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# Insights into pour point depressants: a brief review of their impact on the behavior of waxy crude oil

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## ABSTRACT

A persistent challenge in the petroleum industry involves paraffin wax deposition from crude oils during low-temperature conditions, complicating pipeline flow assurance due to the intricate rheological behaviors exhibited by waxy crude oil gels. These behaviors include viscoelasticity, yield stress, and thixotropy, contributing to issues like flow reduction and pipeline obstruction, adversely affecting overall pipeline performance. Mitigating this problem requires a combination of mechanical and chemical processes, with pour point depressants (PPDs) emerging as an effective chemical solution. PPDs operate by interacting with wax crystals in the oil, disrupting their formation into a continuous network and preventing flow blockage at lower temperatures. The performance of PPDs depends on factors such as base oil type, PPD concentration, and application temperature. Recent advancements in PPDs focus on developing new polymers with enhanced performance and reduced environmental impact, including those derived from renewable resources, biodegradable PPDs, nano-structured PPDs, or hybrid PPDs. Polymeric additives, such as crystalline-amorphous copolymers, ethylene-vinyl acetate copolymers, comb polymers, and nanohybrids, are employed to modify wax crystallization behavior. Understanding the molecular structure of these additives, fluid composition, and pipeline conditions is crucial for optimizing formulations tailored to specific petroleum fluid compositions and transport conditions, ensuring effective wax deposition mitigation.

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## 1. INTRODUCTION

Millions of years ago, the organic materials of living organisms and plants mixed with other sediments were buried and sunk to the seafloor after dying. Under high pressure and temperature conditions, the remains of the organisms transformed into fossil fuels such as coal, natural gas, and petroleum. Petroleum is made up of a complex blend of substances that developed from the deposition and breakdown of organic stuff. Microorganisms and phytoplanktonic algae are the main constituents of this mixture, which are combined with inorganic sediments to form the major constituents of the oil content [1]. Petroleum is not uniformly homogeneous and its composition varies depending on the location and age of the oil field, as well as its depth. Each Petroleum variety derived from various wells or locations has a distinct mix of molecules that determine physical and chemical attributes like viscosity, fluidity, cloud point, pour point, and others.

Today, petroleum reservoirs can be found on land and beneath the ocean's surface. Giant drilling equipment is used to obtain petroleum crude oil. Color differences represent the various chemical compositions of different crude oil suppliers [2]. Although the hue of this crude oil is typically black or dark brown, it can also look yellowish, reddish, tan, or even greenish. Hydrocarbons, such as paraffin, naphthene, and aromatics, are found in crude oil and are categorized into several categories based on the sorts of molecules. Hydrocarbons make up around 50 to 97% of oil, with nitrogen, oxygen, and sulfur accounting for the remaining 6 to 10%, and metals such as copper, nickel, vanadium, and iron accounting for less than 1% [3]. Figure 1 shows wax blockages in subsea pipelines occurring when the crude oil solidifies due to low temperatures, obstructing flow, and necessitating preventive measures.

Waxy crude oil is made up of paraffinic hydrocarbons ($C_{18}$-$C_{36}$), often known as paraffinic wax, as well as some naphthenic hydrocarbons ($C_{30}$-$C_{60}$) [4]. High pressure and temperature in the underground rock formations make crude oil entirely liquefiable. However, when the oil is exposed to lower temperatures or pressures, the wax molecules become less soluble and have a greater chance of crystallizing, separating from the oil phase, and packing on pipeline walls [1]. These waxy crudes can precipitate in cold temperatures, making crude oil production, transportation, and storage challenging. Three steps namely nucleation, growth, and agglomeration lead to the crystallization process of paraffin wax from crude oil [5]. A disordered phase is transformed into a solid ordinate structure by the physical process of crystallization. Due to the oversaturation of paraffin waxes in the oil phase, nuclei develop in the first step. Wax molecules from the fluid bulk are transferred to the nucleus throughout the development process, increasing crystallite size. Wax crystals that have formed during the agglomeration process interact with one another and create networks. Other factors like hydrates, slugs, and emulsions can also lead to flow assurance problems. Figure 2 shows the flow assurance problems in subsea pipelines which can arise due to different factors.

The pour point temperature is the lowest temperature at which a liquid, here crude oil will stop flowing. The flow of crude oil is blocked by wax precipitation creating concerns for operational safety and increasing expenses, as well as several challenges during transportation. The starting of machinery in cold weather conditions might be difficult or impossible due to the high pour point of these oils [6]. Solid wax deposits with carbon numbers between 18 to 75, and having melting points between 40 to 70 °C are a common source of high molecular weight paraffin.

The wax deposition can be managed and prevented using different techniques such as mechanical (by pigging), thermal (by hot water or oil), and chemical approaches. For the mechanical method, pigging technology has been used for a long time since it is less expensive than replacing pipes. It is also one of the most used methods to evaluate the internal health of a pipeline. Recently, high chemical resistance thick film glass-filled materials have been used in pigging. Here, pigs are fired from one end and then retrieved from the other end either by using compressed air, water, or process liquids [7]. Another wax preventive and correction technique is the application of heat. For crude oil pipelines in colder areas, various thermal treatments for eliminating wax accumulation have proven effective. Due to the benefits of raising the temperature above the wax appearance temperature, active heating has been particularly recognized as an effective flow assurance method against this wax. These methods may include the installation of downhole heaters, and radio frequency heaters or insulation [8].

Figure 1. Wax blockage in subsea pipeline [9]

The chemical procedure is the simplest and most economical of all of these techniques. These are the most frequently suggested strategies since they are less expensive than other ways to prevent wax build-up. Chemicals of different kinds, like solvents, dispersants, wax crystal modifiers, pour point depressants, or paraffin deposition inhibitors, can be utilized [10]. The difficulties due to wax deposition can be mitigated through the application of low quantities of polymeric additives. These polymeric wax inhibitors (WIs) are commonly utilized in the pipeline transportation of waxy crude oils to address wax deposition issues. These inhibitors often serve dual purposes, functioning not only as wax inhibitors but also as pour point depressants (PPDs) or flow improvers for waxy crude oils. This dual functionality significantly enhances safety and economic efficiency. This article comprehensively reviews the structural characteristics, types, and mechanisms associated with polymeric wax inhibitors and PPDs.

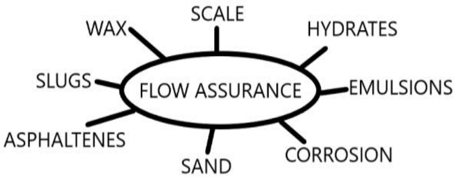


Figure 2. Factors of flow assurance problems

## 2. RHEOLOGICAL BEHAVIOUR OF WAXY CRUDE OIL

Crude oil is a liquid that exists naturally and is obtained from the ground. It has a high viscosity, which means it has a high amount of friction, and it is typically darker in color than refined oil. The viscosity of crude oil can vary depending on its origin and composition. For example, crude oil from North America tends to have higher viscosities than crude from other areas due to the lower natural gas content in North American crude. One of the common sources from the production of petroleum fuel and other chemical products is waxy crude oil. The rheological behavior of waxy crude oil is dependent on temperature which can be represented by a curve of a phase diagram, "Viscosity-temperature graph" which is shown in Figure 3.

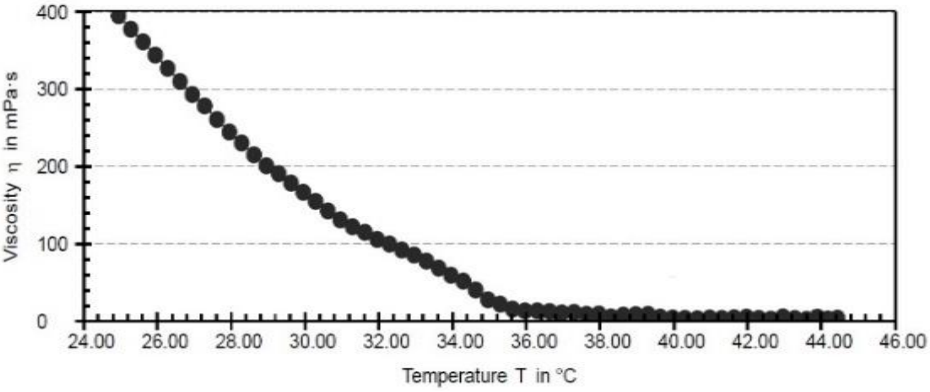


Figure 3. Viscosity-temperature graph for waxy crude oil having pour point at 33 °C

The viscosity of waxy crude oil decreases as temperature increases. The rheology of oil refers to how oil changes as it flows through a pipeline. It is important for this reason as it may clog the pipeline causing damage or even failure if it loses its ability to flow at an acceptable rate. The viscosity of waxy crude oil can vary from very light to very heavy depending on the temperature at which it is kept. The viscosity also depends on the measurement method used as measurements made using a differential refractometer give results that are lower than those obtained using conventional methods such as a burette or pipette. Wax begins to precipitate and become suspended in the Newtonian base liquid below a specific critical temperature or wax appearance temperature (WAT). Crude oils are mostly Newtonian liquids above this temperature. The precipitated wax may stick to cold surfaces and cause wax deposition. This happens at a higher temperature when there is more wax in the oil. Additionally, the rheological behavior becomes decidedly non-Newtonian as more wax precipitates with continued temperature decline. When this happens the pipeline flow assurance becomes more difficult as the waxy crude oil gels complicate the rheological characteristics, yield stress, viscoelasticity, and thixotropy properties [11].

## 3. WAX DEPOSITION AND FLOW ASSURANCE ISSUES

Flow assurance issues have been in the oil and gas sector since the very beginning. The key issues in flow assurance revolve around preventing and controlling solid deposits that could obstruct product flow. Hydrocarbon fluids are efficiently transferred from the reservoir to the end user over the course of a project in any environment using a technique known as "flow assurance," which is an engineering analytical process. With flow assurance, solids like hydrates [12], wax, asphaltenes, and scale can be controlled [13]–[15].

Wax deposition is a major problem in crude oil transportation. It can cause flow restrictions and pipeline blockages. Waxes are complex organic compounds that can solidify and deposit on the walls of pipelines at lower temperatures, especially during the transportation of crude oil with high paraffin content. To prevent wax deposition, pipeline operators use a variety of methods, including insulation, mechanical methods, heating, and chemical inhibitors. Insulation and heating can help maintain the temperature of the crude oil above the wax appearance temperature, preventing the wax from solidifying and depositing on the pipeline walls. Chemical inhibitors can also be injected into the crude oil to prevent wax deposition by disrupting the crystal structure of the waxes. In addition to preventative measures, pipeline operators also use pigging, a process of sending a mechanical device through the pipeline to remove any accumulated wax. This is particularly important for pipelines that are not continuously operated, such as those in remote or offshore locations [16].

The mechanism of wax deposition in crude oil pipelines involves the cooling and subsequent crystallization of waxy components present in the oil. When the temperature falls below the WAT or pour point, certain hydrocarbons in the crude oil begin to solidify and form wax crystals. The wax crystals can adhere to the inner surface of the pipeline, initiating the deposition process. The deposition is influenced by factors such as the composition of the crude oil, the concentration of waxy components, and the pipeline operating conditions. Crude oils with higher concentrations of long-chain paraffins are more prone to wax deposition. The deposition process is exacerbated in areas where the flow rate decreases, such as bends or areas with reduced pipeline diameter, as well as in regions of low pipeline insulation. These areas experience lower flow velocities, allowing more time for wax crystals to settle and adhere to the pipeline walls. Additionally, the presence of impurities and other solid particles in the crude oil can serve as nucleation sites for wax crystals, further promoting deposition. PPDs are commonly used to mitigate wax deposition issues. PPDs function by modifying the crystallization behavior of waxy components, preventing the formation of large and obstructive wax deposits. Understanding the mechanisms behind wax deposition is crucial for implementing effective strategies to prevent or manage the issue in crude oil pipelines, ensuring smooth and efficient oil transportation. The recent studies of pour point and wax content values of waxy crude oil are shown in Table 1.

Table 1. Recent studies (2019-2023) on pour point and wax content values of waxy crude oil

| Sl No | Waxy Crude Oil/Location | Pour Point (°C) | Wax content(wt%) | Reference |
|---|---|---|---|---|
| 1 | Akshabulak oil field (Kazakhstan) | 19 | 17.1 | [17] |
| 2 | North Qarun field, Qarun Company (Egypt) | 27 | 12.42 | [18] |
| 3 | Three crude oils of Daqing Oilfield, Heilongjiang, China | 34, 32, 34 | 18.3, 17.6, 18.1 | [19]–[21] |
| 4 | Qarun Petroleum Company, Egypt | 21 | 9.52 | [22] |
| 5 | Two crude oils of Niger Delta, Nigeria | 27, 30 | 14.4, 15 | [23] |
| 6 | Three crude oils of (oils A−C) China | 16, 30, 23 | 11.34, 16.38, 10.02 | [24] |
| 7 | Iranian heavy crude oil | 15 | 11.4 | [25] |
| 8 | Jing'an Block (Changqing Oilfield), China | 24 | - | [26] |
| 9 | Shengli (SL) waxy crude oil, China | 32 | 21.23 | [27] |
| 10 | Egyptian Waxy crude oil from Qarun (Egypt) | 27 | 12.3 | [28] |
| 11 | Western Indian oilfield | 38 | 14 | [29] |
| 12 | Kerteh, Terengganu, Malaysia | 11 | 28 | [30] |

## 4. WAX DEPOSITION AND FLOW ASSURANCE ISSUES

### 4.1. Crystalline amorphous polymers

Crystalline and amorphous polymers are two types of polymers that can be used as PPDs for crude oil and other petroleum products. Crystalline polymers have an ordered, repeating structure, and they can form crystalline regions with distinct melting points. Examples of crystalline polymers are polyethylene and polypropylene. Crystalline PPDs work by disrupting the formation and growth of wax crystals, which lowers the pour point of the fluid. Amorphous polymers, on the other hand, have a disordered, random structure and lack distinct melting points. Examples of amorphous polymers are styrene-butadiene copolymers and ethylene-propylene copolymers. Amorphous PPDs work by absorbing onto the surface of the wax crystals and preventing them from agglomerating and blocking pipelines or equipment. Both crystalline and amorphous polymers can be used alone or in combination with other PPDs to achieve the desired pour point reduction. Figure 4 shows the structure of crystalline, amorphous, and semi-crystalline polymers. Crystalline polymer structure features highly organized molecular chains arranged in repeating patterns, resulting in regions of densely packed segments known as crystallites, contributing to the material's stiffness, strength, and distinct melting points. Amorphous polymers lack long-range molecular order, exhibiting random arrangement of chains without distinct crystalline regions, leading to properties like flexibility, transparency, and a broad glass transition temperature range, making them suitable for various applications including packaging materials and adhesives.

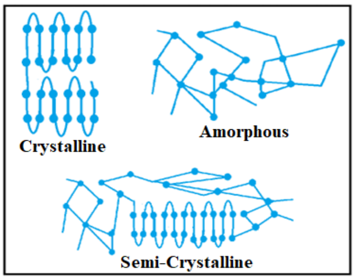


Figure 4. Crystalline amorphous polymers

In a study, investigates the impact of polyethylene-vinyl acetate (EVA) on the flow behavior of degassed crude oil treated with supercritical carbon dioxide ($scCO_2$), employing various analyses. The results reveal that $scCO_2$ extraction disrupts the solvation layer of asphaltenes, forming asphaltene aggregates that hinder their role as natural wax crystal modifiers. Consequently, smaller and more abundant wax crystals are precipitated, leading to increased pour point and apparent viscosity at low temperatures. Moreover, the addition of EVA enhances wax solubility, altering the wax crystal morphology from needle-like to compact clusters. Interestingly, the asphaltene aggregates induced by $scCO_2$ still interact with EVA, facilitating EVA adsorption on asphaltene aggregates and resulting in a more efficient EVA/asphaltene composite. This synergistic effect leads to more compact wax crystal structures, improved flow behavior, and higher liquid oil content in the crude oil samples [31].

### 4.2. Polymethacrylates

Polymethacrylates are a family of polymers that are derived from methacrylic acid or its esters. They can be synthesized by a variety of methods, including radical polymerization, anionic polymerization, and cationic polymerization. The resulting polymers can have a range of properties, depending on the specific monomers and conditions used in the polymerization process. They can be added to petroleum products to lower their pour point. They work by reducing the size of the wax crystals that form at low temperatures, making them easier to disperse and preventing them from blocking pipelines or equipment [32]. Figure 5 represents a terpolymer that comprises chains with alternating units of methyl methacrylate (MMA), propyl acrylate (PA), and maleic anhydride (MAH), forming a copolymer structure. The MMA units contribute rigidity, PA adds flexibility, and MAH provides functional groups for crosslinking or reactivity.

In a wide range of temperature settings, including the dramatic temperature swings experienced in laboratory tests, polymethacrylate additives are renowned for their adaptability and effectiveness. Because of their versatility, these additives can perform well under a variety of operating situations, which is advantageous. Polymethacrylate additives can be particularly made to increase the viscosity index of oils in addition to their ability to lower pour points. The viscosity index evaluates an oil's resistance to variations in viscosity brought on by temperature changes. Higher viscosity index values suggest less pronounced temperature-related fluctuations in the oil's viscosity [32], [33].

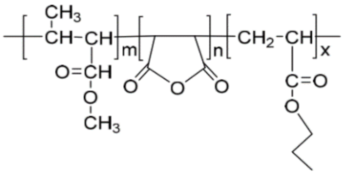


Figure 5. Chemical structure of the PPD with three monomers of methyl methacrylate, propyl acrylate, and maleic anhydride [27]

Kazemi *et. al.* [34] performed studies where a novel polymeric nanocomposite PPD, consisting of polymethyl methacrylate (PMMA) and montmorillonite (MMT) clay, was synthesized and characterized for its efficacy in treating a model waxy crude oil. Comparative analyses with neat PMMA were conducted, revealing that the PMMA/clay nanocomposite exhibited superior performance. The addition of 400 ppm of PMMA and 800 ppm of PMMA/clay nanocomposite to the waxy crude oil resulted in a remarkable 120% reduction in pour point, reaching -3 °C. Rheological tests demonstrated that both PMMA and PMMA/clay nanocomposite reduced yield stress and gelation point, with the nanocomposite displaying significantly higher effectiveness. Moreover, the nanocomposite altered the morphology and dispersity of waxy solid-phase particles, preventing the formation of a waxy network and enhancing the rheological properties and flowability of the waxy crude oil.

### 4.3. Alkyl acrylate copolymer

Alkyl acrylate copolymers are copolymers of two or more alkyl acrylates, such as stearyl acrylate and behenyl acrylate, and are often used in combination with other PPDs to achieve the desired pour point reduction. The resulting copolymer can be tailored to have a specific composition and molecular weight, which can affect its effectiveness as PPD.

Figure 6 shows an example where the combination of stearyl acrylate and behenyl acrylate forms stearyl acrylate-co-behenyl acrylate copolymer which is used as flow improver or PPD. The alkyl acrylate copolymers work by adsorbing onto the wax crystals that form in the crude oil at low temperatures, preventing them from agglomerating and clogging the flow of the crude oil. This type of polymer has excellent corrosion resistance, high strength, and high toughness. The copolymers also have a steric hindrance effect, which prevents the wax crystals from growing and forming larger aggregates [35].

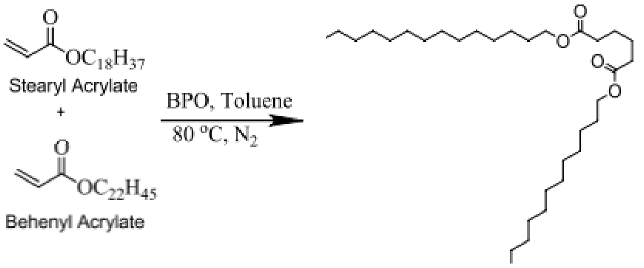
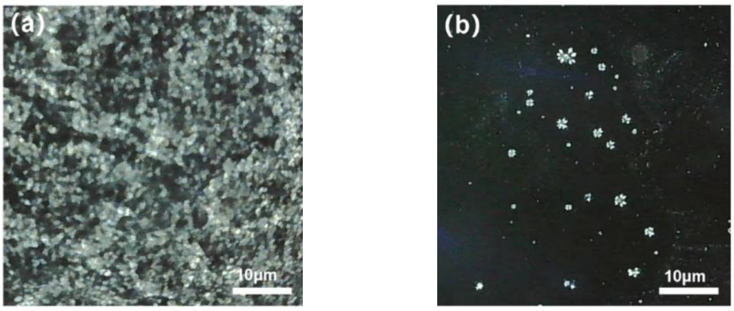


Figure 6. Structure of stearyl acrylate-co-behenyl acrylate copolymer [30]

Figure 7 illustrates polarized microscopy images capturing the crude oil in two scenarios: one without a pour point depressant and the other with the inclusion of 200 ppm of pour point depressant at a temperature of 20 °C. The absence of a pour point depressant resulted in small wax crystal sizes, relatively loose wax crystal distribution, and even dispersion in the oil phase. Upon introducing the PPD, the wax crystal particles in the crude oil exhibited increased size, forming large spherical crystal aggregates through agglomeration. The addition of the pour point depressant altered the wax crystallization pattern, reducing the amount of encapsulated liquid oil, diminishing the flocculation tendency of wax crystal aggregates, weakening the spatial grid structure's strength, and ultimately enhancing the flowability of the crude oil [27].



(a) (b)

Figure 7. Polarized microscopy images of crude oil of (a) virgin crude oil and (b) crude oil with 200 ppm concentration of PPD at 20 °C [27]

### 4.4. Ethylene-vinyl acetate copolymers

Ethylene-vinyl acetate copolymers (EVAc) are used as PPD for crude oil and lubricating oils. They work by disrupting the crystallization of waxes, which lowers the pour point and improves low-temperature flow. The use of EVAc as a PPD for crude oil is well-established and has been studied extensively. Researchers have investigated various factors that can affect the performance of EVAc as a PPD, including the molecular weight, vinyl acetate content, and dosage. Additionally, researchers have explored the possibility of using EVAc in combination with other additives to enhance its performance as a PPD [17], [36]. Figure 8 shows the ethylene-vinyl acetate copolymer structure.

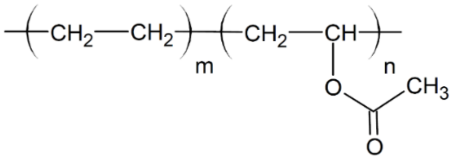


Figure 8. Ethylene-vinyl acetate copolymer structure

According to Marenov *et al.* [17], combining EVAc with gossypol (CG) acts as an efficient PPD for crude oils. One of the possible explanations for the improved properties could be the appearance of additional nonpolar and polar groups caused by the formation of the EVAc/CG composition. This combination may have introduced new chemical functionalities or modified the surface properties of the PPD, enhancing its performance in reducing the pour point of the crude oil. Further exploration and optimization of the copolymer structures such as the alkyl chain length with the presence of specific functional groups such as benzene ring or other polar groups could enhance the performance of the copolymers as PPDs [37]. Xia *et al.* [38] studied the addition of laurylamine (LA) to vinyl acetate copolymer pour point depressants (EVA PPD) which seems to have a significant impact on the interaction between the EVA and polar asphaltenes. The authors propose that a small amount of LA can weaken the interaction force between the resin and polar asphaltenes. However, the authors also note that an excessive amount of LA can have negative consequences. Too much LA can cause the asphaltenes to clump together, which can result in a small decline in the rheology of the oil samples. This suggests that an optimal amount of LA should be used to achieve the desired modification effect without negatively impacting the overall rheological properties of the oil. These findings highlight the importance of carefully controlling the LA concentration in EVA PPD formulations. By optimizing the LA content, it may be possible to enhance the performance of the EVA PPD in terms of modifying the asphaltenes and improving the rheology of the oil samples.

### 4.5. Polyolefin copolymers

Polyolefin copolymers are used as pour point depressants for diesel fuels and heating oils petroleum products. They work by modifying the crystalline structure of the waxes that form at low temperatures, reducing their size and preventing them from blocking pipelines or equipment [39]. Polyolefins, such as polyethylene and polypropylene, are effective pour point depressants in heavy crude oils due to their ability to modify the wax and asphaltene crystal structure. They adsorb onto the surface of the wax and asphaltene particles, preventing their growth and aggregation, and thus reducing the pour point of the crude oil. The degree of pour point depression achieved depends on several factors, including the type and concentration of the polyolefin used, the wax and asphaltene content of the crude oil, and the temperature at which the crude oil is being processed [31]. Polyolefin pour point depressants have been shown to be effective in reducing the pour point of heavy crude oils by as much as 20-30 °C.

### 4.6. Comb polymers

Comb polymers are macromolecules that consist of a backbone chain and side chains that are attached to the backbone like the teeth of a comb. Figure 9 shows a comb-type polymer. These side chains can be tailored to have different chemical properties, such as polarity, charge, or hydrophobicity. Comb polymers can exhibit unique properties due to their structure, such as the ability to self-assemble into specific patterns or to form stimuli-responsive materials. Comb polymers can be effective PPDs because their side chains can interact with the wax crystals and prevent them from aggregating and forming large, rigid networks that can block the flow of the oil. The length, density, and chemical composition of the side chains can be tuned to optimize the PPD performance for specific applications and operating conditions [40], [41].

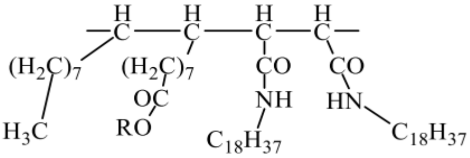


Figure 9. Structure of poly benzyl oleate-co-maleic anhydride polymer [42]

### 4.7. Nano-hybrid PPDs

Nano-hybrid pour point depressants (NHPPD) are an improvement over traditional PPDs, which have been used for decades to improve the flow rate of crude oil through long-distance pipelines. These new NHPPDs use a combination of nanotechnology and chemistry to create a more effective method for controlling the viscosity of crude oil. Nano-hybrid PPDs are made by combining two or more types of PPD additives: a conventional PPD and a nanomaterial, such as carbon nanotubes, graphene, or other nano-size materials. In comparison to pure polymers, the addition of dispersed nanoparticles enhances the mechanical and thermal stability, abrasion resistance, and tenacity of nanocomposite materials. The combination of these materials creates a synergistic effect, resulting in a more effective pour point depressant with improved performance at lower concentrations [26].

In Figure 10, the pour point change in a model oil with 15 wt% wax is depicted after the addition of various types and doses of PPDs. The trend observed indicates an initial decrease followed by an increase in pour point with the rise in PPD dosage. Notably, compared to the conventional methacrylate PPD PM18, non-polymeric pour point depressants (NPPDs) demonstrate a superior effect in reducing the pour point, with significantly lower optimal dosages. The most effective pour point depression is achieved with a 300 mg·kg−1 dosage of PM18/SiO2 and PM18-g-NSiO2, resulting in pour point reductions from 30 to 17 and 11 °C, respectively. Moreover, PM18-g-NSiO2, when compared to the same dosage of PM18/SiO2, further enhances the low-temperature fluidity of the oil. This improvement is attributed to the crucial role of polymer coverage on nanoparticle surfaces, where establishing a stable chemical bond through grafting enhances polymer stability, prevents shedding, and effectively improves the overall performance of NPPDs [43].

In this section, the impact of graphene oxide (GO)-PPD and EVA on the morphology of wax crystals was investigated, as illustrated in Figure 11. In Figure 11(a), without any chemical additive, sword-like wax crystals were observed, forming a three-dimensional network as their quantity increased. However, the introduction of EVA in crude oil led to the effective dispersion of wax crystals, accompanied by a notable reduction in both quantity and size, as depicted in Figure 11(b). The presence of GO-PPD in the crude oil further enhanced wax crystal dispersion, with smaller crystal sizes compared to those observed with EVA. This suggests that GO-PPD holds promise as a pour point depressant, effectively inhibiting wax formation and promoting the flowability of the crude oil from Changqing [26].

However, it should be noted that all the above studies were conducted using crude oil from a specific oil field, and the effectiveness of the different PPD compositions may vary depending on the properties of the crude oil.

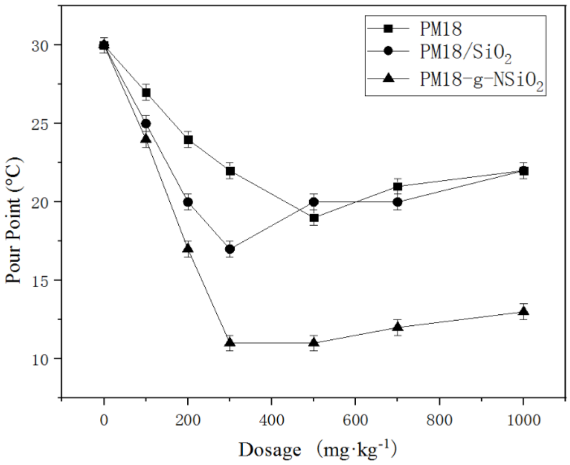
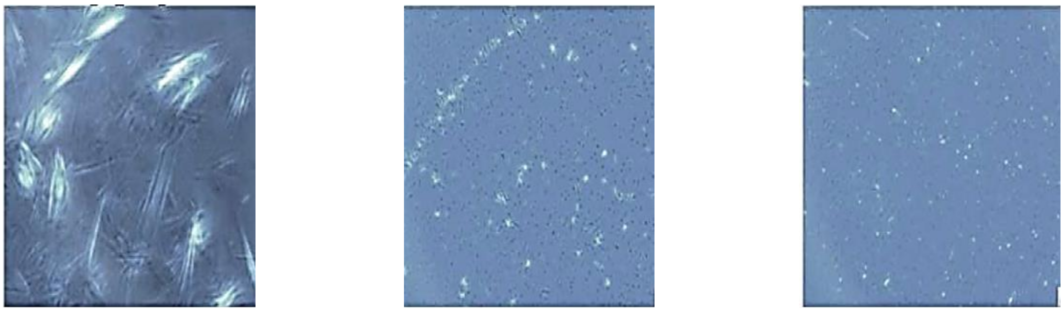


Figure 10. Pour point of 15 wt% model oil adding different kinds of NPPD [43]



(a) (b) (c)

Figure 11. Wax morphology of samples consisting of (a) raw sample, (b) raw sample+500 mg/kg EVA sample, and (c) raw sample+500 mg/kg GO-PPD [26]

## 5. FACTORS AFFECTING THE PERFORMANCE OF POUR POINT DEPRESSANTS ON CRUDE OIL

The efficacy of PPDs in crude oil is influenced by various factors. The chemical composition of the crude oil, including wax content and wax type, plays a pivotal role, with higher concentrations or different PPD types being required for crude oils featuring elevated wax content or intricate wax structures. Temperature is a critical factor, as PPD effectiveness diminishes at temperatures nearing the pour point, where these additives modify wax crystals forming at lower temperatures.

Table 2 presents the performance of poly (BA-co-SMA-co-MA) as a paraffin inhibitor at a consistent stirring rate of 200 rpm and varying operating temperatures (5, 10, 15, 20, and 25 °C). At 5 °C, the inhibitor achieved the maximum paraffin inhibition efficiency (PIE) of 45.6%. The volume of wax decreased slightly at higher temperatures, especially when the crude oil temperature approached its WAT. The study indicates that poly (BA-co-SMA-co-MA) effectively reduced wax deposition with decreasing temperatures [44].

Table 2. Effects of temperature on the amount of wax deposits [44]

| Temperature (°C) | | 0 | 15 | 20 | 25 |
|---|---|---|---|---|---|
| Amount of wax deposits of blank crude oil (g) | 1.14 | 0.77 | 0.51 | 0.22 | 0.08 |
| Amount of wax deposits after using BA-co-SMA-co-MA (g) | 0.62 | 0.50 | 0.32 | 0.18 | 0.06 |
| Paraffin inhibition efficiency. PIE (%) | 45.6 | 35.06 | 36.60 | 19.70 | 20.83 |

The concentration and type of PPD used significantly impact performance, as diverse chemical structures and properties among PPDs influence their interactions with wax crystals. Table 3 shows the efficient reduction in pour point achieved by various additives. The untreated crude oil had a pour point of 38 °C. PMMA-1% GO exhibited the most significant pour point depression, reaching 23 °C at 1500 ppm. PMMA-0.5% GO at the same concentration showed a 16 °C depression. Phoenix at 1250 ppm resulted in a 14 °C pour point depression, while PMMA at the same concentration achieved an 11 °C depression. The pour points for PMMA-1% GO, PMMA-0.5% GO, Phoenix, and PMMA were 15, 22, 24, and 27 °C, respectively, at their optimum concentrations. Above the optimum concentration, there was a sudden increase in pour point due to suspended additives causing gelling in crude oil, making it heavier. The nanocomposite additives, especially PMMA-1% GO, demonstrated superior pour point depression compared to commercial PPD. This improvement is attributed to the nanocomposites altering wax crystal morphology, providing nucleation sites that prevent the formation of an interlocking wax network. The nanocomposites act as templates for wax molecules, promoting compact crystal formation and reducing gelation, resulting in enhanced flowability and pour point depression, with PMMA-1% GO showing superior performance compared to PMMA-0.5% GO [29].

The optimal PPD concentration and type depend on specific crude oil characteristics and operating conditions. Furthermore, the mixing and shear conditions during blending can affect PPD effectiveness, emphasizing the importance of proper blending to enhance dispersibility and overall performance. The effectiveness of PPD polymers is intricately influenced by the length of the pendant alkyl chain, a key structural feature impacting their ability to bind to wax in crude oil. Shorter alkyl polymers are effective in low pour point oils, while longer alkyl polymers prove more adept at lowering the pour point in oils with higher pour points. The presence of a polar moiety on the wax surface, facilitated by the insertion of a long chain alkyl group into the wax crystal, contributes to a reduction in wax crystal size. However, if alkyl chains are too short, they may be adsorbed on the wax below the pour point, hindering the depressant's efficacy. Conversely, excessively long alkyl chains may lead to polymer crystallization at temperatures beyond the pour point [45]. Optimal performance is achieved when the pendant alkyl chains closely match the paraffin in crude oil. Additionally, operating conditions, including pressure, flow rate, and temperature, play a crucial role in PPD performance, necessitating adjustments in type and concentration based on variations. Furthermore, the interactions between PPDs and other additives in crude oil, such as friction modifiers, dispersants, and detergents, can be synergistic or antagonistic, depending on their chemical properties and concentrations, thereby impacting overall PPD effectiveness.

Overall, the performance of PPDs on crude oil is a complex interaction between the crude oil composition, PPD properties, and operating conditions. Proper selection and optimization of the PPD can improve its performance and provide effective pour point depression [46].

Table 3. Pour point of crude oil treated with different additives (°C) and concentrations [29]

| Concentration (ppm) | Phoenix | PMMA (10 wt% xylene) | PMMA-0.5% GO (1- wt% xylene) | PMMA-1%GO (10 wt% xylene) |
|---|---|---|---|---|
| 0 | 38 | 38 | 38 | 38 |
| 250 | 36 | 36 | 35 | 35 |
| 500 | 33 | 33 | 33 | 32 |
| 750 | 30 | 31 | 39 | 28 |
| 1000 | 27 | 28 | 27 | 25 |
| 1250 | 24 | 27 | 26 | 21 |
| 1500 | 26 | 28 | 22 | 15 |
| 1750 | 29 | 30 | 25 | 19 |

## 6. SELECTION OF POUR POINT DEPRESSANTS

Chemicals that are used to regulate wax should be rigorously assessed. They are greatly influenced by the type of oil, its characteristics and composition, and also the operating environment. For instance, the efficiency of the comb-shaped copolymers is significantly influenced by the length of the alkyl side chain. A lengthy, high molecular-weight copolymer may be enough massive to interact with itself and, in addition, may alter the polymer's solubility, whereas a short, low-molecular-weight copolymer may not be sufficient to disrupt crystallization. As a result, the side chain length should fall within the range of the n-alkane distributions in the particular oil. This may be the major justification for testing a wide range of wax inhibitors before choosing the ones that work best in the given situation. When selecting PPDs for crude oil, several factors should be considered, such as:

### 6.1. Based on compatibility

Compatibility of a PPD refers to its ability to mix with and not adversely affect the properties of the base oil or lubricant. The compatibility of a PPD can be affected by a variety of factors, including the chemical structure of the PPD, the base oil or lubricant type, and the presence of other additives or contaminants. Some PPDs may be more compatible with certain types of base oils or lubricants than others, depending on their chemical composition and molecular weight. Incompatibility between a PPD and a base oil or lubricant can result in a variety of negative effects, including the formation of insoluble deposits, changes in viscosity or other flow properties, and reductions in the effectiveness of the PPD in lowering the pour point. To ensure compatibility of a PPD with a base oil or lubricant, it is important to evaluate the PPD under the specific conditions of use and to conduct compatibility testing before use. Compatibility testing typically involves mixing the PPD with the base oil or lubricant and monitoring the mixture for any changes in viscosity, sediment formation, or other indicators of incompatibility. It is important to select a PPD that is compatible with the specific base oil or lubricant being used and to conduct appropriate testing to ensure that the PPD does not adversely affect the performance or properties of the crude oil or lubricant.

### 6.2. Based on efficiency

The PPD should be effective at reducing the pour point of the crude oil to the desired level. The degree of pour point depression required depends on the specific application and operating conditions. The efficiency of a PPD can be measured by its ability to reduce the pour point of a base oil or lubricant. The lowest temperature at which oil will move naturally is known as the pour point. Generally, the greater the reduction in pour point achieved by a PPD, the more efficient it is considered to be. Other factors that can impact the efficiency of a PPD include the type and concentration of other additives used in the formulation, as well as the operating conditions of the equipment or machinery in which the PPD is used. For example, the efficiency of a PPD may be reduced at high temperatures or in equipment with high shear forces, which can disrupt the crystal structure of the PPD and reduce its effectiveness. It is important to evaluate the performance of different PPDs under the specific conditions of use to ensure that the chosen PPD provides the desired level of improvement in pour point and flow properties [47].

### 6.3. Based on cost

The cost of the PPD should be balanced against its effectiveness and other benefits, such as improved flow properties, stability, and wear resistance. The cost of production of PPDs can vary widely depending on the specific type of polymer or copolymer used, the manufacturing process, and other factors such as raw material costs and energy prices. Generally, PPDs are produced using a variety of chemical synthesis methods, such as free radical polymerization or anionic polymerization. The raw materials used to produce PPDs can include monomers, initiators, solvents, and other additives. The cost of these materials can vary depending on the market prices and availability. In addition to raw material costs, other factors that can impact the cost of production of PPDs include the scale of production, labor costs, energy costs, and regulatory compliance costs. For example, large-scale production may result in lower costs per unit due to economies of scale, while increased regulatory compliance requirements may increase production costs. Therefore, it is difficult to provide a specific cost estimate for the production of PPDs as it can vary widely depending on the factors mentioned above. However, the cost of production of PPDs is likely a significant factor in the pricing of these chemicals, which may vary depending on the manufacturer, supplier, and intended use of the PPD.

### 6.4. Based on environmental and safety considerations

The PPD should be environmentally friendly and safe to handle, transport, and use. This includes factors such as biodegradability, toxicity, and flammability. PPDs can have both positive and negative environmental and safety impacts depending on their specific properties and the manner in which they are used. Environmental considerations may include biodegradability, ecotoxicity, and disposal. Some PPDs may be biodegradable, while others may persist in the environment and contribute to pollution. PPDs may be toxic to aquatic organisms or other wildlife if they are released into the environment. Improper disposal of PPDs can contribute to environmental pollution and harm wildlife. Safety considerations may include flammability, and skin and eye irritation. PPDs may be flammable and toxic, and pose a fire hazard if not stored and handled properly. Some PPDs may be irritating to the skin and eyes and can cause allergic reactions in sensitive individuals. PPDs may be toxic if ingested or inhaled and may pose a risk to human health if not used properly. To minimize environmental and safety risks, it is important to use PPDs in accordance with manufacturers' instructions and to follow proper safety and disposal procedures. PPDs should be stored in a cool, dry place away from sources of heat or flame, and should be kept out of reach of children and animals. In addition, PPDs should be disposed of in accordance with local regulations, and spills or leaks should be cleaned up promptly to prevent environmental contamination.

### 6.5. Based on regulatory compliance

The PPD should comply with applicable regulations and standards, such as those related to health, safety, and environmental protection. In most countries, PPDs are considered to be specialty chemicals that are subject to regulatory oversight. The specific regulations that apply will depend on the country and the intended use of the PPD. PPDs may also be subject to local, state, or national regulations depending on the specific application and intended use of the chemical. Manufacturers and users of PPDs should consult with regulatory agencies and legal counsel to ensure compliance with all applicable regulations.

### 6.6. Based on the chemical structure

The chemical structure of the PPD should be carefully evaluated, including its molecular weight, branching density, and polarity, to ensure that it is suitable for the specific crude oil and application. The type of PPD, whether it is a polymeric, oligomeric, or low molecular weight additive can also be considered based on the needs of the application. PPDs are polar or polarizable functional groups that are present in high molecular weight polymers or copolymers. Depending on the particular polymer employed, the precise molecular composition of a PPD will vary, but common examples of functional groups include esters, amides, ethers, and alkyl groups. Depending on the maker and the intended use, a PPD's precise chemical composition can change, but they typically have a polymeric backbone with polar or polarizable functional groups that help lower the oil's pour point. PPD selection and usage are crucial for guaranteeing optimum performance and extending the longevity of oil formulations and transportation along with reducing equipment damage at low temperatures. When the PPD dosage is chosen correctly, even at low concentrations, low-temperature performance is improved. However, if PPD concentration is increased, a minimal amount of extra improvement is noticed. Since these flow improvers themselves contain waxy properties, it is important to keep the wax build-up under control when you add the specified amount of PPD to avoid having the opposite effect.

## 7. RECENT ADVANCEMENTS OF POUR POINT DEPRESSANTS

### 7.1. Biodegradable PPDs

Researchers have developed PPDs that are biodegradable and environmentally friendly. These PPDs are typically derived from natural sources, such as plant oils or biopolymers, and can provide effective pour point depression while reducing the environmental impact of crude oil production and transportation. Figure 12 shows the effect of bio-additives on the wax crystallization mechanism.

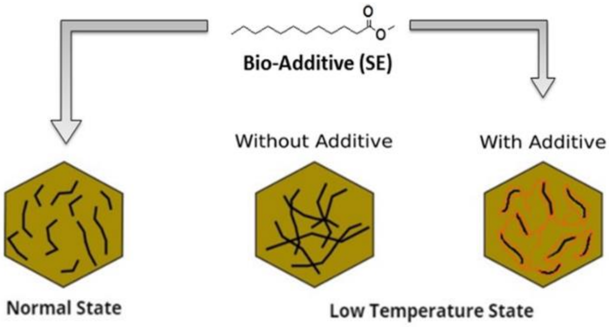


Figure 12. Effect of bio-additive on wax crystallization mechanism [48]

Biodegradable PPDs (BPPDs) work by altering the crystal structure of wax in crude oil, converting them into fine and dispersed particles that can flow easily through pipelines. BPPDs have been tested extensively and have shown promising results in reducing the pour point and viscosity of crude oil, improving flowability, and reducing pumping costs. Additionally, BPPDs are biodegradable and non-toxic, making them an environmentally friendly alternative to conventional PPD [49]. Examples are poly (n-dodecyl linoleate –co- succinic anhydride) and poly (n-dodecyl ricinoleate –co- succinic anhydride) from the naturally obtained vegetable oils fatty acids, which were subsequently evaluated as PPDs for a waxy crude oil by Deka *et al*. [49]. BPPD has a bright potential to be used in the petroleum business for pipeline transportation of waxy crude due to its biodegradability and nontoxic nature [50].

### 7.2. Nano-structured PPDs

Nano-structured PPDs have been developed using advanced materials and nanotechnology. The nano-particles have a wide range of potential applications because of the distinct size effect, global quantum mechanical tunneling effect, and distinct morphological structure. These PPDs are composed of nanosized particles that have a high surface area-to-volume ratio, which enhances their effectiveness in reducing the pour point of crude oil [51]. The use of nano-structured PPDs has shown promising results in improving the flowability of waxy crude oil, reducing the viscosity of crude oil, and minimizing pumping costs. Additionally, the small particle size of nano-structured PPDs allows them to disperse easily in crude oil and avoid agglomeration, which can lead to clogging and other flow issues [52]. The addition of NPPD facilitates the heterogeneous nucleation that contributes to the reduction in yield stress. Studies also found that an optimal magnetic field intensity and frequency can further reduce the yield stress. However, the effect of the magnetic field on yield stress is weakened when the magnetic field intensity and frequency are increased beyond the optimal value [53]. However, the synthesis and application of nanostructured PPDs require careful consideration of their potential impact on the environment and human health, as well as their long-term stability and effectiveness in real-world conditions. These PPDs can have enhanced solubility and dispersibility in crude oil, and can effectively inhibit the growth and aggregation of wax crystals at low concentrations [26], [28].

### 7.3. Hybrid PPDs

Hybrid PPDs have been developed by combining different types of PPDs or other additives to achieve synergistic effects. For example, a hybrid PPD may combine a polymeric PPD with a surfactant to improve its dispersibility and effectiveness [54]. The presence of a mixed surfactant system reduces interfacial surface tension and the presence of a non-ionic surfactant helps to maintain stability and flow-respond at low temperatures [55]. To achieve the desired properties, a good combination of non-ionic and anionic surfactants is essential. The ratio and type of surfactants used can impact the stability, particle size, and performance of the emulsion. The non-ionic surfactant can enhance the thermal stability, freeze-thaw stability, and mechanical properties of the emulsion, making it more robust and resistant to temperature changes and mechanical stress. On the other hand, the anionic surfactant can reduce the particle size and provide electrostatic stabilization to the emulsion, resulting in improved stability and reduced coalescence [56].

### 7.4. Effect of magnetic field on PPD

Studies exploring the impact of an alternating magnetic field, varying in intensity and frequency, on the yield stress of waxy model oil, both with and without PPDs, provide valuable insights into the optimal conditions for such modifications. The findings by Huang *et al.* [53] look into how a magnetic field, when applied in the right way, can help make waxy oils flow better in pipelines, which is crucial for pipeline safety. There's an ideal strength and frequency for the magnetic field that works best in reducing the yield stress of the waxy oil, which essentially means making it flow more easily. When the NPPD is added, it helps in making the waxy oil flow better by changing how the wax crystals form. Interestingly, the magnetic field is most helpful in reducing the yield stress at a lower frequency and strength before reaching the ideal values. However, if the magnetic field is increased beyond these ideal values, its effectiveness decreases. This happens because the shape of the wax crystals changes under the magnetic field, releasing the trapped oil and making it flow better.

Table 4 shows the effect of the magnetic field on PPD. At the WAT, wax crystals connect, forming a network with temperature-dependent yield stress. In a 20 Hz magnetic field, at 20 °C, yield stress decreases from 41 to 16 Pa (60.9% reduction), and at 25 °C, it varies from 24 to 9 Pa (62.5% reduction). In EVA-doped waxy model oil (20 °C), yield stress reduces from 16 to 4 Pa (75% reduction), 46 to 8 Pa (82.6% reduction at 15 °C), and 102 to 23 Pa (77.4% reduction at 10 °C) under a 0.3 T, 20 Hz magnetic field. NPPD-doped waxy model oil shows a reduction from 7 to 1 Pa (85.7% reduction at 20 °C), 30 to 5 Pa (83.3% reduction at 15 °C), and 50 to 14 Pa (72% reduction at 10 °C) under the same conditions. Comparatively, undoped waxy model oil at 15 °C has a 35.2% reduction (196 to 127 Pa), while synergistic modification of NPPD or EVA with a magnetic field results in an 83.3% reduction (30 to 5 Pa) for NPPD-doped and 82.6% reduction (46 to 8 Pa) for EVA-doped waxy model oil. This synergy demonstrates a more significant reduction compared to the magnetic field alone, emphasizing the combined impact of magnetic field and additives on yield stress [53].

Table 4. Yield stresses of wax model oil under magnetic field (0.3 T, 20 Hz) samples [53]

| Samples | Temperature, °C | Yield stress, Pa<br>Magnetic field<br>Without | <br><br>0.3 T, 20 Hz | Reduction, % |
|---|---|---|---|---|
| Undoped waxy model oil | 15 | 196 | 127 | 35.2 |
| | 20 | 41 | 16 | 60.9 |
| | 25 | 24 | 9 | 62.5 |
| EVA-doped waxy model oil | 10 | 102 | 23 | 77.4 |
| | 15 | 46 | 8 | 82.6 |
| | 20 | 16 | 4 | 75.0 |
| NPPD-doped waxy model oil | 10 | 50 | 14 | 72.0 |
| | 15 | 30 | 5 | 83.3 |
| | 20 | 7 | 1 | 85.7 |

### 7.5. Renewable PPDs

Renewable PPDs are derived from renewable sources, such as biomass or waste materials, and can provide effective pour point depression while reducing reliance on traditional PPDs derived from fossil fuels. These PPDs can also help to reduce the carbon footprint of crude oil production and transportation [57]. One example of a renewable PPD is methyl oleate, which is derived from renewable sources such as vegetable oil [58]. It has been shown to be effective in reducing the pour point of crude oil and other hydrocarbons, while also providing other benefits such as improved lubricity and biodegradability. Another example is a PPD derived from lignocellulosic biomass, such as wood or agricultural waste. These PPDs are produced by extracting and modifying lignin, a natural polymer found in plant cell walls. Lignin-derived PPDs have been shown to be effective in reducing the pour point of crude oil and other hydrocarbons, while also offering advantages such as biodegradability, low toxicity, and renewable sourcing [59].

## 8. CONCLUSION

PPDs play a crucial role in the transportation and processing of waxy crude oil. They are widely used to prevent the formation and growth of wax crystals that can cause flow restriction and reduce the efficiency of pipelines, tanks, and equipment. Over the years, researchers and industry professionals have developed and optimized various types of PPDs to meet the diverse needs of crude oil producers, refiners, and transporters. This review paper has discussed the different aspects of PPDs, including their mechanisms of action, factors affecting their performance, and other advancements in their development. Polymeric flow improvers, ethylene vinyl acetate copolymers, polyalkylmethacrylates, hydrocarbon-based flow improvers, and comb polymers are among the widely used types of PPDs. Recent advancements in PPDs have focused on improving their performance, reducing their environmental impact, and meeting the changing needs of the oil and gas industry. In conclusion, PPDs are crucial additives that enable the efficient transportation and processing of waxy crude oils. By effectively inhibiting wax crystal formation and growth, PPDs can reduce pour points and prevent flow restriction, thereby improving the safety, reliability, and profitability of crude oil production and transportation. Further research and development in PPDs are necessary to meet the evolving demands of the industry and address the challenges of sustainability, safety, and regulatory compliance.

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## REFERENCES

[1] B. C. Lemos *et al.*, “Synthesis, structure-activity relationship and evaluation of new non-polymeric chemical additives based on naphthoquinone derivatives as wax precipitation inhibitors and pour point depressants to petroleum,” *Fuel*, vol. 220, no. January, pp. 200–209, 2018, doi: 10.1016/j.fuel.2018.01.121.

[2] O. W. Duru, “History of oil and gas,” *SSRN Electron. J.*, pp. 1–8, 2012, doi: 10.2139/ssrn.2137976.

[3] D. A. T.Jarullah, “Composition and classification of crude oils,” *Pet. Refin.*, vol. 4, pp. 1–5, 2020.

[4] F. Yang, Y. Zhao, J. Sjöblom, C. Li, and K. G. Paso, “Polymeric wax inhibitors and pour point depressants for waxy crude oils: a critical review,” *J. Dispers. Sci. Technol.*, vol. 36, no. 2, pp. 213–225, 2015, doi: 10.1080/01932691.2014.901917.

[5] Davidson Chukwudi Onwumelu *et al.*, “Crude oil and the problem of wax deposition on pipeline systems during transportation: a review,” *World J. Adv. Res. Rev.*, vol. 15, no. 1, pp. 781–798, 2022, doi: 10.30574/wjarr.2022.15.1.0770.

[6] I. A. Struchkov and M. K. Rogachev, “The challenges of waxy oil production in a Russian oil field and laboratory investigations,” *J. Pet. Sci. Eng.*, vol. 163, pp. 91–99, 2018, doi: 10.1016/j.petrol.2017.12.082.

[7] J. Zhou, T. Deng, J. Peng, G. Liang, X. Zhou, and J. Gong, “Experimental study on pressure pulses in long-distance gas pipeline during the pigging process,” *Sci. Prog.*, vol. 103, no. 1, pp. 1–23, 2020, doi: 10.1177/0036850419884452.

[8] W. Böser and S. Belfroid, “Flow assurance study,” *Energy Procedia*, vol. 37, no. December 2013, pp. 3018–3030, 2013, doi: 10.1016/j.egypro.2013.06.188.

[9] Z. Patel, P. Modi, and A. Nagar, “An overview of wax deposition in the pipeline,” *Int. J. Mod. Trends Sci. Technol.*, vol. 7, no. 12, pp. 137–143, 2021.

[10] T. Ragunathan, H. Husin, and C. D. Wood, “Wax formation mechanisms, wax chemical inhibitors and factors affecting chemical inhibition,” *Appl. Sci.*, vol. 10, no. 2, pp. 1–18, 2020, doi: 10.3390/app10020479.

[11] S. Correra, D. Merino-Garcia, A. Fasano, and L. Fusi, “Formation and growth of wax deposit in the pipelining of crude oils,” no. 1, pp. 307–311, 2008, doi: 10.1007/978-3-540-71992-2_41.

[12] Z. T. Al-Sharify, M. Lahieb Faisal, L. B. Hamad, and H. A. Jabbar, “A review of hydrate formation in oil and gas transition pipes,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 870, no. 1, 2020, doi: 10.1088/1757-899X/870/1/012039.

[13] H. Husin, M. Eissa Mohyaldinn Elhaj, and C. D. Wood, “Evaluation of asphaltenes deposition inhibition factors in heavy crude oil pipelines,” *Process. Heavy Crude Oils - Challenges Oppor.*, 2019, doi: 10.5772/intechopen.88160.

[14] M. Askari, M. Aliofkhazraei, and S. Afroukhteh, “A comprehensive review on internal corrosion and cracking of oil and gas pipelines,” *J. Nat. Gas Sci. Eng.*, vol. 71, no. August, p. 102971, 2019, doi: 10.1016/j.jngse.2019.102971.

[15] M. S. Kamal, I. Hussein, M. Mahmoud, A. S. Sultan, and M. A. S. Saad, “Oilfield scale formation and chemical removal: a review,” *J. Pet. Sci. Eng.*, vol. 171, no. July, pp. 127–139, 2018, doi: 10.1016/j.petrol.2018.07.037.

[16] F. Alnaimat and M. Ziauddin, “Wax deposition and prediction in petroleum pipelines,” *J. Pet. Sci. Eng.*, vol. 184, no. April, p. 106385, 2020, doi: 10.1016/j.petrol.2019.106385.

[17] B. T. Marenov, K. S. Nadirov, M. K. Zhantasov, and R. K. Nadirov, “Ethylene-vinyl acetate copolymer/crude gossypol compositions as pour point depressants for waxy oil,” *Int. J. Chem. Eng.*, vol. 2020, 2020, doi: 10.1155/2020/4195382.

[18] T. Mahmoud and M. A. Betiha, “Poly(octadecyl acrylate-co-vinyl neodecanoate)/oleic acid-modified nano-graphene oxide as a pour point depressant and an enhancer of waxy oil transportation,” *Energy and Fuels*, vol. 35, no. 7, pp. 6101–6112, 2021, doi: 10.1021/acs.energyfuels.1c00034.

[19] H. Yu, Z. Sun, G. Jing, Z. Zhen, Y. Liu, and K. Guo, “Effect of a magnetic nanocomposite pour point depressant on the structural properties of daqing waxy crude oil,” *Energy and Fuels*, vol. 33, no. 7, pp. 6069–6075, 2019, doi: 10.1021/acs.energyfuels.9b00689.

[20] Y. Liu, Z. Sun, G. Jing, S. Liu, Y. Yang, and J. Xu, “Synthesis of chemical grafting pour point depressant eval-go and its effect on the rheological properties of daqing crude oil,” *Fuel Process. Technol.*, vol. 223, no. August, p. 107000, 2021, doi: 10.1016/j.fuproc.2021.107000.

[21] X. Jia *et al.*, “Submicron carbon-based hybrid nano-pour-point depressant with outstanding pour point depressant and excellent viscosity depressant,” *Arab. J. Chem.*, vol. 15, no. 10, p. 104157, 2022, doi: 10.1016/j.arabjc.2022.104157.

[22] S. M. Ahmed, T. T. Khidr, and E. S. Ali, “Preparation and evaluation of polymeric additives based on poly(styrene-co-acrylic acid) as pour point depressant for crude oil,” *J. Dispers. Sci. Technol.*, vol. 43, no. 11, pp. 1634–1641, 2022, doi: 10.1080/01932691.2021.1878038.

[23] S. Williams and O. Uche, “Evaluation of local pour point depressant on waxy crude oil,” *Int. J. Energy Power Eng.*, vol. 11, no. 2, p. 30, 2022, doi: 10.11648/j.ijepe.20221102.12.

[24] H. Li *et al.*, “Effect of pour point depressants on the impedance spectroscopy of waxy crude oil,” *Energy and Fuels*, vol. 35, no. 1, pp. 433–443, 2021, doi: 10.1021/acs.energyfuels.0c03378.

[25] N. Hazrati, M. Abdouss, A. A. Miran-Beigi, and A. A. Pasban, “Long chain alkylated ionic liquids as pour point depressant and rheology improver for crude oil,” *Pet. Chem.*, vol. 61, no. 2, pp. 206–213, 2021, doi: 10.1134/S0965544121020079.

[26] H. Wen *et al.*, “Effect of nano pour point depressant on the flow properties of the waxy crude oil from Changqing oilfield,” *E3S Web Conf.*, vol. 329, 2021, doi: 10.1051/e3sconf/202132901050.

[27] D. Yuan *et al.*, “Synthesis and performance testing of maleic anhydride–ene monomers multicomponent co-polymers as pour point depressant for crude oil,” *Polymers (Basel).*, vol. 15, no. 19, 2023, doi: 10.3390/polym15193898.

[28] A. M. Al-Sabagh, M. A. Betiha, D. I. Osman, and T. Mahmoud, “Synthesis and characterization of nanohybrid of poly(octadecylacrylates derivatives)/montmorillonite as pour point depressants and flow improver for waxy crude oil,” *J. Appl. Polym. Sci.*, vol. 136, no. 17, pp. 1–15, 2019, doi: 10.1002/app.47333.

[29] R. Sharma, V. Mahto, and H. Vuthaluru, “Synthesis of PMMA/modified graphene oxide nanocomposite pour point depressant and its effect on the flow properties of Indian waxy crude oil,” *Fuel*, vol. 235, no. March 2018, pp. 1245–1259, 2019, doi: 10.1016/j.fuel.2018.08.125.

[30] B. Elarbe, I. Elganidi, N. Ridzuan, K. Yusoh, N. Abdullah, and S. Vijayakumar, “Synthesis, characterization and evaluation of stearyl acrylate-co-behenyl acrylate copolymer as a pour point depressant of waxy crude oil,” *J. Pet. Explor. Prod. Technol.*, vol. 12, no. 7, pp. 1811–1828, 2022, doi: 10.1007/s13202-021-01408-7.

[31] S. Yang, C. Li, F. Yang, X. Li, G. Sun, and B. Yao, “Effect of polyethylene-vinyl acetate pour point depressants on the flow behavior of degassed changqing waxy crude oil before/after scCO2 extraction,” *Energy and Fuels*, vol. 33, no. 6, pp. 4931–4938, 2019, doi: 10.1021/acs.energyfuels.9b00561.

[32] R. A. Soldi, A. R. S. Oliveira, R. V. Barbosa, and M. A. F. César-Oliveira, “Polymethacrylates: pour point depressants in diesel oil,” *Eur. Polym. J.*, vol. 43, no. 8, pp. 3671–3678, 2007, doi: 10.1016/j.eurpolymj.2006.07.021.

[33] A. M. Al-Sabagh, M. A. Betiha, D. I. Osman, A. I. Hashim, M. M. El-Sukkary, and T. Mahmoud, “Preparation and evaluation of poly(methyl methacrylate)-graphene oxide nanohybrid polymers as pour point depressants and flow improvers for waxy crude oil,” *Energy and Fuels*, vol. 30, no. 9, pp. 7610–7621, 2016, doi: 10.1021/acs.energyfuels.6b01105.

[34] M. A. Kazemi, A. Reza, S. Nazar, and Y. Karimi, “The performance of polymethyl methacrylate / clay nanocomposite as novel pour point depressant on rheological properties of model waxy crude oil,” *J. Pet. Sci. Technol.*, vol. 10, pp. 67–74, 2020, doi: 10.22078/jpst.2020.4177.1675.

[35] P. Ghosh, M. Das, M. Upadhyay, T. Das, and A. Mandal, “Synthesis and evaluation of acrylate polymers in lubricating oil,” *J. Chem. Eng. Data*, vol. 56, no. 10, pp. 3752–3758, 2011, doi: 10.1021/je2003435.

[36] G. Chen *et al.*, “Application of polymethacrylate from waste organic glass as a pour point depressor in heavy crude oil,” *J. Pet. Sci. Eng.*, vol. 165, no. August, pp. 1049–1053, 2018, doi: 10.1016/j.petrol.2017.12.041.

[37] N. Li, W. Wu, and G. Mao, “Effect of modified ethylene vinyl acetate copolymers pour point depressants on flow properties of crude oil and corresponding mechanism analysis,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 630, p. 127602, 2021, doi: 10.1016/j.colsurfa.2021.127602.

[38] X. Xia *et al.*, “Performance improvement of ethylene−vinyl acetate copolymer pour point depressant (EVA PPD) by adding small dosages of laurylamine (la),” *Pet. Sci.*, vol. 19, no. 5, pp. 2472–2482, 2022, doi: 10.1016/j.petsci.2022.04.002.

[39] I. E. Nifant’ev *et al.*, “Tandem synthesis of ultra-high molecular weight drag reducing poly-α-olefins for low-temperature pipeline transportation,” *Polymers (Basel).*, vol. 13, no. 22, pp. 1–16, 2021, doi: 10.3390/polym13223930.

[40] P. E. A. Gibson, “United States patent (19),” no. 19, 1996.

[41] C. Zhang *et al.*, “Synthesis of comb bipolymers and their pour point depressing properties,” *Pet. Sci.*, vol. 11, no. 1, pp. 155–160, 2014, doi: 10.1007/s12182-014-0327-4.

[42] M. R. Elkatory, M. A. Hassaan, E. A. Soliman, V. C. Niculescu, M. S. Raboaca, and A. El Nemr, “Influence of poly (benzyl oleate-co-maleic anhydride) pour point depressant with di-stearyl amine on waxy crude oil,” *Polymers (Basel).*, vol. 15, no. 2, 2023, doi: 10.3390/polym15020306.

[43] Z. N. Sun, B. Yan, G. L. Jing, Y. H. Yang, H. J. Li, and F. N. Zhang, “Influence of chemical grafting method on the performance of SiO2 nanocomposite pour point depressant,” *Processes*, vol. 11, no. 4, 2023, doi: 10.3390/pr11041159.

[44] I. Elganidi, B. Elarbe, N. Ridzuan, and N. Abdullah, “Synthesis, characterisation and pre-evaluation of a novel terpolymer as pour point depressants to improve the Malaysian crude oil flowability,” *J. Pet. Explor. Prod. Technol.*, vol. 12, no. 7, pp. 2067–2081, 2022, doi: 10.1007/s13202-021-01445-2.

[45] H. P. Soni, D. P. Bharambe, A. Nagar, and Kiranbala, “Synthesis of chemical additives and their effect on Akholjuni crude oil (Gujarat, India),” *Indian J. Chem. Technol.*, vol. 12, no. 1, pp. 55–61, 2005.

[46] J. S. Manka and K. L. Ziegler, “Factors affecting the performance of crude oil wax-control additives,” *Proc. - SPE Prod. Oper. Symp.*, pp. 639–645, 2001, doi: 10.2523/67326-ms.

[47] M. Kurniawan, J. Norrman, and K. Paso, “Pour point depressant efficacy as a function of paraffin chain-length,” *J. Pet. Sci. Eng.*, vol. 212, no. October 2021, p. 110250, 2022, doi: 10.1016/j.petrol.2022.110250.

[48] B. Pal and T. Naiya, “Application of novel fruit extract for flow assurance of Indian field waxy crude oil,” *SPE J.*, vol. 27, no. 5, pp. 3178–3195, 2022, doi: 10.2118/209789-PA.

[49] B. Deka, R. Sharma, and V. Mahto, “Synthesis and performance evaluation of poly (fatty esters-co-succinic anhydride) as pour point depressants for waxy crude oils,” *J. Pet. Sci. Eng.*, vol. 191, no. August 2019, p. 107153, 2020, doi: 10.1016/j.petrol.2020.107153.

[50] B. Pal and T. K. Naiya, “Application of synthesized novel biodegradable pour-point depressant from natural source on flow assurance of Indian waxy crude oil and comparative studies with commercial pour-point depressant,” *SPE J.*, vol. 27, no. 1, pp. 864–876, Feb. 2022, doi: 10.2118/208578-PA.

[51] F. Wang *et al.*, “The effect of nanohybrid materials on the pour-point and viscosity depressing of waxy crude oil,” *Chinese Sci. Bull.*, vol. 56, no. 1, pp. 14–17, 2011, doi: 10.1007/s11434-010-4174-4.

[52] M. Mansourpoor, R. Azin, S. Osfouri, and A. A. Izadpanah, “Effect of DSO, EVA, and SiO2 and clay nanohybrids on rheological properties of waxy oil mixtures,” *Mater. Res. Express*, vol. 5, no. 9, 2018, doi: 10.1088/2053-1591/aad858.

[53] H. R. Huang *et al.*, "Synergistic effect of magnetic field and nanocomposite pour point depressant on the yield stress of waxy model oil," *Pet. Sci.*, vol. 17, no. 3, pp. 838–848, 2020, doi: 10.1007/s12182-019-00418-9.
[54] A. C. Egerton, "Chemical technology," *Nature*, vol. 177, no. 4515, pp. 861–862, 1956, doi: 10.1038/177861a0.
[55] N. E. S. Umoruddin, M. R. H. Rosdi, and A. Ariffin, "Mixed surfactant enabled EVA emulsion for PPD applications," *J. Dispers. Sci. Technol.*, vol. 40, no. 3, pp. 361–368, 2019, doi: 10.1080/01932691.2018.1469413.
[56] J. Yang and R. Pal, "Investigation of surfactant-polymer interactions using rheology and surface tension measurements," *Polymers (Basel).*, vol. 12, no. 10, pp. 1–20, 2020, doi: 10.3390/polym12102302.
[57] R. S. Kamal, G. Michel, A. Ageez, and R. K. Farag, "Waste plastic nanomagnetite pour point depressants for heavy and light Egyptian crude oil," *ACS Omega*, vol. 8, no. 4, pp. 3872–3881, 2023, doi: 10.1021/acsomega.2c06274.
[58] M. A. H. Altaie, R. B. Janius, U. Rashid, Y. H. Taufiq Yap, R. Yunus, and R. Zakaria, "Cold flow and fuel properties of methyl oleate and palm-oil methyl ester blends," *Fuel*, vol. 160, no. July, pp. 238–244, 2015, doi: 10.1016/j.fuel.2015.07.084.
[59] D. Wang, Z. Cai, Z. Zhang, X. Xu, and H. Yu, "Laboratory investigation of lignocellulosic biomass as performance improver for bituminous materials," *Polymers (Basel).*, vol. 11, no. 8, pp. 1–18, 2019, doi: 10.3390/polym11081253.

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