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*Review*

# Effect of Pour Point Depressant (PPD) for Efficient Transport of Waxy Crude Oil: A Critical Review

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**Abstract:** The transportation of waxy crude oils is often challenged by high pour points and wax deposition, which significantly increase pipeline viscosity, energy consumption, and operational costs. Pour point depressants (PPDs) have emerged as effective chemical additives to modify wax crystallization behavior, reduce pour point, and improve crude oil flowability. In this study, the role of PPDs in enhancing pipeline transportation of waxy crude oil is discussed with emphasis on their mechanisms of action, such as adsorption on wax crystal surfaces, inhibition of crystal growth, and modification of crystal morphology. Various classes of PPDs, including ethylene–vinyl acetate copolymers, polymethacrylates, and comb-like copolymers, are evaluated for their efficiency in lowering pour point and mitigating wax deposition. Laboratory assessments and field applications demonstrate that optimized PPD formulations can reduce pour points by more than 10-20°C, ensuring uninterrupted transportation under sub-ambient conditions. This literature review summarizes the importance of molecular structure, crude oil composition, and operating parameters in determining PPD performance, providing insights for the design of next-generation flow assurance additives.

**Keywords:** Pour Point Depressant; waxy crude oil; Polymer, Additives

## 1. Introduction

Crude oil is considered as a promising class of fuel as it is an energy source and it supplies energy to each corner of the world. Crude oils are classified on the basis of API gravity provided by American Petroleum Institute (API) as light (API>38), medium (38>API>29) and heavy (29>API) [1]. Wax rich crude oil  oil is characterized by high pour point, high viscosity and non-Newtonian flow [2]. Waxy crude oil comprises paraffins, aromatic hydrocarbons, lighter distillates methane hydrates, resins and asphaltenes [3]. The presence of paraffin waxes creates flow assurance problems for waxy crude oil industry. Every year the wax deposition causes a loss of a billions of dollars worldwide [4]. When the inner wall temperature decreases below wax appearance temperature (WAT), the wax starts to deposit in the pipeline walls which undergo a two-phase dispersion with wax solid particle and causes a reduction of the diameter of the pipelines [5]. These deposited waxes create several problems such as recovery, production, storage, replacement of pipelines, failure of the equipment, consumption of high horse power, extra man power as well as transportation of the crude oil [6]. Various techniques have developed to resolve the above-mentioned problems such as heating, dilution with lighter crudes and preparing emulsion of oil-water [7]. However, these techniques provide some challenges such as environmental pollutions, consumption of high energy, time, geological restriction and difficulties in post-processing [8]. Pour point is considered as a representative of the rheology of crude oil at low temperature [9]. Application of pour point depressant (PPD) or flow improvers (FI) offers a cost effective and safe solution to address these issues [10].

Over the decades a number of researchers have developed several methods for the synthesis of different kinds of PPDs and became popular in the oil filed due to ease of synthesis and cost effectiveness. The polymeric PPD forms smaller wax crystals of high volume-to-surface ratio which enables the crystals' ability to diminish the interlocking and intergrowing of wax crystals which enhances the rheology of the waxy crude oil [11].

### *1.1. Historical Background*

Reports about the discovery of polymeric PPD surfaced in early 1930s For the first time ever, Zimmer, Davis, and Frolich reported on polymeric PPDs in 1933 [12] They investigated how three-dimensional networks of waxes formed, which caused crude oil to gel. In the meantime, the polymeric PPD, polyalkylmethacrylates (PAMAs), was patented in 1937 by Rohm and Haas Co [13]. Encouraged by their development of PPD, Ruehrwein et al. studied the specificity of n-alkylpolymethacrylate in the series of dodecyl, tetradecyl, hexadecyl and octadecyl after almost 15 years. It was reported that the polymers containing longer alkyl chains are very effective as PPD for high pour point oils and polymers with shorter alkyl chains are effective for low pour point oils [14]. IInyckyj and C. O. Cole in the year 1976 assumed that dual functioning flow improvers can improve the flow property of crude oil [15]. They believed that amongst the two functions, one can act as a wax growth arrestor and the other acts as a nucleating agent. Thereafter, a number of works have been performed on the basis of combination of two or three compounds as flow improver. The functional groups used here are often polar in nature in the year 1996, Borthakur et al. synthesized a copolymer based on vinyl acetate-behenyl fumerate which was used as a PPD for high waxy crude oil. This group arrived at the conclusion that the copolymer's molecular weight has a significant impact on the polymer's pour point depression efficiency. They claimed that a variety of polymeric chemicals can be employed as flow enhancers. Examples of polymeric compounds that can be used as a PPD include polyalkyl acrylates and methacrylate copolymers, alkyl esters of styrene maleic anhydride copolymers, alkyl acrylate-alkyl maleate copolymers, ethylene-vinyl acetate copolymers, and alkyl fumerate-vinyl acetate copolymers [16]. Later on in the year 1997, El-Gamel et al. concluded that polymeric structures with long alkyl chain (C20-C26) acrylic-α-olefin copolymers are very effective PPD for the high pour point waxy crude oil. In 1999, Liao and Zhai have made a kind of esterified copolymer of maleic anhydride with a mixture of olefins, acrylic alkyl ester and styrene (MOAS). They showed how well this copolymer lowers the pour point of Daqing crude oil. They have unique features in contrast to PPDs made in China. The PPD stated above showed a simple synthesis procedure, and the equipments used are of cost-effective and safe for the environment [17]. After a few years in 2001, Machado et al. synthesized a copolymer, poly (ethylene-co-vinyl acetate) as a flow improver and they concluded that the performance of PPDs highly depend on the composition of copolymer and for better efficiency there must be an optimum concentration of the copolymer. Recently in the year 2015, Cunzhe et al. synthesized a novel nano-hybrid PPD (NPPD) as flow improver for crude oil [18]. The rheological results indicated that the NPPD exhibit better viscosity improvement, yield stress and pour point depression of crude oil than the conventional polymeric PPDs. Since the preparation of the polymer blend is a cost-effective, simple, and time-efficient technique, PPDs based on polymer blend have garnered a lot of attention recently. This study examines a number of synthesis methods related to distinct PPDs, their mechanisms for enhancing flow, and the many PPD research projects undertaken till date [19].

**Table 1.** Summary of some synthesized PPDs and different synthetic approaches

| Year | Title of Article | Materials and crude oil used | Preparation methods | Conclusion |
|---|---|---|---|---|
| **1999** | A study on alcohols mixture esterified copolymer of maleic anhydride with mixed olefins, acrylic alkyl ester and styrene as pour-point depressant for diesels | Materials: Maleic anhydride, Mixed u-Olefins, Acrylic alkyl ester, Styrene.<br>Crude oil: Diesels produced from Daqing crude oil. | Polymerization, esterification. | It is a new way to improve low-temperature fluidity of them. The synthetic path is reasonable. The equipment investment and cost are low. |
| **2005** | A Regular, Hydrophobically Modified Polyampholyte as Novel Pour Point Depressant [2]. | Materials: poly[(N,N-diallyl-N-octadecylamine-alt-(maleic acid)) (50–300 ppm), isopropanol.<br>Crude oil: Akshabulak oil field. | Free-radical copolymerization. | In the presence of the new PPD, the amount of paraffin crystals is drastically reduced, and the size of the aggregates become much smaller than that after heat treatment. |
| **2009** | Multifunctional Additives Viscosity Index Improvers, Pour Point Depressants and Dispersants for Lube Oil | Materials: Benzene and one mole of maleic anhydride, Dodecyl alcohol, Dodecyl amine,<br>Hexadecyl alcohol, Hexadecyl amine, Octadecyl alcohol, Octadecyl amine, Docosanol<br>Crude oil: NA | Esterification, copolymerization | Viscosity index increases with increasing the conc. of the additives. The aminated copolymers have very good dispersancy for sludge and solid particles. |
| **2012** | Modified Maleic Anhydride Co-polymers as Pour-Point Depressants and Their Effects on Waxy Crude Oil Rheology | Materials: Acrylic acid, maleic anhydride, and p-toluenesulfonic acid, Octadecanol, dodecanol, dodecylamine, benzyl alcohol, dibenzoyl peroxide, and hydroquinol<br>Crude oil: Changqing (CQ) waxy crude oil. | Esterification, free radical polymerization, | Good efficiency as PPD and low asphaltene content. |
| **2012** | Investigation into a Pour Point Depressant for Shengli Crude Oil | Materials: Acrylic acid, maleic anhydride, p-toluenesulfonic acid, vinyl acetate, toluene, methanol octadecanol, dodecylamine, dibenzoyl peroxide, and hydroquinol.<br>Crude oil: Shengli Crude Oil | Copolymerization | Pour point of the crude oil was depressed 11°C. The interaction between asphaltene and resin had an impact on the process of wax crystallization in the crude oil. |

| Year | Title of Article | Materials and crude oil used | Preparation methods | Conclusion |
|---|---|---|---|---|
| **2015** | Adsorption of Polymeric Additives Based on Vinyl Acetate Copolymers as Wax Dispersant and Its Relevance to Polymer Crystallization Mechanisms | Materials: Vinyl acetate, maleic anhydride, dodecyl alcohol (DA), stearyl alcohol (SA), behenyl alcohol (BA), benzoyl peroxide (BP), and P-toluene sulfonic acid monohydrate (PTSA) Benzene, dimethylformamide (DMF), and xylene<br>Crude oil: Egyptian waxy crude oil (Norpetco, Egypt) was delivered from Fardous field. | Copolymerization, Esterification. | The composition of VASM greatly affects the Performance of the additive. While the copolymer VASM with mole ratio 2:1 was the best additive in improving the crude oil yield shear stress and improving the flow properties of crude oil. |
| **2016** | Influences of the Molecular Weight (MW) and Its Distribution (MWD) of Poly(styrene-alt-octadecyl maleimide) as a Flow Improver for Crude Oils | Materials: Styrene, Maleic anhydride, 1-Phenylethyl phenyldithioacetate (PEPDTA), Chloroform, anhydrous methanol, THF, 2-butanone, ethylbenzene, and n-heptane, xylene, n-Decane, n-Octadecyl amine (ODA), n-tetracosane.<br>Crude oil: Shanghai Research Institute of Petrochemical Technology | RAFT copolymerization | The MW and MWD of the prepared flow improvers were found to play critical roles in defining their effectiveness as flow improvers. |
| **2017** | Oil dispersible polymethylsilsesquioxane (PMSQ) microspheres improve the flow behavior of waxy crude oil through special hindrance effect | Materials: Methyltrimethoxysilane (MTMS), hydrochloric acid (37 wt%), ammonia (25 wt%), ethanol, n-heptane and n-dodecane<br>Crude oil: PetroChina Co., Ltd. | Two-step sol-gel route | Adding the PMSQ microspheres dramatically decrease the gelation point; yield stresses of the oil samples are also greatly decreased after the addition of the PMSQ microspheres. |
| **2018** | A new kind of nanohybrid poly(tetradecyl methyl acrylate)-graphene oxide as pour point depressant to evaluate the cold flow properties and exhaust Gas emissions of diesel fuels. | Materials: Graphite flakes (400 mesh), Tetradecyl methyl-acrylate (MA14, 99%), benzoyl peroxide (BOP, 75%), N, N-Dimethylformamide (DMF, 99.8%), $NaNO_3$ (99%), $KMnO_4$ (≥99.5%), $H_2SO_4$ (98%) and $H_2O_2$ (31%).<br>Crude oil: Diesel fuel purchased from China Petrochemical Corporation. | Modified Hummers method, in-situ free radical polymerization. | PMA-GO PPDs increased the crystallization temperature of diesel and modified crystallization behavior of the wax crystals. So, PMA-GO PPDs effectively improved the cold flow properties of diesel fuel. |

### *1.2. Interaction of Waxes with PPD*

To resolve the wax deposition problem, one needs to address how to overcome the adhesive force of the gel at lower temperature and a PPD is proved as the best choice to reduce the pour point of the waxy crude oil. The flow improvers or PPDs have the ability to change the morphology of the wax crystal which in turn, inhibits the growth of the wax crystals in the crude oil pipeline. The interaction mechanism of PPDs with wax crystals can be represented with the help of the following phases:

#### *1.2.1. Nucleation*

The nucleation starts with the formation cluster of tiny solid aggregates known as nuclei. The nuclei are very stable in crude oil which facilitates the growth of wax crystal [20]. When the temperature drops below WAT, the attractive force between the wax molecules becomes stronger than that between the oil and wax molecules. This results in the precipitation of wax molecules from the oil phase. The precipitated wax molecules start forming the wax crystal. At this lower temperature high molecular weight polymeric PPDs can precipitate preferentially than that of the lower molecular weight PPDs. These precipitated PPDs behave as a crystalline nuclei [21]. After that some bigger sub-critical crystalline nucleus is formed by polynucleation mechanism. These crystalline nuclei then inhibit the growth of the wax crystal. It also facilitates the formation of smaller wax crystals. Small sized wax crystals promote better fluidity of the crude oil [22].

#### *1.2.2. Adsorption*

When the temperature is near or below WAT, the wax molecules start getting adsorbed on the surface of the polymeric PPDs. This adsorption can inhibit the growth of the wax crystal by modifying the morphology of the wax crystal. This modification reduces the crystal-crystal adhesion which prevents the growth of the crystal. The PPD molecules adsorbed on the wax crystal triggers the formation of some smaller and more isotropic crystals, which does not affect the flowability of the crude oil [23].

#### *1.2.3. Co-crystallization*

Co-crystallization is the process through which the wax molecules are adsorbed on the surface of the polymeric PPDs. Co-crystallization changes the interaction mode between the wax crystals and modifies its composition. It inhibits the formation of cage or three-dimensional network which are formed by the interlocking of the wax molecules. This inhibition causes the crystal deformation of crude oil waxes. After the deformation, waxes are not able to undergo aggregation; so the fluidity of the waxy crude oil increases. X-ray diffraction pattern showed that the paraffin crystals exhibit well-resolved low angle spectra in the absence of flow improver. However, upon addition of additives such as poly (ethylene butane), PEB copolymer and poly (maleic anhydride amide-co-α-olefin) the low angle scattering from the layered structure disappeared. This implies that the additives associate with the wax crystal via co-crystallization. Yang et al. (2020) proposed a mechanism where N-containing PPDs can act as a flow improver for the crude oil. They showed that the N-containing PPDs with long side chain alkyl group co-crystallizes with the n-alkanes of analogous chain length at room temperature. The exposed N-containing polar group of PPDs broke the prompt growth and unordered stacking of the wax crystal. This rupturing of the cross-linking of the wax crystal improved the fluidity of the crude oil [24].

### *1.2.4. Dissolution*

Instead of long stick or plate-like crystals, sphere-like crystals form when the PPD concentration in crude oil rises. The solution becomes unstable due to the extremely high solid-liquid interface energy in the absence of polymeric PPDs. When PPD is added, polar groups are induced to adsorb onto the eutectic surface, forming a molecular layer. Later, a solvation layer is formed adjacent to the first molecular layer which changes the nature of solid-liquid interface i.e., the wax crystal and the liquid, which leads to the decrease in energy of the surface, thereby inhibiting the association between the wax molecules which impede the formation of three dimensional network [25].

## 2. Types of Pour Point Depressant

Till date, a significant number of PPDs have been employed for getting improved result of fluidity of the crude oil at low temperature with varying degree of success. The PPDs are used for the manipulation of the crude oil because of the several advantages such as cost effectiveness, low energy consumption, low pollution, good effect and no subsequent processing. [26] A PPD is comprised of two parts, one is non-polar which is formed by alkyl group and the other is polar. The alkyl group interacts with the wax molecule and polar group modifies the wax crystal structure thereby inhibit the growth of wax crystal [27]. Following sections discuss about different types of PPDs used as flow improver.

### *2.1. Ethylene-vinyl Acetate (EVA) Copolymer*

The pour point depression activity of a copolymer is always better than that of a homopolymer. EVA copolymer exhibits better performance in the rheology of waxy crude oil [28]. It is observed that the wax crystals formed in presence of EVA copolymer are more compact and numerous. On the other hand, strong van der Waal interaction between the wax crystal and the functional group present in EVA copolymer is a reason of decreasing WAT and increase of solubility of wax molecule [28]. The two active oxygen atoms with one methyl and methylene group make VA a polar compound. The oxygen atoms present in the EVA copolymer forms an intermolecular interaction with the wax crystal, which helps in the prevention of wax crystal formation. The side chain co-crystallizes into paraffin by leaving the polar group which interferes with the new incoming wax molecule alignment [29].

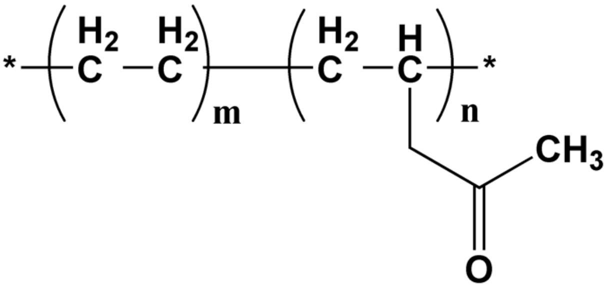

**Figure 1**. Chemical structure of EVA copolymer

In the year 2001, Machado et al. demonstrated EVA copolymer with numerous VA content which influence on the viscosity as well as pour point of the Brazilian crude oil. They confirmed that there is a significant role of VA content in the pour point of the crude oil [30]. Wu et al. in the year 2005 studied the simulation of molecular dynamics on EVA copolymer to see the interactions between EVA copolymer and the wax crystal. They showed that the EVA copolymer modifies the shape of the wax crystal and governs the growth of wax crystal in different directions [31].

### *2.2. Comb-type Copolymers*

Comb-type copolymers have different crystal structures than EVA copolymer. Comb polymers are widely used as flow improvers because of the flexibility it possesses. These copolymers contain polyvinyl backbone with different alkyl chains. This kind of flow improver is useful due to its exceptional ability to improve the flow of waxy crude oil. The comb-type copolymers also have two parts; one is non-polar group and the other is polar group [26]. The non-polar part consists of long chain alkyl groups and the polar part consists of different types of groups such as aromatic base, ester bonds, amine bonds etc. The non-polar groups affect the formation of wax crystals, thereby hindering the formation of three-dimensional network of wax crystal. On the other hand, the polar group that enters into the interior of wax disturbs the interaction between the wax molecules which, in turn, improves the fluidity of the crude oil. The wax crystals are attached between non-polar alkyl chains and long chain paraffins through co-crystallization process [32]. The polar portion inhibits the formation of crystal structure by dispersing the wax in the decentralized state. This interaction between the PPD and wax crystal enhance the flowing of the crude oil.

### *2.3. Acrylate Based Polymer*

Acrylate based polymers are widely used as pour point depressants because of low cost and effectiveness to reduce the pour point. Acrylate polymers contain different alkyl groups. At room temperature the acrylate polymers are in solid state [33].

**Table 2.** Viscosity of PPD at 25°C [33]

| Type of PPD | Viscosity, cP |
|---|---|
| Solvent based PD90 | Solidified |
| Emulsified PD90 | 16 |
| Other emulsified PPD | <10 |

Alkyl acrylate and alkyl methacrylate-based polymers contain alkyl substituents ranging from C14 to C26 in alcohol moiety are one of the most widely used class of pour point depressant [34]. A number of pendant alkyl chains for acrylate and methacrylate polymers have been synthesized as flow improver. Behenyl acrylate which is a mixture of C18, C20 and C22 is widely used in the preparation of polymeric PPD [35]. Nonetheless, poly(alkyl methacrylate) that combines alkyl chains with high and low molecular weights is considered as efficient as a pour point depressant.

Yao et al. introduced poly (octadecylacrylate) (POA)/clay nanocomposite as a PPD for the Changqing waxy crude oil. The pour point of the waxy crude oil was initially relatively high (28°C). Upon addition of 800 mg POA per kg of clay the pour point reduces by 9°C [36]. Thus, acrylate-based polymers are successfully prepared and applied for improving the pour point and flowability of the waxy crude oil.

### *2.4. Crystalline-amorphous Polymers*

This type of polymers are a combination of two homopolymers. Among them one is crystallizable and another one is amorphous in nature. Some examples are polyethylene-polyethylene propylene (PE-PEP) and polyethylenebutene (PEB) [37]. In PE-PEP, which is a diblock copolymer, the PE block is crystallizable in nature and PEP block can exist as amorphous form. Together they form a plate like aggregate with PE core within a PEP brush layer. The crystallizable PE core can initiate the nucleation in the presence of crystallizable paraffin molecule. The soluble PEP brush layer offers a steric stabilization to the wax crystal. Earlier studies revealed that the diblock copolymer PE-PEP can control the size and rheological properties of wax crystals in the middle distillate fuel and crude oils. The PE-PEP diblock copolymers are considered as an emerging class of wax crystal modifiers and PPDs even at lower concentration [38].

### *2.5. Nano-hybrid PPDs*

Nano-hybrid materials have turned out to be a research hotspot for enhancing the flow improving properties of crude oil in petroleum and petrochemical field. Various types of inorganic nanoparticles are introduced in the polymeric matrix of PPD such as silica, titania, montmorillonite, grapheme oxide to prepare the nano-hybrid PPD. Compared to pure polymeric PPD, the nanocomposite PPDs are highly effective due to their improved mechanical properties, thermal stabilities and abrasion resistance. Development of polymeric/inorganic nano-composites or nano hybrids are now considered useful for petroleum industry [39]. Compared with the conventional polymeric PPDs, the NPPDs combine the advantages of both nanomaterials as well as the conventional polymeric PPDs. Thus, they increase the performance of the conventional polymeric PPDs [40].

Kazemi et al. stated in 2020 that polymethyl methacrylate/clay nanocomposites have the ability to block wax. Two components make up the polymeric PPDs: a polar component and a non-polar component. The non-polar portion of the polymeric PPD is where the wax crystals are adsorbed, while the polar portion is in charge of reducing the contact between crystals and between crystals and oil, which prevents the formation of a three-dimensional network of wax crystals. This results in the waxy crude oil's viscosity, pour point, and gelation point decreasing, which enhances the oil's rheological characteristics [41].

The change in pour point reduction between the pure EVA copolymers and the NPPD is summarized in table 3 [41].

**Table 3.** Effect of polymeric PPD on the pour point of crude oil

| **Sample** | **PP (ºC)** |
|---|---|
| Native crude oil | 30.5 |
| EVA treated crude oil | 23.0 |
| Nano-hybrid EVA treated crude oil | 16.5 |

### *2.6. Organic Solvents*

For the reduction of viscosity of crude oils, dilution is a very effective method which improves the flowability of crude oil through the pipelines. The conventional diluents include gas condensates, naphtha, and kerosene [42]. The organic solvents based on their octane number with polar group in their alkyl chain have been extensively used as PPDs for the heavy crude oil prior to the emerging of polymeric WIs. The two main types of solvent used on the oilfields are light ends and organic solvents. Benzene, chlorinated hydrocarbons, and carbon disulphide are other effective organic solvents which proved successful for the flow improvement of crude oil, but they are environmentally hazardous. It is proved that $CO_2$ is also act as a solvent for flow improvement of waxy crude oil [43].

### *2.7. Conventional Surfactant*

Conventional surfactants can be prepared from Alkyl sulfonates and fatty amine ethoxylates, that can be used as a PPD. In the presence of water, these PPDs can act as wax deposition inhibitors or wax growth inhibitors; thereby dispersing these wax molecules to a small size so that they can be carried with the oil stream which prevents wax deposition in the crude oil pipelines.

The accumulation of wax crystals is inhibited by PPDs adhering to the developing wax crystals. By forming an oil-water emulsion, the PPD molecules stop wax crystals from forming. In contrast to the crude deposited wax, the polymeric PPDs produced tougher deposited wax with a higher average molecular weight. The deposited wax was found to be softer with a lower average molecular weight when the emulsion was present [44].

### *2.8. Bio-based Flow Improver*

The bio-based PPDs have interesting properties such as biodegradability, non-toxicity and cost-effectiveness. Pseudomonas putida and Halomonas xianhensis are two bacterial strains that are isolated from oil polluted sites in Egypt. They exhibit a good pour point reducing property. Surfactant extracted from Madhuca Longifolia which is tropical Indian plant is widely used as a flow improver for heavy crude oil [45]. Most of the bio surfactants exhibit the best surface activity at neutral pH. Recently it was reported that the synthetic fatty acids esters and vegetable oils show a positive result on the pour point reduction in crude oils [46]. Some vegetable oils such as jatropha, rubber and castor are also capable of reduction of pour point and viscosity of waxy crude when used in an appreciable amount. Olive oil based tertiary polymer is also effective as PPD. Upon addition of 1000 ppm of the polymeric PPD, the pour point of the crude oil was depressed by 8°C [47].

**Table 4.** Physicochemical properties of biological surfactant extracted from Madhuca Longifolia [45]

| **Color and appearance** | **Brownish red and liquid** |
|---|---|
| Specific conductance (25°C) | 73µS |
| Total organic content (TOC) | 14.32% |
| Non-ionic content | 10.67% |
| Anionic content | 0.73% |
| Cationic content | 2.92% |

In Table 5, effect of biological surfactant extracted from Madhuca Longifolia on the properties of heavy crude oil have been shown.

**Table 5.** Effect of Surfactant Concentration on Raw Crude Oil Properties [45]

| **Surfactant concentration on raw crude oil (ppm)** | **Behaviour index (n)** | | | **Consistency index (k)** | | | **Viscosity at 300 $s^{-1}$ shear rate (Pa.s)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | 30°C | 40°C | 50°C | 30°C | 40°C | 50°C | 30°C | 40°C | 50°C |
| 0 | 0.34 | 0.55 | 0.66 | 23.43 | 18.39 | 16.2 | 6.23 | 5.01 | 3.81 |
| 500 | 0.36 | 0.54 | 0.68 | 22.34 | 18.36 | 15.23 | 5.48 | 4.21 | 3.03 |
| 1000 | 0.39 | 0.56 | 0.76 | 20.1 | 17.66 | 14.35 | 3.95 | 3.01 | 2.35 |
| 1500 | 0.48 | 0.63 | 0.8 | 17.68 | 16.83 | 10.34 | 3.52 | 2.34 | 1.28 |
| 2000 | 0.52 | 0.8 | 0.87 | 4.43 | 2.198 | 2.16 | 1.58 | 0.57 | 0.19 |

## 3. Factors Influencing the Behavior of PPDs

Numerous types of polymeric additives are extensively used as PPDs or flow improvers. They are capable of modifying the morphology of wax crystal structure which results in the inhibition of the formation of three-dimensional wax crystal networks. A combination of effect that a polymeric PPD exhibit is pour point depression, viscosity reduction and yield stress reduction to a large extent. The pour point depression is greatly affected by the difference of wax constitution in the crude oil [48].

### *3.1. The Polymeric Backbone and Pendant Chains of PPD*

The performance of a polymeric PPD will be better when the structure i.e. the backbone and pendant chains are similar with the wax molecule. Xu et al. reported a comb-type copolymer based on maleic anhydride [49]. They synthesized different Maleic anhydride-α-octadecene copolymer derivatives with different chains and proposed that the aromatic fragments (AMAC) in a copolymer partially damage the aggregation of asphaltenes which improve the flow ability of the crude oil than that of the naphthalene (NMAC) as well as alkyl fragment (MAC). Thus, by molecular simulation they concluded that the order of flow ability is AMAC (phenyl group) >MAC (alkyl group) >NMAC (naphthyl group).

Zhao et al. in 2016 studied the effect of heteroaromatic pendant chains in comb polymers on the cold flow ability of crude oil. The crude oil contains the paraffin crystals are irregular and small in size. With the addition of co-polymeric PPD, the amount of paraffin crystals in crude oil is significantly reduced, in the manner of MACO > MACP > MACB [50].

### *3.2. Concentration of PPD*

Concentration plays an important role in the performance of polymeric additives. More the concentration of polymeric additives, lower will be the pour point of the oil. Machado et al. reported about poly (ethylene-co-vinyl acetate) as pour point depressant and concluded that the copolymer composition and an optimum concentration of EVA copolymer greatly influence the efficiency of the EVA copolymer as a PPD [30]. Concentration of PPD also plays an important role in the flow improvement of crude oil. With the increase in concentration of polymeric additives, the pour point of the wax molecule decreases to a significant amount. M.V. Kok in 2013 reported that when the concentration of PPD increased from 500 to 2000 ppm, the pour point of the crude oil was decreased to a considerable amount. It was observed that the additives work well with the crude oil which has low asphaltene content [51].

Table 6 given below shows the depression in pour point with the concentration of additives

**Table 6.** Effect of Additive (Pour point Depressant) Concentration on the Pour Points of Crude Oils [51]

| Crude oil | Concentration, ppm | Pour point, ºC |
|---|---|---|
| **Crude oil-1** | 0 | 15 |
| | 500 | 12 |
| | 1000 | 9 |
| | 2000 | 6 |
| **Crude oil-2** | 0 | -3 |
| | 500 | -3 |
| | 1000 | -6 |
| | 2000 | -9 |
| **Crude oil-3** | 0 | -15 |
| | 500 | -30 |
| | 1000 | -42 |
| | 2000 | -48 |

**Table 7.** Acrylate polymer as flow improver for wax rich crude oil [53]

| Polymer No. | Composition | MP (°C) | MW | PDI | Pour Point Depression (K.M.) | Pour Point Depression (S.) |
|---|---|---|---|---|---|---|
| **1** | NAFOL 2022 acrylate homopolymer | 55–56 | 27,900 | 2.96 | 3 | 27 |
| **2** | NAFOL 1822 acrylate homopolymer | 61–62 | 36,980 | 4.85 | 6 | 30 |
| **3** | NAFOL 2022 methacrylate homopolymer | 45–46 | 55,160 | 1.79 | 3 | 15 |
| **4** | NAFOL 1822 methacrylate homopolymer | 47–48 | 14,650 | 1.4 | 0 | 15 |
| **5** | NAFOL 2022 acrylate–NAFOL 2022 methacrylate copolymer | 65 | 90,270 | 2.54 | 9 | 3 |
| **6** | NAFOL 2022 methacrylate–vinyl acetate copolymer | 45 | 23,460 | 1.24 | 15 | 6 |
| **7** | NAFOL 2022 acrylate–acrylic acid–vinyl acetate terpolymer | 45 | 14,220 | 1.28 | 9 | 9 |

### *3.3. Average Molecular Weight and PDI of PPD*

The applications of polymeric PPDs are greatly influenced by the molecular weight and its distribution (Table 7). They are the polymeric additives with molecular weight ranging from

25000 to over one million, among which polyalkyl methacylates are notable ones [52]. The polymeric PPDs with molecular mass of 5000 to 50000 usually give better result than that of the smaller ones i.e., below 2000 and bigger molecules whose molecular mass is above 100000. El-Gamal et al. in 1994 showed that in case of acrylate/methacrylate copolymers, when the molecular weight distribution is broad i.e. high polydispersity index (PDI), the inhibition capability of the wax also increases which reveal the better pour point depression of the PPD [53].

In general, with the increase of average molecular weight, the activity of PPD also increases. Thus, by assessing their structure, molecular weight, physical and chemical structure, functional group presence, and various elemental composition, high performance PPD can be synthesized.

Chanda et al. showed that polybehenyl acrylate having low molecular weight and narrow molecular weight distribution exhibit better performance for crude oil with high asphaltene content [54].

### *3.4. Polarity of PPD Molecule*

The effect of polar and non-polar groups in comb-type copolymers on the flowability of the waxy oil was demonstrated by Xu and his group [55]. They synthesized poly(maleic acid alkylamide-co-α-octadecene) copolymer by varying the ratio of polar and non-polar groups via amidation process. In 2016, Yang et al. studied about different functional groups on the performance of poly (octadecyl acrylate) PPDs. They used the polar moieties such as VA, MA and Styrene for their study [56]. An evaluation of modified ethylene-vinyl acetate copolymer was performed by Ren et al. for the Jianghan crude oil. The results from different experiment show that EVAL exhibit better performance in decreasing the pour point of the waxy crude oil and reduction of viscosity than EVA copolymer. The EVAL copolymer has the ability to change the wax crystal habit thereby lowering the wax precipitation amount [57].

It was observed that the pour point and yield stress of crude oil is reduced by MAC at different dosage of MACs. The MAC with 0.5% MAC exhibit better effect on reducing pour point of the crude oil than that of the MAC with 0.3% MAC content. They concluded that in terms of asphaltene, the polar groups such as carboxyl group and amide linkage are able to disperse the asphaltene which can improve the cold flowability of the crude oil. But for crude oil having higher paraffin content, the MAC possesses medium r shows better result in cold flowability of the crude oil [55].

### *3.5. Monomer to Monomer Ratio*

There must be a suitable ratio between the comonomers for better performance of a polymeric additive. Recently in the year 2020, Fu et al. studied about the influence of monomer on the activity of poly(Octadecylacrylate-co-Styrene) as PPD. They took a controlled amount of styrene to synthesize the copolymer via copolymerization with octadecyl acrylate and found that the ratio between octadeyl acrylate and styrene at 3:2 will give an optimum performance in the pour point depression of the Shengli crude oil [58].

Their research revealed that with the increase in molar ratio of styrene in PPD, the pour point of the model waxy oil first starts to increases and then decreases. This result shows that the pour point of the waxy oil can be regulated by the content of polar group in styrene [58].

### *3.6. Solubility of the Additives*

The solubility parameter is an important factor for the performance of a flow improver. It is proved that the alteration of solubility parameter of the solvent always affect the WAT of the model oil when there is no additive involved. It does not affect the pour point of the model oil. However, upon addition of the additive, the effect on WAT remains same, but the pour point was significantly affected. As the polymer-solvent interaction increases, the polymer-polymer interaction decreases which results in the expansion of polymer coil. This expansion increases the hydrodynamic radius of polymer which increases the intrinsic viscosity of model oil [59].

## **4. Different Synthesis Approaches**

There are so many synthetic approaches have been proposed till today for the synthesis of various pour point depressant as flow improver. The methods which are commonly used for the preparation of these flow improvers are mentioned below,

### *4.1. Free-radical Polymerization*

Researchers have already reported about various free radical polymerization techniques in the last few decades [60]. In the year 1994, Gamal et al. reported the synthesis of acrylate/methacrylate polymers for the flow improvement of waxy crude oil. They used monomers in presence of benzoyl peroxide as an initiator and benzene as a solvent for the polymerization reaction. The reaction was heated at about 70±5°C for 20 minutes under $N_2$ atmosphere. Then the mixture was stirred at that temperature utilizing a nitrogen blanket for 3 hours. The prepared homopolymer was precipitated out with an excess volume of methanol and then filtered. After that, purification was done by dissolution of polymer in benzene and re-precipitated with methanol. The precipitate was then allowed to dry at 40°C for 3 hours in vacuum. The resulting product was white solid powder. They concluded that acrylate/methacrylate polymers were considered as an effective flow improver for both Salam (S) and Khalda mixture (K.M.) waxy crude oil [53]. In the same year, Borthakur et al. reported a synthesis procedure of alkyl fumerate-vinyl acetate co-polymer in association with alkyl acrylate as flow improver for Borholla crude oil [13]. They prepared the flow improver additives by esterification followed by polymerization/ co-polymerization, except in case of styrene-behenyl maleate where they performed co-polymerization first and then esterification was carried out. In esterification, they used fumaric acid, acrylic acid and styrene-maleic anhydride copolymer and esterified with appropriate amount of alcohol. The solvent used was toluene and p-toluene sulphonic acid (PTSA) was used as catalyst. The reaction mixture was then repeatedly washed with distilled water to remove unreacted acid and PTSA. Then with a suitable solvent, the product was precipitated out. After that polymerization/ copolymerization of acrylate, fumerate and vinyl acetate was carried out using BPO as initiator in nitrogen atmosphere at 80-85°C. Finally, the prepared copolymers were precipitated out in a suitable solvent. Later on in the year 1996, they reported about the synthesis of dialkylfumerate-vinyl acetate copolymer by similar method as a flow improver for Indian waxy crude oil. Meanwhile in 2002, Ashbaugh et al. reported about diblock copolymer synthesis through anionic polymerization followed by hydrogenation. In this report they synthesized PE-b-PEP diblock polymer which are of well-defined molecular weight [37]. A flow improver for Akholjuni crude oil was synthesized by Soni and his group [61]. They synthesized alkyl ester-maleic anhydride copolymer through the process of esterification followed by copolymerization. From different experimental data they found that the optimum length of pendant chain certainly affects the pour point depression and viscosity reduction of this polymeric PPD [62]. Deshmukh and Bharambe in 2009 reported four polymeric PPDs which can be used as pour point depressants for Limbodara waxy crude oil through the free radical co-polymerization of maleic anhydride and n-alkyl undecylenates. The results from various experiment showed that those prepared additives can act as both wax depressant and flow improvers because of the presence of polar group in the structure [62].

### *4.2. Controlled Radical Polymerization*

Controlled radical polymerization (CRP) is currently considered as one of the best tools to synthesis of different polymeric additives because of its ease of synthesis. It is an efficient method for the synthesis of polymeric materials with well-defined molecular structure and weight and with narrow molecular weight. Different CRP techniques such as Atom Transfer Radical Polymerization (ATRP), Activator Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET-ATRP), Reversible Addition Fragmentation Transfer (RAFT) are significant for the synthesis of polymeric PPD for improving the rheology and depressing the pour point of the waxy crude oil.

#### *4.2.1. Atom Transfer Radical Polymerization (ATRP)*

In polymer chemistry it is of great interest to synthesize polymers with well-defined composition, design and functionalities. The ATRP approach enables us to synthesize a polymer of predetermined molecular weight upto Mn= 105 and narrow molecular weight distribution, $M_w/M_n$=1.10. ATRP can be used for a broader class of monomer such as methylmethacrylate, methacrylate, styrene etc. which enables us to synthesize a wide range of tailor-made polymers. The transition metal catalysts in ATRP are of low oxidation state such as Cu (I), Fe (II), Ru (II) etc. But this ATRP techniques has two major disadvantages:

- The halide species, R-X are toxic, as they are volatile, corrosive, and environmentally unsafe. Secondly, their handling and waste disposal are problematic in large-scale applications.
- Oxidation of catalyst Mn/LX by oxygen in air. Because It readily oxidizes the lower oxidation state metal catalyst into a higher oxidation state, which disturb the redox equilibrium required for controlled polymerization. On the other hand, it may lead to loss of control over molecular weight and dispersity.
- To overcome these drawbacks, Matyjaszewski et al. and Teyssie et al. used conventional initiator AIBN in presence of transition metal catalyst in higher oxidation state and referred as reverse and alternative ATRP process [63]. Arvind et al. in 2016, provided a new way for an efficient PPD which was a non-aqueous lubricant additive from functionalized grapheme oxide. They synthesized a nanocomposites of graphene oxide/poly(Cn-acrylate) (GOPA18). The incorporation of graphene oxide enhances the solubility of grapheme derivative and provides a multifunctional hybrid material. In their work they performed a surface-Initiated Atom-Transfer Radical Polymerization (SI-ATRP) of long-alkyl-chain (C10−C18) acrylates [64]. From various analytical techniques they concluded that the

GOPA18 nanocomposite was a potential lubricating nanoadditives with enhanced flowing properties in base oil.

### *4.2.2. Activator Regenerated by Electron Transfer Polymerization (ARGET-ATRP)*

In the year 2018, Savoji and his group reported about poly (alkylmethacrylate) grafted polyolefin as viscosity modifier for engine oil. They synthesized this graft polymer through ARGET-ATRP process. This group had performed successive ring opening metathesis copolymerization (ROMP) and ARGET-ATRP for grafting alkyl methacrylate on an unsaturated polyolefin backbone. The molar mass of the backbone was tuned by the incorporation of cis-4-octene as a chain transfer agent. The unsaturated polyolefin precursor was then used in a grafting from reaction of the methacrylate monomer through ARGET ATRP prior to chemical hydrogenation. They used two alkyl methacrylate monomers for the preparation of side chain such as butylmethacrylate and laurylmethacrylate. After that, grafting of methacrylate monomer was done by ARGET-ATRP approach using tinethylhexanoate $Sn(EH)_2$ as reducing agent and degassed with argon [65].

### *4.2.3. Reversible Addition/Fragmentation Chain Transfer Polymerization (RAFT)*

The development of RAFT polymerization was on the basis of radical addition fragmentation process which was developed in 1970s. To control the molecular weight and end-functionalities of a polymer chain RAFT polymerization is considered to be the best way [66]. For the RAFT polymerization process, a RAFT agent is quite necessary. In 1995, methacrylate macromonomer were appeared as a RAFT agent for performing free radical polymerization in a controlled way. In 2010, Yao et al. reported a well-defined block copolymer having one polystyrene segment and another poly(styrene-alt-maleic anhydride) segment with RAFT polymerization. The objective of this work was to synthesize a uniform diblock copolymer PS-b-Poly(St-alt-MAn) with both narrow molecular weight and strictly alternating SMA segments [67].

Inspiring from this novel synthetic approach, Cao et al. in 2015 synthesized a polymeric flow improver through RAFT polymerization technique. They synthesized a well-defined copolymer of styrene (St) and maleic anhydride which further modified by octadecyl amine. The wax crystal becomes fewer and smaller after the addition of this flow improver [68]. The synthesized styrene-maleic anhydride copolymer via RAFT polymerization exhibit a quite narrow polydispersity less than 1.3.

A comb-like copolymer-POSS (polyhedral oligomeric silsesquioxane) nanocomposite was synthesized by Yao et al. via in-situ RAFT polymerization. They synthesized POA-POSS, POA-VA-POSS and POA-St-POSS nanocomposite PPD. The monomers they used for the RAFT polymerization were octadecyl acrylate (OA), vinyl acetate (VA), maleic anhydride (MA) and styrene (St). The RAFT agent used was 2-cyanoprop-2-yldithiobenzoate (CPDB) [69]. In the year 2019, Moriceau et al. reported about alkyl Functional Poly (Styrene-co-Maleic Anhydride) (PSMA) as pour point and viscosity modifiers for Lubricating Oil. The copolymer was synthesized by RAFT polymerization process. They observed that better pour point depressant activity was obtained with polymeric PPD having higher density of side chain [70].

### *4.3. Anionic Polymerization*

The anionic polymerization is applicable for that system where the alkali metals are involved. This alkali metal transfers electrons from metal to the monomer. Ashbaugh et al. prepared a random copolymer of poly (ethylene butadiene) via anionic polymerization. They polymerize 1, 3-butadiene in a mixture of hexane and triethylamine with tert-butyl lithium as initiator. Study from their experiment revealed that these copolymers modify the wax crystal structure which further affects the rheology of crude oil [71].

### *4.4. Cationic Polymerization*

Cationic polymerization involves transfer of charge from a cationic initiator to a monomer unit which further becomes reactive. The reactive monomer undergoes a polymerization reaction with the other monomer result in the formation of a polymer. El-Gamal et al. synthesized a high molecular weight poly-α-olefin which can be used as a PPD for Egyptian waxy western desert gas oil through cationic polymerization. The result from their experiment showed that the prepared polymer has the potential to reduce the pour point of the desert gas oil. They also conclude that the molecular weight distribution is an important factor for the performance of polymeric PPD [72].

### *4.5. Melt Blending Technology*

Melt blending is an approach which is commonly used for preparing clay/polymer nanocomposites. In this method, the polymer is allowed to melt and then combined with a required amount of intercalated clay with the help of an extruder. This process is carried out in presence of inert gases such as argon, nitrogen etc. Since this process lacks organic solvent, hence it is an environment friendly approach. In 2016, Yao et al. reported a flow improver based on nanocomposites via melt blending method. They synthesized POA/clay nanocomposite PPD using melt blending approach. They observed that compared to solvent blending, melt blending shows better performance over the synthesis of polymeric nanocomposites [73].

Study showed that the nanocomposites PPD particles have the ability to control the dispersion of POA molecule in oil phase by adsorbing POA molecule on the surface of the particle. The PPD can modify the microstructure of the gelled waxy crude oil which results in the reduction of solid-liquid interfacial area, thereby weakening the microstructure of the wax crystal which greatly enhances the performance of the nanocomposites PPDs.

## 5. Challenges

Although PPDs are widely used as flow improvers, yet there are many challenges to address. Such additives are very selective, and no single type of PPD has universal application to every waxy crude oil due to the differences in crude oil compositions [74]. To be effective for a particular oil, a PPD should have certain physical characteristics which maybe ineffective in other oils [75]. Thus, certain experimental techniques are required to assess an effective flow improver for each type of waxy crude oil. Most of the chemical additives typically have a wax like paraffinic part that co-crystallizes with wax forming components of oil and a polar component limiting the degree of co-crystallization [76]. These polymeric additives are very selective i.e. not all additives are sufficiently effective for every crude oil. Besides these, the long molecular chain, large molecular weight and high thermostability of the polymeric PPDs make them hard to decompose in the oil refining process.

The dosage of PPDs required in laboratory tests may not be the representative of oil filed dosage and it is always be higher than that of the field dosage. The mechanism of interaction of PPDs is often hypothesized and till date it is not clearly understood as different crude oil is used for each study, therefore it is challenging to get an accepted theory to explain the experimental result [77], [78]. At present, the polymeric PPD is mainly produced via free radical polymerization, which leads to random structure of polymer formation of invalid fragment [79], [80]. These fragments may arise because free radical polymerization occurs in a random manner, so monomers may connect in an uncontrolled way [81], [82] Controllable preparation of block polymer with relatively accurate structure can minimize the amount of invalid fragment and improve the performance of polymer PPD [83].

## 6. Conclusions

Polymeric additives serve multiple functions in the transportation of waxy crude oil, acting as pour point depressants (PPDs), wax inhibitors, and flow enhancers. By reducing the pour point of crude oils, these additives significantly improve its flowability. Typically, polymeric PPDs consist of one polar group and one non-polar group. These functional groups interact with wax crystals through mechanisms such as nucleation, adsorption, and co-crystallization, thereby modifying the crystal morphology.

The efficiency of polymeric PPDs is strongly influenced by factors such as the length of the alkyl chain, the monomer grafting ratio, and the number of polar moieties. In addition, the chemical composition and molecular structure of the wax present in crude oil play a critical role in determining PPD performance. However, a unified theory describing the interaction between polymeric PPDs and waxy crude oil is still lacking, as different additives show varying effects depending on the type of crude oil.

To better evaluate the efficiency of polymeric PPDs, theoretical modeling is required to predict their interactions with wax molecules. Since free radical polymerization often produces PPDs with random structures, controlled synthesis strategies are essential to minimize inactive fragments and enhance overall effectiveness.

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## Conflicts of Interest

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## Declaration on AI Usage

This manuscript has been prepared without the use of AI tools.

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