Petroleum and Coal

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Synthesis and Performance of Some Homopolymer and Copolymers as Paraffin Crystallizations Modifiers in Egyptian Waxy Crude Oil

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Received April 8, 2024; Accepted July 19, 2024

Abstract

Numerous tactics have been employed to reduce the issues costing the petroleum sector billions of dollars annually. This paper describes performance based design, synthesis characterizide and evaluation of comb shaped homo and copolymeric additives. The alkylacrylate 1822C were prepared by esterification of acrylic acid with Nafol1822C (C_{av}=22), the synthesized homompolymer and copolymerized with styrene/vinyl acetate in different molar ratios. All the prepared monomer, homopolymer and copolymers were characterized by using infra-red (FTIR), and Gel permeation chromatography (GPC). The performance of the synthesized modified homopolymer and copolymers as pour point depressors and viscosity index improvers for the Egyptian waxy crude oil. The prepared additives were evaluated as pour point depressants and it was found that the pour point decreases with increasing the concentration of the additives used. The Nafol acrylate 1822C - vinyl acetate copolymers of (PPD6 to PPD9) showed better results than homopolymer Nafol 1822C acrylate (PPD1) and the copolymers of Nafol 1822C- styrene (PPD2-PPD9). Nafol 1822C acrylate - vinyl acetate copolymers PPD7 exhibited the best performance at optimum dosage of 1000ppm as it depresses the pour point by 21ºC from the blank.

Keywords: *Homopolymer; Copolymers; Additives; Crude oil; Pour point depressant; Viscosity index; Photo micrography.*

1. Introduction

Waxy crude oils are produced in many countries worldwide. The waxes present in these oils pose significant challenges to the processing industry. The chemical composition, temperature, pressure, and past thermal history of the oil all have a strong influence on the flow characteristics of waxy oils. High wax content oils have high viscosities and pour points [1]. If the waxy oils are allowed to cool, wax will crystallize, agglomerate and entrap the oil into its structure. This phenomenon often happens if the ambient temperature is below the pour point of the waxy oils [2]. Wax is the high molecular weight paraffin fraction of crude oil that can be separated with reduction in oil temperature below pour point of oil. Millions of dollars are invested to diminish the output problems with paraffinic wax deposition in production, storage, and transportation [3].

The pour point is the lowest temperature at which oil can flow while being pulled by gravity. The pour point is the name given to gravity in order to avoid these operational issues. Polymeric additives, also known as pour point depressants or flow improvers, can be used to stop wax precipitation and the ensuing disruption of the oil flow, which can cause operational issues [4]. Consequently, various crude oil flow enhancers have been employed to enhance the flowability of heavy oil [5]. Some of the usual techniques include heating and dilution with lighter crudes or alcohols; however, the use of alcohols is quite expensive and depends on the feedstock of the lighter crudes. As long as these additives increase the flowability of crude oil, they can generally be categorized as crude oil flow improvers. The molar mass and structure of polymeric additives are two factors that affect their performance. The additive may co-crystallize

with the wax in a waxy system, changing the crystals' surface shape and slowing or even stopping their agglomeration [6]. Preventive measures for these issues include the use of pour-point depressants (PPDs), flow improvers, and wax inhibitors to increase fluid viscosity and alter crystal formation [7-8]. The mechanisms of pour point depressants (PPDs) are now being explained by ideas including adsorption, co-crystallization, nucleation, and increased wax solubility [9-10].

A preventive and economic strategy using chemical additives [11]. Represents one of the most viable solutions to this problem that can prevent wax deposition in pipelines and down hole by serving as wax crystals modifiers and PPDs. To suppress Wax appearance temperature WAT, pretreatment with a small dose of wax dispersants or PPDs should be used . Industrial PPDs may be produced by adding and varying the polar and nonpolar group ratios that enhance the cold flow properties [12]. The nonpolar carbon chains have a high chemical affinity for the paraffin molecule while the polar groups can suppress the growth of paraffin crystals.

Comb-type polymers are generally effective at improving flow. Their primary backbone is joined to lengthy pending alkyl chains that make up their macromolecule architectures. The polymers also exhibit a characteristic that lies in between linear and branching structures [13-14]. Typically, unsaturated dicarboxylic acid esters such as fumaric, maleic, acrylic, and methacrylic acids are copolymerized with other comonomers to create comb-structured polymers. Amphiphilic structures function with paraffins and asphaltenes, having components that are both polar (carboxylic groups) and nonpolar (long alkyl groups) [15]. The most effective additives for reducing the pour point of crude oils are thought to be comb-shaped polymers having side chains made up of more than 18 carbons [16–18].

In the present context, we have prepared Nafol 1822C acrylate, homopolymer of Nafol 1822C acrylate and its copolymers with styrene and vinyl acetate separately at different percentage compositions. Also, the synthesized modified performance homopolymer and copolymers as pour point depressant at different dosages of was (250-2000ppm) and as viscosity index improvers on the Egyptian waxy crude oil were evaluated. Additionally, the influence of their addition on the morphology of wax crystals modification was examined by photomicrographic analysis.

2. Experimental

2.1. Materials

Acrylic acid (AA), styrene (ST), vinyl acetate (VA), p-toluene sulphonic acid as a catalyst, hydroquinone as an inhibitor and xylene were obtained as analytical reagents from Aldrich chemical, and used as received. The initiator benzoyl peroxide (BPO) was re-crystallized from methanol. A linear long-chain alcohol blend and (NAFOL 1822 C) were supplied from CONDEA chemical company with the typical analysis listed in Table 1. Egyptian waxy crude oil (CO) was submitted from Qarun Petroleum Company. The physicochemical properties are listed in Table 2. The n-paraffin distribution of the isolated waxes was determined by gas chromatography analysis according to ASTM D 2887 standards.

Table 1. Typical analysis of linear long chain alcohol blends (Nafol 1822C).

Alcohol composition (wt.%)	C_{16-OH}	0.1
	C_{18-OH}	5.0
	C_{20-OH}	16.5
	C_{22-OH}	77.6
	C_{24-OH}	0.8
Average carbon number (calculated)	C_{av} = 21.5~22	
Density (g/cm^3) approx.	at 80°C = 0.802	
Solidification point (oC) approx.	64	
Flash point (oC) approx.	204	
Ester No. (mg KOH/g)	0.14	
Acid No. (mg KOH/g)	0.05	
Iodine No. (mgI/100 mg)	0.31	
Water (Wt.%)	0.04	

Table 2. Physical characteristics of waxy crude oil.

Properties	Method	Crude oil
Density at 20°C (g/cm^3)	ASTMD 1298	0.8557
Kinematics viscosity (cSt)	ASTMD 445	
at 40°C		12.330
at 100 °C		2.710
Pour point (pp), °C	ASTMD 97	21
Sulfur content (wt%)	ASTMD 4294	0.21
n-paraffin (wt%)	ASTMD 2887 (GLC)	89.05
Iso-paraffins (wt%)	ASTMD 2887 (GLC)	7.70
Total paraffins content (wt%)	ASTMD 2887 (GLC)	96.75
Average carbon number (n)	IP 372 / 85 (GLC)	21.75
Asphaltene content,wt.%	IP 143/84	00.728
Wax content,wt%	UOP 46/64	10.920

2.2. Preparation of additives

2.2.1. Esterification of acrylic acid with Nafol 1822C

Nafol 1822C acrylates were synthesized by using the esterification process, which involved reacting one mole of Nafol 1822C with one mole of acrylic acid. Using the Dean-Stark apparatus, the reaction was carried out in the presence of 1% p-toluene sulfonic acid as a catalyst, 0.6% hydroquinone as an inhibitor, and xylene (an azeotropic solvent) as a solvent. Nafol 1822C acrylate (NA) was either a pale yellow or a milky white final product. Scheme 1 depicted the 1822C acrylate synthesis procedure. Esterification reactions occurred under a slow stream of nitrogen, and the refluxing was continued at 130°C for 6 h with continuous stirring [19]. The obtained ester was purified, refluxed for 4 h, filtered off repeatedly to ensure the complete removal of unreacted acid then the produced ester was left on $CaCl_2$ overnight for drying.

2.2.2. Preparation of homopolymer and copolymers

The polymers (homo and copolymers) were synthesized by free radical polymerization (scheme1) at different percentage composition of monomers illustrated in Table 3 in presence of (BPO) as initiator (0.5% w/w, with respect to the total monomer). The entire reaction process was conducted under inert static nitrogen gas condition. At the beginning, as the temperature of increased to 110°C, 5% benzoyl peroxide in xylene solvent as an initiator was added to the a forementioned reaction for 1 h. The whole reactants were refluxed for 8 h, with constant stirring. For purification, the copolymer precipitated from the solvent by excess methanol and filtration. Final products were obtained after a vacuum drying for 12 h. The process of polymerization and purification of polymer [20] illustrated in Scheme 1

2.3. Characterizing the artificially produced copolymeric and homopolymeric additions

2.3.1. Fourier transform infrared (FTIR) spectroscopy

The purified esters, produced homopolymer, and copolymer have all been identified using the infrared spectra acquired with an FTIR spectrometer of the type Mattson-Infinity Series Bench top 961.

2.3.2. Gel permeation chromatography (GPC)

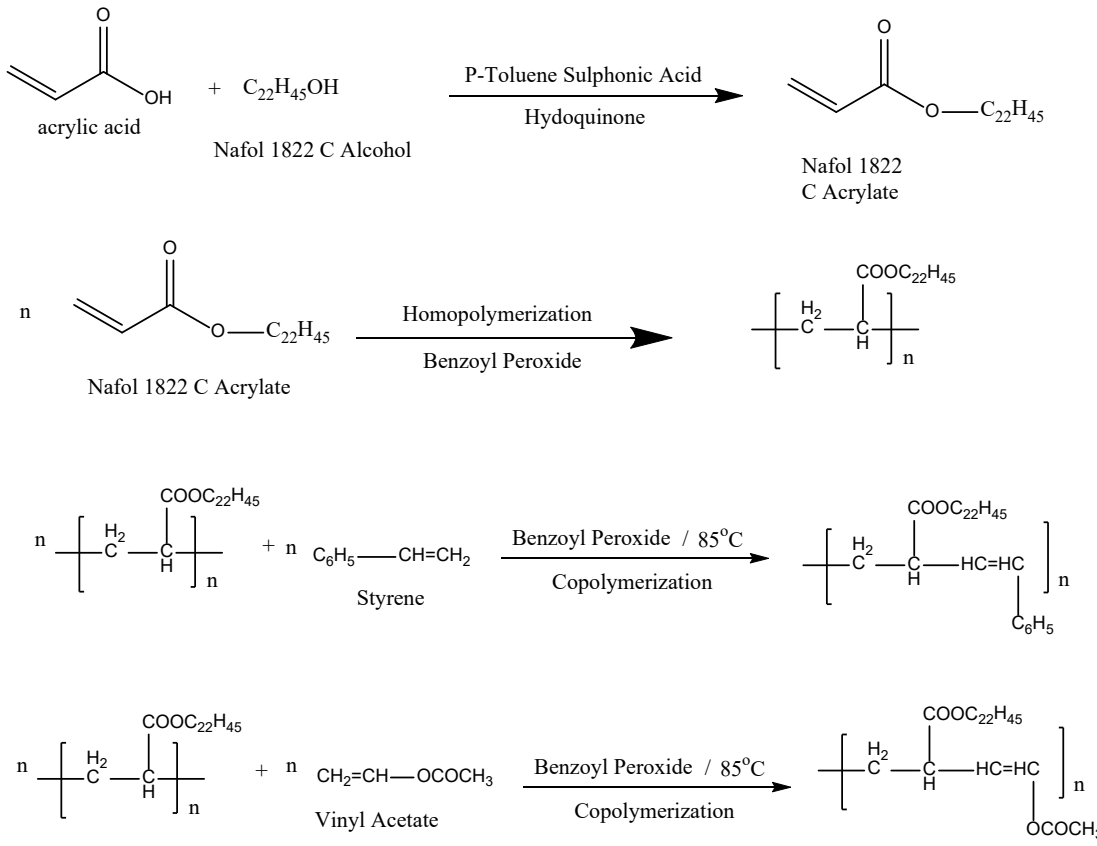
The synthesized homopolymer and copolymer's weight average molecular weight (Mw) and polydispersity index (PDI) were measured using Gel permeation chromatography (GPC) at

40°C with a model water (Model 510), a polystyrene standard, an Ultra-styragel column, and tetrahydrofuran as an eluent illustrated in Table 3.

Table 3. Percentage composition M_w and PDI of additives (PPD1-PPD9)

Additive designations	NA	ST%	VA%	Mw	PDI
PPD1	100	-	-	45682	2.1123
PPD2	95	5	-	59682	2.2266
PPD3	90	10	-	78666	2.7132
PPD4	85	15	-	85516	2.8913
PPD5	80	20	-	95911	2.8531
PPD6	95	-	5	49013	3.1525
PPD7	90	-	10	36512	1.5310
PPD8	85	-	15	67330	1.3400
PPD9	80	-	20	86315	1.2100

NA = Nafol 1822C acrylate; ST = styrene; VA = vinyl acetate; M_w = average molecular weight ; PDI = poly dispersity index



Scheme 1. Synthesis of Nafol 1822C acrylate, Nafol 1822C acrylate homopolymer and Nafol 1822C acrylate – styrene/ vinyl acetate copolymers.

2.4. Performance evaluation of the synthesized homopolymer and copolymers

2.4.1. As pour point depressants (PPDs) in waxy crude oil

The efficacy of the synthesized compounds as pour point depressants for crude oil was assessed using varying doses of the homopolymer and copolymer (250, 500, 750, 1000, and 2000 ppm). The samples of waxy crude oil were injected at a temperature of 60°C. Next, the pour point (PP) of the treated and untreated crude oil samples was determined by evaluating them in accordance with ASTM D97.

2.4.2. Evaluation of the synthesized homopolymer and copolymers as viscosity index improvers for waxy crude oil

The synthesized copolymers were evaluated as viscosity index improvers using free additive crude oil through the viscosity index test (VI) according to the ASTM D- 2270 -87. The Kinematic viscosity of the oil contains the synthesized compounds was determined at 40°C and 100°C. Different concentrations 250, 500, 750, 1000 and 2000 ppm synthesized additives concentration on (VI).

2.4.5. Photomicrographic analysis

For photomicrographic examination of the wax crystallization characteristics, a ZEISS Axiolab 5 digital laboratory optical polarizing microscope equipped with a Leica MC190 HD microscope camera was utilized. Both untreated samples and samples treated with the modified PPD2 and PPD7 additives at a concentration of 1000 ppm were inspected. A cooling thermostat was connected to the microscope slide in order to control the temperature of the sample being examined. The magnification of the microscope was adjusted at100μm for observation and analysis.

3. Results and discussion

3.1. Crude oil characterization

The physicochemical characteristics of waxy crude oil were analyzed to establish the average molecular weight distribution of wax. The gas chromatography technique according to the IP/372/85 system is used. Data presented in Table 2, indicate that the average distribution of carbon numbers is 21.75 for the collected crude oil and represented its physical characteristics. Also, the obtained data of wax and asphaltene contents reveal that the collected crude oil has a waxy nature.

3.2. Characterization of the synthesized ester, homopolymer and copolymers FTIR spectroscopy

With FTIR spectroscopy, the esterification reaction's conclusion and the effective synthesis of Nafol 1822C acrylate (NA) were clarified. This leads to the following observations: the carboxylic acid characteristic band is absent at around 3200 cm^{-1}; the ester carbonyl group band appears at 1755 cm^{-1} [21]; two bands characteristic for the (C-O-C) group appear at 1136 and 1232 cm^{-1}; the CH2 groups scissoring vibration band appears at 1470 cm^{-1}; and two strong characteristic bands for the alkyl group's CH3- and -CH2- appear at 2922 and 2847 cm^{-1}, respectively. Additionally, the presence of the non-conjugated alkene's double bond (C=C str) is indicated by the strong band detected at 1630 cm^{-1}. The remaining peaks at 1406, 1266, 1161, 975, and 810 cm^{-1} can be explained by the ester group's symmetric C–H bending, the C–O stretching of the ester group, and the C–O–C str. At 718 cm^{-1}, one can discern the usual swing absorption bands of the -CH2- in the long-chain alkyl groups.

The C-H bond bending at 1728 cm-1 is visible in the IR absorption band of the Nafol 1822C acrylate homopolymer. The peaks at 2853 cm-1 and 2924 cm-1 for the CO stretching vibration and at 1465.8, 1404, 1229, 1215, and 1150 cm-1 for the –CH2CH3 group appeared as a result of their presence.

The IR spectrum of copolymers of Nafol 1822 C methacrylates with styrene (PPD2 to PPD5) are similar and exhibited the following results: The absorption band for ester carbonyl group at 1728 cm^{-1} shifted to 1720 cm^{-1} in the copolymer and the peaks at 745cm^{-1} and 700 cm^{-1} were due to the C-H bond of the phenyl group of styrene. For the copolymers of Nafol 1822 C acrylate and vinyl acetate (PPD6 to PPD9) the IR spectrum are similar and showed the following results: Peaks at 1723 cm^{-1} and 1710 cm^{-1} indicate the presence of ester carbonyl groups and the peaks at 2855 cm^{-1} and 2924 cm^{-1} are for the $–CH_2CH_3$ group. The peaks at 1450 cm^{-1}, 1320 cm^{-1}, 1260 cm^{-1} and 1002 cm^{-1} were due to CO stretching vibration and absorption bands at 820 and 708 cm^{-1} were for bending of C-H bond.

3.3. Evaluation of the prepared homopolymer and copolymer

3.3.1. As pour point depressants (PPDs) for waxy crude oil

The synthesized homopolymer and copolymers were tested as PPDs for waxy crude oil at various concentrations (250, 500, 750, 1000 and 2000 ppm) and added at the injection temperature of 60 °C to the collected waxy crude oil samples. The resultant data of the synthesized homopolymer and copolymers additives effect on the PPD of the waxy crude oil samples listed in Table 4 and shows that the increase in their concentrations up to 1000 ppm enhances the pour point depression of the treated crude oil compared with untreated crude oil . The experimental values of pour point are given in Table 4 and Figures 1 and 2.

Table 4. Effect of additives on the pour point of the waxy crude oil.

Additive label	Pour point (°C) of additives doped crude oil (ppm)					
	Nil	250	500	750	1000	2000
PPD1	21	12	12	9	6	6
PPD2	21	18	9	9	3	3
PPD3	21	15	12	9	6	6
PPD4	21	15	12	12	9	9
PPD5	21	21	18	18	15	15
PPD6	21	9	9	6	3	3
PPD7	21	12	9	3	0	0
PPD8	21	12	6	6	3	3
PPD9	21	18	15	15	12	12

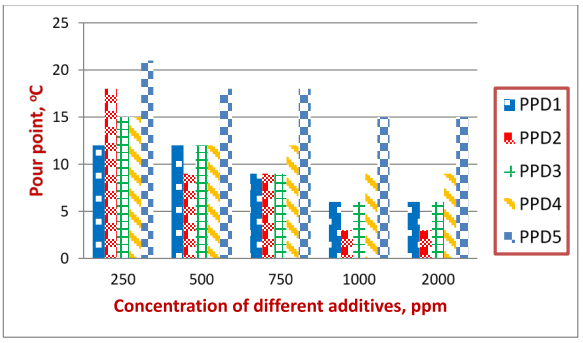


Figure 1. Effect different concentration of copolymer additives PPD1-PPD5 on pour point of crude oil.

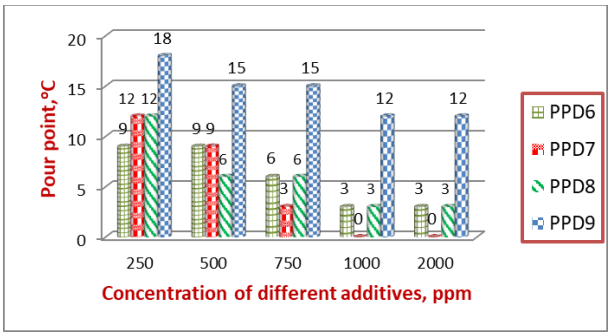


Figure 2. Effect different concentration of copolymer additives PPD6-PPD9 on pour point of crude oil.

The values suggest that all the synthesized homopolymer PPD1, copolymers Nafol 1822Cacrylate- styrene(PPD2 to PPD5) and copolymers Nafol 1822C acrylate vinyl acetate (PPD6 to PPD9) can be used effectively as pour point depressants (PPDs) for waxy crude oil. The copolymers (PPD2 to PPD9) are better than the homopolymer (PPD1) as PPDs for crude oil. But with varying concentration, the pour point values do not linearly co-relate. In case of the copolymers of Nafol 1822C acrylate and styrene (PPD2 to PPD5), PPD2 copolymer with the lowest percentage of styrene (5%) acts as the better PPD than the others(PPD3-PPD5) and using1000ppm of the copolymer PPD2 we get the lowest pour point of 3°C. Increase in the percentage of styrene results in increasing the phenyl content in the additive. Hence it may be the reason behind that PPD3 to PPD5 copolymers with higher percentage of styrene gradually showed higher pour point at 1000ppm PPD5 copolymer with highest percentage of styrene shows highest pour point of 15°C at 1000ppm. But the copolymers of Nafol 1822C acrylate and vinyl acetate copolymers (PPD6 to PPD9) showed better results than the copolymers of Nafol1822C acrylate–styrene(PPD2-PPD5).These copolymers are better PPDs and may be due to absence of phenyl group which reduces the adsorption of the polymer molecule on the wax crystals [22] that happened in case of styrene copolymers. The PPD7 copolymer Nafol 1822C acrylate- vinyl acetate having 10% (w/w) vinyl acetate proved to be the best

PPDs among all the synsesized copolymers. At 1000ppm concentration this copolymer showed lowest pour point of 0°C.

3.3.2. Performance evaluation as viscosity index improver for waxy crude oil

The effect of the homopolymer and copolymer compounds as viscosity index improvers depends mainly on the behavior of polymer molecules in the dispersed phase (crude oil). The synthesized compounds (PPD1-PPD9) were tested for their effectiveness as viscosity index improvers for the crude oil. In this respect, the kinematic viscosity of the undoped oil, and oil containing different concentrations of the tested additives was determined at 40 and 100°C [23]. The viscosity index of the crude oil is given in Table 5 and Figures 3 and 4.

Table 5. Effect of additives on the viscosity index of the waxy crude oil.

Additive label	Viscosity index of additives doped crude oil (ppm)					
	Nil	250	500	750	1000	2000
PPD1	90	90	90	93	94	95
PPD2	90	90	94	96	98	100
PPD3	90	90	90	92	94	94
PPD4	90	90	90	91	92	92
PPD5	90	92	92	94	95	96
PPD6	90	100	105	104	106	107
PPD7	90	105	108	110	112	115
PPD8	90	102	105	106	108	110
PPD9	90	90	91	93	94	95

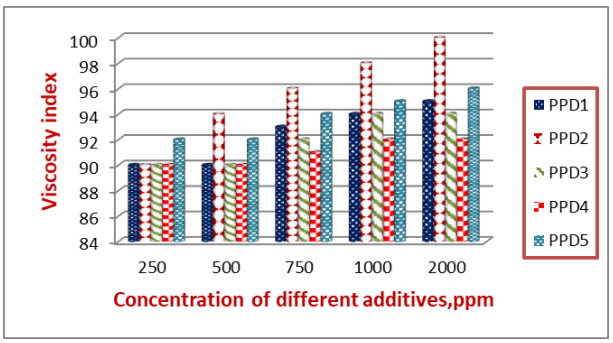


Figure 3. Effect different concentration of copolymer additives PPD1-PPD5 on viscosity index of crude oil.

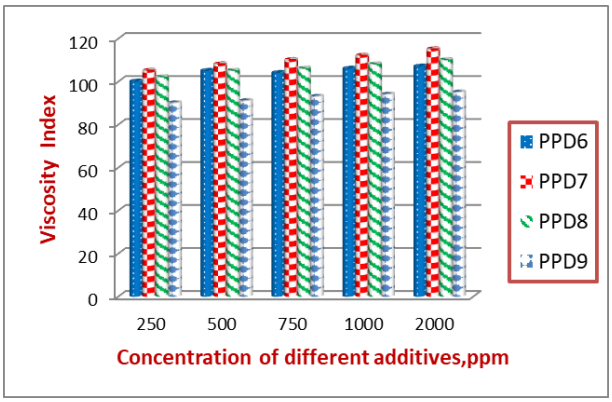


Figure 4. Effect different concentration of copolymer additives PPD6-PPD9 on viscosity index of crude oil.

3.3.2.1. Effect of additive concentration on viscosity index of crude oil

The effect of the additive concentration on VI was investigated using a range of concentrations of the synthesized additives, including 250, 500, 750, 1000, and 2000 ppm. The data are tabulated in Table 5 and Figures 3 and 4, showing that the VI increases as the concentration of the synthesized additives in solution increases.

The viscosity of a particular fluid is not constant, however, but varies with temperature. As oil is heated, its viscosity decreases, and becomes thinner. The polymer– oil interaction at low temperature is minimal but increases as the temperature rises. This interaction of the polymer with the base oil at elevated temperatures increases the effective hydrodynamic volume of the polymer, thereby increasing the effective volume fraction of the viscosity modifier. This, in turn, leads to an increase in crude viscosity [24]. The increase in the concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution. Consequently, a high concentration of polymer will impart a higher viscosity index than a low concentration of the same polymer.

3.3.2.2. Effect of molecular weight of the synthesized additives on viscosity index of crude oil

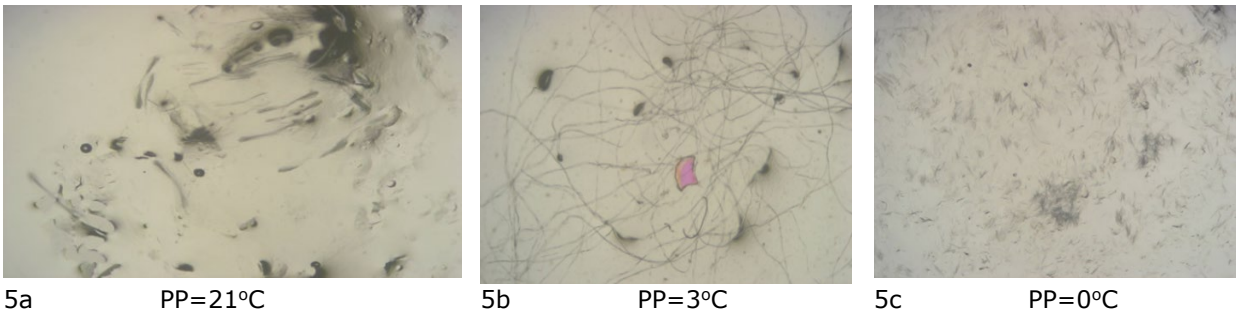
The effect of molecular weight on the efficiency of the synthesized additives as viscosity index improvers for crude oil is indicated at Table 3, 5 and Figures 3 and 4 , which indicates that the efficiency increasing with decreasing the molecular weight with copolymer Nafol 1822 C -Vinyl acetate (PPD7). This may be due to lower molecular weight and the influence of the molecular weight on the effective coil radius and hence the viscosity index.

3.3.2.3. Influence of the molar ratios of the various investigated copolymers on their effectiveness in terms of viscosity index improvers

The effectiveness of the viscosity index improvers is related to molar ratio of copolymers Nafol 1822C acrylate and styrene / molar ratio of copolymers Nafol 1822C acrylate and vinyl acetate. The effectiveness of copolymers increases in copolymer 1822C acrylate-styrene in the order PPD2> PPD3> PPD4> PPD5, but in copolymer 1822C acrylate-vinyl acetate in the order PPD7> PPD6= PPD8> PPD9. The effectiveness of the viscosity index improvers is related to the molar ratio of Nafol 1822C acrylate-styrene /Nafol 1822C acrylate - vinyl acetate. Due to its moderate polarity and molar ratio, it was discovered that the copolymer PPD7 (NA:VA) (90: 10) has a stronger effect as viscosity index improvers. The present study's outcome is in agreement with previous research findings [25], indicating that a somewhat polar structure is required in the viscosity index improver to enhance its interaction with precipitated paraffin, as opposed to a non-polar or highly polar structure.

3.3.3. Effect of copolymer type on wax crystal modification

Phototo micrographs analysis are illustrated in Figure 5(a-c) show variant wax morphology changes according to types of additives photo analysis confirms with pour point test that evaluate the cold flow properties of untreated/treated waxy crude oil through wax crystallization behaviors. Copolymers PPD2 and PPD7 act through surface adsorption onto the wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. Photo analysis confirms other standard flow tests that evaluate the cold flow properties of untreated/treated crude oil through wax crystallization behavior [26-27]. It is applied herein for accessing the action of the previously prepared copolymers flow additives as wax inhibitor/pour point depressant through wax modification according to their type. Results are illustrated in Figure 5 from which it is apparent that untreated waxy crude oil Figure 5a displays elongated thick rod- like crystals which on treatment with copolymer different types of additive PPD2 and PPD7 at 1000ppm show a significant reduction of wax crystal size. Results show in Figure 5b explain PPD2 show the wax crystal size becomes gradually smaller wax crystal and with PPD7 in Figure 5c formation of abundant number of very fine dispersed crystals.



5a PP=21°C 5b PP=3°C 5c PP=0°C

Figure 5. Photomicrographs of a: Crude oil (CO) untreated, b: (CO)+ PPD2, c: (CO)+ PPD7 at 1000 ppm

3.4. The interaction mechanism discussion

The mechanism of the PPD7 on the pour point (PP) of waxy crude oil was studied at the molecular level based on the findings of the experiments. Figure 6 illustrates that the straight

alkanes in the untreated crude oil effectively precipitated and aggregated into a 3 D network structure at low temperatures, resulting in crude oil solidification. For PPD7 -treated crude oil, the PPD7 molecular structure is typically composed of a linear hydrocarbon chain and polar group segment. As a result, the PPD7 generally inhibits wax deposition via linear hydrocarbon chains that interrelate with wax crystals and hence, disperse them in crude oil using the polar groups to avoid aggregation.

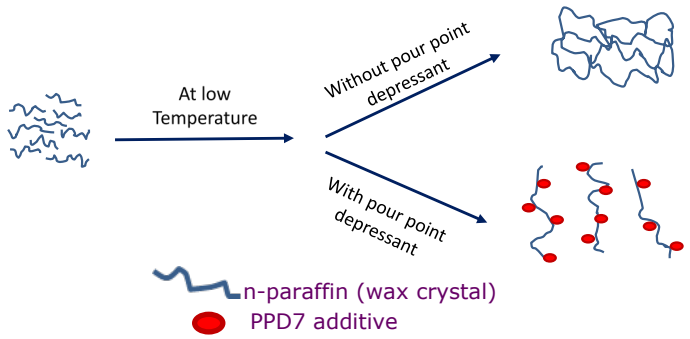


Figure 6. Mechanism of PPD7 on the pour point depression of waxy crude oil.

4. Conclusion

In this instance, we have synthesized a homopolymer of Nafol 1822C acrylate and its co-polymers using styrene and vinyl acetate separately at different percentage compositions. FTIR and GPC were two of the methods used to characterize each produced homopolymer and copolymers. Additionally, the efficacy of homopolymer and copolymers as viscosity index enhancers and pour point depressant on Egyptian waxy crude oil was assessed. The vinyl acetate-based copolymers are better as pour point depressant than styrene based copolymers. Moreover, it was also found that copolymer PPD7 with lower molecular weight are more effective as pour point depressant than copolymers PPD5 with higher molecular weight. As a result, the current work presents innovative synthetic copolymers that hold promise as efficient, safe, and effective depressant additives for the environment.

References

[1] Yuping S, Tianhui R, Xisheng F, and Xiaohong X. Study on the relation between the structure and activities of alkyl methacrylate – maleic anhydride polymers as cold improvers in diesel fuels. Fuel Processing Technology, 2005; 86(6), 641-650. https://doi.org/10.1016/j.fuproc.2004.05.011

[2] Ilyushin PYu, Vyatkin KA and Kozlov AK. Investigation of rheological properties of oil during the formation of wax deposits, Results Eng., 2022; 14:100434. https://doi.org/10.1016/j.rineng.2022.100434

[3] Deng Q, Slan_y, Zhang H, Gu X, Li Y, Du, W and Chen G. Synthesis of alkylaliphatic hydrazine and application in crude oil as flow improvers. Energies. 2021;14 (15):4703. https://doi.org/10.3390/en14154703

[4] Al-Sabagh, A M, Nasser N M, Mahmoud T. Investigation of Kinetic and Rheological properties for the demulsification process. Egyptian Journal of Petroleum. 2013; 22(1), 117–127.

[5] Gentili DO, Khalil CN, Lucas EF. Evaluation of phosphoric ester polymer additives as paraffin crystallization modifiers. Polímeros 2004; 14: 283–288. https://doi.org/10.1590/S0104-14282004000400016

[6] Emad A, Soliman EA, Elkatory MR, Hashem AI and Ibrahim HS. Synthesis and performance of maleic anhydride copolymers with alkyl linoleate or tetra-esters as pour point depressants for waxy crude oil. Fuel.2018; 211, 535–547. https://doi.org/10.1016/j.fuel.2017.09.038

[7] AL-Shamy OA, Khidr, AK, and Badr EE. Studies The Effect of HydrazideDerivatives as Flow Improvers for Waxy Crude Oil. Petroleum and Coal 2019; 61(3): 533-539.

[8] Khidr TT, Alternating copolymerized derivative as pour point depressant for gas oil. Petroleum and Coal 2020; 62(4): 1420-1426.

[9] Al-Sabagh AM, Sabaa MW, Saad GR, Khidr TT, and Khalil TM. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. Egyptian J. Pet., 2012; 21:19–30.
[10] Yang S, Li, C Yang F, Li, X, Sun, G and Yao B. Effect of polyethylene-vinyl acetate pour point depressants on the flow behavior of degassed Changing waxy crude oil before/after scCO2 extraction. Energy & Fuels 2019; 33 (6):4931–4938. https://doi.org/10.1021/acs.energyfuels.9b00561
[11] Yao B, Chen W, Li C, Yang F, Sun G, Wang G and Xu H.. Polar asphaltenes facilitate the flow improving performance of polyethylene-vinyl acetate. Fuel Processing Technology 2020; 207:106481. https://doi.org/10.1016/j.fuproc.2020.106481
[12] Xie M, Chen F, Liu J, Yang T, Yin S, Lin H, Xue Y, and Han S. Synthesis and evaluation of benzyl methacrylate-methacrylate copolymers as pour point depressant in diesel fuel. Fuel 2019 ; 255:115880. https://doi.org/10.1016/j.fuel.2019.115880
[13] Plate NA and Shibaev, VP Comb-like polymers. Structure and properties, J. Polym. Sci.: Macromolecules. 1974; 8 (1):117–253, https://doi.org/10.1002/pol.1974.230080103
[14] Al-Sabagh AM, El-Hamouly SH, Khidr TT, El-Ghazawy RA, Higazy S A. Preparation the esters of oleic acid-maleic anhydride copolymer and their evaluation as flow improvers for waxy crude oil. J. Dispersion Sci. Technol. 2013; 34 (11) :1585–1596. https://doi.org/10.1080/01932691.2012.739857
[15] Al-Sabagh AM, Khidr TT, Moustafa, H. Investigating the synergistic effect between oil soluble surfactants and styrene– maleic anhydride copolymers to enhance the flow properties of waxy crude oil. Petroleum Science and Technology. 2017; 33: 1381 -1388. https://doi.org/10.1080/10916466.2017.1331243
[16] Al-Sabagh AH, El-Hamouly SH, Khidr T, El-Ghazawy A, and Higazy SA. Synthesis of phthalimide and succinimide copolymers and their evaluation as flow improvers for an Egyptian waxy crude oil. Egyptian J. Pet., 2013; 22:381–393.
[17] Ahmed SM, Khidr TT, and Ismail DA. Effect of gemini surfactant additives on pour point depressant of crude oil. Journal of Dispersion Science and Technology, 2018; 39(8): 1160-1164. https://doi.org/10.1080/01932691.2017.1385483
[17] Khidr TT, and Omar MA. Anionic/nonionic mixture of surfactants for pour point depression of gas oil. Egyptian J. Pet., 2003; 13: 21–26.
[19] Kim YW, Eom G T, Hong JS, and Chung. KW. Fatty acid alkyl esters as feedstocksfor the enzymatic synthesis of alkyl methacrylates and polystyrene-co-alkyl methacrylatesfor use as cold flow improvers in diesel fuels. Journal of the American Oil Chemists' Society 2011; 88 (11):1727–1736. https://doi.org/10.1007/s11746-011-1834-8
[20] Ghosh P, Das M, Upadhyay M, Das T and Mandal A. Synthesis and evaluation of acrylate polymers in lubricating oil. J. Chem. Eng. Data. 2011;56:3752–3758. https://doi.org/10.1021/je2003435
[21] Soliman E A, Elkatory M R, Hashem A I and Ibrahim HS. Synthesis and performance of maleic anhydride copolymers with alkyl linoleate or tetra-esters as pour point depressants for waxy crude oil. Fuel. 2018; 211:535–547. https://doi.org/10.1016/j.fuel.2017.09.038
[22] AL-Shamy OA, Khidr TT and Badr EE. Studies The Effect of Hydrazide Derivatives as Flow Improvers for Waxy Crude Oil. Petroleum and Coal. 2019; 61(3): 533-539.
[23] Ahmed NS, Nassar AM, Nasser RM, Khattab AF, Abdel-Azim AA Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil. Pet. Sci. Technol. 2008; 26: 1390–1402. https://doi.org/10.1080/10916460701272195
[24] Rizvi SQA. Lubricant additives and their functions. In: Friction, lubrication, and wear technology. ASM handbook, vol18, 10th edn. ASM International, Material Park, 1992; 98–112.
[25] Berkhof R and Kwekkboom HJ. Reprint, 3rd Servo Oil Field Chemicals Symposium, Moscow, USSR, October, 1985.
[26] Khidr TT. Alternating Gas Oil Copolymerized Derivative As A Pour Point For Gas Oil. Petroleum and coal, 2020; 62: 1420-1426.
[27] Table El-Tabei AS, Khidr TT, Amira E. El-Tabei, and Elsayed.A.Elsharaky Synthesis, Characterization, and Performance of New Polymeric Nonionic Surfactants as Flow Improvers and Wax Dispersants for Waxy Crude Oil. Egyptian Journal of Chemistry 2023; 66 (6): 205 - 216.

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