fluids

MDPI

Article

Ester and Amide Functionalization of Maleated Polyolefins as Pour Point Depressants for Kumkol Waxy Crude Oil

Assel Begimova, Zhanna Nadirova *, Kazim Nadirov, Gulmira Bimbetova and Berik Sakybayev

Department of Petroleum Engineering, M. Auezov South Kazakhstan University, Tauke Khan Avenue 5, Shymkent 160012, Kazakhstan; as_86_ar@mail.ru (A.B.); nadirovkazim@mail.ru (K.N.); gulmirabimbetova@gmail.com (G.B.); neftehimstroy@mail.ru (B.S.)

* Correspondence: zhanna.nadirova@inbox.ru; Tel.: +7-775-315-22-77

Abstract

Pour point depressants (PPDs) based on functionalized polyolefins were obtained and evaluated for their efficiency in pour point reducing of Kumkol waxy crude oil (Kazakhstan), which contains 15.2 wt.% paraffin and has a pour point of +17 °C. An ethylene–propylene copolymer (EPR-505A) was treated through grafting of maleic anhydride (MA-g-PO) and then converted into three different derivatives that had an identical polymer backbone: an ester-functionalized, an amide-functionalized, and a combined ester–amide additive. The obtained products were tested at 500 g/t through kinematic viscosity measurements, equilibrium and kinetic interfacial tension analysis, pour point determination, cooling curve analysis, and optical microscopy. The ester derivative reduced the pour point by 7 °C, the amide derivative did so by 5 °C, and the combined additive achieved a 10 °C pour point reduction and a more than twofold decrease in kinematic viscosity at 0 °C. Interfacial tension measurements and adsorption kinetics allowed us to assume that ester groups govern macromolecular solubility and diffusion mobility, while amide groups enhance adsorption affinity at paraffin crystal surfaces. Their combined action shifts crystallization from a collective to a dispersed regime. These findings establish structure–activity relationships between polar group architecture and PPD efficiency.

Keywords: pour point depressant; waxy crude oil; polyolefin; maleic anhydride; ester functionalization; amide functionalization; flow assurance; paraffin crystallization

1. Introduction

The presence of many long-chain n-alkanes (C_{16}–C_{35}) in waxy crudes makes them very problematic to deal with when trying to extract these oils from the ground, transport them through pipelines, and store them in cold weather. When the temperature of the oil falls below the wax appearance temperature, paraffin molecules crystallize and join together to form a network by interlocking with one another, resulting in an increase in viscosity and gel strength, and ultimately producing a total loss of flowability [1–3]. Paraffin crystallization is governed by thermodynamic and kinetic factors, including temperature, pressure, and oil composition. The effect of pressure on wax deposition has been demonstrated by Quan et al., who showed that increasing pressure shifts the wax appearance temperature and accelerates deposition from wax–solvent mixtures [4]. The thermodynamic modeling of paraffin precipitation using DSC-based solid–liquid equilibrium approaches has been described by Coto et al., providing a quantitative framework for predicting wax phase behavior in petroleum mixtures [5].

Check for updates

Academic Editor: Rajinder Pal

Received: 14 April 2026
Revised: 13 May 2026
Accepted: 17 May 2026
Published: 20 May 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

In addition, some crude oils have pour points above the ambient temperature, such as crude oils that are produced in Kumkol (Kazakhstan), where the amount of solid paraffins can be anywhere from 14.0 to 16.3 wt.%, and these crude oils can be predicted to be non-flowable (lacking the ability to flow) at temperatures of +9 to +12 °C. Therefore, in order to ensure that these types of crude oils remain flowable at reduced temperatures, a chemical intervention must be made [6].

Chemical solutions for addressing the problem of paraffin wax build-up, specifically in pipeline systems, would usually include wax additives. Among these wax additives are pour point depressant (PPD) products that fall within the category of polymer-based or polymeric-type additives that interact with and modify the behavior of paraffin crystals. Therefore, based on the chemical structure and composition, these PPDs modify the way in which the paraffin crystals are able to develop and increase their size, and in some cases, PPDs create altered forms of paraffin crystals ('crystal morphology') so that the paraffins do not create crystalline meshes in the oil and thus prevent the entire bulk of the oil from solidifying [7–10]. The most commonly researched and discussed types of PPDs are polyacrylate types, ethylene–vinyl acetate (EVA) copolymers and maleic anhydride copolymers, all of which use a polymeric additive base with a flexible, nonpolar backbone and either polar or amphiphilic groups that provide interactivity with the surface of crystallizing paraffin [11]. All of these share the common structural principle of combining a flexible non-polar backbone, which ensures compatibility with polar or amphiphilic pendant groups capable of interacting with crystallizing paraffin surfaces [12–14]. For a PPD to be effective, it is important for its chemical structure to contain nonpolar hydrocarbon chains and polar groups so that it is able to co-crystallize with paraffins and sterically prevent the formation of a crystalline network [15].

The type and density of polar functional groups on depression activity have a well-defined conceptual basis; however, many aspects of the quantitative measurements of this relationship still remain unclear. One significant reason for this is that various studies have applied many different types of polymer backbones; therefore, it is difficult to verify whether functional group contributions are isolated from those associated with matrix effects. For instance, Quan et al. studied the changes in viscosity, pour point, and wax appearance temperature of crude oil with 15 wt.% wax content treated by 12 different commercial wax inhibitors and found that EVA wax inhibitors have a pronounced effect on pour points and apparent viscosity, whereas they only marginally influence wax appearance temperatures [16]. Machado et al. found that the addition of copolymers such as polyacrylates, polymethacrylates, or EVA can inhibit the deposition phenomenon, but this effect is specific: similar copolymers present different performance depending on their physicochemical properties in solution [17].

In particular, ester- and amide-functionalized polyolefins have been investigated separately in the literature, and both have shown PPD activity toward waxy crudes. Wu et al. conducted a systematic examination of maleic anhydride-based polymer copolymers and their respective derivatives containing varying polar and/or aromatic pendant groups and reported that those four copolymers contain polymeric additives that worked well as flow-modification agents within Changqing Waxy Crude Oil [18], thus proving that how good or bad the performance of the various products is depends on the chemistry involved with the pendant group. On the amide-based side of the research project, Deshmukh et al. prepared poly(n-alkyl acrylates-co-N-hexadecylmaleimide) from reactions of maleic anhydride copolymers with hexadecylamine, which permitted these nitrogen-containing copolymers to also act as both flow improvement agents and wax dispersants [19]. Zhubanov et al. performed research specifically on wildcat crude oil from Kazakhstan by synthesizing a series of copolymers made from α-olefins and maleic anhydride that were subsequently modified

by reacting with amines (e.g., hexadecylamine and octadecylamine), resulting in improved rheological properties and lower pour points of the wildcat crude oil from the Akshabulak field [20]. Marenov et al. further improved ethylene-vinyl acetate (EVA)-based PPD activity for Akshabulak crude by compounding the EVA copolymer with crude gossypol, demonstrating that adding non-polar and polar functional group options provide better wax crystal inhibition performance than what was available without using those types of additives [21]. At the field application level, Mun et al. mentioned that the modified EVA-based graft copolymers (gEVAp) were better than commercial PPDs on Kumkol oil with a +12 °C to −3 °C pour point depression and formation of compact platelet-shaped wax crystals. Field pigging tests also showed considerably less wax accumulation on the pipeline [11].

However, a systematic, side-by-side comparison of ester, amide, and combined ester–amide functionalities on an identical polymeric scaffold together with a mechanistic interpretation spanning rheological interfacial crystallization and microstructural levels has not been reported. In this context, it is necessary to have a balance between nonpolar and polar groups such that the solubility of additives in the oil is adequate [18]; however, knowing how the chemical structure of the polar component influences the kinetics of adsorption, the stability of the interfacial layer, the suppression of crystal formation, and, ultimately, macroscopic flow of the liquid would allow for rational PPD design for the next generation of PPDs.

This study fills the existing gap by using a functionalization technique on a single polymer precursor. As the backbone, an ethylene–propylene copolymer (EPR-505A) was selected due to its hydrocarbon nature, good compatibility with waxy crude oils, and the thermochemical stability it has during both synthesis and service conditions. The non-polar EPR backbone is capable of good solubility and dispersibility in paraffin-rich oil. However, it does not contain functional groups that can direct paraffin crystallization. To add reactive sites, EPR was grafted with maleic anhydride, resulting in a maleated polyolefin (MA-g-PO) with anhydride moieties on the side chains. These anhydride nodes serve here as chemical handles for later transformations without changing the hydrocarbon backbone. From a single MA-g-PO intermediate, three structurally different PPD additives were made by turning the anhydride groups into ester fragments through the reaction with oleic acid (MA-g-PO-ester), amide fragments through the reaction with hexadecylamine (MA-g-PO-amide), or a hybrid mixture of both ester and amide fragments (MA-g-PO-EA). Since the polymer matrix is the same in all three cases, changes in the activity observed can be linked to the type of polar functional group.

We evaluated the impact of additives on Kumkol crude oil by conducting a series of experiments involving measurement of kinematic viscosity of the oil over a temperature range of 5 to +40 °C, determination of both equilibrium and kinetic interfacial tension at the oil–air interface, pour point determination, analysis of cooling curves, and polarized-light microscopy of the paraffin microstructure. The aim of this paper is twofold: first, to develop quantitative structure–activity relationships that link the type of polar functional group grafted onto the polyolefin chain to the ability of the resulting polymer to suppress paraffin crystallization in Kumkol crude oil, and second, to get more insight into the physicochemical mechanism responsible for the paraffin crystallization inhibition.

2. Materials and Methods

2.1. Synthesis of PPD Additives

The polymeric backbone of the three PPD samples that were analyzed in this work was the commercially available ethylene–propylene copolymer EPR-505A (Sinopec, Beijing, China; weight-average molecular weight ~60,000 g/mol). Maleic anhydride (Tianjin Damao

Chemical Tianjin, China, 99%) was the functionalizing agent. Oleic acid (Tianjin Fuchen, Tianjin, China, 99%) and hexadecylamine (Aladdin, Shanghai, China, 95%) were the long-chain hydrophobic modifiers used for the ester and amide derivatives, respectively. The functionalization was performed in two steps. For the first step, 50 g of granulated EPR-505A was dissolved in 250 mL of xylene, and 10 wt.% maleic anhydride in the presence of 0.5 wt.% benzoyl peroxide (initiator) was added at 165 ± 5 °C. The reaction was kept at that temperature for 4 h under stirring, and then the mixture was cooled down to 60 °C and filtered to obtain the maleated copolymer (MA-g-PO). The second step consisted in reacting the MA-g-PO intermediate (10 g) with the selected modifier in toluene at 120 C for 3 h: oleic acid (0.1 mol) for the ester derivative (MA-g-PO-ester), hexadecylamine (0.1 mol) for the amide derivative (MA-g-PO-amide), or an equimolar mixture of both reagents (0.05 mol each) for the combined ester-amide derivative (MA-g-PO-EA).

Products were isolated by precipitation into isopropanol (200 mL, 0 °C) with stirring, filtered through a Büchner funnel, washed three times with fresh isopropanol (3 × 50 mL) to remove unreacted modifiers and residual toluene, and dried under vacuum at 60 °C to constant mass.

2.2. Crude Oil Characterization

Crude oil from the Kumkol field (Kyzylorda region, Kazakhstan) was used as the test medium. Its physicochemical characteristics are summarized in Table 1. Prior to testing, the oil was allowed to settle for 48 h at 20 °C to sediment mechanical impurities, after which the supernatant layer was decanted and filtered through a qualitative paper filter. The prepared oil was stored in sealed 1 L glass bottles at +4 °C.

Table 1. Physicochemical characteristics of Kumkol crude oil.

Property	Value
Density at 20 °C	816 kg/m^3
Kinematic viscosity at 20 °C	6.04 mm^2/s
Pour point	+17 °C
Sulfur content	0.48 wt.%
Resin content	6.7 wt.%
Asphaltene content	0.41 wt.%
Wax content	15.2 wt.%
Mechanical impurities	<0.01 wt.%

Oil–additive mixtures were prepared by adding the PPD (0.10 wt.%, equivalent to 500 g/t) to oil preheated to 60 °C, stirring with a magnetic stirrer for 30 min, and then holding at 60 °C for a further 1 h.

2.3. Acid Number Determination

The anhydride conversion rate was calculated by acid–base titration according to ASTM D974. A 0.5 g measure of each sample was dissolved in 20 mL of xylene at 80 °C, followed by addition of 5 mL of distilled water. The resulting solution was titrated with 0.1 M KOH in isopropanol using phenolphthalein as indicator. The acid number (AN) was calculated as

$$AN = (V \times C \times 56.1)/m$$

where V is the volume of KOH solution consumed (mL), C is the KOH concentration (mol/L), 56.1 is the molar mass of KOH (g/mol) and m is the sample mass (g).

Each measurement was performed in triplicate. The anhydride conversion rate X was calculated as

$$X = (AN_0 - AN_P)/AN_0 \times 100\%$$

where AN_0 is the acid number of MA-g-PO and AN_P is the acid number of the corresponding derivative.

2.4. Kinematic Viscosity

Kinematic viscosity values was obtained in accordance with GOST 33-2000 using a glass capillary viscometer VPZh-2 (UNIPRO, Moscow, Russia). Measurements were performed over the temperature range from −5 to +40 °C. The temperature was maintained to ±0.1 °C using a liquid thermostat with an electronic controller; each temperature point was equilibrated for at least 10 min prior to measurement. Kinematic viscosity ν was calculated as

$$\nu = K \cdot \tau$$

where K is the viscometer constant (mm^2/s^2) and τ is the efflux time (s). Each measurement was performed in triplicate and the mean value was reported; the relative standard deviation between replicates did not exceed 2% in all cases.

2.5. Interfacial Tension

The temperature dependence of interfacial tension σ was measured at the oil–air interface over the range +20 to +40 °C using a Krüss DSA100 (KRÜSS GmbH, Hamburg, Germany) tensiometer (pendant drop method). For each sample, at least 3 independent droplets were analyzed at each temperature. The reported values represent mean results with a reproducibility of ±0.3 mN/m. Adsorption kinetics (σ vs. time) were recorded isothermally at +20 °C over 300 s immediately after droplet formation.

2.6. Pour Point Determination

Pour points were determined according to GOST 20287-91. Oil samples (with and without PPD at 500 g/t) were preheated to 50 °C, cooled at a controlled rate of 1 °C/min, and the pour point was recorded as the lowest temperature at which the sample retained mobility. Each determination was performed in triplicate.

2.7. Cooling Curve Analysis

Cooling curves were recorded using a custom-built apparatus consisting of a 20 mL sample tube immersed in a programmable cooling bath, with a calibrated thermocouple (±0.05 °C) inserted into the oil sample. After preheating to 60 °C, samples were cooled at 0.5 °C/min and temperature was logged every 10 s. The onset temperature and duration of the isothermal crystallization plateau were used as indicators of paraffin phase behavior.

2.8. Polarized Light Microscopy

The microstructure of the paraffin phase was examined by polarized light microscopy (Olympus BX53, Olympus, Tokyo, Japan, 200× magnification). Samples were heated to 60 °C, placed on glass slides, and cooled to +5 °C at 1 °C/min using a Linkam temperature-controlled stage. Micrographs were acquired in transmission mode with crossed polarizers. Crystal size and morphology were evaluated qualitatively from at least five representative fields of view per sample.

3. Results and Discussion

3.1. Anhydride Conversion and Rheological Behavior

To evaluate the degree of anhydride conversion, acid numbers of MA-g-PO and its derivatives were obtained by KOH titration (Table 2).

Table 2. Acid numbers and anhydride conversion rates of MA-g-PO and its derivatives.

Sample	Acid Number (mg KOH/g)	Conversion (%)
MA-g-PO	48.3 ± 1.2	-
MA-g-PO-ester	14.1 ± 0.8	70.8 ± 2.1
MA-g-PO-amide	6.9 ± 0.5	85.7 ± 1.6
MA-g-PO-EA	3.8 ± 0.4	92.1 ± 1.3

The acid number of the MA-g-PO precursor was 48.3 ± 1.2 mg KOH/g. Upon esterification with oleic acid, it decreased to 14.1 ± 0.8 mg KOH/g, which corresponds to a conversion of 70.8 ± 2.1%. The amide derivative showed a higher conversion of 85.7 ± 1.6% (AN = 6.9 ± 0.5 mg KOH/g). The combined ester–amide derivative exhibited the highest conversion of 92.1 ± 1.3% (AN = 3.8 ± 0.4 mg KOH/g). Figure 1 shows the temperature dependences of the kinematic viscosity of an oil sample in the range from +40 °C to −5 °C in the absence of additives and in the presence of PPDs based on functionalized polyolefins at a dosage of 500 g/t.

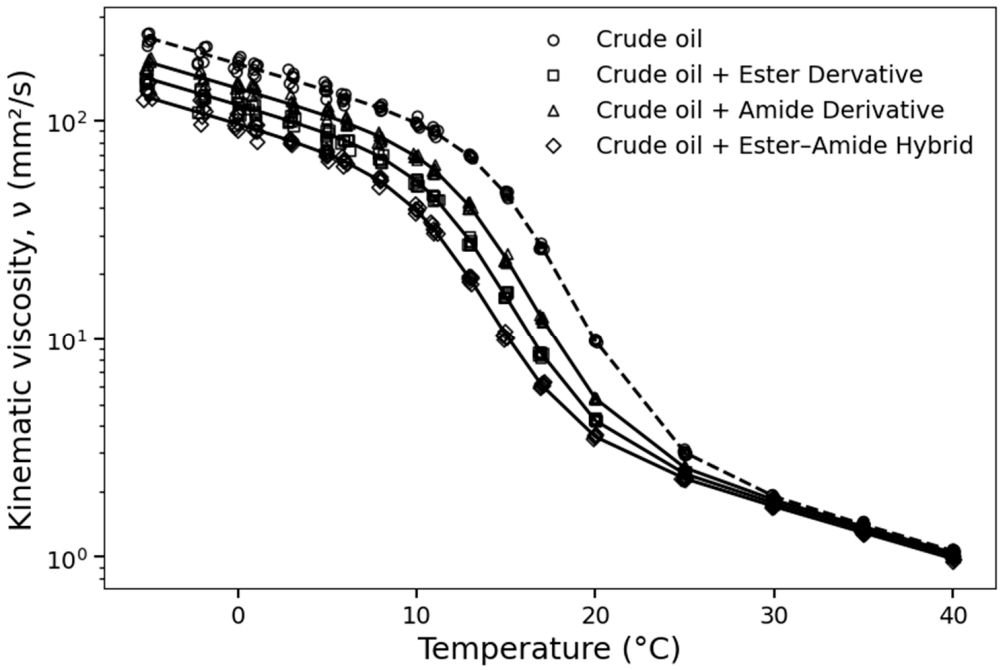


Figure 1. Temperature dependences of the kinematic viscosity of oil from the Kumkol field in the absence and presence of functionalized polyolefin PPDs (500 g/t).

For the initial crude oil without PPDs, the kinematic viscosity at +40 °C is approximately 3.5–4.0 mm^2/s and increases to ~6 mm^2/s at +20 °C. Below +16 °C, a sharp inflection is observed on the curve, which corresponds to the onset of intensive crystallization of the paraffin phase, after which the viscosity increases to 20–25 mm^2/s at +5 °C and exceeds 30 mm^2/s at temperatures around 0 °C [22]. The introduction of ester-functionalized polyolefin leads to a slowdown in viscosity growth upon cooling. Thus, at +10 °C, viscosity values are approximately 12–14 mm^2/s versus 18–20 mm^2/s for the original crude oil,

and at 0 °C they do not exceed 18–20 mm^2/s. The inflection point of the temperature dependence shifts to lower temperatures, down to ~+11–+12 °C. The amide-functionalized polyolefin has a less pronounced effect on rheological behavior. At +10 °C, the viscosity is approximately 15–17 mm^2/s, and at 0 °C it reaches 22–24 mm^2/s. The temperature at which the viscosity begins to increase shifts slightly and remains near +13 –+14 °C. The most pronounced PPD effect is observed for the combined ester–amide additive. In this case, the kinematic viscosity at +10 °C does not exceed 10–12 mm^2/s, and at 0 °C it is approximately 14–16 mm^2/s, which is more than 2 times lower than that of the original oil. An increase in viscosity begins only at temperatures around +9–+10 °C, which indicates effective suppression of paraffin crystal aggregation and network formation. Thus, the data in Figure 2 show that, at the same dosage of 500 g/t, changes in the chemical architecture of the polyolefin additive lead to significant differences in the macroscopic rheological behavior of the oil, with the maximum effect achieved with combined ester–amide functionalization.

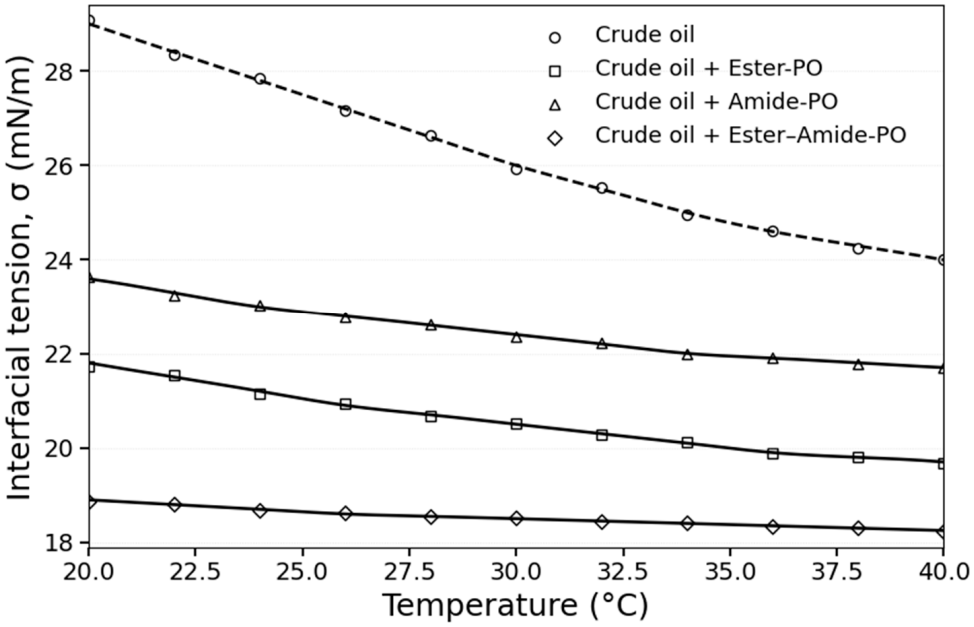


Figure 2. Temperature dependences of the interfacial tension of oil from the Kumkol field in the absence and presence of functionalized polyolefin PPDs (500 g/t).

The obtained kinematic viscosity data reflect the integral rheological behavior of the system but do not allow for a definitive determination of the additives' mechanism of action. Considering interfacial properties allows us to move from a macroscopic description of rheological behavior to an analysis of the molecular mechanisms of action of PPDs. In particular, the change in interfacial tension at the oil–air interface reflects the ability of functionalized polyolefins to adsorb at the interface and form a surface layer that prevents the aggregation of paraffin particles.

3.2. Interfacial Properties and Crystallization Behavior

Figure 2 shows the temperature dependences of the interfacial tension of an oil sample in the range of +20–+40 °C in the absence of additives and in the presence of functionalized polyolefin PPDs at a dosage of 500 g/t.

The original crude oil shows the highest σ values: at +20 °C, they are approximately 29 mN/m and gradually decrease to ~24 mN/m at +40 °C. The reason for this behavior is a decrease in cohesive interactions in the hydrocarbon system with increasing temperature [23]. The introduction of the ester-functionalized polyolefin decreases interfacial tension: at +20 °C, σ decreases to ~21.7–21.8 mN/m and further decreases to

~19.6–19.8 mN/m at +40 °C. This is probably due to the effective adsorption of carbonyl groups at the phase boundary and the orientation of long alkyl chains within the bulk of the oil [24]. The amide-functionalized polyolefin has a less pronounced effect. The σ values are ~23.5 mN/m at +20 °C and decrease to ~21.6–21.7 mN/m at +40 °C. This is likely due to the lower surface activity of amide groups in a non-polar medium and the formation of a less dense adsorption layer. The most pronounced effect is observed for the combined ester–amide additive. In this case, σ at +20 °C is ~18.9 mN/m and decreases only slightly to ~18.2 mN/m at +40 °C. The relatively weak temperature dependence indicates the formation of a stable and saturated interfacial layer with high surface activity. The maximum effect on interfacial tension reduction is achieved for the combined ester-amide structure.

The data in Figure 2 allow us to evaluate the effectiveness of additives under equilibrium conditions. In real oil cooling processes, the interfacial state of the system develops dynamically. Under these conditions, not only is the final value of interfacial tension crucial, but also the rate of its reduction, which determines the adsorption efficiency of functionalized molecules at the interface. To evaluate this effect, the kinetic dependences of interfacial tension σ(t) were studied for the original oil and samples with the most pronounced depressant activity at a dosage of 500 g/t. The corresponding results are shown in Figure 3.

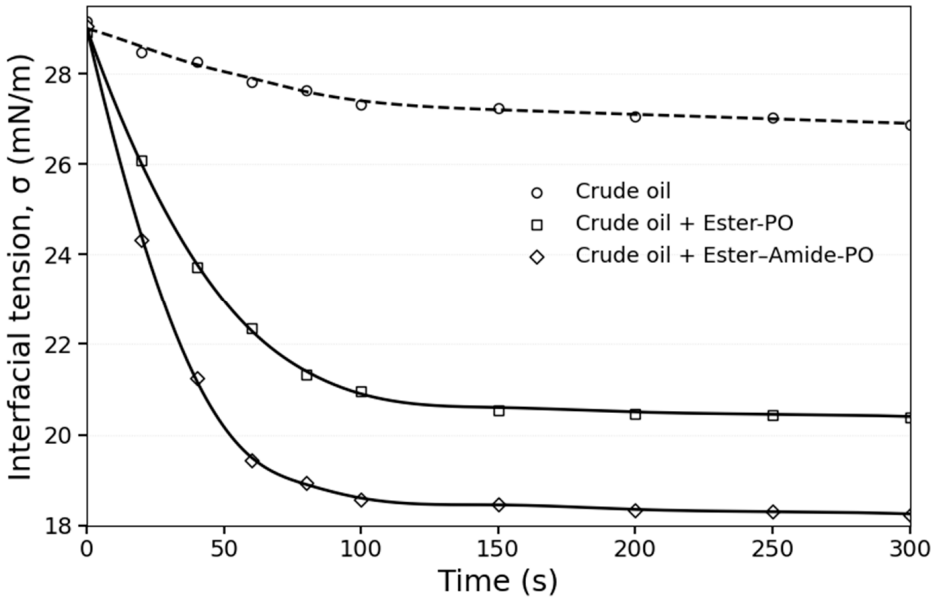


Figure 3. Dynamics of interfacial tension of Kumkol oil over time in the absence and presence of functionalized polyolefin additives (500 g/t).

Without additives, the decrease in σ is slow: at the first moment, the interfacial tension value is ~29 mN/m and decreases to ~27.5 mN/m within the first 100 s, after which further change is insignificant and by 300 s reaches only ~26.8–27.0 mN/m. This fact indicates a low rate of adsorption of the natural surface-active components of the oil. In the presence of the ester-functionalized polyolefin, in contrast, kinetics are significantly faster than before. Already within the first 50–60 s, σ's value decreases from ~29 to ~22–23 mN/m, and by 100 s it reaches ~21 mN/m, then reaches a plateau of about 20.4–20.6 mN/m. This fact indicates the formation of an adsorption layer limited by diffusion and subsequent reorganization of molecules at the interface [25]. The most pronounced effect is observed for the combined ester–amide PPD. In this case, a sharp reduction in interfacial tension occurs within the first 40–50 s: σ decreases to ~19–20 mN/m, and by 80–100 s, it reaches a steady-

state value of approximately 18.3–18.5 mN/m. Rapid relaxation and a low equilibrium σ value indicate high surface activity and the ability of the molecules to form a dense and stable interfacial layer.

Overall, the results presented in Figure 3 show that the effectiveness of the considered PPDs is determined not only by the equilibrium reduction in interfacial tension but also by the speed at which the mentioned equilibrium is established. The combined ester–amide structure is the most effective and provides both rapid formation of the interfacial layer and its high stability.

Cooling curves of oil in the absence of additives and in the presence of functionalized polyolefin PPDs at a dosage of 500 g/t are presented in Figure 4.

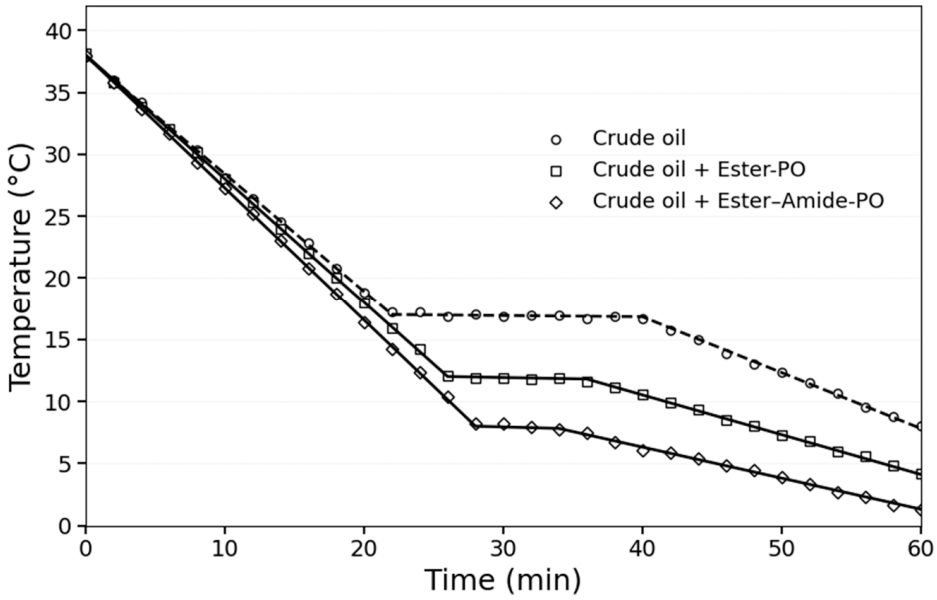


Figure 4. Cooling curves of Kumkol oil in the absence and presence of functionalized polyolefin PPDs (500 g/t).

Original crude oil demonstrates a defined isothermal region that is observed in the diapason of ~16.8–17.2 °C, persisting for ~22–40 min. The virtually horizontal nature of this region indicates an intense and synchronous release of latent heat of crystallization, which corresponds to the rapid formation of a bound spatial structure of paraffin crystals within the system [26]. The introduction of the ester-functionalized polyolefin leads to a qualitative change in the shape of the curve. The plateau shifts to the range of ~11–12 °C and becomes sloping, while its duration decreases to ~8–10 min. The sloping nature of the region indicates a prolonged crystallization process and a decrease in the rate of heat release, which indicates a disruption in the synchronicity of crystal growth and a decrease in the degree of their aggregation. For the system with a combined ester–amide additive, the isothermal region virtually disappears. At ~7–8 °C, just a slight inflection point is observed on the curve, without the formation of a plateau, and the temperature decreases continuously over the whole observation time. The absence of a pronounced thermal plateau indicates that the crystallization process is dispersed, without the formation of a large-scale structure capable of accumulating and releasing latent heat in the form of an isothermal region. The onset temperatures extracted from the cooling curves were 17.0 ± 0.2 °C (blank), 13.5 ± 0.3 °C (MA-g-PO-amide), 11.5 ± 0.3 °C (MA-g-PO-ester), and 7.5 ± 0.4 °C (MA-g-PO-EA), confirming the progressive suppression of paraffin crystallization with increasing functional group complexity. The difference between the crystallization onset temperature and the pour point remains relatively narrow across all systems

(0–1.5 °C), suggesting that in all cases, crystal network formation proceeds rapidly once nucleation begins. The primary effect of the additives is therefore the depression of the onset temperature itself rather than a broadening of the crystallization window.

Analysis of the cooling curves (Figure 4) shows that functionalized polyolefin additives significantly alter the crystallization pattern of the paraffin phase. However, to quantitatively evaluate their effectiveness, it is necessary to determine the pour point of the oil, which is an integral parameter. The pour point reflects the moment of formation of a continuous crystalline structure, leading to a loss of system flowability, and is a key indicator of the depressant activity of additives. Unlike cooling curves, which characterize the dynamics of a phase transition, this parameter allows for a direct comparison of the effectiveness of different types of functionalization. For this purpose, the pour points of an oil sample were determined in the absence of additives and in the presence of functionalized polyolefin additives at a dosage of 500 g/t. The corresponding results are presented in Figure 5.

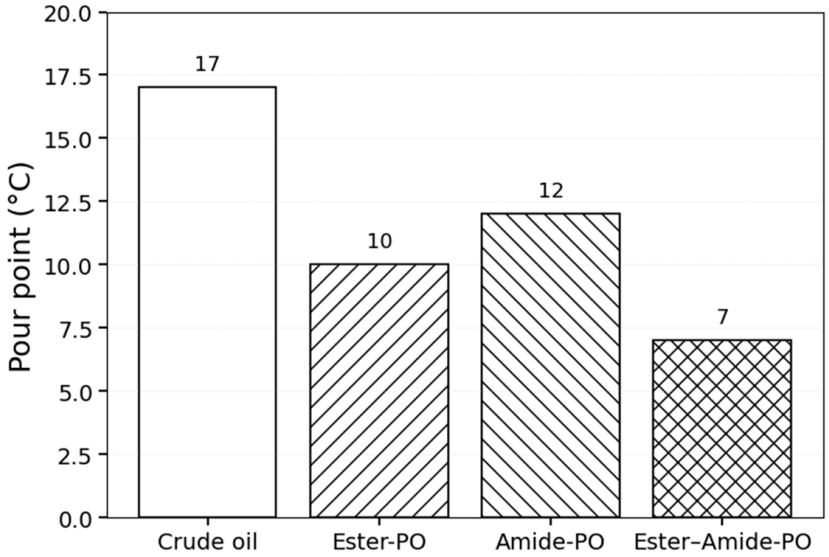
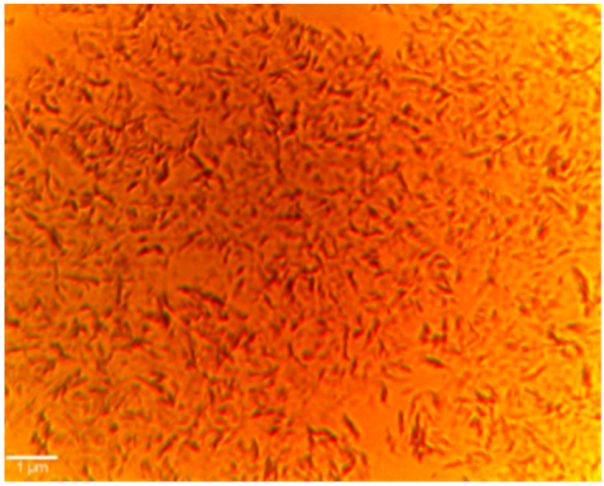


Figure 5. Pour point of oil from the Kumkol field in the absence and presence of functionalized polyolefin additives (500 g/t).

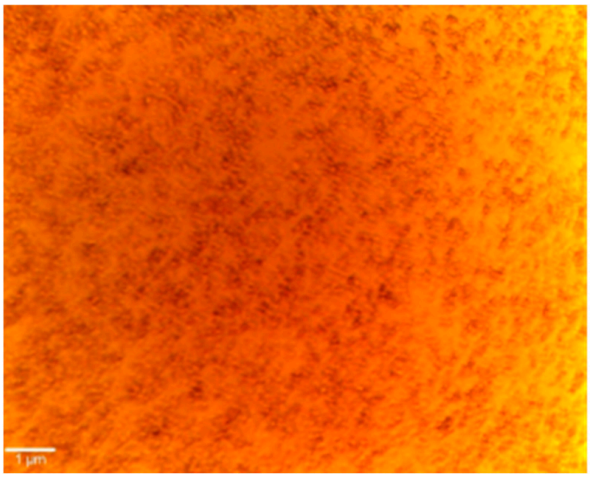
Without any additives, the pour point is +17 °C, which corresponds to the formation of a crystalline structure of the paraffin phase, and is confirmed by the presence of a pronounced plateau on the cooling curves (Figure 5). The introduction of the ester-functionalized polyolefin decreases the pour point to ~+10 °C ($\Delta T \approx -7$ °C). When using the amide-functionalized polyolefin, the pour point is ~+12 °C ($\Delta T \approx -5$ °C). In both cases, the decrease in the pour point is accompanied by a decrease in the intensity and duration of the crystallization plateau. The most significant decrease in the pour point is observed for the combined ester-amide additive: this value decreases to ~+7 °C ($\Delta T \approx -10$ °C). This result is consistent with the absence of a pronounced plateau on the cooling curves and indicates the suppression of the formation of a continuous crystalline network of paraffin crystals.

3.3. Microstructure and Mechanism of Action

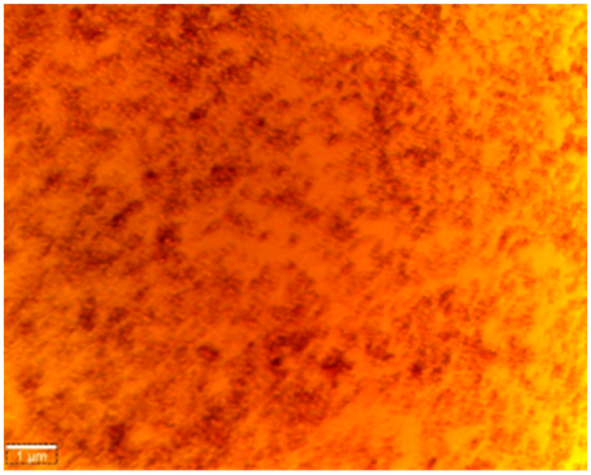
Figure 6 shows micrographs of the paraffin phase of an oil sample in the absence of additives and in the presence of functionalized polyolefin PPDs at a dosage of 500 g/t. The image scale is approximately 1 μm.



(**a**)



(**b**)



(**c**)

Figure 6. Microstructure of the paraffin phase of Kumkol oil: (**a**) without additive; (**b**) with ester-functionalized polyolefin; (**c**) with a combined ester–amide additive (500 g/t).

The initial oil (Figure 6a) is characterized by the formation of a dense structure consisting of elongated needle-like crystals oriented in various directions and overlapping each other. The crystals are approximately 1–3 μm long and form an interconnected network, which is consistent with the presence of a pronounced plateau in the cooling curves and a

high value of pour point. In the presence of the ester-functionalized polyolefin (Figure 6b), the morphology changed. In this case, the crystals become more dispersed, their characteristic size decreases to ~0.5–1 μm, and the degree of overlap decreases. For the combined ester–amide additive system (Figure 6c), the structure has a different character. Small, predominantly isotropic aggregates with a characteristic size of less than 0.5 μm, uniformly distributed throughout the volume, are observed. There are no signs of the formation of a continuous crystalline network, which indicates the suppression of the aggregation of paraffin crystals and is consistent with the absence of a pronounced plateau on the cooling curves and the minimum values of the pour point.

3.4. Discussion of Physicochemical Mechanism

The obtained results demonstrate that altering the chemical structure of the polyolefin polymer (EPR) by grafting maleic anhydride (MAH, $–C_2H_2(CO)_2O–$ fragment) and subsequent modification leads to changes in the interfacial and phase characteristics of the oil. The key role is played by the transformation of anhydride groups into ester (–COOR) and amide (–CONHR) fragments, which determine the balance of polarity and solubility of the macromolecule.

For the starting oil sample, the interfacial tension at 20 °C is $\sigma \approx 29$ mN/m, decreasing to ~24 mN/m at 40 °C. Adsorption kinetics are relatively slow, and after 300 s, the σ value decreases just to ~27 mN/m. This indicates a low concentration of natural surfactant components and high interfacial energy of the system. Under the mentioned conditions, crystallization of n-alkanes (C_nH_{2n+2}, $n \approx 18–30$) took place via a collective growth mechanism, accompanied by the formation of crystals ~1–3 μm long and a pronounced plateau at ~17 °C in the cooling curves. Accordingly, the pour point is +17 °C, and the kinematic viscosity at 0 °C exceeds 30 mm^2/s.

The introduction of an ester-functionalized polyolefin lowers σ to 21.8 mN/m at 20 °C and 19.6–19.8 mN/m at 40 °C, with a corresponding equilibrium value for σ being about 20.5 mN/m. The kinetics of adsorption is enhanced, and its characteristic time of relaxation equals about 70–100 s. Ester carbonyl groups are oriented towards the nascent crystal surface, while their non-polar chain remains dissolved in oil. This reduces the crystals' growth rate and their characteristic size to 0.5–1 μm, shifts the plateau on cooling curves to 11–12 °C with a shortening to 8–10 min, and decreases the pour point down to +10 °C ($\Delta T \approx -7$ °C). Viscosity of the oil at 0 °C drops to 18–20 mm^2/s. σ-values of amide-functionalized polyolefin (23.5 mN/m at 20 °C, $\sigma_{eq} \approx 21.5$ mN/m) were higher and had less pronounced kinetics ($\tau > 100$ s). While the polar –CONH– group provides a donor–acceptor interaction, it is ineffective in non-polar solvents, probably due to partial macromolecule association and lower mobility. As a result, the pour point decreases to only ~+12 °C ($\Delta T \approx -5$ °C), and the crystal structure remains partially bound.

The better effect in pour point depression is obtained for the combined system, which contains both ester and amide fragments. In this case, σ at 20 °C decreases to ~18.9 mN/m, and the equilibrium value reaches ~18.3 mN/m. Adsorption kinetics accelerate significantly: the characteristic time is $\tau \approx 30–50$ s, which indicates rapid formation of the interfacial layer. The ester groups ensure the solubility and diffusion of the macromolecule, while the amide groups enhance adsorption on the crystal surface due to local polar interactions. The superior performances of the combined ester–amide derivative are explained by a molecular synergy between the two functional groups. The ester groups, bearing a carbonyl flanked by an alkoxy substituent, exhibit moderate polarity and good solubility in the hydrocarbon medium, ensuring effective diffusion of the macromolecule towards the surfaces of the nascent paraffin crystals—as evidenced by the rapid adsorption kinetics ($\tau \approx 30–50$ s) observed for MA-g-PO-EA. The amide groups, for their part, have a

greater donor/acceptor capacity for hydrogen bonds thanks to the N-H group, which facilitates specific polar interactions with the ordered crystal lattice of the paraffin and anchors the macromolecule to the crystal surface. When they are present simultaneously on the same skeleton, the ester groups control the transport step while the amide groups control the adsorption step, resulting in a bifunctional mechanism that neither group can carry out alone. This cooperative action is reflected in the lowest equilibrium interfacial tension ($\sigma \approx 18.3$ mN/m), the most pronounced depression of the crystallization start temperature ($\Delta T = 9.5$ °C. relative to the white), and the complete suppression of the crystallization plateau. The cooling curves do not exhibit a pronounced plateau; only a slight inflection is observed at ~7–8 °C. The pour point decreases to ~+7 °C ($\Delta T \approx -10$ °C), and the viscosity at 0 °C decreases to ~14–16 mm^2/s.

4. Conclusions

This study shows that the controlled functionalization of an ethylene–propylene maleated copolymer by combined ester, amide and ester–amide polar groups makes it possible to obtain PPDs with different performances on Kumkol waxy crude oil. The ester derivative reduces the pour point by 7 °C, the amide derivative by 5 °C and the combined ester–amide additive by 10 °C. The latter also reduces the kinematic viscosity at 0 °C by more than half. The interfacial tension measurements and the adsorption kinetics revealed the mechanistic origin of this hierarchy: the ester groups determine the macromolecular solubility and the diffusion mobility, while the amide groups improve the adsorption affinity on the surface of the paraffin crystals. Acting together, these two functionalities modify the crystallization mechanism, passing from a collective lattice formation to a dispersed regime, as confirmed directly by polarized light microscopy and the analysis of the cooling curves.

These results establish a structure–activity relationship between the architecture of the polar groups and the effectiveness of the depressant agent and provide a rational basis for the future development of polyolefin-based PPDs. In particular, the systematic variation in the ester/amide ratio, the length of the alkyl chain and the molecular weight of the polymer represents a promising route for obtaining additives having an optimized solubility-adsorption balance. The modular functionalization strategy presented here is also applicable to other crude oils with a high wax content.

The combined ester–amide derivative represents a promising candidate for industrial evaluation as a pipeline PPD for waxy crude oils produced in cold climates. Future work will focus on systematic variation in the ester/amide ratio, alkyl chain length, and polymer molecular weight to further optimize the solubility–adsorption balance, as well as on field-scale testing under realistic pipeline conditions.

Author Contributions: Conceptualization, K.N.; methodology, Z.N. and A.B.; formal analysis, Z.N. and G.B.; investigation, A.B., Z.N., G.B. and B.S.; resources, K.N.; data curation, K.N. and Z.N.; writing—original draft preparation, Z.N., A.B. and B.S.; writing—review and editing, K.N. and G.B.; visualization, Z.N. and B.S.; funding acquisition, K.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant no. BR24992809).

Data Availability Statement: The data supporting the results can be made available from the corresponding author upon request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Elkatory, M.R.; Soliman, E.A.; El Nemr, A.; Hassaan, M.A.; Ragab, S.; El-Nemr, M.A.; Pantaleo, A. Mitigation and remediation technologies of waxy crude oils' deposition within transportation pipelines: A review. *Polymers* **2022**, *14*, 3231. [CrossRef]
2. Ansari, F.; Shinde, S.B.; Paso, K.G.; Sjöblom, J.; Kumar, L. Chemical additives as flow improvers for waxy crude oil and model oil: A critical review analyzing structure–efficacy relationships. *Energy Fuels* **2022**, *36*, 3372–3393. [CrossRef]
3. Liu, Y.; Sun, Z.N.; Ji, S.Z.; Yang, Y.H.; Xu, J.Q.; Jing, G.L. Effect of nanocomposite pour point depressant EVAL/CNT on flow properties of waxy crude oil. *Pet. Sci.* **2023**, *20*, 3807–3818. [CrossRef]
4. Quan, Q.; Ran, W.; Yang, L.; Gao, G.; Wang, S.; Gong, J. The effect of pressure on wax deposition from wax-solvent mixtures with natural gas. *J. Pet. Sci. Eng.* **2018**, *171*, 1318–1325. [CrossRef]
5. Coto, B.; Martos, C.; Espada, J.J.; Robustillo, M.D.; Peña, J.L. Analysis of paraffin precipitation from petroleum mixtures by means of DSC: Iterative procedure considering solid–liquid equilibrium equations. *Fuel* **2010**, *89*, 1087–1094. [CrossRef]
6. Boranbayeva, L.; Boiko, G.; Sharifullin, A.; Lubchenko, N.; Sarmurzina, R.; Kozhamzharova, A.; Mombekov, S. Analysis of the processes of paraffin deposition of oil from the Kumkol group of fields in Kazakhstan. *Processes* **2024**, *12*, 1052. [CrossRef]
7. Li, B.; Guo, Z.; Du, M.; Han, D.; Han, J.; Zheng, L.; Yang, C. Research status and outlook of mechanism, characterization, performance evaluation, and type of pour point depressants in waxy crude oil: A review. *Energy Fuels* **2024**, *38*, 7480–7509. [CrossRef]
8. Nadirov, K.; Zhantasov, M.; Ketegenov, T.; Nadirova, Z.; Batkal, A.; Kamunur, K.; Bimbetova, G.; Nadirov, R. Novel pour point depressants for crude oil derived from polyethylene solution in hexane and coal fly ash. *Fluids* **2024**, *9*, 121. [CrossRef]
9. Nadirova, Z.; Begimova, A.; Nadirov, K.; Zhantasov, M.; Bimbetova, G.; Botashev, Y.; Sadyrbayeva, A. Development of composite depressant additives based on poly (maleic anhydride-ethanolamine) and butyl linoleate for waxy crude oils. *J. Dispers. Sci. Technol.* **2025**, 1–10. [CrossRef]
10. Shi, E.; Li, J.; Yang, M.; Ma, S.; Han, J.; Li, B.; Yang, C.; Luo, H.; Liu, W. Research status and challenges of mechanism, characterization, performance evaluation, and type of nano-pour point depressants in waxy crude oil. *ACS Omega* **2024**, *9*, 35256–35274. [CrossRef] [PubMed]
11. Mun, G.A.; Bekbassov, T.; Beksultanov, Z.; Yermukhambetova, B.B.; Azhgaliyev, B.; Azhgaliyev, N.; Dergunov, S.A. Modified graft copolymers based on ethylene vinyl acetate as depressants for waxy crude oil and their effect on the rheological properties of oil. *J. Pet. Sci. Eng.* **2022**, *213*, 110298. [CrossRef]
12. Zou, Y.; Zheng, H.; Luo, X.; Tang, J. Study on the influence of polar groups in pour point depressant on flow properties of Karamay crude oil. *J. Dispers. Sci. Technol.* **2024**, *45*, 851–858. [CrossRef]
13. Kuzmin, K.A.; Kosolapova, S.M.; Rudko, V.A. Investigating the mechanism of action of polymer pour point depressants on cold flow properties of biodiesel fuels. *Colloids Surf. A Physicochem. Eng. Asp.* **2024**, *702*, 134971. [CrossRef]
14. Kurniawan, M.; Norrman, J.; Paso, K. Pour point depressant efficacy as a function of paraffin chain-length. *J. Pet. Sci. Eng.* **2022**, *212*, 110250. [CrossRef]
15. Martins, M.F.; de Sousa, I.V.J.B.; da Silva, V.A.M.C.; Severo, P.V.R.; Alves, B.F.; Nunes, R.d.C.P.; Alvares, D.R.S.; Lucas, E.F. Modifying Commercial Poly (ethylene-vinyl acetate) to Improve Its Performance as a Pour Point Depressant: A Study in Waxy Model Oils at Different Concentrations. *ACS Omega* **2025**, *10*, 42392–42402. [CrossRef] [PubMed]
16. Quan, Q.; Jin, W.; Sun, N.; Wang, Y.; Wang, S. Effect of ethylene vinyl acetate on pour point and wax deposition characteristics of high-pour-point and viscous waxy crude oil. *Fuel* **2025**, *395*, 135269. [CrossRef]
17. Machado, A.L.; Lucas, E.F.; González, G. Poly (ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: Oil viscosity, pour point and phase behavior of organic solutions. *J. Pet. Sci. Eng.* **2001**, *32*, 159–165. [CrossRef]
18. Wu, Y.; Ni, G.; Yang, F.; Li, C.; Dong, G. Modified maleic anhydride co-polymers as pour-point depressants and their effects on waxy crude oil rheology. *Energy Fuels* **2012**, *26*, 995–1001.
19. Deshmukh, S.; Bharambe, D.P. Synthesis of polymeric pour point depressants for Nada crude oil (Gujarat, India) and its impact on oil rheology. *Fuel Process. Technol.* **2008**, *89*, 227–233. [CrossRef]
20. Zhubanov, A.A.; Kozhabekov, S.S.; Donenov, B.K.; Sigitov, V.B.; Zhuragat, G. Synthesis of copolymers based on maleic anhydride and α-olefins and modification with primary amines as pour point depressant (PPD) for waxy crude oils. *Pet. Sci. Technol.* **2023**, *41*, 2017–2035.
21. Marenov, B.T.; Nadirov, K.S.; Zhantasov, M.K.; Nadirov, R.K. Ethylene-Vinyl Acetate Copolymer/Crude Gossypol Compositions as Pour Point Depressants for Waxy Oil. *Int. J. Chem. Eng.* **2020**, *2020*, 4195382. [CrossRef]
22. Ilyin, S.O.; Arinina, M.P.; Polyakova, M.Y.; Kulichikhin, V.G.; Malkin, A.Y. Rheological comparison of light and heavy crude oils. *Fuel* **2016**, *186*, 157–167. [CrossRef]
23. Hassan, M.E.; Nielsen, R.F.; Calhoun, J.C. Effect of pressure and temperature on oil-water interfacial tensions for a series of hydrocarbons. *J. Pet. Technol.* **1953**, *5*, 299–306. [CrossRef]
24. Yao, B.; Li, C.; Yang, F.; Sun, G.; Xia, X.; Ashmawy, A.M.; Zeng, H. Advances in and perspectives on strategies for improving the flowability of waxy oils. *Energy Fuels* **2022**, *36*, 7987–8025. [CrossRef]

25. Miller, R.; Aksenenko, E.V.; Fainerman, V.B. Dynamic interfacial tension of surfactant solutions. *Adv. Colloid Interface Sci.* **2017**, *247*, 115–129. [CrossRef]
26. Schou Pedersen, K.; Skovborg, P.; Roenningsen, H.P. Wax precipitation from North Sea crude oils. 4. Thermodynamic modeling. *Energy Fuels* **1991**, *5*, 924–932. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.