

Comparative Study of Polymethyl Acrylate, its Hydrazone Derivative with Commercial Surfactants for Flow Improvements in Waxy Crude Oil

S. Hesham¹, N. S. Yousef², Ehssan Nassef^{2*}

¹ Amreya Petroleum Refining Co. (APRC), Mergham, Cairo-Alex Desert Road, Egypt

² Petrochemical Department, Faculty of Engineering, Pharos University, Alexandria, Egypt

Received October 9, 2019; Accepted December 29, 2019

Abstract

Methyl acrylate polymer and its hydrazone derivative were synthesized, and their structure was confirmed by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. These polymers were tested as flow improvers for two types of Egyptian waxy crude oil (light-1, heavy-2), and their results were compared with commercial surfactants such as linear alkyl benzene (LAB), linear alkyl benzene sulfonate (LAS) and the sodium salt of linear alkyl benzene sulfonate (Na-LAS). For both crude oils, poly-methyl acrylate and its hydrazone derivative exhibited better pour point depressant properties when compared with LAB, LAS and Na-LAS. For crude oil 1, the pour point declined from 24°C to 12°C and from 24°C to 15°C by the addition of poly-methyl acrylate and its hydrazone derivative, respectively, at a level of 1000 ppm. For oil 2, the same parameter declined from 21°C to 6°C and from 21°C to 9°C on using poly-methyl acrylate and its hydrazone derivative, respectively, at a concentration of 1000 ppm.

Keywords: Flow improvers; polymers; pour point; de-asphalting; waxy crude oil.

1. Introduction

The pour point of the oil is defined as the temperature at which the flow of crude oil stops. Under this temperature, the oil solidifies and loses its flowability [1]. Paraffin wax and asphaltenes are the main components of crude oil, and these components create several problems in transportation in reservoir, wellbore, production tubing and surface flow lines. As these crude oil reserves are mainly located offshore with the ambient amount of seawater and low temperatures, they are subjected to below pour point temperatures. As a result, the waxy constituents tend to deposit on cold surfaces of the pipelines and continuous deposition of the waxy layer leads to gelation. Under these conditions, the crude oil undergoes three dissimilar phase transformations. Due to variation in pressure and temperature, the wax crystals aggregate to form wax gels. Further, the wax gels combine with each other to form net-like and cage-like structures. This decreases the accessible area in the channel for oil transportation, which elevates the pressure drop between the two terminals of the oil channel. This leads to a decrease in flow rate and an increase in energy consumption for transportation [2]. Another significant hurdle in this arena is the pipeline use after an extended closedown for repairing. At lower temperatures, the oil transforms into a gel structure over long periods of storage, resulting in high yield stress on the pipelines [3-4]. To circumvent the above-mentioned problems, extensive research and study of pour point depressants (PPD's) are important to encounter the global oil demands.

Polymeric additives are well established as PPDs. They are added in ppm levels to reduce the yield stress, viscosity, and pour point of crude oil for easy transportation. These polymers increase the fluidity of waxy crude, thereby reducing energy consumption and improving propelling efficiency [5-7]. Following are important properties necessary for flow improvers and PPDs: (i) should have wax character, possess linear alkyl chains of 14 to 25 carbon atoms, and co-crystallize with oil's wax; (ii) have good solubility in oil depending on their typical

molecular weights; (iii) monomer to monomer ratio, amorphous and crystalline parts of flow improver; (iv) physical and chemical stability [8-10]. Generally, there are two types of PPDs known as alkyl aromatic polymers and poly methylacrylates. Alkyl aromatic polymers are also well known for their use as PPDs. Besides alkyl aromatic polymers, acrylate copolymers and their derivatives are important additives used to increase the pour points of crude oil, gasoline and naphtha for easy transportation. These polymers were deposited on the emerging crystals, hindering their development and leading to the formation of small wax crystals [11-14]. While abundant literature is available for alkylaromatic polymers, poly methylacrylates are less explored.

Here, we report the synthesis of a poly(methylacrylate) polymer [1] and its hydrazide derivative [2]. Structures of these polymers were confirmed by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Spectroscopy (SEM). These polymers were investigated as PPDs using two types of Egyptian waxy crude oil (light and heavy). Further, these results were compared with commercially available surfactants: linear alkyl benzene (LAB), linear alkyl benzene sulfonate (LAS), and the sodium salt of linear alkyl benzene sulfonate (Na-LAS).

2. Materials and methods

2.1. Materials

Technical grades of methyl acrylate, potassium bromate, sodium hydrogen sulfite, sodium chloride, polyethylene, and acetone were used for the preparation of poly(methyl acrylate) without further purification. Analytical grades of dimethyl sulfoxide, hydrazidne hydrate (80%), and poly-methyl acrylate were used to prepare poly(methyl acrylic acid hydrazide). Na-LAS was prepared by using NaOH. Alexandria Petroleum Company in Egypt, light crude oil and heavy crude oil. De-asphalting crude oils were done using n-heptane as a solvent. Determinations of paraffin wax content in crude oils were done by using acetone, Fuller's earth, and petroleum naphtha.

2.2. Preparation of poly-methyl acrylate

Methyl acrylate (300 mL of 5%) was poured in a 1 liter conical flask. Both potassium bromate solution and sodium hydrogen sulfite solution were added as the following: KBrO_3 solution (5 ml, 0.1 M) and NaHSO_3 solutions (5 ml, 0.45 M) were added to methyl acrylate solution, and the mixture was swirled vigorously for 15 minutes until it formed a homogenous milky emulsion. Coagulation of polymer was done by pouring NaCl solution (300 mL, 5 M) to the milky emulsion. Isolated polymers were washed by water to remove salts and traces of unreacted monomer present, followed by squeezing. Polymers were cut/tear into small pieces and dissolved in acetone (1 g/10 mL) and were agitated using a glass stick. Thin films were then prepared after acetone is evaporated after the obtained mass was dense and viscid [15].

2.3. Preparation of hydrazide derivative of poly methyl acrylate

A solution of poly-methyl acrylate (2 g) in 60 mL dimethylsulfoxide was added with 20 mL of hydrazine hydrate and heated to reflux on a hot plate with stirring for 20 h and then subsequently cooled. This solution was added with constant stirring to 400 mL of methanol. The precipitated poly methyl acrylic acid hydrazide polymer was filtered and dried under vacuum, purified by dissolution in the least amount of water, and then re-precipitated from CH_3OH . The obtained polymer was filtered and dried with a vacuum desiccator for ten days over concentrated sulfuric acid [15].

2.4. Preparation of Na-LAS sodium salt of linear alkyl benzene sulphonate

Alexandria Petroleum Company in Egypt provided LAS, and this was reacted with NaOH to obtain Na-LAS.

2.5. De-asphalting of crude oil

Crude oils 1 and 2 (ALAMIN and AGIBA), obtained from Alexandria Petroleum Company, were analyzed and given in Table 1.

Table 1. Characterization of oil 1 and 2

Properties	Oil 1 (Alamin)	Oil 2 (Agiba)
Crude type	Light crude	Heavy crude
Specific gravity	0.8155	0.8761
Pour point (°C)	24	21
Wax content %wt	3.4	4
Asphaltene content %wt	1.2	1.8

Crude oils were de-asphalted in the following manner. A three neck flask was set up, followed by the addition of 2 grams of crude oil and 200 mL *n*-heptane. The mixture was heated to reflux with gentle stirring for 30 min on a hot plate and cooled at room temperature gradually for 1 h. The slurry obtained was filtered through a sintered glass funnel under vacuum. The precipitate obtained was washed with *n*-heptane and was then transferred to a crucible and dried in an oven at 107°C. The drying was pursued until a steady weight was reached. The filtrate was distilled to remove the solvent and dried. Drying was continued until a constant weight was obtained at 107°C which is the weight of asphaltene [16].

2.6. Determination of paraffin wax content in crude oil

Two grams of crude oils were weighed and dissolved in 500 mL petroleum naphtha (boiling point range: 40-60) in 1 L Erlenmeyer flask. Then 15 g of Fuller's earth was added to the mixture, stirred for 15 min, and filtered through a filter paper. Petroleum naphtha was evaporated from the filtrate on a steam bath. A mixture containing 75% acetone and 25% petroleum naphtha (200 mL) was added to the concentrate under a temperature of about 50°C. The resulting solution was cooled to 0°C and filtered through filter paper. Wax obtained after filtration was washed with a hot solution of acetone-naphtha mixture and then the filtrate was evaporated. The produced wax and the flask were weighed to near 0.01 mg [17].

2.7. Determination of pour point in crude oil

Crude oil was heated until it was just sufficiently fluid and then poured into the level mark of the standard measuring flask. The flask was tightened with the cork carrying the high-pour thermometer. The thermometer was placed inside the jacket, 25 mm from the bottom. Chilling the flask resulted in paraffin wax crystals with minimal disturbance. At temperature nearer to pour point, the jar needed to be tilted; the movement of liquid was then checked and analyzed. When there was no flow, the jar was placed horizontally for 5 sec. If the liquid did not flow, 3°C was supplementary to the present temperature and was considered as pour point. After the specimen has been cooled, and paraffin wax crystals are formed, great care should be taken in order not to lose the network of wax crystals, which could lead to error in results [18-19].

2.8. Characterization of poly methyl-acrylate and its hydrazide derivative

2.8.1 SEM analysis

SEM images were obtained for both poly methyl-acrylate and its hydrazide derivative using SEM (Model: JSM-5500 LV; JEOL, Ltd-Japan).

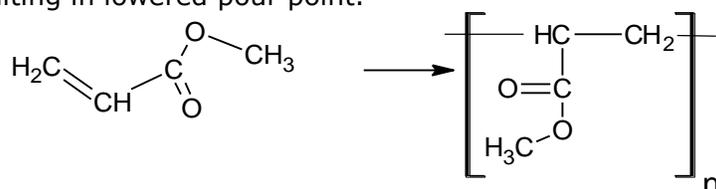
2.8.2 IR analysis

IR spectra were obtained for both poly methyl-acrylate and its hydrazide derivative using a Perkin-Elmer (BX-II FT-IR) instrument.

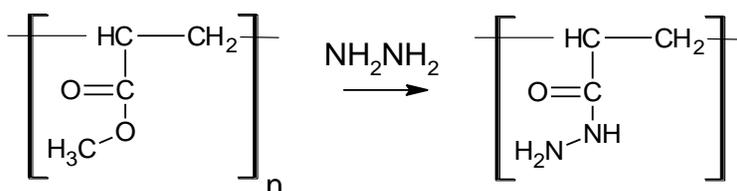
3. Results and discussions

3.1. Synthesis of polymers

Synthesis of polymethyl acrylate polymer (1) (Scheme 1) was achieved by the reaction of methyl acrylate with potassium bromate and sodium hydrogen sulfite. Hydrazide derivative (2) of acrylate polymer 1 was achieved by the reaction of polymethyl acrylate with hydrazine hydride in DMSO. The molecular weight of polymers was determined by Gel Permeation Chromatography. The choice of polymethyl acrylate polymer and its hydrazide derivative are due to their ability to slither and wiggle past and around each other easily, facilitating the easy flow of oil and resulting in lowered pour point.



Scheme 1. Synthesis of polymethyl acrylate from methyl acrylate



Scheme 2. Synthesis of hydrazide derivative of polymethylacrylate

3.1.1. Scanning electronic microscopy (SEM)

Figures 1 and 2 represent the SEM image of the morphology of poly methyl-acrylate and its hydrazide derivative, respectively. The average length of the poly methyl-acrylate polymer was 5 μm , whereas the same for poly-methyl acrylic acid hydrazide polymer was 10 μm .

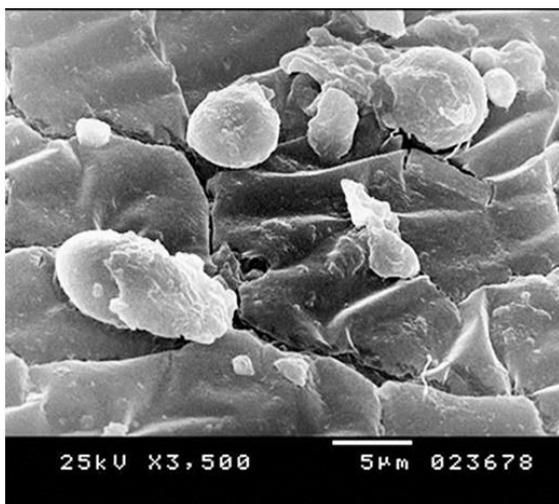


Figure 1. SEM image of poly methyl-acrylate polymer

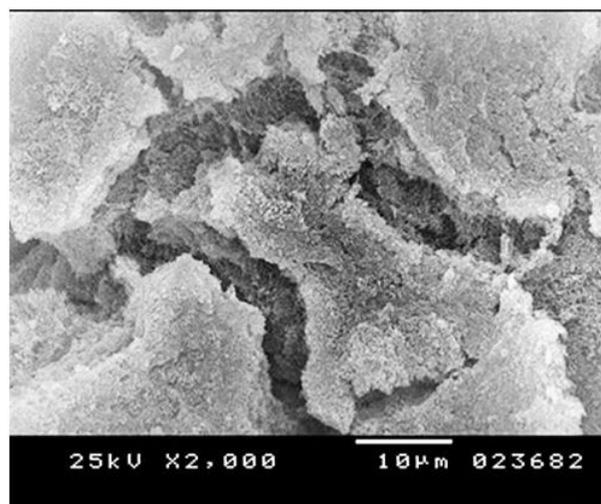


Figure 2. SEM image of poly-methyl acrylic acid hydrazide polymer

3.1.2. IR Analysis

IR spectra (Figure 3) of the poly methyl acrylate and its hydrazide derivative were obtained using a Perkin-Elmer (BX-II FT-IR) instrument. Poly-methyl acrylate (1) showed a signal at 1716 cm^{-1} , representing CO stretching. The absorption signals at 2854 cm^{-1} and 2927 cm^{-1}

represent CH₂ groups of the polymer. The spectra of hydrazide polymer (2) showed a series of bands corresponding to the hydrazide group (-CO-NH-NH₂) with signals at 3400-3100 cm⁻¹ corresponding to $\gamma_{\text{sym}}(\text{NH}_2)\gamma_{\text{asym}}(\text{NH}_2)$ (3200 cm⁻¹) attributable to the stretching of secondary NH group. Similar to amides, the hydrazide group also showed the spectra of acid hydrazide and acid hydrazine. IR bands also showed C=O in plane deformation and without plane deformation at 670 cm⁻¹ and 510 cm⁻¹, respectively.

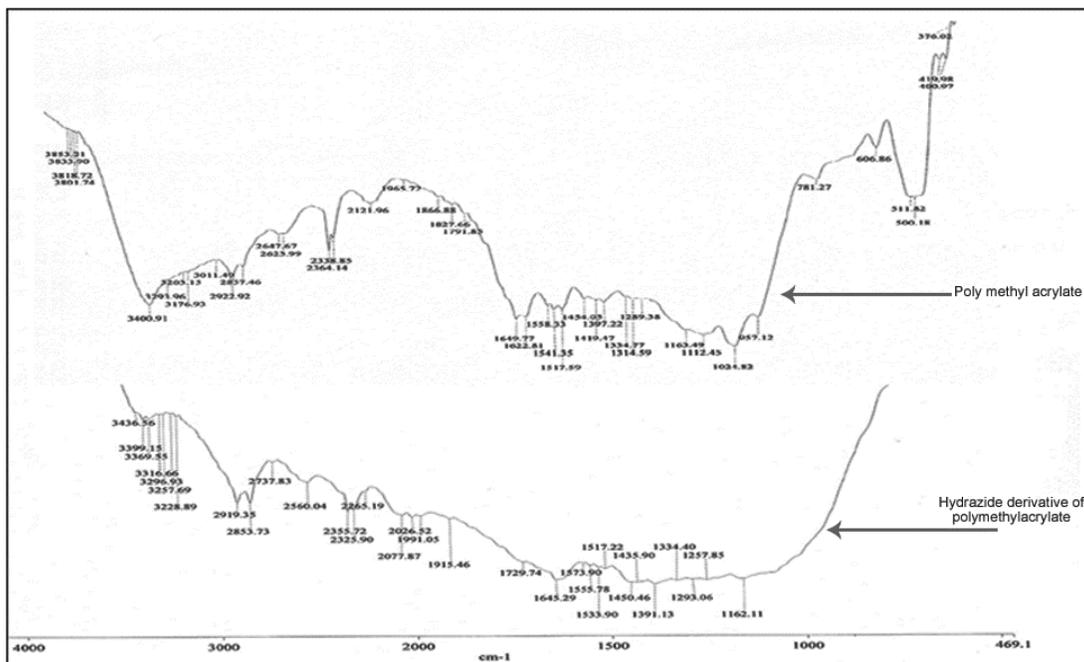


Figure 3. IR spectra of the poly methyl acrylate (1) and its hydrazide derivative (2)

3.2. Characterization of crude oils

The crude oils selected were ALAMIN (crude 1) and AGIBA (crude 2). The properties of crude 1 and crude 2 are given in table 1. Crude 1 had a specific gravity of 0.8155 g/cm³ and a pour point of 21°C. The wax content and asphaltene contents were 3.4% and 1.2%, respectively. Crude 2 had a specific gravity of 0.8761 g/cm³ and a pour point of 24°C. The wax content and asphaltene contents were 4% and 1.8%, respectively. Crude 2 is heavy in character when compared with crude 1.

3.3. Effect of poly-methyl acrylate as a PPD in crude 1 and 2

Figure 4 shows the influence of polymer concentration on the pour points of oil 1 and 2. For both crudes, pour point decreased in a linear fashion with an increase in polymer concentrations. In the light crude oil (crude 1), the pour point decreased from 24°C to 12°C with an increase in the concentration of polymer to 1000 ppm. On the other hand, in the heavy fraction crude oil (crude 2), the pour point decreased from 21°C to 6°C on the same concentration levels of the polymer. This showed that poly-methyl acrylate was more effective as a pour depressant in crude 2 when compared with crude 1.

3.4. Effect of poly-methyl acrylate hydrazide as a pour point depressant on crude oils 1 and 2

Figure 5 shows the influence of the concentration of hydrazide polymer 2 on oils 1 and 2. The pour point decreased with the increase in polymer concentration. In a light fraction crude oil (crude 1), the pour point reduced in the range of 24°C to 15°C with an increase in the concentration up to 1000 ppm. On the other hand, the heavy fraction crude oil (crude 2) pour

point reduced in the range of 21°C to 9°C with an increase in polymer concentration. In essence, the addition of both polymers 1 and 2 resulted in a decrease in pour point in both crude oils 1 and 2. For both polymers 1 and 2, the decrease in pour point was more significant in crude 2 when compared with crude 1.

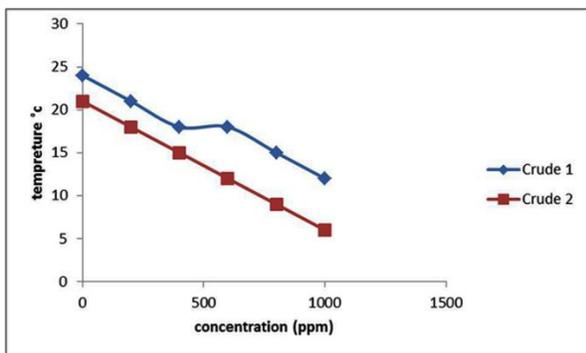


Figure 4. Effect of poly-methyl acrylate on crude oils 1 and 2

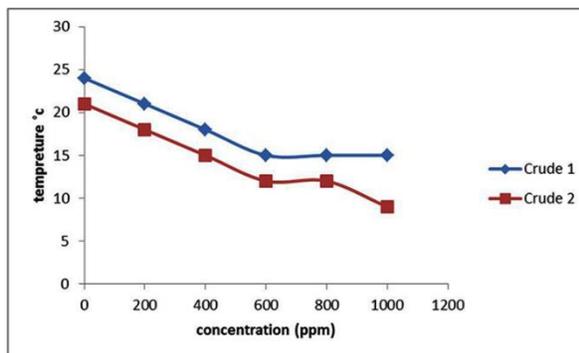


Figure 5. Effect of poly-methyl acrylate hydrazide on different crude oils

3.5. Effect of linear alkyl benzene (LAB) as a pour point depressant on crude oils 1 and 2

Figure 6 showed the influence of LAB concentration on the pour point of heavy and light oils. For both the crude oils 1 and 2, the pour point decreased with the initial addition of LAB up to 200 ppm from 24°C to 20°C and 21°C to 18°C, respectively. Afterwards, no significant change was observed in pour point up to 600 ppm. Further addition of LAB up to 800 ppm in oil 1 reduced pour point in the range of 20°C to 18°C. On the other hand, in the heavy crude oil 2, the pour point increased in the range of 18°C to 21°C upon increasing the concentration to 800 ppm.

3.6. Influence of LAS as PPD on crude oils 1 and 2

The effect of LAS concentration on crude oils 1 and 2 is shown in Figure 7. For both crude oils, the initial increase in the concentration of LAS up to 200 ppm resulted in no significant increase in pour point. An increase from 200 ppm to 400 ppm resulted in a decrease in pour point from 24°C to 21°C and 21°C to 18°C in crude oils 1 and 2, respectively. Further addition of LAS resulted in no change in the pour point of crude oil 1. On the other hand, in crude oil 2, the addition of LAS above 800 ppm increased pour point.

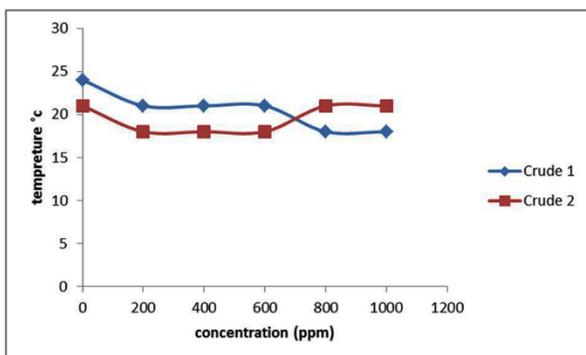


Figure 6. Influence of LAB for oils 1 and 2

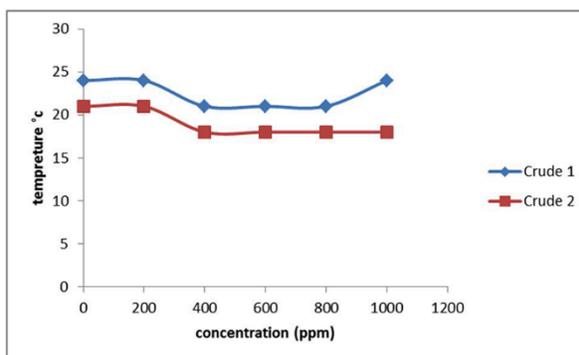


Figure 7. Influence of LAS on crude oils 1 and 2

3.7. Influence of Na-LAS as PPD on crude oils 1 and 2

The influence of Na-LAS concentration on the pour point of heavy and light fractions of crude oils 1 and 2 are given in Figure 8. For both crude oils, the initial increase in the concentration of Na-LAS up to 200 ppm resulted in no significant increase in pour point. An increase from 200 to 800 ppm resulted in a decrease in pour point in the range of 24°C to 18°C and

21°C to 15°C in crude oils 1 and 2, respectively. Further addition of LAS resulted in no change in the pour point of both crude oils.

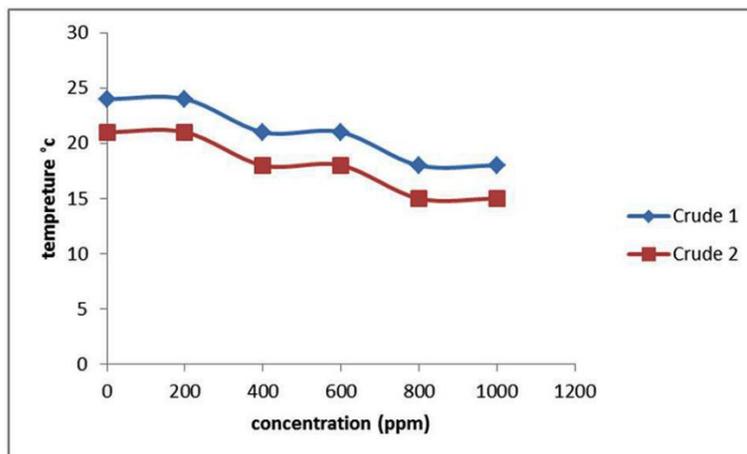


Figure 8. Effect of sodium salt of linear alkyl benzene sulfonate on different crude oils

3.8. Mechanism of flow improvers in methyl acrylate polymer and its hydrazide derivative

The following are the characteristics of flow improvers:

When both flow improvers and wax undergo the nucleation process, the molecules of wax form the crystalline nucleus. But as the molecular weight of the polymer is higher than wax, the crystalline nucleus undergoes self-assembling to form micelle structure, leading to smaller wax crystals. Smaller crystals improve flowability.

- (i) Waxes adsorbed on the uppermost layer of polymers due to Van der Waals's interactions. This changes the topography of wax crystals, leading to an increase in flowability.
- (ii) Van der Waals interactions between wax and the polymers elevate the solvability of both oils and, thereby, increases the flowability [20].

Here, methyl acrylate polymer has an ester group with two oxygen atoms. The oxygen atoms exhibit a strong Van der Waals interaction with a hydrogen atom in n-alkyl chains of wax, thereby, inhibiting the growth of wax crystals. Similarly, the hydrazide derivative of poly methyl acrylate has CO as well as NH, NH₂ functionalities favoring strong Van der Waals interaction. Our results showed that methyl acrylate polymer was a better flow depressant than its hydrazide derivative with a higher decrease in pour point. Also notable is that both these polymers have better flow depressant behavior in heavy crude oil 2 than its light-weight counterpart oil 1. This can be interpreted as the polymers had better interaction with crude where the wax content was more. On the other hand, commercial flow depressants LAB, LAS and Na-LAS showed the same level of PPDs in crude 1 and crude 2.

4. Conclusions

In this work, poly-methyl acrylate (1) and hydrazine derivative of poly-methyl acrylate (2) were synthesized and characterized by FTIR and SEM. Their effectiveness as PPD for two varieties of oils 1 and 2 was investigated and compared with the commercial LAB, LAS, and Na-LAS. Both polymers acted as a PPD and flow improvers. Below are the conclusions derived from this study:

- For both crude oils 1 and 2, the poly-methyl acrylate and its hydrazine derivative exhibited better PPD properties when compared with LAB, LAS, and Na-LAS.
- PPD of oil 1 lessened from 24°C to 12°C and from 24°C to 15°C by the addition of poly-methyl acrylate and its hydrazide derivative, respectively, at 1000 ppm.
- For oil 2, the pour point diminished in the range of 21°C to 6°C and from 21°C to 9°C on using poly-methyl acrylate and its hydrazine derivative, respectively, at a concentration of 1000 ppm.

- For LAB, LAS, and Na-LAS, the changes in pour points of oils were minimal with 3-4°C, where the same was significant with 10-12°C for poly-methyl acrylate and its hydrazine derivative.

References

- [1] Ronningnsen HP, Bjorndal B, and Hansen AB. Wax precipitation from North Sea crude oils 1. Crystallization and dissolution temperature, and Newtonian and non-Newtonian flow properties. *Energy Fuels*, 1991; 5(6): 895-908.
- [2] Pauly JP, Daridon JL, and Coutinho JAP. Liquid-solid equilibria in n-decane + multi paraffins system. *Fluid Phase Equilibria*, 1998; 149(1-2): 191-207.
- [3] Pauly JP, Daridon JL, and Coutinho JAP. Solid deposition as a function of temperature in the nC10 + (nC24-nC25-nC26) system. *Fluid Phase Equilibria*, 2004; 224(2): 237-244.
- [4] Thanh NX, Hsieh M, and Philip RP. Waxes and asphaltenes in crude oils. *Organic Geochemistry Journal*. 1999; 30(2-3): 119-132.
- [5] Bott TR and Gudmundsson JS. Deposition of paraffin wax from kerosene in cooled heat exchanger tubes. *The Canadian Journal of Chemical Engineering*. 1977; 55(4): 381-385.
- [6] Carnahan NF. Paraffin deposition in petroleum production. *Journal of Petroleum Technology*, 1989; 41(10): 2024-2025.
- [7] Elsharkawy AM, AL-Sahhaf TA, and Fanhim MA. Wax deposition from Middle East crudes. *Fuel*, 1999; 79(9): 1047-1055.
- [8] Altgelt KH and Boduszynski M. *Composition and analysis of heavy petroleum fractions*. CRC Press, Taylor and Francis Group, Dekker, New York. 1993.
- [9] Burger ED, Perkins TK, and Striegler JH. Studies of wax deposition in the trans Alaska pipeline. *Journal of Petroleum Technology*, 1981; 33(6): 1075-1086.
- [10] Musser BJ and Kilpatrick PK. Molecular characterization of wax isolated from a variety of crude oils. *Energy Fuels*, 1998; 12(4): 715-725.
- [11] Nermen HM and Magdy TZ. Separation of microcrystalline waxes from local crude petrolatums using solvent-antisolvent mixtures. *Petroleum Science and Technology*, 2004; 22(11-12): 15553-15569.
- [12] Handoo J, Gupta AK, and Agrawal KM. Characterization of total waxes derived from some Indian crude oils by fractionation. *Petroleum Science and Technology*, 1997; 15(3-4): 347-356.
- [13] Pedersen WB, Hansen AB, Larsen E, and Nielsen AB. Wax precipitation from North Sea oils, Solid phase content as function of temperature determined by pulsed NMR. *Energy Fuels*, 1991; 5(6): 908-913.
- [14] Li H, Zhan J, and Yan D. Correlations between the pour point /gel point and the amount of precipitated wax for waxy crudes. *Petroleum Science Technology*, 2005; 23(11-12): 1313-1322.
- [15] Al-Shafey HI, Hashem AI, Abdel Hameed RS, and Dawood EA. Studies on the Influence of Long Chain Acrylic Esters Co-Polymers Grafted with Vinyl Acetate as Flow Improver Additives of Crude Oils. *Advances in Applied Science Research*, 2011; 2(5): 476-489.
- [16] Abdel Azim AAA and Rash MAA. Polymeric additives for improving the flow properties and viscosity index of lubricating oils. *Journal of Polymer Research*, 2001; 8(2): 111-118.
- [17] *Standard Methods of de-asphalting of Petroleum Oils, ASTM D-3279. Standard methods for analysis and testing of petroleum products. Annual Book of ASTM standards, American Society for Testing and Materials, Philadelphia. 1974.*
- [18] *Universal oil products of determination of wax content in oil, UOP 46.*
- [19] *Standard Methods of Test for Pour Point of Petroleum Oils, ASTM D-97, Standard methods for analysis and testing of petroleum products, Annual Book of ASTM standards, American Society for Testing and Materials, Philadelphia. 1974; pp.81-84.*
- [20] Hao LZ, Al-Salim HS, and Ridzuan N. A review of the mechanism and role of wax inhibitors in the wax deposition and precipitation. *Pertanika Journal of Science & Technology*, 2019; 27(1): 499-526.

To whom correspondence should be addressed: Professor Ehssan Nassef, Petrochemical Department, Faculty of Engineering, Pharos University, Alexandria, Egypt, E-mail: ehssan.nassef@pua.edu.eg