	CTAC, CTAB, OTAC	cocrystallization
India[21]	poly(hexyl oleate-cetylmaleamide-co-n-alkyl oleate)	cocrystallization
Egypt[22]	Maleic anhydride ester—vinyl acetate copolymer	improvement of wax dispersion
simulate oil[23]	large-aperture POA-co-DVB	cocrystallization, nucleation
India[27]	poly(triethanolamine dioleate)	cocrystallization
Iranian[24]	poly(ethylene vinyl acetate)	nucleation, adsorption
Kazakhstan[25]	poly(ethylene vinyl acetate)/ nanocomposites	cocrystallization
Egypt[28]	triethanolamine	cocrystallization
Malaysia[26]	poly(phenyl acrylate-co-stearyl methacrylate-maleic anhydride)	cocrystallization, nucleation
China (Xuzhou)[29]	montmorillonite nanocomposites	cocrystallization, nucleation
China (Changqing)[30]	poly(octadecyl ester)/clay nanocomposites	cocrystallization
simulate oil[33]	poly(octadecyl acrylate) (POA)/ silica nanoparticle hybrids	improvement of wax dispersion
India[34]	PPDR-GO	nucleation, solubilization
China (Daqing)[9]	PAA-18/carbon-based nanomaterials	nucleation
simulate oil[35]	POA/SiO_2	nucleation

3. PREPARATION AND CHARACTERIZATION

3.1. Preparation and Modification of Nanomaterials.
In recent years, the application and development of nano-composite anticoagulants (NPPDs) has become a hot research topic.[5,36−40] Compared with conventional PPDs, NPPDs have a stronger anticoagulant effect.

Today, the main pour point depressants for waxy crude oils are ethylene−vinyl acetate copolymers, acrylates, and maleic anhydride after alcoholysis or aminolysis. In practical engineering applications, traditional pour point depressants show poor stability and require changes in the stability and other properties of polymers, while nanoparticles can significantly affect the heat deflection temperature, crystallinity, and grain size of polymer nanocomposites;[41] for example, silicon-based materials such as nanoclay,[42] carbon-based materials such as graphene,[43,44] and metal-based materials such as magnetic

nano-Fe_3O_4[45] have all become hotspots for research on nano-pour point depressants.

Montmorillonite is a nonmetallic nanomineral formed by the stacking of very thin silicate flakes with negatively charged surfaces, and its particular intergranular structure is characterized by high surface polarity and a strong cation exchange capacity, which is most commonly used in the manufacture of nano-pour point depressants. Montmorillonite is hydrophilic and oleophobic, has good swelling properties, and is inexpensive, but it has poor compatibility with polymers.[46] It is therefore necessary to modify montmorillonite to reduce the polarity of its surface and to increase the lipophilicity and interlayer spacing. The organic modifiers commonly used are cationic agents, anionic agents, nonionic surfactants and coupling agents. Among the cationic agents, the most commonly used are organic quaternary ammonium salts.[47] Organic quaternary ammonium salts are relatively large and enter the montmorillonite interlayer to increase interlayer spacing, reduce interlayer forces, and promote plugging reactions.[48] Cui et al.[49] modified montmorillonite using long alkane chain quaternary ammonium salts and investigated the effect of long alkane chain quaternary ammonium salts on the intercrystalline structure of the modified montmorillonite. They found that the interlayer spacing of the modified montmorillonite increased with the increase in the amount of quaternary ammonium salts, the number of carbon atoms, and the number of alkane chains and that quaternary ammonium salts with different numbers of alkane chains had different cation arrangements in the interlayers of the lamellae. Yao et al.[50] modified the nanoclay organically through a cation exchange reaction. X-ray diffraction showed the appearance of long carbon chain alkyl side chains of OTAC on the surface of the nanoclay and in the interlayers, and the interlayer spacing was significantly increased, which helps to compound with polymer pour point depressants and improve the coagulation reduction effect. This is confirmed by the study carried out by Lin et al.[51] Cheng et al.[52] used cetyltrimethylammonium bromide (CTAB) as a modifier to obtain organically modified montmorillonite through the ultrasonic technique, and neo-prene/organically modified montmorillonite nanocomposites were obtained by mechanical mixing and the intercalation method. Cao et al.[53] modified montmorillonite by intercalation on the basis of CTAB supplemented with methyl silicone oil and honey ammonium phosphate salt and found that the surface of honey ammonium phosphate salt-modified mont-morillonite was smooth, the particles were arranged in a regular manner, and the layer spacing was maximal, which gave the best surface modification effect.

Graphene-based nanomaterials mainly include graphene (Gr), graphene oxide (GO) and reduced graphene oxide (rGO). Graphene has unique structural and physicochemical properties that make it an ideal material for the fabrication of polymer nanocomposites. The bonding of carbon atoms between the monatomic layers of graphene forms a honey-comb structure, giving graphene a theoretical specific surface area of up to 2630 m^2/g. However, because polymers tend to agglomerate in graphene, the performance of pristine graphene materials used to make polymer nanocomposites is unsat-isfactory.[54,55] As a product of graphene oxidation, graphene oxide (GO) is a material of interest in the petroleum industry due to its structural similarity to graphene and the variety of functional groups it contains.[56] Many researchers have shown[57,58] that the addition of graphene derivatives such as

GO to the polymer matrix can effectively reduce polymer agglomeration.

There are several methods to obtain graphene oxide from graphite, the most prominent of which is the Hummers method,[59] in which $NaNO_3$ and $KMnO_4$ are dissolved in concentrated sulfuric acid, which avoids the risk of explosion present in previous preparation methods and has the advantage of rapid synthesis but suffers from the disadvantages of the emission of toxic gases (NO_2 and N_2O_4) and low preparation efficiency. Many researchers have tried to improve the Hummers method[60−65] through methods such as extending the reaction time,[60] optimizing the amount of oxidizer,[61] adding sodium nitrate auxiliary agents,[62,63] and post-treatment techniques such as dialysis or centrifugation,[64,65] but the various improvements of the Hummers method still suffer from two problems: first, the high consumption of oxidizing and embedding agents is unavoidable, and second, most of the synthesis times are very long; both these problems lead to higher costs and poorer practical applicability. Chen et al.[66] prepared graphene oxide using a modified Hummers method by providing an acidic environment using concentrated sulfuric acid with gradual stirring and cooling to add a strong oxidant $KMnO_4$, and the synthesis scheme is shown in Figure 3. This
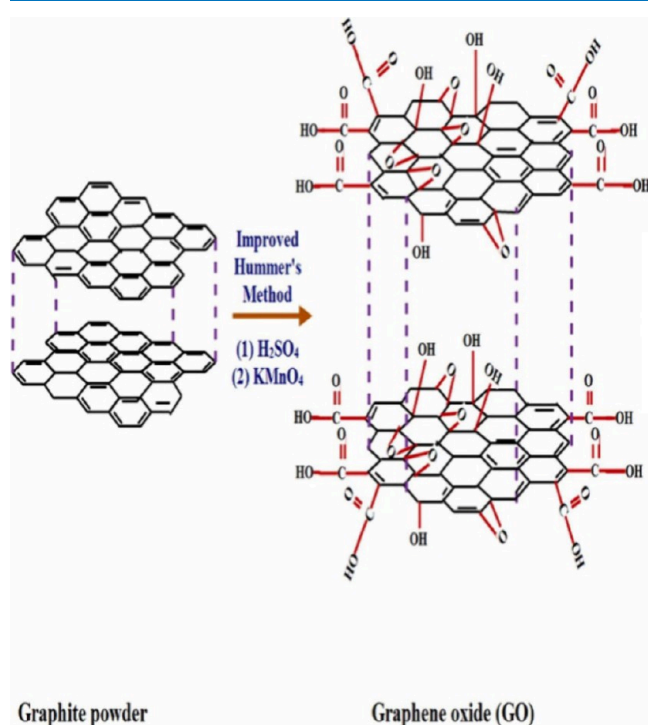

Figure 3. Schematic diagram of graphite synthesis of GO and VGO. Reproduced with permission from ref 34. Copyright 2017 American Chemical Society.

suggests that the most important factor affecting the efficiency of graphene oxide preparation is the filtration rate, and it is difficult to remove the residual acid, so the focus of the modified research can be placed on the purification of the graphene oxide suspensions containing acids and metal ions.

Due to the high oxygen content of graphene oxide, which does not work well in all application scenarios, GO can be reduced to produce rGO with a lower oxygen content. Reduced graphene oxide restores the original sp^2 structure, which gives rGO mechanical strength, stability, dispersion, and

reactivity different from GO.[67] One or more methods such as thermal treatment, chemical reduction, or thermochemical methods can be used to produce different grades of rGO.[68−71] Xu et al.[72] used the chemical reduction method to deposit metal nickel nanoparticles uniformly on the surface of rGO, graphene, and magnetic metal Ni to form an electromagnetic coupling interaction in addition to multiple scattering and reflection caused by the nanosize effect; the reduced graphene oxide exhibited excellent electromagnetic performance, which was far superior to that of graphene oxide. Wang et al.[73] successfully synthesized covalently modified reduced graphene/polyaniline (E-RGO/PANI) composites by in situ polymerization, and the schematic route is shown in Figure 4. E-RGO has a layered structure with a large specific surface area, which increases the number of sites for redox reactions, and the PANI network is tightly wrapped around the E-RGO sheets to form a lamellar structure, which is connected by covalent bonds and has a strong $\pi-\pi$ conjugation effect with excellent physicochemical properties.

Carbon nanotubes (CNTs) were first discovered by the Japanese scientist Lijima in 1991 while producing C60 using the electric arc process. Carbon nanotubes (CNTs) are allotropes of carbon that can be thought of as sheets of graphene rolled into cylinders of nanoscale diameter, with a large specific surface area, good electrical conductivity, and excellent mechanical properties.[74] Photoelectron spectroscopy studies of carbon nanotubes show that both multiwalled carbon nanotubes and single-walled carbon nanotubes (schematic structure shown in Figure 5) incorporate a certain number of functional groups on their surfaces, whereas carbon nanotubes obtained by a variety of different preparation methods have different functional groups on their surfaces, and different postprocessing methods also result in CNTs with different surface structures.

Commonly used carbon nanotube preparation methods mainly include arc discharge, laser ablation, chemical vapor deposition (CVD), and so on. Among them, the CVD method has the advantages of low temperature, low energy input, and easy to control parameters, and it is currently the main method for preparing carbon nanotubes.[7] Makris et al.[75] used hot filament chemical vapor deposition (HFCVD) to grow carbon nanotubes (CNTs) on nickel catalysts using H_2 and CH_4 as gas precursors; Abdullah et al.[76] proposed a floating catalyst chemical vapor deposition (FCCVD) method using CNT aerogels as the object of study, in which the carbon source and the catalyst were directly and simultaneously introduced into the reactor and hydrogen and sulfur were added to the high-temperature reactor to induce high-speed growth of carbon nanotubes in the gas phase, enabling the large-scale production of carbon nanotube aerogels. Williams and his team[77] described the preparation of carbon precursors for production using hydrocarbons produced by the pyrolysis of waste plastics. The reaction conditions of the pyrolysis and catalytic processes were controlled, and a viable solution for producing carbon nanotubes from waste plastics was investigated. Periyasamy et al.[78] investigated the stability of carbon nanotubes in six different base oils and confirmed their feasibility as nano-substrate carriers for pour point depressants in highly waxy crude oils.

C60 and higher fullerenes have excellent properties with significant chemical reactivity and are expected to be used as novel nanosubstrates for compounding with polymers.[79] As fullerenes have been found to have excellent properties that
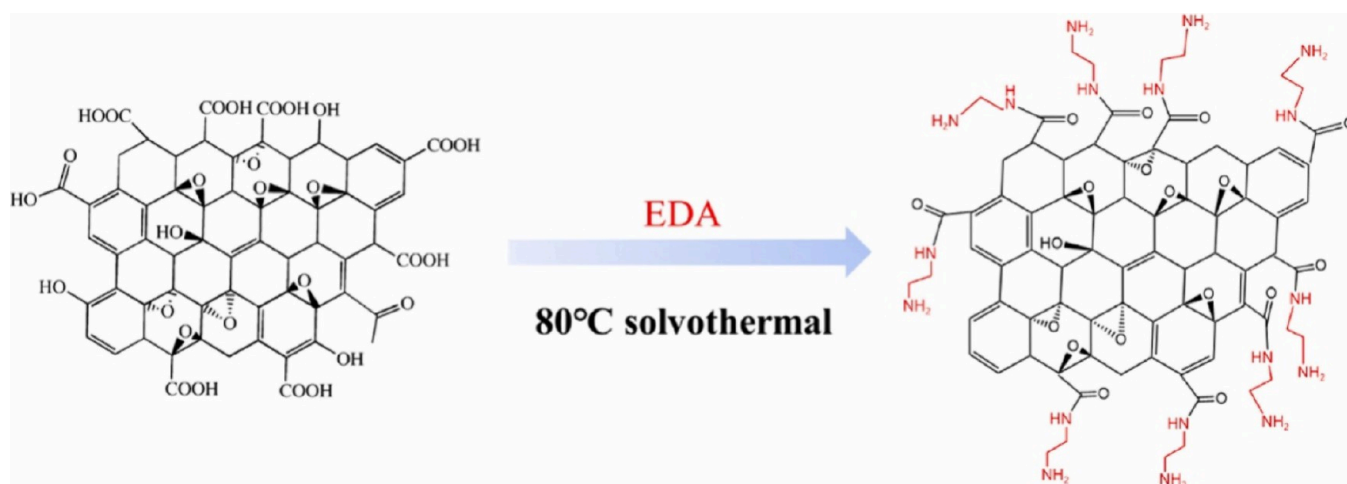
Figure 4. Schematic of the synthesis routes of E-RGO. Reproduced with permission from ref 73. Copyright 2023 Shandong University.
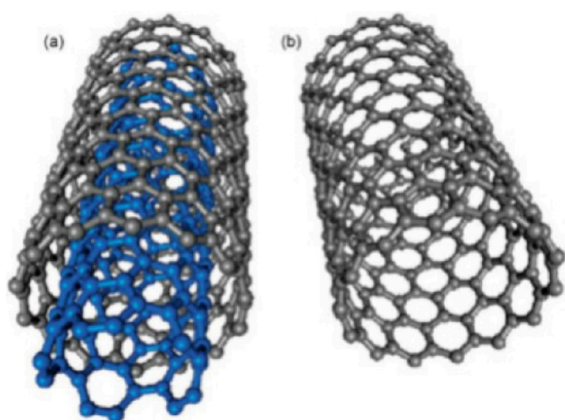

Figure 5. (a) Multiwalled carbon nanotubes (MWCNTs) and (b) single-walled carbon nanotubes (SWCNTs). Reprinted from ref 7. Copyright 2009 American Chemical Society.

dealing with the hybridization of typical 1D and 2D nanomaterials the two compositions may have different topologies, resulting in the formation of nanohybrids.

3.2. Preparation and Modification of Nano-Pour Point Depressants. Nano-pour point depressants combine the principles of nanotechnology and traditional polymer pour point depressants by incorporating inorganic nanoparticles into the polymer matrix to form composites with unique properties. Nano-pour point depressants are usually made by polymerizing small-molecule compounds and then modifying the polymer side chain by changing the length, number, and type of functional groups to improve the anticoagulant effect and the bonding effect with nanosubstrates.

Commonly used methods for the preparation of nano-pour point depressants include solution blending and melt blending. Solution blending involves dissolving and reacting polymers and nanomaterials in a solvent; after distillation to remove the solvent, nanocomposite pour point depressants are obtained, and PPDs are usually coated on the surface of the nanoparticles in the form of physisorption. Therefore, it is important to improve the compatibility of the nanoparticles with organic pour point depressants. At the same time, the polymerization temperature, the polymerization time, the type and content of polar groups, the type and amount of solvent, and the type and amount of initiator during the solution

can be combined with other materials to achieve even better performance, it is necessary to perform research on fullerene nanohybrids to meet more potential applications. Chen and his team[80] reported a method to prepare graphene-C60 hybrid materials via a simple coupling reaction between graphene oxide and pyrrolidine fullerene, and Zhang[79] found that when
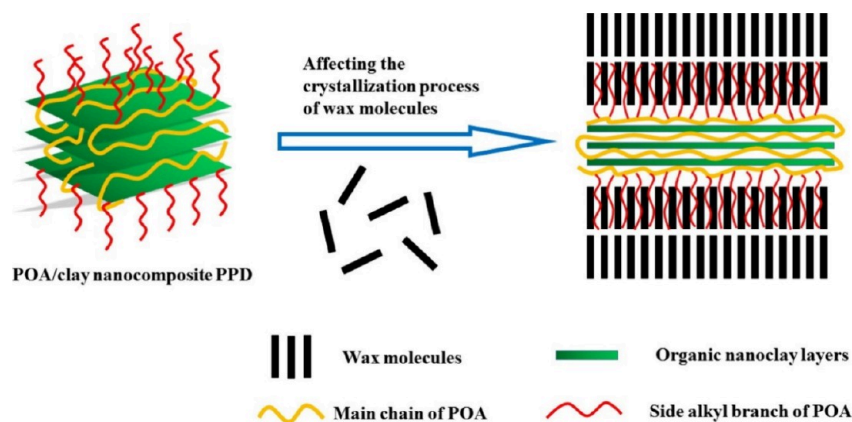

Figure 6. Possible mechanism of POA/clay nanocomposite PPD for improving the flowability of waxy crude oil. Reproduced with permission from ref 50.
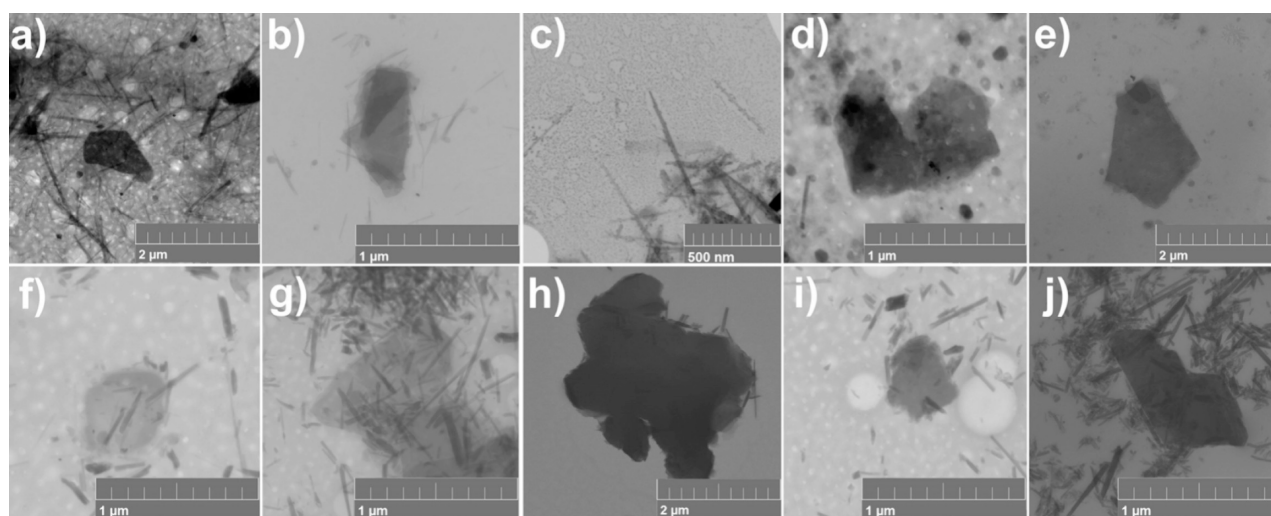
Figure 7. TEM analyses of: (a) EVA:PALY(90:10)S1/FD, (b) EVA:PALY(90:10)S2/FD, (c) EVA:PALY(95:5)S2/FD, (d) EVA:MMT(90:10)-S2/FD, (e) EVA:MMT(95:5)S2/FD, (f) EVA:HALLO(90:10)S2/FD, (g) EVA:HALLO(90:10)S1/OV, (h) EVA:HALLO(95:5)S2/FD, (i) EVA:HALLO^C(90:10)S2/FD, and (j) EVA:HALLO^C(95:5)S2/FD. Reproduced with permission from ref 86. Copyright 2022 Elsevier.

polymerization process have a certain influence on the polymerization process because it is necessary to choose a suitable solvent to dissolve the polymer and the nanomaterials. In addition, this method requires the recovery and disposal of a large amount of organic solvents in practical applications.

Yao[50] prepared a composite pour point depressant by the solution blending method using OTAC-modified nanoclay (shown in Figure 6) and analyzed the effect of organochemical modification on the effect of the pour point depressant, and POA/nanoclay composite pour point depressant had a stronger viscosity reduction effect than the pure POA at the same POA content. Ridzuan et al.[3] prepared nano-pour point depressants by dissolving sodium salts of nanoparticles in cyclohexane at 60 °C with stirring for solution mixing and sonicated the mixture in an ultrasonic bath at 25 °C for 1 h. It was concluded that the combination of PPDs and nanoparticles can show excellent performance in reducing the amount of wax caking and viscosity by the effect of viscosity, shear stress, and wax deposition. Sun[81] prepared two types of nano-pour point depressants by blending octadecyl acrylate/MAH polymer with unmodified and modified nano-SiO$_2$, respectively, using toluene as a solvent. The structures of the two types of nano-pour point depressants were characterized using infrared testing (FTIR), scanning electron microscopy (SEM), etc., and it was found that modified nano-pour point depressants had a better pour point depressant effect. The study found that the modified nano-pour point depressants have a better coagulation reduction effect.[82] Sixteen novel nanohybrid PPDs based on poly(methyl acrylate) (PMA), an ethylene–vinyl acetate copolymer, polyolefin, and organically modified nanoclay were synthesized by the solution blending method, and the morphology of the wax crystals and the crystalline behavior of the wax crystals at low temperature of diesel fuel were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The addition of the nanohybrid PPDs reduced the cold filter plugging point and solidification point by 14 and 16 °C, respectively. Ding et al.[83] prepared organic nanosilica-blended PMMA wax inhibitors by the solution blending method using γ-aminopropyltriethoxysilane to organically modify the nanosilica, which improved the lipophilic properties while increasing the high-temperature stability. Sun et al.[84] prepared PM18-g-NSiO$_2$ by an amidation reaction using amino-modified silica nanoparticles and an octyl methacrylate–maleic anhydride copolymer and compared it with PM18/SiO$_2$ prepared by the solution mixing method. Characterization results from Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) showed that different synthesis methods affect the coverage of the polymer on the surface of the nanoparticles and thus the effectiveness of the pour point depressant.

Melt blending is a method of melt blending nanoparticles with polymers at high temperatures to produce nanocomposite pour point depressants without the use of solvents. Yao[50] prepared POA/nanoclay composite pour point depressants using a micro-twin-screw extruder by directly blending the nanoclay with polymer-based pour point depressants in the molten state for better dispersion of the nanoclay in the polymer matrix, which resulted in composite pour point depressant particles with smaller dispersed particle sizes in the oil phase and confirmed that the nanoclay with a lower percentage of the mass used produced a better modifying effect. Yang et al.[85] prepared a nanocomposite pour point depressant by melting modified montmorillonite and polyethylene vinyl acetate at 150 °C. Compared with a conventional pour point depressant, the nanocomposite pour point depressant can significantly reduce the wax precipitation point of the waxy crude oils and has a better coagulation and viscosity reduction effect due to the improvement of the polymer and the compatibility of the organic montmorillonite in the melting and blending process.

Alves et al.[86] compared nano-pour point depressants prepared by melt blending at different content ratios and found that increasing the amount of clay minerals relative to polymers reduced the efficiency of the nanocomposites, although it was still higher than that of pour point depressants prepared by solution blending. Transmission electron microscope images of nano-pour point depressant with different content ratios prepared by the melt mixing method are shown in Figure 7. The nomenclature of each different group of nano-pour point depressants consists of EVA:clay mineral (ratio)/preparation method/drying method. Among them, PALY,
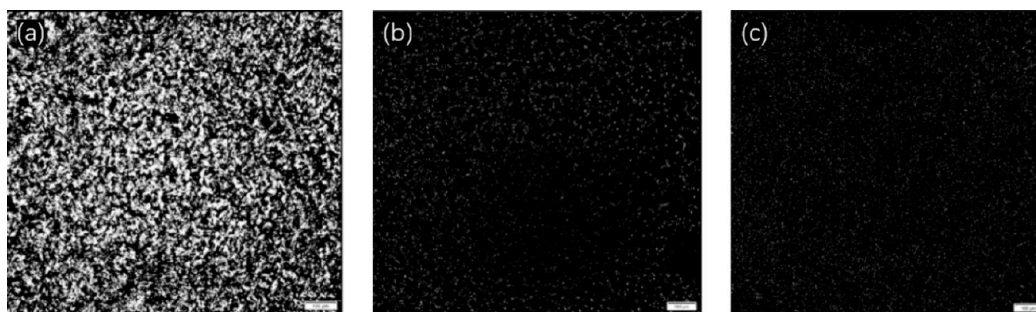
Figure 8. XRD microscopic images illustrating changes in the wax morphology of (a) virgin crude oil, (b) MALN-beneficiated crude oil, and (c) MARC-beneficiated crude oil. Reproduced with permission from ref 99. Copyright 2020 Elsevier.

MMT, HALLO, and HALLO^C correspond to palygorskite, montmorillonite, halloysite, and commercial halloysite; S1 and S2 denote two different methods of solution preparation, with the S1 method being 10 wt/v % of clay mineral + polymer in 100 mL of toluene and the S2 method being 2.78 wt/v % of clay mineral + polymer in 10 mL of toluene; and OV and FD denote the oven drying method and freeze-drying method, respectively.

There are two main modification methods for nano-pour point depression agents: one is to improve the coagulation reduction mechanism to enhance the effect of coagulation reduction by modifying the pour point lowering agent, and the other is to organically modify the nanosubstrate material, which makes the formulation of the nano-pour point depression agent easier to achieve; additionally, the content of organic polymer molecules existing in the nanosubstrate material is higher, which better meets the needs of practical applications. Zhang[87] obtained an oil-soluble improver by modifying acetic anhydride and waste polystyrene by mixing them 1:1 to change the crystalline behavior of waxes by cocrystallization with saturated hydrocarbons. Zhu et al.[88] prepared grafted polymer nanocomposites using polypropylene with reactive functional groups (PP-OTMS) as a matrix with organically chemically modified SiO$_2$ and found that surface modification of SiO$_2$ by a silane coupling agent helps the dispersion of SiO$_2$ and thus promotes in situ grafting during melt bonding of reactive matrix and nanofillers. In their investigation into the effect of EVA/SiO$_2$ nanohybrids on the rheological properties of crude oil, Ning et al.[89] found that asphaltenes and gums in crude oil are easily adsorbed on waxes. The nanoparticles can adsorb asphaltenes and inhibit the formation of wax crystals. Nanohybrids will aggregate and precipitate with an increase in concentration. Analysis of the optimal silica dosage based on the field crude oil rheological data can assist in the development of a more practical pour point depressant. Ahamad et al.[90] investigated the application of PMMA nanohybrids as an example of PMMA-GO nanocomposites, noting that the agglomeration phenomenon is prevalent in GO. They further observed that the GO agglomeration problem is mainly caused by surface hydrophilicity, which can be suppressed by modification with the addition of inorganic silica in order to improve the solubility and dispersion of the graphene sheets and nanoparticles.

3.3. Characterization Method. In the field of research into pour point depressants, Fourier transform infrared (FTIR) spectroscopy is frequently employed to identify the chemical structure and functional groups of the prepared pour point depressants,[91,92] while lattice diffraction peaks are analyzed by X-ray diffraction (XRD)[93] in order to determine the lattice

morphology. Furthermore, scanning electron microscopy is utilized. Transmission electron microscope images can be employed to visually assess the state of wax crystal aggregation, thereby characterizing the impact of coagulation reduction. Thermogravimetric analysis (TGA)[94,95] can be utilized to determine the thermal stability of the prepared nanocomposites and calculate the percentage weight loss (PWL) of the samples with increasing temperature. This allows for an analysis of the preparation and modification of the NPPD.

Wulanawati et al.[92] successfully prepared copolymers of natural rubber and maleic anhydride as crude oil pour point depressants, and infrared spectroscopic analysis demonstrated the emergence of a novel functional group at a wavelength of 1748 cm^{-1}. X-ray diffraction (XRD) analysis by Elkatory et al.[93] demonstrated that the nonpolar alkyl branching of the polymer additives impedes copolymer chain stacking, resulting in lattice distortion and structural disorder that in turn weakens the crystalline structure. Huang[96] characterized the long period, radius of gyration, and thickness of the interfacial layer of paraffin hydrocarbon grains using small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD). El-Segaey et al.[97] prepared novel copolymers (AEs) of hexadecylmaleimide (HDM) and octyloleate (OOE) using solution polymerization, and nanonanohybrids were prepared by emulsion polymerization in the presence of silicon dioxide. The polymeric nanohybrids were characterized by high-resolution transmission electron microscopy (TEM) and dynamic light scattering (DLS) plots, which demonstrated their synthesis on the nanoscale. Wang et al.[98] conducted an investigation into the impact of nanohybridized PPD on the crystallization of crude oil utilizing polarized optical microscopy and X-ray diffraction. The polarized optical microscopy (POM) images demonstrate that the wax crystals in the untreated crude oil are dense, with minimal interstitial space between them. Furthermore, the wax crystals tend to aggregate to form a three-dimensional network, which results in an increase in the apparent viscosity of the waxed crude oil. Following the addition of nanohybrid PPD, the number of wax crystals decreased, the wax crystals were sparse, and the gaps between wax crystals widened, indicating that the apparent viscosity of the crude oil with NPPD was lower. The results demonstrated that the addition of nanohybrid PPD resulted in a reduction in the crystalline strength of wax-containing crude oils, accompanied by a notable decrease in apparent viscosity, with a reduction of approximately 87.4% at 50 s^{-1}. Furthermore, the pour point was observed to be approximately 14.0 °C lower. The incorporation of nanohybrid PPDs resulted in a reduction in the number of wax crystals, prevented their aggregation, and lowered the temperature at which the crude
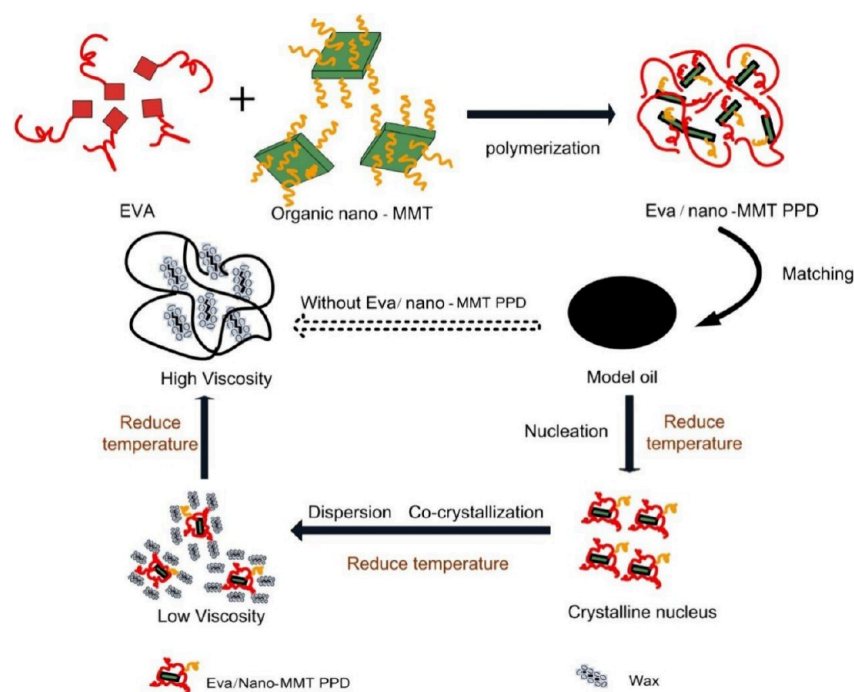
Figure 9. Graphical depiction of the interaction of EVA/nano-MMT composite PPDs with waxes. Reproduced with permission from ref 102. Copyright 2018 Elsevier.

oil crystallized. This indicates that the freezing/pouring point reduction, shear resistance, and fluidity of the nanohybrid PPDs were significantly superior to those of the conventional EVAs.

Deka et al.[99] observed that the polar groups of the two PPDs, namely, poly(*n*-dodecyl linoleate-*co*-succinic anhydride) (MALN) and poly(*n*-dodecyl ricinoleate-*co*-succinic anhydride) (MARC), confer upon the PPDs the capacity to form stronger hydrogen bonds with the gums and asphaltenes. This stronger bonding negates the hydrogen bonding between the gums and asphaltenes, thus preventing them from overlapping. This phenomenon reduces the viscosity of the crude oil considerably, which is clearly observed in the SEM images (Figure 8) of the PPD-treated oils. Yu et al.[100] doped Fe_3O_4 magnetic nanoparticles in EVA and observed the morphology of wax crystals after their action by polarized optical microscopy. The wax crystals at a 100 ppm dose were found to be dense and regular, which verified the nonhomogeneous nucleation in the mechanism of action of the depressant with crude oil. Maleki et al.[24] conducted a comparative analysis of microscopic images of crude oil wax crystals before and after NPPD treatment. They concluded that the spherical shape of the wax crystals is a consequence of the nanomaterials being dispersed effectively in the crude oil medium. They act as sphere-forming nucleation sites that facilitate the development of the wax crystal network.

4. CATEGORY

The nature of the matrix material directly determines the intrinsic composition and microstructure of the pour point depressant, which, in turn, affects its coagulation reduction performance. Therefore, nano-pour point depressants are classified based on the nature of the matrix. With the continuous exploration of nano-pour point depressants, they are mainly classified into silicon-based nano-pour point depressants, carbon-based nano-pour point depressants, and

magnetic metal nano-pour point depressants. The polymerization phase formed by dispersed nanoparticles can be used to prepare polymeric nanocomposite pour point depressants; this provides a framework for the selection of different nano-substrates, the polymerization of the composite, the modification method, and the study of the effect of coagulant reduction, which is important for the in-depth understanding of the mechanism of nano-pour point depressants.

4.1. Silicon-Based Nanomaterial Pour Point Depressants.
Silicon-based materials are known for their excellent chemical and thermal stability and their ability to maintain stable performance in extreme environments such as high temperatures and severe corrosion. Nanomontmorillonite (MMT), a naturally occurring nanomineral commonly used to improve the rheology of crude oil, has been the focus of research in the field of pour point depressants as a "general purpose material". Due to its hydrophilic nature, nano-montmorillonite usually requires organic modification to become organic montmorillonite (OMMT).

Gao et al.[101] investigated the effect of organic montmorillonite on the yield stress of model waxy oils and found that the incorporation of montmorillonite nanosheets significantly reduced the yield stress, which was attributed to the inhibition of wax gelation by the montmorillonite nanosheets. Li et al.[102] prepared a series of novel nanohybridized pour point depressants of nanomontmorillonite (MMT) and ethylene–vinyl acetate copolymers (PPDs), which could control the size and morphology of wax crystals compared to the same content of pure EVA pour point depressants and effectively changed the morphology of wax crystals from fluffy feathery to dense rod-like as shown in Figure 9, where the wax crystals grew together with the EVA/OMMT PPDs, which acted as smaller crystalline nuclei that precipitated earlier than the waxes. The new crystalline nuclei influenced wax precipitation through wax crystal overlap and interactions that were detrimental to the formation of wax crystal networks but favored the formation of
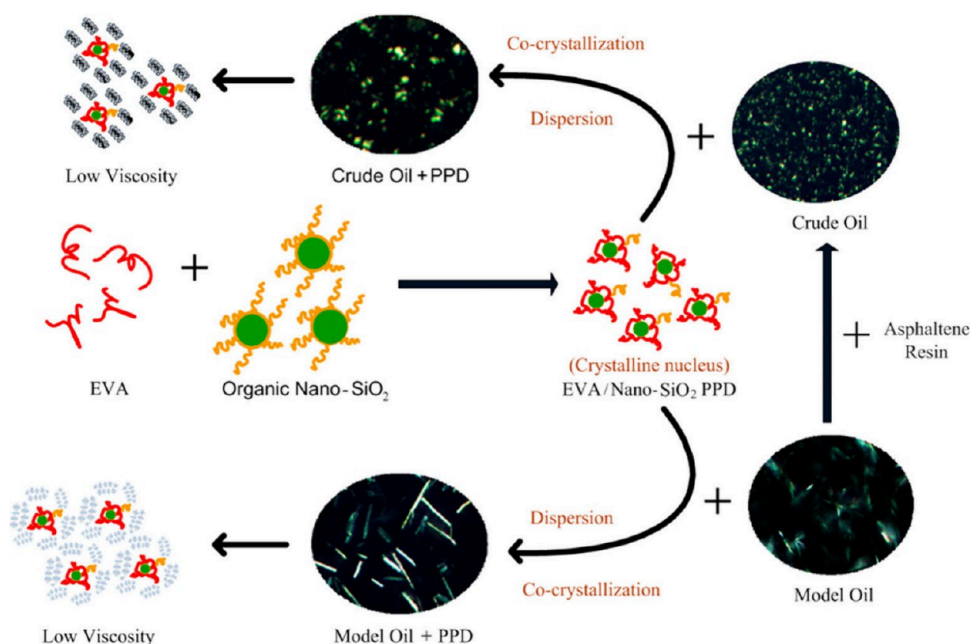
Figure 10. Mechanism analysis of EVA/SiO₂ PPD on oil. Reprinted with permission from ref 108. Copyright 2018 American Chemical Society.

small wax crystals dispersed in the oil phase. Al-Sabagh et al.[103] successfully dispersed inorganic nanolayers of MMT clay on organic polymer matrices by in situ radical polymerization with different ratios to prepare a series of novel poly(octadecyl acrylate derivative)−montmorillonite (ODA/MMT) nano-hybrids, and it was confirmed by a series of characterizations such as high-resolution transmission electron microscopy (HRTEM) and XRD that these polymers provide more nucleation sites for inhibiting or modifying wax crystals. Yao et al.[104] prepared nano-MMT/POA (poly(octadecyl acrylate)) nanohybrids by solution blending and found that POA molecules further enhanced the lipophilicity of the nanoclay. It is believed that the MMT/POA composite particles dispersed in crude oil were able to provide solid−liquid interfacial sites of a minute size that acted as wax precipitation templates, resulting in a larger and denser wax morphology. The large wax crystal size (reduced wax crystal/oil interface) and dense structure (less liquid oil trapped in the wax crystal structure) are conducive to the formation of a reticulated structure, which is conducive to improvement of the rheological properties of waxy crude oils.

Nano-SiO₂ is an important new inorganic material with a strong surface adsorption capacity, high chemical purity, and good dispersion; however there are a large number of hydroxyl and unsaturated bonds on the surface of nano-SiO₂ that result in high surface energy and thermodynamic instability, making it prone to agglomeration and affecting its dispersion performance and hybridization effect in polymers. In recent years, many researchers have used SiO₂ nanocomposites to improve the flow properties of oil products through in situ polymerization and chemical grafting.

Song et al.[105] investigated the effect of SiO₂ nanoparticles on wax crystallization and the fluidity of model oils and concluded that SiO₂ nanoparticles could adsorb and disperse asphaltenes to prevent their aggregation, thus inhibiting the nucleating effect of asphaltenes on wax crystallization. Norrman's team[35] developed a novel nanohybrid PPD by coating poly(octadecyl acrylate) (POA) on the surface of silica nanoparticles, a new

type of nanohybrid PPD. The complete coverage of POA nanoparticles significantly reduced the wax gel strength, and the presence of nanoparticles altered the nature of wax crystallization. Mao et al.[106] used a silane coupling agent, KH570, to surface modify SiO₂ nanoparticles and found that organically modified silica nanoparticles could modulate the aggregation state of wax crystals in the oil phase and act as a crystallographic nucleus to change the morphology of wax crystals and make the aggregates formed by wax crystals denser. The polar groups on the surface of nanosilica adsorbed on the surface of wax crystals and hindered the aggregation, growth, and formation of the wax crystals. Jing et al.[107] prepared a composite pour point depressant of EVA and nanosilica by mixing them with toluene solution and found that as the content of polar groups in EVA increased, the compatibility of the modified nanosilica with EVA became weaker. This reduced compatibility resulted in easier desorption of EVA from the surface of nanosilica, leading to a weaker effect of nanohybridized PPD, and it was concluded that a more suitable EVA could be selected based on the type of oil used and the compatibility factor.

In a study by Ning et al.,[8] the wax crystallization inhibition properties of pure EVA were compared with those of EVA adsorbed onto SiO₂NPs. The results demonstrated that EVA/SiO₂ greatly improved the oil flowability of the nanohybrids compared to pure EVA addition. It can be observed that the SiO₂ nanoparticles can adsorb the asphaltenes and colloids in the crude oil as nuclei, thus inhibiting the deposition of wax crystals. Furthermore, the nanoparticles can also act as nucleation sites for the crystallization of wax molecules. Due to the complexity of crude oil, the interactions between nanoparticles and other components are more intricate. For instance, both agglomeration of nanoparticles and an increase in the concentration can precipitate complex alterations. Consequently, there is an effective saturation concentration of the nanoparticles. The authors thus concluded that adsorbed asphaltenes and colloids act as nuclei on SiO₂NPs, while EVA cocrystallizes with wax crystals and inhibits the formation of a

wax crystal network. Li et al.[108] prepared EVA/SiO$_2$ nano-pour point depressants and compared their viscosity-reducing effects on model oil and crude oil, and the mechanism of action of the EVA/SiO$_2$ nano-pour point depressants on model oils and crude oils is shown in Figure 10. The reduced efficacy of depressants in crude oils can be attributed to the propensity of asphaltenes and colloids in crude oils to aggregate and attach to waxes at low temperatures, which impedes wax crystallization. Maleki et al.[24] investigated the application of polyacrylamide (PAM) in wax deposition inhibition and found that a composite of the most effective pour-point-lowering agents with silica NPs were found to be those containing SiO$_2$, which has the capacity for asphaltene adsorption and the ability to cocrystallize with wax crystals. The adsorbed asphaltene reduces the agglomeration of its aggregates and acts as a template for the nucleation of wax crystals. Furthermore, the highly dispersed nanocomposites are capable of adsorbing a greater quantity of asphaltenes due to the high content of asphaltenes in heavy crude oil. Consequently, the ability of nanocomposites to improve the properties of light oil may not be as significant as that for heavy crude oil. Table 2 illustrates the silica-based nanocomposite pour point depressants.

Table 2. Silica-Based Nanocomposite Pour Point Depressants

NPPD	method	conclusion
EVA-MMT[102]	toluene solution co-mingling	earlier precipitation as smaller nuclei, reducing wax crystal network formation
ODA-MMT[103]	in situ radical polymerization	provides additional nucleation sites for inhibition or modification of wax crystals
POA-MMT[104]	electrostatic adsorption of cationic surfactants (OTAC)	POA alkyl side chains provide nucleation sites for nonhomogeneous wax crystals
POA-SiO$_2$[35]	fully coated surfaces	inhibition of nucleation by dispersed asphaltene
EVA-SiO$_2$[107]	toluene solution co-mingling	an increase in polar groups decreases compatibility, leading to a decrease in the hybridization effect
EVA-SiO$_2$[8]	xylene solution co-mingling	composites can increase the crystallization sites between EVA and waxes
PMA-SiO$_2$[24]	vapor acid method	nanoscale SiO$_2$ adsorbed asphaltene cocrystals and reduced wax crystal agglomeration

4.2. Carbon-Based Nanomaterial Pour Point Depressants. Carbon-based nanomaterials are nanoscale structures composed of carbon atoms that possess unique properties and a wide range of applications. Graphene nanosheets (GNS), one of the most recent two-dimensional (2D) carbon-based nanomaterials to emerge, is a monolayer honeycomb lattice nanostructure consisting of tightly aligned sp^2-hybridized carbon atoms,[109−111] which combines excellent mechanical, electrical, and thermal properties.[112] Graphene is mainly prepared by micromechanical cracking,[113] epitaxial growth,[114,115] chemical vapor deposition (CVD),[116,117] and chemical redox.[118] Although the crystal structure of graphene prepared by traditional physical methods is more complete, the requirements for experimental conditions are more stringent and the output rate of graphene is lower, rendering it unsuitable for large-scale production and practical applications.[79] In order to fully expand the application fields of graphene, efficient and low-cost graphene preparation methods urgently need to be developed and intensively researched. With regard to the cost and processability of graphene

preparation, the redox method is typically employed to extract graphene from natural graphite, expandable graphite, or graphite derivatives (e.g., graphite oxide).

Sharma[119] characterized a polymer nanocomposite, poly-(methyl methacrylate)−graphene oxide (PMMA-GO), prepared by in situ radical polymerization and observed its wax crystal shape in Indian waxy crude oil. He concluded that GO sheets in the nanocomposites acted as nucleation templates for the precipitation of wax crystals, which explains the mechanism of the wax deposition action of the synthesized polymer nanocomposite. The nanocomposite prevents wax crystal overlap and the formation of a wax crystal network. Jaberi et al.[120] prepared a nanocomposite consisting of a monolayer of graphene oxide (GO) nanolayer and polyethylene glycol (PEG) hydrophilic polymer by solution blending. The wax precipitation temperature was significantly reduced, confirming the efficacy of the prepared nano-pour point depressant, as demonstrated by DSC calorimetry. Liu et al.[121] successfully synthesized grafted products of graphene oxide (GO) and alcoholized ethylene vinyl acetate−ethylene vinyl alcohol copolymer (EVAL) by chemical grafting. Their findings indicated that the composite pour-point depressant disrupts the aggregation of colloidal and asphaltene molecules overlapping in planes, leading to sparsity of the aggregation structure. Furthermore, the ordering of the material was reduced. Sharma et al.[122] conducted the laboratory synthesis and preparation of a novel nanocomposite poly(2-ethylhexyl acrylate)−graphene oxide [P(2-EHA)-GO], in which graphene was incorporated. The synthesis steps are listed in Figure 11. This material was found to improve the selectivity of NPPD for waxy crudes, as confirmed by the authors through microscopic image characterization. The study demonstrates that NPPD disperses wax crystals through nucleation and cocrystallization mechanisms, thereby avoiding precipitation. The work of numerous academics and research teams has shown that graphene nanosubstrates can be used in the development of numerous products for flow assurance technology in the petroleum industry, with significant potential for growth.

Mohammadi et al.[123] synthesized single-walled nanotubes (SWCNTs) with the objective of investigating their effect on the formation and growth of asphaltene and wax deposits in crude oil under real production conditions. The high specific surface area of carbon nanotubes allows for the formation of strong π−π interactions between the aromatic ring electron cloud of SWCNTs and asphaltene molecules, adsorbing asphaltene to the surface of the nanoparticles and providing nucleation sites. The presence of these sites facilitates the formation of wax crystals, resulting in a reduction in the melting point of the wax (WAT from 32.6 to 23.2 °C) and the inhibition of the gelation process (GP from 21.5 to 14.7 °C). Jia et al.[9] employed a poly(α-olefin-acrylate) polycarbenol ester pour point depressant (PAA-18) as a pour point depressant in conjunction with three carbon-based nanomaterials of varying sizes, namely graphene oxide. The carbon-based hybrid nano-pour point depressant was prepared by an esterification polymerization reaction using GO, carbon nanorods (Cna's), and oxidized carbon nanotubes (OCNTs), respectively. The molecules are illustrated in Figure 12. Figure 12 depicts the schematic structure and inhibition mechanism of the molecules. All three pour point depressants exhibit excellent thermal stability, high crystallinity, and an excellent coagulation reduction effect. A comparison of the pour point reduction effects of the three composite pour point depressants with
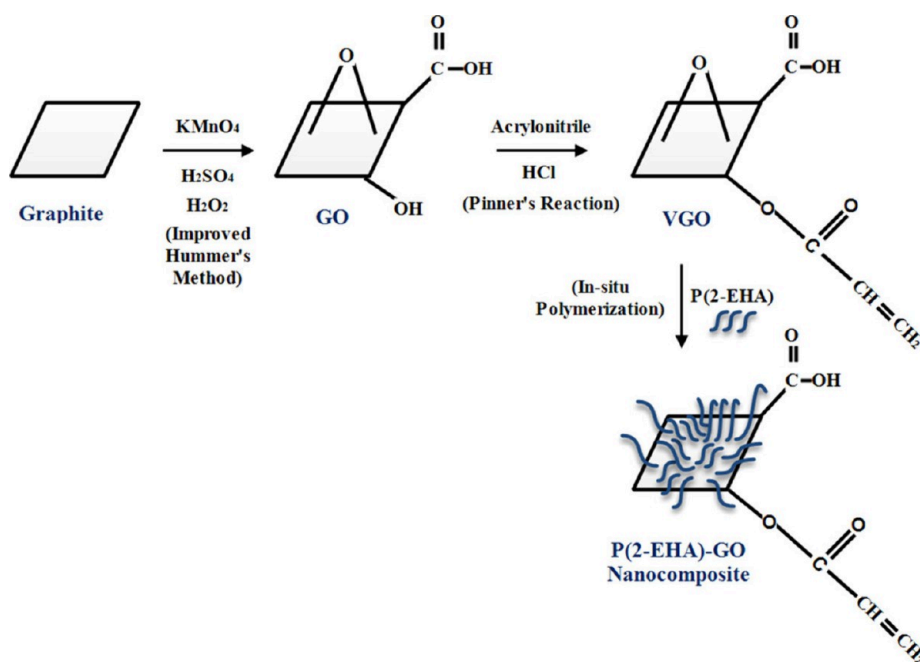
Figure 11. Schematic diagram illustrating the stepwise synthesis of GO, VGO, and nanocomposites. Reprinted with permission from ref 122. Copyright 2019 American Chemical Society.
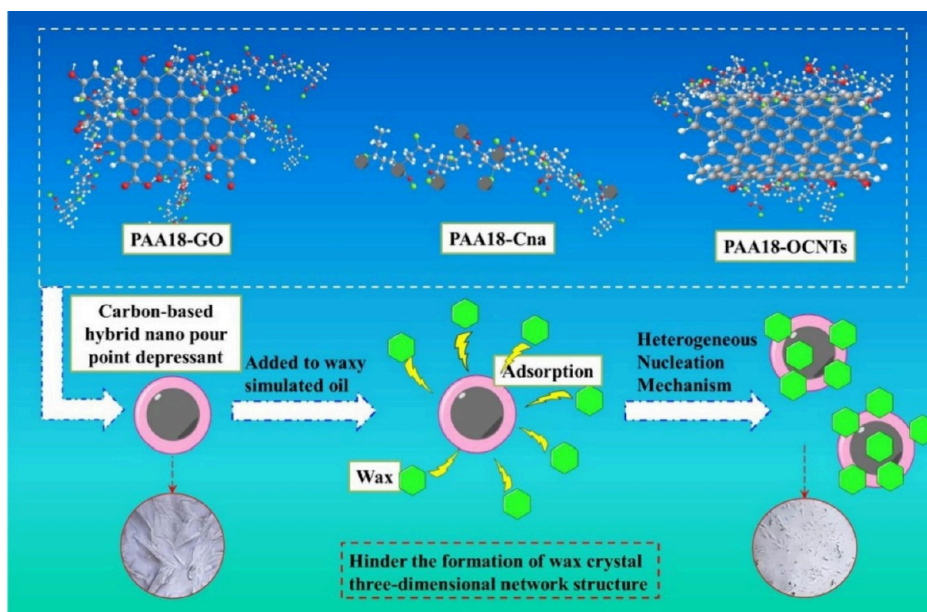

Figure 12. Mechanistic map of carbon-based hybridized nanoinhibitors. Reproduced with permission from ref 9. Copyright 2022 The Authors.

Table 3. Carbon-Based Nanocomposite Pour Point Depressants

| NPPD	method	conclusion
PMMA-GO[119]	in situ radical polymerization	GO can be employed as a nucleation template to reduce wax crystal interlocking
PEG-GO[120]	solution mixing method	the formation of large-sized crystals is prevented by hydrophilic materials.
EVAL-GO[121]	chemical grafting	disruption of overlapping aggregates of colloidal and asphaltene molecules
[P(2-EHA)-GO][122]	optical microscopy	dispersion of wax crystals by nucleation and eutectic mechanisms
SWCNTs[123]	CVD	carbon nanotubes retard asphaltene/wax formation and control their growth in oil media
EVAL-CNT[124]	chemical grafting by esterification	carbon nanotubes provide nucleation sites for inhomogeneous nucleation processes
PAA18-OCNTs[9] PAA18-GO[9] PAA18-Cna[9]	esterification and polymerization by Hummers' Method	the high surface energy of carbon-based nanomaterials provides new nucleation sites
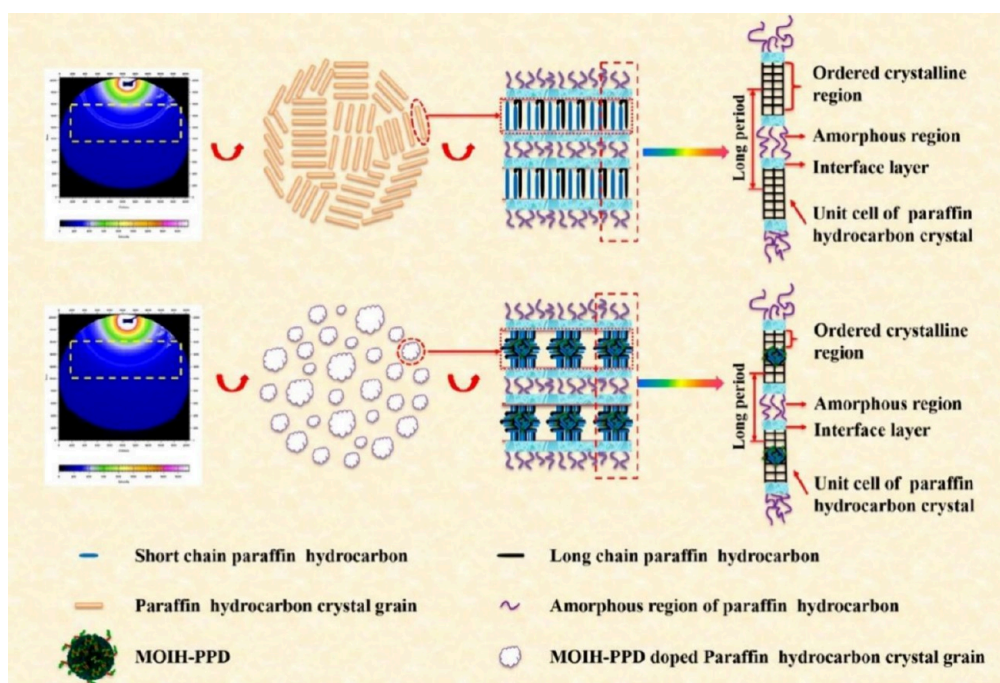
Figure 13. Mechanism of the interaction of MOIH-PPD with paraffinic hydrocarbon molecules. Reprinted with permission from ref 96. Copyright 2020 American Chemical Society.

those of the polymer pour point depressants reveals that the addition of carbon nanomaterials effectively improves the pour point reduction effect of PAA18. The order of the pour point reduction effect is PAA18-OCNTs > PAA18-GO > PAA. Carbon nanotubes have been demonstrated to exhibit excellent pour point and viscosity reduction effects. This is attributed to the unique tubular shape of carbon nanotubes, which allows for greater spatial sites.

In a study by Liu et al.,[124] ethylene vinyl alcohol copolymer (EVAL) and carboxylated multiwalled carbon nanotubes (O-MWCNTs) were used to synthesize the nanocomposite pour point depressant, EVAL-CNT. The grafting process was conducted through an esterification reaction, and the rheological performance of the new pour point depressant on the wax−oil system was investigated through macro-rheological measurements and microelectron microscopy observation. It was observed that the pour point depressant performance was superior to that of EVAL-GO, which was attributed to the fact that the carbon nanotubes served as nucleation sites for the nonhomogeneous nucleation process, which further narrowed the crystal−liquid interface. Additionally, the carbon nanotubes were isolated from each other without interfering with each other, which could enhance the activity of the polymer pour point depressant. Table 3 presents the results of the pour point depressant tests conducted on carbon-based nanocomposite materials.

4.3. Magnetic Metal Nanomaterial Pour Point Depressants. Magnetic nanoparticles are nanomaterials consisting of magnetic elements, and their compounds show great potential for applications in various fields due to their nanoscale size. Ferrite nanoparticles are the most studied magnetic nanoparticles, and their surfaces are usually modified by surfactants and silica, organosilicon, or phosphate derivatives to increase their stability in solution. It has been demonstrated by scholars[125,126] that Fe_3O_4 nanoparticles modified with SiO_2, GO, and polythiophene coatings all

adsorb asphaltenes and inhibit asphaltene precipitation, thus improving the fluidity of asphaltene-containing crude oil. Setoodeh et al.[127] conducted an investigation into the adsorption capacity of asphaltenes from crude oil in the case of magnetic Fe_3O_4 coated with polythiophene (PT), graphene oxide (GO), SiO_2 nanoparticles, and chitosan, respectively. The results demonstrated that the polythiophene-coated Fe_3O_4 magnetic nanoparticles exhibited the highest asphaltene adsorption capacity. The authors hypothesize that this is due to the fact that the presence of sulfur atoms and the polycyclic structure of PT, as a cyclic organic compound with multiple sulfur heterocycles, greatly enhances the polarity of polythiophene. Consequently, it interacts with the N, S, and O atoms in the asphaltene molecule with stronger polarity, electrostatic interactions, and van der Waals forces. Tazikeh et al.[128] also investigated polythiophene-coated magnetic Fe_3O_4 nanomaterials to explore the mechanism of asphaltene aggregation at the micro- and nanoscale from the perspective of molecular dynamics simulations. It was demonstrated that functional groups and aromatic rings in the asphaltene structure are responsible for asphaltene adsorption on solid surfaces (e.g., nanoparticles and substrates). Furthermore, Fe_3O_4 and polythiophene-coated nanoparticles were observed to slow asphaltene precipitation through asphaltene adsorption, which helped to reduce asphaltene cluster formation.

Huang[45] confirmed the synergistic effect of magnetic metal nanomaterials in the presence of a magnetic field, demonstrating a superior pour point reduction effect through the investigation of the impact of an alternating magnetic field on the yield stress of different model oils. Huang[96] investigated the effect of a $NiCo_2O_4$/EVA magnetic nano-pour point depressant on the structure of waxes in model oils in the presence of a magnetic field (as illustrated in Figure 13). At a conditioned temperature of 15 °C, the yield stress was reduced by 181 Pa with the addition of the nano-pour point depressant, whereas the yield stress was only reduced by 149 Pa with the

doping of pure EVA. This indicates that the nano-pour point depressant has a stronger ability to reduce coagulation. The conditions were kept constant throughout the experiment, and the combined effect of NiCo$_2$O$_4$/EVA and a magnetic field was observed to reduce the yield stress of the model oil by 195 Pa. This result further confirmed the synergistic effect of the magnetic field. Wang et al.[129] conducted an investigation into the effect of a ferromagnetic nanocomposite pour point depressant (FNPPD) on wax deposition under the influence of a magnetic field. Their findings indicated that the unfavorable effect of FNPPD, which resulted in an increase in wax content and hardness within the deposited layer, could be mitigated by the synergistic effect of the magnetic field. However, the constant magnetic field would appear to have the opposite effect, reducing the impact of FNPPD. This indicates that the magnetic field exerts an influence on the effect of the magnetic nano-pour point depressant in the reduction of coagulation of crude oils. The mechanism of the synergistic effect remains unclear, presenting an avenue for further research.

In a study by Odutola et al.,[130] blends of polyethylene—butene (PEB) and aluminum oxide nanoparticles (Al$_2$O$_3$) were found to greatly reduce crude oil viscosity at low temperatures with the addition of varying concentrations of PEB/Al$_2$O$_3$. However, at higher operating temperatures, temperature plays a more critical role in reducing the viscosity of the crude oil, and at this point it will not be possible to accurately assess the pour point depressant performance.

Yu et al.[100] employed a composite ethylene vinyl acetate (EVA) with magnetic spherical Fe$_3$O$_4$ nanoparticles, along with polarized optical microscopy and rheological tests, to study the wax crystal morphology and the rheological properties of Daqing crude oil compared with the same size of nano-EVA-SiO$_2$. The results demonstrated that magnetic nanomaterials exert a nonhomogeneous phase nucleation effect, which effectively enhances the efficacy of the nano-composite pour point depressant. The team of Huang[96] prepared a magnetic metal oxide organic—inorganic hybrid (MOIH-PPD) for the reduction of crude oil coagulation. MOIH-PPD acted as a nucleation template for paraffin hydrocarbon molecules, regulating the crystallization process. Furthermore, this work demonstrated the modifying effect of a magnetic field on MOIH-PPD, reducing the yield stress of paraffin. In a study by Mahmoudi et al.,[131] MWCNT-Fe$_2$O$_3$ nanocomposites were synthesized with the objective of controlling the formation and growth of asphaltene particles in unstable crude oil. The composites were found to have a higher asphaltene adsorption potential and the ability to control asphaltene aggregation. The authors postulated that a more pronounced coagulation reduction effect could be achieved by utilizing a smaller molar amount of metal particles, potentially due to the robust hydrogen bonding between the iron oxide and the asphaltene active sites. The investigation of the MWCNT-Fe$_2$O$_3$ nanocomposites indicates the potential for enhanced asphaltene inhibitors and dispersants, which will effectively reduce the reliance on metal-based nanoparticles and their associated environmental impacts. Table 4 presents a series of magnetic metal nanocomposite pour point depressants.

5. CONCLUSION

The Review reviews the current state of research on nano-pour point reducing agents, analyzing the preparation, modification,

Table 4. Magnetic Metal Nanocomposite Pour Point Depressants

NPPD	method	conclusion
Fe$_3$O$_4$-EVA[100]	melt mixing method	denser petal-like wax crystals observed
NiCo$_2$O$_4$-EVA[96]	magnetic field synergy	constant magnetic field reduces the viscosity reduction effect.
PEB-Al$_2$O$_3$[130]	solution mixing method	higher temperatures are more critical to pour point depressant effectiveness
Fe$_3$O$_4$—PT[127]	coprecipitation	cyclic structure increases electrostatic repulsion and van der Waals forces
Fe$_3$O$_4$—PT[128]	molecular dynamics simulation	significant reduction in the number of molecules and average size of asphaltene aggregates
MOIH-PPD[96]	magnetic field synergy	regulating paraffin crystallization as a nucleation template
MWCNT-Fe$_2$O$_3$[131]	CVD, deionized water washing	strong hydrogen interactions between iron oxide and asphaltene active sites

and characterization methods of nano-pour point reducing agents to meet the current research needs. The aim is to provide a strong reference for theoretical construction and practical application in this field. A summary is made of the different nanosubstrate compounding methods, and the coagulation reduction ability is analyzed by means of characterization, which provides some ideas for nano-pour point lowering agent compounding.

(1) The effect of polymer pour point depressants is influenced by their own structure. The nonpolar part (long-chain alkyl group) achieves coagulation reduction through the eutectic effect, while the part that is more polar due to the existence of functional groups (such as ester group) can effectively enhance dispersion to achieve the purpose of coagulation reduction. The incorporation of nanosubstrates enables the pour point depressant to retain an adequate alkyl side chain length, ensuring polarity through the active electrons present in the pores or interlayers and thereby enhancing the pour point depressant ability. The nucleation sites provided by the nanoparticles facilitate the crystallization of the wax molecules, allowing a multitude of coagulation reduction mechanisms to operate in concert and thereby ensuring the coagulation reduction ability. The incorporation of nanosubstrates has led to a notable enhancement in the mechanical properties and thermal stability of the pour point depressant, accompanied by a broader selectivity to crude oil, which is of practical significance for industrial applications.

(2) The utilization of melt blending in lieu of solution blending during the synthesis of nano-pour point depressant results in the formation of smaller particles dispersed within the oil phase, accompanied by a more pronounced pour point reduction effect. The grafting of polymers to enhance polarity can effectively enhance the dispersion of wax crystals, while the modification of the wettability of nanoparticles through the use of silane coupling agents can improve the compounding effect. The characterization of nanoparticle microparameters represents a crucial indicator for the study of the properties of nanoparticles, including chemical components, lattice parameters, specific surface area, and so forth. The microstructural parameters obtained by means of characterization can be employed to further analyze the influence of different preparation conditions

and methods on the performance of the synthesized nano-pour point depressants. This analysis allows the optimal synthesis conditions to be identified, which is the key to measuring the modification effect and evaluating the results of the nanocomposite pour point depressant preparation.

(3) The exploration of nano-pour point depressants has been deepening, with the majority of these being divided into three main categories: silicon-based nano-pour point depressants, carbon-based nano-pour point depressants, and magnetic metal nano-pour point depressants. Among the silica-based NPPDs, nanoclay exhibits a lower cost and superior wax adsorption ability following surfactant modification. The point-carrying ions in the interlayer enhance the polarity, causing electrostatic repulsion that is conducive to the dispersion of wax. Nano-SiO$_2$, on the other hand, was able to maintain stable descaling performance following modification due to its stronger surface adsorption capacity and dispersibility. The OCNTs in carbon-based NPPDs provide more nucleation sites due to their tubular structure and have a better coagulation reduction ability than GO and Cna. The advantage of magnetic metal nanoporous point depressants is that they can synergistically reduce the consumption of energy and chemical agents through the addition of an alternating magnetic field, which can promote the effectiveness of coagulation reduction.

Given the excellent compatibility with crude oil systems, remarkable dispersibility, higher specific surface area, and superior grafting activity of NPPDs, the development of NPPDs with excellent properties will remain a core topic for future research, particularly for cutting-edge products such as magnetic NPPDs and NPPDs derived from novel materials, which indicate broad potential for development and application. Future research efforts need to elucidate the mechanism of action of NPPDs and conclude that the addition of nanoparticles affects the wax deposition, gelation, and aggregation-crystallization processes by comparing it with the mechanism of a conventional polymer pour point depressant, in order to design superior NPPDs that will drive the overall advancement of NPPDs technology. Through continued exploration and innovation, it is anticipated that more effective strategies for the efficient application of NPPDs in crude oil treatment and other related industries will be developed.

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Notes

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