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PREPARATION OF TERPOLYMER ADDITIVES AND USED THEIR AS POUR POINT DEPRESSANT FOR CRUDE OIL

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Abstract

To investigate the influence of structure variables of terpolymeric additives on the pour-point depression and rheological behavior of waxy crude oil. Four different alkyl chain length of n-alkyl methacrylate-styrene-maleic anhydride terpolymers were synthesized by radical polymerization and distinguished by FTIR and GPC. The capacity of the prepared terpolymers were studied for their capability as pour point depressants (PPD) and flow improvers for Egyptian waxy crude oil to solve the difficulty of wax deposition during transportation and storage. From the evaluation, it was found that, the maximum depression of PP was obtained by additive (TC22M) with long chain alcohol (C_{22}-OH) from 27°C to 9°C ($\Delta pp_{2000ppm} = 18°C$). On the other side, it was remarked that low diminition obtained by additive (TC12M) which esterified by alcohol (C_{12}-OH) from 27°C to 21C ($\Delta pp_{2000ppm} = 6°C$) at the same condition. The depression of pour point influences was discussed on the light of polymers structure, molecular weights, and their concentrations. The decrease of pour point and rheological parameters after additive addition largely related to the terpolymer structure. Photomicrographic analysis showed that a clear effect of the terpolymer additives on the wax crystal modification which is in agreement with above results.

Keywords: Ester; Terpolymer; Pour point depressants; Flow improvers; Crude oil; Rheology.

1. Introduction

With the development of economy and society, the need of crude oil increases day by day. Crude oil contains n-paraffin waxes that tend to be separated from oil when the heat of crude oil falls under the wax appearance temperature. With reducing temperature, the waxes generally crystallize as an interlocking network of fine sheets there by entrapping the remaining liquid fuel in cage-like structures [1-2]. When the temperature approaches the pour point, the oil may gel completely and affecting the cold flow problems such as blockage of flow pipes or production lines. The pour point is the lowest temperature at which oil will flow freely under its own weight under specific test conditions. Some ways [3-4] have been available to progress the low-temperature properties of crude oil. Pretreatment with flow improver (FI) additives is an attractive solution for transportation of waxy crudes via pipelines. Flow improver additives, also known as pour point depressants (PPD)/wax crystal modifiers, can reduce the growth of wax crystals and form smaller crystals of higher volume to surface ratio [5-6]. Flow improvers are very selective in nature. Some additives that result in the highest reduction of viscosity and gel strength do not result in the lowest pour point. However, when an exact fit can be developed, polymeric additives can be remarkably effective in depressing the pour point of a waxy crude. It is generally recognized that wax content is primarily responsible for flow problems: the higher the wax content, the greater are the flow problems [7]. Many factors affecting the flowability behavior of crude oil such as its chemical composition, temperature and the current, as well as previous thermal history [8-9].

In the present revision we have synthesized four alkyl methacrylate-styrene-maleic anhydride terpolymers with different long-chain alkyls by free radical polymerization and evaluated

their influence on the flow properties of crude oil. We also determined the carbon number distribution of n-alkanes in the diesel fuel and studied the rheological behavior and crystallization behavior of crude oil with and without additives. One of the purposes of this research was to observe the affiliation between the influence of n-alkyl chain length of terpolymer and the n-alkanes in crude oil. Another purpose was to study the effect of size, form and accumulation of wax crystals on pour point (PP) and viscosity.

2. Experimental

2.1. Materials

The following chemicals were used, methacrylic acid, styrene maleic anhydride, dodecyl alcohol, hexadecyl alcohol, p-toluene sulphonic acid, toluene were attained as analytical reagents from Aldrich chemical. The initiator benzoyl peroxide was recrystallized from methanol. Two linear long chain alcohol blend (NAFOL 20+A) and (NAFOL 1822 B) were supplied from CONDE chemical company with the typical analysis listed in Table 1.

Table 1. Typical analysis of linear long-chain alcohol blends (NAFOL)

Properties	NAFOL 20+A	NAFOL 1822 B	Properties	NAFOL 20+A	NAFOL 1822 B
Composition , wt %			Density g/cm^3 at 80°C	0.803	0.802
C16-OH	0.9	0.2	Solidification point, °C	56-60	63-65
C18-OH	24.3	15.0	Ester number, mg KOH/g	9.9	0.16
C20-OH	24.4	14.8	Acid number, mg KOH/g	0.05	0.01
C22-OH	38.2	69.8	Water, wt%	0.06	0.04
C24-OH	9.9	0.2	Flash point , °C	208	204
C26-OH	2.3	-	Iodine number, mg I$_2$/100 mg	8.2	0.23
Average carbon number(calculated)	C$_{av}$= 20	C$_{av}$= 22			

2.2. Crude oil used

Egyptian waxy crude oil was submitted from Qarun Petroleum Company. Their physico-chemical 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 showed in Figure 1.
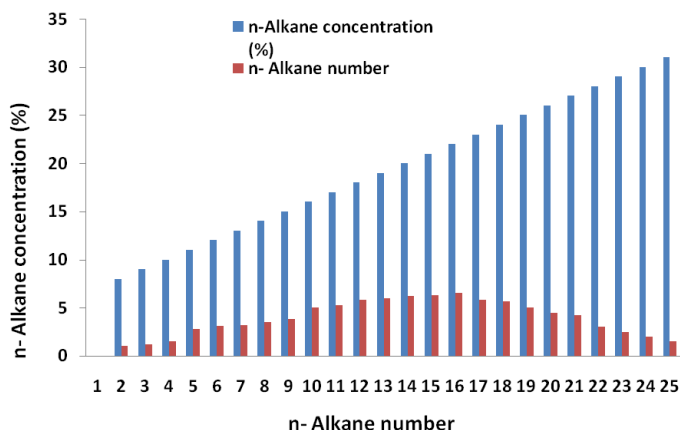

Figure 1. Concentration distribution of n- alkanes in the crude oil

Table 2. Physicochemical properties of the investigated crude oil

Test	Method	Result	Test	Method	Result
Density@15°C, kg/L	ASTM D1298	0.8662	Sulfur content, wt%	ASTM D4294	0.869
Pour point, °C	ASTM D97	27	Wax content, wt%	UOP 46/64	10.01
Kinematic viscosity at 40°C, Cst	ASTM D445	11.440	n-paraffins, wt%	ASTM D2887	85.27
at 100°C, Cst		2.400	Iso- paraffin, wt%	ASTM D2887	6.12
Asphaltene content, wt.%	IP 134	0.725	Total paraffins content, wt%	Urea adduct	91.39

2.3. Esterification and terpolymer reaction

2.3.1 Synthesis of n-alkyl methacrylate

The n-alkylmethacylate were prepared by the reaction methacrylic acid (1.2 mole) with a series of n-alkyl alcohols which have increasing number of carbon atoms, dodecyl alcohol C_{12}, hexadecyl alcohol C_{16}, blend of alcohol NAFOL 20+A (C_{av}=20) and NAFOL 1822 B (C_{av}=22) (1 mole) in a round bottom flask furnished with a Dean and Stark trap to remove the water of reaction azeotropically as it is formed [8]. The reaction was conducted in the presence of toluene (100 mL) as a solvent, at reflux temperature, hydroquinone as a polymerization inhibitor. The reaction was carried out until the theoretical amount of water of the reaction was collected. The four prepared monomers dodecyl methacrylate, hexadecyl methacrylate, NAFOL 20+A methacrylate and 1822 B methacrylate were then purified by cleaning off the solvent at the end of esterification at reduced pressure. The reaction mixture was then extracted with n-hexane, washed a number of times with distilled water to remove the catalyst and any unreacted acid until the washing converts neutral, then the organic material was collected and dry.

2.3.2. Terpolymer of alkyl methacrylate – styrene - maleic anhydride

The above synthesized n- alkyl methacrylate and styrene-maleic anhydride liquefied in toluene in a 1:1:1 mole ratio was taken in a four necked round bottom flask [9]. At the start the contents were subjected to nitrogen flushing for twenty minutes, then gradually heated to 95°C, the desired weight of initiator (benzoyl peroxide) liquefied in toluene as initiator was added drop by drop, was heated for 8 hours. When the reaction was completed, the temperature was allowed to reduce at room temperature, then the reaction mixture was powered droplet by droplet in chilled methanol with continues rousing, filtered off and dry. The prepared additives are named as TC12M, TC16M, TC20M and TC22M correspondingly.

2.4. Characterisation of terpolymer

The structures of the prepared monoester alkyl methacrylate and terpolymer with styrene and maleic anhydride were confirmed by using Infrared spectroscopic analysis. The infrared spectra photometer a doping KBr technique. Description of terpolymer is illustrated in Table 3.

Table 3. Characterization of the synthesized terpolymer additives alkyl methacrylate-styrene- MA

Additive designation	Composition	M_w (g/mol)	Poly dispersity index
TC12M	Terpolymer (dodecyl methacrylate-styrene – maleic anhydride)	41 513	1.70
TC16M	Terpolymer (hexadecyl methacrylate-styrene – maleic anhydride)	38 513	1.52
TC20M	Terpolymer (NAFOL 20+A methacrylate-styrene – maleic anhydride)	30 512	1.41
TC22M	Terpolymer (NAFOL 1822 B methacrylate-styrene – maleic anhydride)	28 858	1.25

Molecular weights of terpolymers were determined by a Waters gel permeation chroma-tography (GPC) includes Waters 515 HPLC pump system equipped with 2410 refractive index detector, were used for construction of calibration curve. Tetrahydrofuran was used as the mobile phase, at a flow rate of 1 ml/min.

2.5. Evaluation of the synthesized additives

2.5.1. Pour point (PP) measurements (ASTM) D97)

Solutions of the synthesized terpolymers (TC12M, TC16M, TC20M and TC22M.) in xylene containing 50% active material were prepared with different concentrations (500, 1000, 2000 and 3000 ppm) of each of the prepared solutions. The solutions were injected into the crude oil at 60ºC to assurance complete dissolution of the crude oil paraffin content, stirred for homo-genization, then subjected to pour point test according to the ASTM D97 standard procedure deprived of reheating.

2.5.2. Viscosity measurements

The prepared additives were evaluated as flow improver for waxy crude oil through rheo-logical dimensions at concentration 2000 ppm. The measurements were carried out for the untouched and touched crude oil samples at different temperatures above your head and under pour point of crude oil ranging from (17.27 and 37°C) using Brookfield DV-II+ program-mable viscometer operating instructions manual no. M/97-164-D1000. The experimental procedure starts when the additives were mixed with crude oil at the prescribed concentration at 60°C. Meanwhile , the viscometer cup is preheated to the same temperature , then loaded with 25 mL of the sample and then the temperature is brought down to a constant tempe-rature, at which the measurements will be achieved, at a low shear rate of 0.024 s^{-1} (dynamic cooling). Shearing was continued for 15 minute at the test temperature for estimation. The shear stress-shear rate correlation was detailed for the tested samples.

3. Result and discussion

3.1. Concentration distribution of n-alkanes in the crude oil

It is well recognized that the series of n-alkanes and their distribution play a major role in wax crystal formation [10]. Figure. 1 shows the concentration distribution of n-alkanes. The carbon number of n-alkanes ranges from 8 to 31 and mainly from 20 to 23. The content of n C23 is the most. The content of nC22 and nC23 is also great and the nC23 content is somewhat higher than nC22. But the content of nC31 is much a smaller amount than them.

3.2. Chemical structures of the prepared terpolymers

The structures of the four terpolymers were confirmed by Fourier Transform Infra-Red spectrophotometer. It can be clearly seen the distinctive CH_3 and CH_2 stretcheing of the alkyl group adsorption peaks at 2920 and 2856cm^{-1}, the characteristic C=O stretching peaks of maleic anhydride at 1850 and 1780 cm^{-1} and the characteristic C=O adsorption peaks of alkyl metha-crylate at 1736 cm^{-1}. And we can see the intensity of CH_3 and CH_2 bands increases with the increase of the length of the alkyl groups [2]. The complete loss of C=C bands1636 cm^{-1}, distinctive of the monomers, definite the formation of the terpolymer.

3.3. The influence of additive on pour point of crude oil

The four prepared additives were tested for reduction of pour point at different concen-trations namely 500, 1000, 2000and 3000ppm. The pour point depression results for alkyl Methacrylate-styrene- Maleic anhydride were measured and illustrated in Figure 2.
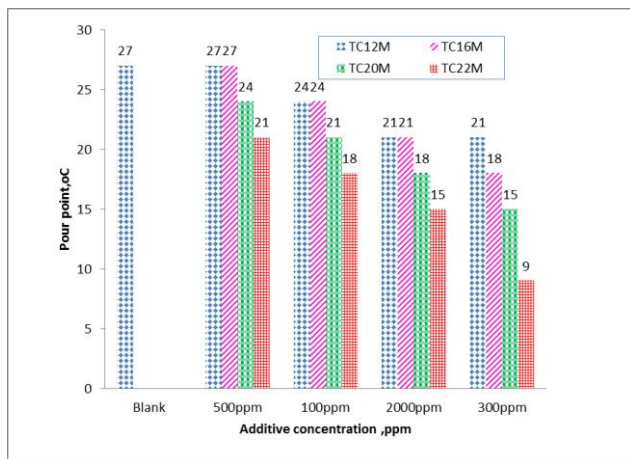
Figure 2. Effect of terpolmeric additives on the pour point of crude oil

Pour point of the crude oil sample is 27°C. The reduced extent of the four terpolymers with changed n-alkyl chain lengths $TC_{12}M$, $TC_{16}M$, $TC_{20}M$ and $TC_{22}M$ at several concentrations to pour point is shown in Figure 2. It can be seen from Table 4, the n-alkyl chain extent and concentrations of PPDs have very important effects on the reduction extent of PP. The influence of n-alkyl chain length of terpolymers is closely related to the content of the corresponding n-alkane in the crude oil, especially for their effect on the PP. The effects of the PPDs on reducing PP sometimes is unpredictable, because PP is closely related to the creation of three-dimensional network. TC22M exhibits the most considerable reduction on PP, at a concentration of 500ppm, TC22M reduces the PP by 6°C. And at a concentration of 3000ppm, TC22M exhibits the best effect on reducing PP. It decreases the PP by 18°C. TC20M has a moderate effect on PP, while TC16M and TC12M almost has no result on PP test.

Table 4.The effect of terpolymeric additives on the pour point of crude oil

Additive designation	Crude oil Additive concentration, ppm							
	Nil	500		1000		2000		3000	
	PP	PP	Δ PP	PP	Δ PP	PP	Δ PP	PP	Δ PP
TC12M		27	0	24	3	21	6	21	6
TC16M	27	27	0	24	3	21	6	18	9
TC20M		24	3	21	6	18	9	15	12
TC22M		21	6	18	9	15	12	9	18

3.3.1. Influence of the concentration of the various investigated copolymers on their efficiency in terms of pour point depression

With the progression of concentration of PPDs, the decrease extent of PP is basically a growth trend and Figure 2. The interaction of these additives with crude oil may occur through well matching of the alkyl side chain and polar ester groups of additive with that of n-paraffin of crude oil. The function of the additive's two moieties is further explained. The large proportions of alkyl side chain in combination with the polarity of ester groups formed and the free acid groups impart the additives the function as pour point depressant where the polar groups introduce decent dispersing action through interacting with the wax crystal and impeding the growth of wax crystals, and the extended alkyl side chain of the copolymer will be merged into the wax crystal of the crude oil. It also forms as many as possible active points for excessive nucleation to form a large number of small crystals thereby may prevent the crystal growth of wax crystals in three dimensional networks resulting in small proportions of free paraffin to prevent the oil flow with the reduction in temperature and, consequently, the pour point was reduced. [11].

3.3.2. Influence of the average molecular weights of the various investigated copolymers on their effectiveness in terms as pour point depression

The four synthesized terpolymer (TC12M, TC16M, TC20M and TC22M) were evaluated as PPD/FI at 3000 ppm concentration in fuel oil in terms of pour point depression. Their average molecular weights and polydispersity were determined by GPC analysis. Results are listed in

Table 3. Data obtained showed that the prepared terpolymer additives have different molecular weights varying from 28.858 to 41.513 and that the optimum effectiveness is achieved at the range of 28,858 to 30.512. Moreover, the results in Table 3 showed that TC20M and TC22M , with the lowest molecular weight (30,512 and 28,858) respectively accomplished the optimum pour point depression with respect to the other terpolymers, whereas, terpolymers (TC12M and TC16M), with the highest molecular weight (41.513 and 38.513) respectively achieved the least dejection. The results also show that the presentation of these terpolymers is almost improved with reducing the molecular weight. Thus it is concluded that average molecular weights and polydispersity index are substantial parameters controlling the effectiveness of the used terpolymer additives.

3.4. The influence of additive on rheology of crude oil

The rheological parameters for untreated and treated crude oil with 2000 ppm concentration of TC22M were determined at different temperatures namely 17^0C, 27^0C and 37^0C Figure 3 (a, b and c) represent shear stress against shear rate relationship.
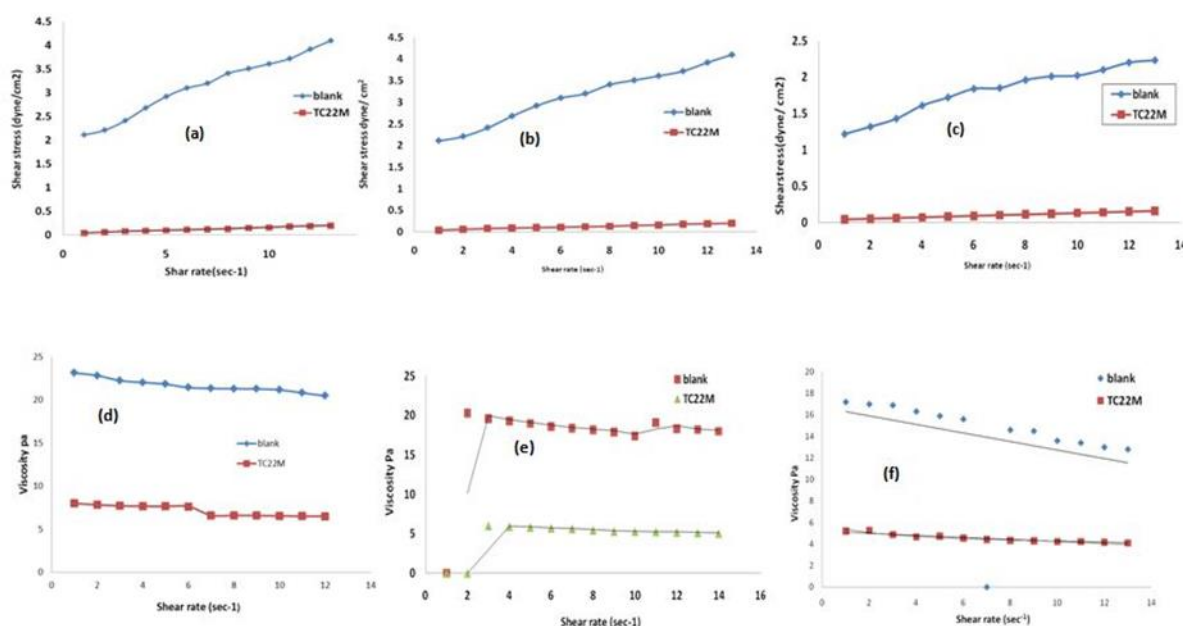

Figure 3. Effect of shear rate on shear stress at (a) 17ºC; (b) 27ºC and (c) 37ºC and the effect of shear rate on viscosity at (d) 17ºC; (e) 27ºC and (f) 37ºC of untreated and treated crude oil with 2000 ppm of TC22M

For the untreated and treated crude oil, shear stress increases sharply with increasing shear rate in such a way that the cold flow pattern follows a non-Newtonian yield pseudo plastic rheological behavior as shown in Figure 3(a, b and c). Increasing the shear rate leads to partial breakdown of the gel wax structure in the crude oil medium, leading to a steep increase in shear stress. The additives reduced the apparent viscosity and the decrease was more significant at lower shear rates. At high shear rates the apparent viscosity reached a constant value, which the equilibrium steady state was attained. The rheological data in Figure 3(d, e and f) are in a scale as apparent viscosity versus shear rate, it was seen that the apparent viscosity decreases with the increase of shear rate at all test temperatures and the rate of decrease was lowered at higher shear rates. This may be explained as follows; at temperatures around the pour point and at low shear rates the energy exerted by shear and dissipated energy in the crude matrix tends to halt down the wax crystals partially. The secondary bonds among the flocculated wax structure, thus leading to the partial decrease of yield stress and reduction of viscosity (thinning effect) without ability to flow. By increasing the shear rate, the dissipated

energy is high enough to overcome the yield stress and start flow, which is replicated by increasing the shear stress of the flow curve. At lower temperatures, the dissolute energy is mostly directed to the decrease of the progressive yield stress and thus less amount of energy is given to the decrease of viscosity, i.e., the diminishing effect is lowered [12-13]. Upon increasing the shear rate, the size of the agglomerates decreases and this process releases some of the continuous phase originally immobilized within the agglomerates. As a result, the effective dispersed phase concentration decreases, and leads to decrease of viscosity. The viscosity decreases with increasing the shear rate until the agglomerates are completely wrecked down into the basic particles. So the waxy crude oil system shows non-Newtonian characteristic [13].

3.5. Effect of flow improver & pour point depressant type on wax crystal modification

Photo analysis confirms other standard flow tests that evaluate the cold flow properties of untouched/ touched crude oil through wax crystallization behavior. It is applied herein for measuring the action of the previously prepared bifunctional flow additives as wax inhibitor /pour point depressant through wax alteration according to the type.

3.6. Type of additive and wax modification

Photomicrographs illustrated in Figure 4(a-e) have showed variant wax morphology changes according to the type of additive.
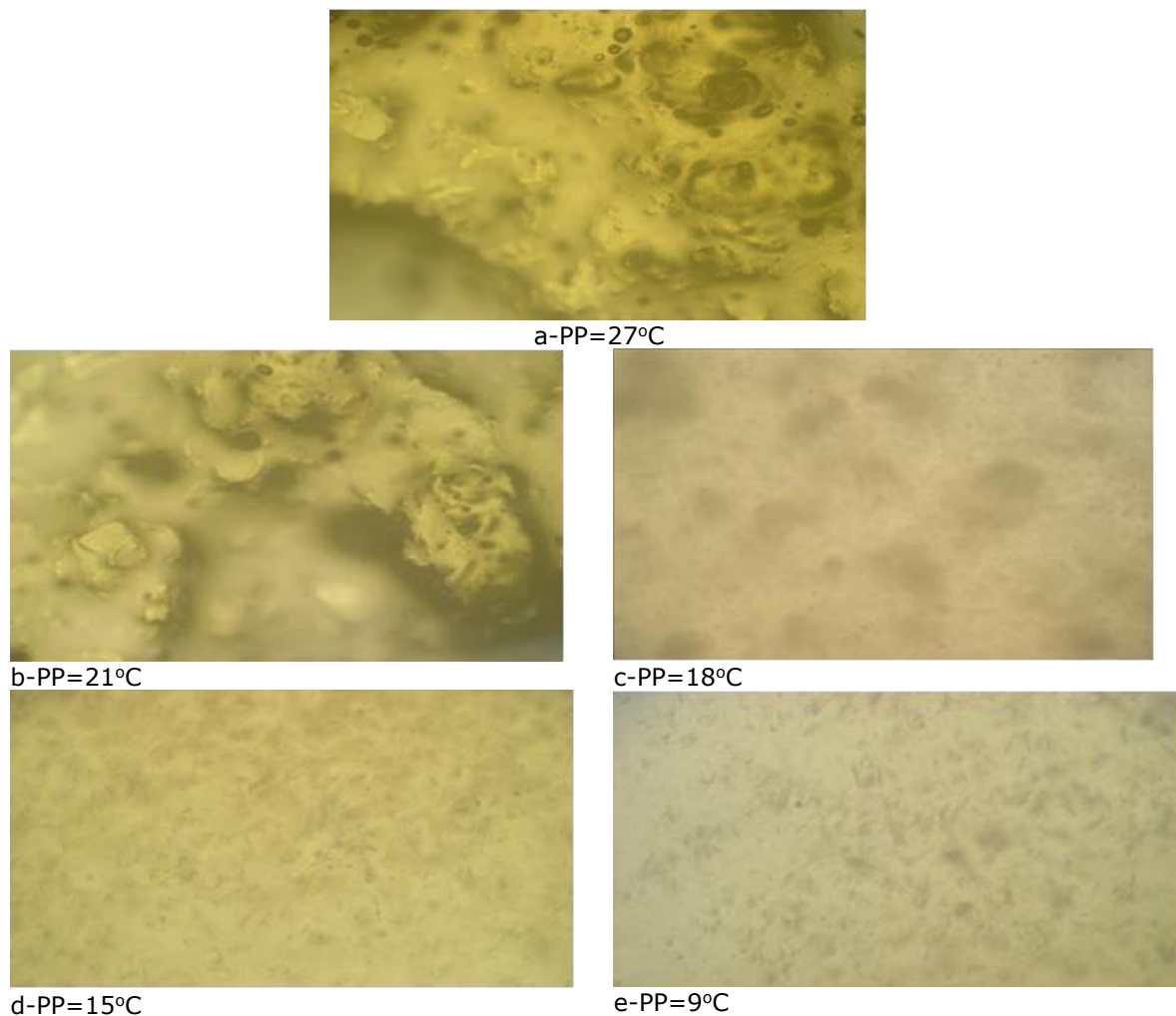

a-PP=27°C

b-PP=21°C   c-PP=18°C

d-PP=15°C   e-PP=9°C

Figure 4. Photomicrographs of a: fuel oil (FO) untreated), b: FO + 3000 ppm TC12M, c: FO +3000 ppm TC16M, and d: FO + 3000 ppm TC20M and f: FO + 3000 ppm TC22M

Figure (4a) of the untreated crude oil showed a large cyclic like crystals (PP=27°C) of approximate size of 100µm which on treatment with 3000ppm TC12M ($PP_{3000\ ppm}$ = 12°C) Figure (4b) has led to momentous reduction of wax crystal size. However, When crude oil was treated with 3000ppm TC16M and 3000ppm TC20M ($PP_{3000\ ppm}$ = 18°C, 15°C) respectively a higher wax variation degree was observed, as shown in Figure 4(c and d). But when the crude oil was treated with 3000ppm TC22M additive ($PP_{3000\ ppm}$ =9°C), the crystal conformation has been modified to involve many fine dispersed crystals, as shown in Figure (4e). From the obtained photography, the wax modification is increased to an upper degree in the order TC22M>TC20M > TC16M >TC12M i.e., there is a good correlation between wax modification and measured flow parameter.

4. Conclusion

The conclusion of this the work can be addressed in following points:

- All the prepared compounds are solvable in crude oil.
- The effects of terpolymers on PP and viscosity are consistent; the terpolymer which has a decent effect on reducing PP also has a good result on reducing viscosity.
- The proficiency of the prepared compounds as pour point depressants increases by growing the concentration and by lessening the molecular weight of the prepared terpolymer additives
- From the data, it was found that theTC12M showed the results (Δ pp = 6°C, at 3000 ppm). In the meantime, theTC22M exhibited the supreme pour point depression of the used crude oil (Δpp = 18°C, at 3000 ppm).
- The flow properties for crude oil were investigated by measuring the rheological parameters. The obtained data showed that, all additives have a positive effect on the dynamic viscosity, if they compared with the original values of the waxy crude oil.
- The photo analysis has been showed that a wax alteration caused by the effective pour point depressant on crystal growth generally alter the irregular large size crystals to form fine depressant wax crystals further enhancement of flow ability and dejections of pour point were obtained.

References

[1]   Khidr TT and Omar AMA. Anionic/Nonionic Mixture of Surfactants for Pour Point Depression of Gas Oil. Egyptian J. Pet., 2003; 13:21–26.
[2]   Al-Sabagh AM, Noor El-Din MR, Morsi RE and Elsabee MZ. Styrene-Maleic Anhydride Copolymers Ester Evaluate as Flow Improvers for Waxy Crude Oil. J. Pet. Sci. Eng. 2009; 65:139–146.
[3]   Khidr TT,.Doheim MM and El-Shamy OAA. Effect of Ethoxylate on Pour Point Depressant of Fuel Oil. Energy Sources,Part A Recovery, Utilization and Enviromental Effects, 2015; 37:1697-1703.
[4]   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 in Relation to Depressants for Lube Oil in Rheological Flow Properties. Egyptian Journal of Petroleum, 2012; 21: 19 -30.
[5]   Khidr TT and Ahmed SM. The effect of Cationic Surfactant Additives on Flow Properties of Crude Oil. Petroleum Science and Technology, 2016; 34: 1219-1225.
[6]   Al-Sabagh AM, Khalil TM, Sabaa MW, Khidr T T and Saad GR. Poly(n-Alkyl Itaconate-Co-Vinyl Acetate) as Pour Point Depressants for Lube Oil in Relation to Rheological Flow Properties. J. Dispers. Sci. Technol. 2012; 33:1649–1660.
[7]   Khidr TT, Azz EMS, Mutawaa SS and Omar AMA. Study of Some Anionic Surfactants as Pour point Depressants Additives for a Waxy Gas Oil. Indust. Lubricat. Tribol, 2007; 57: 64–68.
[8]   El-Gama, IM, Khidr TT and Guiba FM. Nitrogen – based copolymers as wax dispersants for paraffinic gas oils. Fuel, 1998; 77:375–385.
[9]   Al-Sabagh AH, El-Hamouly SH, Khidr TT, 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.
[10]   Al-Sabagh AH, El-Hamouly SH, Khidr TT, El-Ghazawy A and Higazy SA. Preparation the Esters of Oleic Acid-Maleic Anhydride Copolymer and their Evaluation as Flow Improvers of waxy Crude Oil. J. Dispers. Sci. Technol. 2013; 34: 1585–1596.

[11]   Ray SS, Pandey NK and Chatterjee AK. Effect of aromatics and isoalkanes on the pour point of different types of lube oils. Fuel 2009; 88: 1629–1633.

[12]   Al-Sabagh AH, Khidr TT, Moustafa HY, Mishrif MR, Al-Damasy MH. Synergistic effect between surfactants andpolyacrylates-maleinanhydride copolymers to improve the flow properties of waxy crude oil. Journal of Dispersion Science and Technology, 2017; 38: 1055-1062.

[13]   Li, H. and Zhang, J., A generalized model for predicting- Newtonian viscosity of waxy crudes as function of temperature and precipitated wax, Fuel, 2003; 82: 1387.

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