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Abstract - The main target of this work is to solve the transportation problems associated with the waxy crude oil particularly the deposition of paraffin wax during transportation and storage if the temperature of the crude drops below certain temperatures. This work aims to prepare different copolymers based on vinyl acetate and methacrylic acid monomers. The reactions involve copolymerization of vinyl acetate with methacrylic acid in different monomer ratios. The prepared copolymers then esterified using stearyl and behenyl alcohols. The chemical structure of the prepared copolymers and their characteristics were evaluated using FTIR and ¹HNMR spectroscopic techniques. The molecular weight of the polymeric additives was measured using GPC. The efficiency of the prepared copolymers were studied for their capability as pour point depressants (PPD) and flow improvers for Egyptian waxy crude oil to solve the problem of wax deposition during transportation and storage. The study showed that generally the CoVASMA esters were efficient in the role of both pour point depressant and flow improver for the tested crude oil.

Keywords : pour point, rheology, flow improver, pour point depressant, vinyl acetate methacrylate copolymer.

1. INTRODUCTION

In the last quarter of the 20th century, global demand for crude oil had a very stable yearly growth rate averaging 1%. This has changed radically in the first years of the 21st Century due to "Emerging Countries" like China and India whose dynamic economies resulted in a remarkable 1.8% global growth in demand for crude oil in 2009. Serious international studies still foresee that in the next 20 years, at least 80% of the world's energy requirements will come from petroleum, natural gas and coal. Consequently, oil will remain the dominant source of energy for the next half century. Crude oils are complex hydrocarbon mixtures containing nonpolar *n*-paraffins and polar components such as asphaltenes. According to some estimates from the International Energy Agency (IEA), heavy oil represents at least half of the recoverable oil resources of the world. Heavy oil is defined as petroleum which has a density equal or lower

than 20 API, but if petroleum has 10 API or less it is considered as extra heavy oil or bitumen, which is denser than water.

The incorporation of heavy oil to energy markets presents important challenges that require significant technological developments in the production chain. The transportation of heavy and extra-heavy oil presents many operational difficulties that limit their economical viability.

Pipelining is the most convenient mean for transportation of crude oils and derived products continuously and economically. However, transportation of heavy and extra heavy crude oils through pipelines is difficult due to the low mobility and flowability of the crude and wax and asphaltene deposition on pipeline wall surfaces.

Waxy crude oils always suffer serious problems during transportation and storage, particularly in cold environments; this arises from the presence of significant amounts of paraffin wax in the crude oil that impede the flow of crude oil due to wax precipitation. Regarding the composition of the waxy crudes, the high molecular weight *n*-alkanes (*n*-paraffins) are the main components in wax deposits.^{1,2} Waxes are heavy paraffinic solids that settle out of a crude oil to form a gel structure. Wax formation is a liquid-solid phase transition from a liquid mixture which is largely sensitive to a drop in temperature.³ In the petroleum industry, wax precipitation is undesirable because it may cause plugging of pipelines and process equipment. Wax precipitation is an old problem⁴⁻⁷. In this respect the wax deposition problem has been thoroughly studied both chemically and thermodynamically.⁸ The crude oil pipelining at temperatures lower than the pour point temperature (PPT) of the crude oil change the flow behavior of the crude oil dramatically, below this temperature there is no any flow behavior of crude oil.

Solid wax deposition is a challenging problem in crude oil production, transportation, and storage and causes huge economic losses for the petroleum industry.¹ The wax crystals deposition leads to higher viscosity of crude oil, with high transportation costs arises from the increased energy consumption for pumping, the decreased pumping capacity, and the

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reduction of the effective cross sectional area of the pipe via wax deposition. Wax deposition also increases the pipeline roughness which results in an increase in pressure drop.¹⁰ Avoiding and/or solving the wax deposition problems is therefore an economically beneficial target which can be highly achieved by introducing a polymeric chemical additive in the ppm level to the crude oil in order to reduce its pour point temperature.¹¹⁻¹⁴ Although, crude oil treatment with chemical additives is not the only known solution for inhibition of wax deposition, it remains the preferred solution over other options like pigging, heating, and biological treatments. Pour point depressants (PPD) and flow improvers are polymeric additives that used to decrease the pour point and enhance the flow characteristics of crude oil, respectively. In doing that PPD's and flow improvers should possess oil-loving long chains in addition to polar groups such as ester, amine, and hydroxyl groups.¹⁵⁻²¹ This study involves the preparation and evaluation of vinyl acetate methacrylic acid copolymer as pour point depressant PPD by changing the feed ratios of the two monomers and incorporating different alkyl side chains into the polymer backbone via esterification. Egyptian waxy crude oil was used to evaluate the efficiency of the above mentioned esters through measurements of pour point and rheological properties of untreated and additive treated crude oil.

II. EXPERIMENTAL

a) Materials

Vinyl acetate (VA), methacrylic acid (MAA), stearyl alcohol (SA), behenyl alcohol (BA), dibenzoyl peroxide (BP), and P-toluenesulfonic acid (PTSA) were obtained as analytical grade from Aldrich chemicals Co. (Germany). Butanone, dimethyl formamide (DMF), methanol and xylene were obtained from Adweic Chemicals Co. Egypt. Egyptian Waxy crude oil produced from Norpetco (Egypt) and delivered without treatment from Fardous field. The physicochemical characteristics and composition of Norpetco crude oil are listed in **Tables (1)**

Table 1 : The Physicochemical properties of Norpetco crude oil

Test	Method	Value
API gravity at 60 F	ASTMD-1298	41.1
SPECIFIC GRAVITY @ 60/60 F	ASTM D-1298	0.820
Wax content, (Wt%)	UOP 46/64	8.4
Asphaltene content, (Wt%)	IP 143/84	3
Water content vol%	IP 74/70	0.23
Kinematic Viscosity(cSt)@ 50 60 °C	ASTM D-445	7 4.3
Pour Point °C	QPC procedure	30

b) Copolymerization

The copolymerization reaction was carried out in three-neck glass flask equipped with magnetic stirrer, thermometer, nitrogen gas inlet and a reflux condenser. The reaction carried out using butanone as solvent in which vinyl acetate monomer dissolved. Dibenzoyl peroxide (0.1% by weight of the total monomer weight) is dissolved in suitable amount of butanone and used as initiator. The solution of dibenzoyl peroxide is added in four proportions during the first two hours of the reaction. In the beginning of the reaction the reaction flask was swept with nitrogen gas, then the temperature of the reaction mixture is raised to 80 °C and methacrylic acid monomer is continuously introduced during the reaction progress. At the end of the six hours of the reaction the copolymer was precipitated from solution in methanol. The precipitate was collected, washed with methanol, and dried in vacuum oven at 40 °C.

The above mentioned procedure were repeated with different mole ratios of the reacting monomers to produce copolymers with feed ratios namely (1:1), (1:2) and (2:1).

c) Esterification

The esterification reaction of the prepared copolymers was carried out in three-necked reaction flask fitted with reflux condenser, thermometer, and Dean stark separator at constant stirring. The reaction mixture is a solution of 0.02 mol of copolymer with one of the previously described ratios with 0.01 mole of alcohol (stearyl, or behenyl alcohol) was refluxed in 50 ml DMF in the presence of 0.1 % (wt/wt) PTSA as catalyst. The reaction was carried out at the refluxing temperature until theoretical amount of water was collected in the Dean stark trap. The resulting esters were washed out with water to remove the catalyst and any unreacted materials.

d) Characterization

The prepared esters, stearyl methacrylate- vinyl acetate copolymers (CoVASMA), and behenyl methacrylate- vinyl acetate copolymers (CoVABMA), were analyzed by FTIR as spectroscopic technique. Infrared (IR) spectra were performed on a Bio-Rad FTS 165 FTIR spectrophotometer using KBr pressed pellets or KBr salt plate for solid and liquid compounds, respectively.

¹HNMR using a 300 MHz Varian NMR 300 spectrometer using Dimethyl sulphoxide (DMSO) as solvent.

The molecular weight were characterized (in terms of Mw and Mn) and polydispersity index using Shimadzu's gel permeation chromatograph equipped with refractive index detector and polydivinylbenzene mix gel-D column. Tetra Hydro Furan (THF) with a flow rate 1 mL/min was used as mobile phase. Polystyrene was used as the standard.

e) Evaluation Tests

The additives consisted of 10 ml of toluene containing 3 g of each copolymer; each solution was stirred for 10 min at a doping temperature for homogenization.

Pour point test was made according to ASTM D97 test procedure at different concentrations of the prepared additives namely 1000, 2000, 3000, 4000, and 5000 ppm.

Viscosity and flow curves (Rheogram) were measured using Brookfield viscometer equipped with thermostated cooling system for temperature adjustment. To obtain consistent results with accurate rheological measurements, the memory of the evaluated crude oil samples has to be removed by heating at 80 °C while stirring. Tests started by heating the preconditioned untreated crude oil samples to 60 °C in an ultrasonic bath and then loading them into a hermetic bottle with an appropriate amount of flow improver. Finally, the temperature of the sample in the ultrasonic bath was maintained at 60 (1 °C for 30 min). The prepared additives were evaluated as flow improver for wax crude through rheological measurements at concentrations of 2000 ppm. Measurements were carried out at different temperatures below pour point of crude oils ranging from 21 to 12 °C. The experimental procedure started when the additives were mixed with crude oil at the prescribed concentration at 65 °C. Meanwhile, the viscometer cup is preheated to the same temperature, then loaded with 25 ml of the treated sample, and then the temperature is brought down to a constant temperature, at which the measurements will be achieved, at a low shear rate of 7.29 S⁻¹ (dynamic cooling). Shearing was continued for 15 minute at the test temperature before evaluation. The shear stress-shear rate relationship was recorded for the tested samples.

III. RESULT AND DISCUSSION

Free radical polymerization is a common method for the synthesis of many polymers. One drawback of free radical polymerization is uncontrolled structure of the produced polymer. In the present work, solution copolymerization of VA and MAA was carried out in 2-butanone as a solvent to control radical polymerization. The type and amount of initiator, temperature, and delayed monomer feeds have all been used to control the final structure and size of the polymer particles. Random copolymers of MAA with VA are difficult to produce by free radical polymerization, since MAA has a much higher reactivity than the VA monomer.²² In order to prepare PVAMA copolymer, MAA was added into the reactor fluid for a longer period of time during the reaction.

a) Chemical structures of the prepared additives

The FTIR spectra of PVAMA copolymer with different mole ratios, not given here for brevity, show bands at about 2950 cm⁻¹ represent the stretching absorption of -CH aliphatic present in both vinyl acetate and methacrylic acid, and the bands at about 1700 cm⁻¹ assigned for the absorption of carbonyl group. Also, the presence of broad band at in the range of 3400 cm⁻¹ is indicative for the presence of OH group in free carboxyl group of methacrylic acid. The absence of bands in the range of 1640-1680 cm⁻¹ which characterizes the C=C group indicate the completion of polymerization.

Also, the structure of PVAMA copolymer was confirmed by ¹HNMR as follow. **Figure 1** represents the ¹HNMR spectrum of PVAMA copolymer with composition ratio (1:2). The figure shows chemical shift at about 1.0 ppm due to the methyl protons present in MAA and signal at about 2.0 ppm assigned to the protons of methyl group from VA. Also, the figures contain bands at chemical shift 2.5 ppm which indicate the methylene protons from VA and signals at chemical shift about 3.5 ppm assigned to methylene protons from MAA, and the band at chemical shift about 5.3 ppm for CH protons adjacent to the acetate group in the vinyl acetate moieties. The clear signal at about 12.3 ppm is resulting from the free carboxyl group of MAA. The disappearance (or the presence of very weak bands) in chemical shift range of 6 – 6.5 ppm indicate the absence of vinyl protons and completion of polymerization.

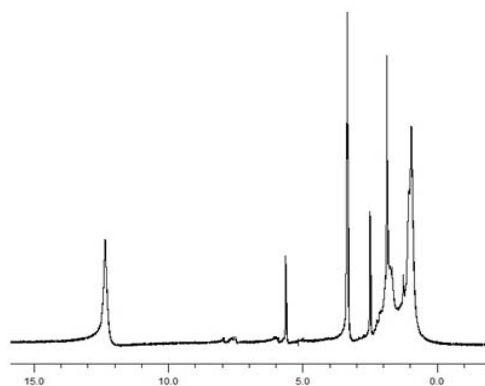


Figure 1 : ¹HNMR of VA: MAA 1:2 copolymer

Molecular weights data of the prepared polymers with the different feed ratios, number average molecular weight (M_n), weight average molecular weights (M_w) and polydispersity (PD= M_w/M_n), were determined using gel permeation chromatography (GPC) using THF as eluent and the results are summarized in **Table 2**. The molecular weight results indicated that the molecular weight increased by increasing either vinyl acetate or methacrylic acid

content. While the polydispersity increased with equimolar ratios of VA and MAA.

Table 2 : The average molecular weight of the prepared copolymer at different mole ratios

Polymer composition	PD	Molecular weight (g/mol)	
		Mw	Mn
PVAMA (1:1)	2.4	10,190	4,231
PVAMA (1:2)	1.69	170,015	100,382
PVAMA (2:1)	1.96	163,105	82,995

b) The influence of additive on pour point of crude oil

The solubility of paraffin in the lighter alkanes is greatly dependent upon temperature. When temperature drops below certain value, PPT, solid paraffin deposits appear and prevent the crude oil from flowing. The paraffin content of the tested crude oil was determined by urea adduction, and then subjected to gas liquid chromatographic analysis for determination of average molecular weight distribution. The structure and

composition of wax in crude oil are very important to select the suitable structure of wax dispersant to increase its flowability. However, still in most cases the wax dispersants having highly polar functional groups are used for improving flowability of wax crude oil. The n-paraffin content in the crude oil was found 12 wt % by urea adduction. Further analysis of n-paraffins by GLC for Norpetco crude oil was carried out to determine the carbon numbers as shown in **Figure 2**. From data represented in **Figure 2**, it has been concluded that the average carbon number was 44 and the molecular weight distribution expressed in $W_{1/2}$ has a broad distribution. It is obvious that the concentration of 50 wt % of the n-paraffin content in the crude oil in a broad range and a high average carbon number (44.2) tends to precipitate suddenly in the form of a solid at a fairly high temperature above the pour point. These n-paraffins have the ability to construct rapidly a massive interlocking network that hinders the response of the crude to additive at a preceding stage of formation of fine crystals.

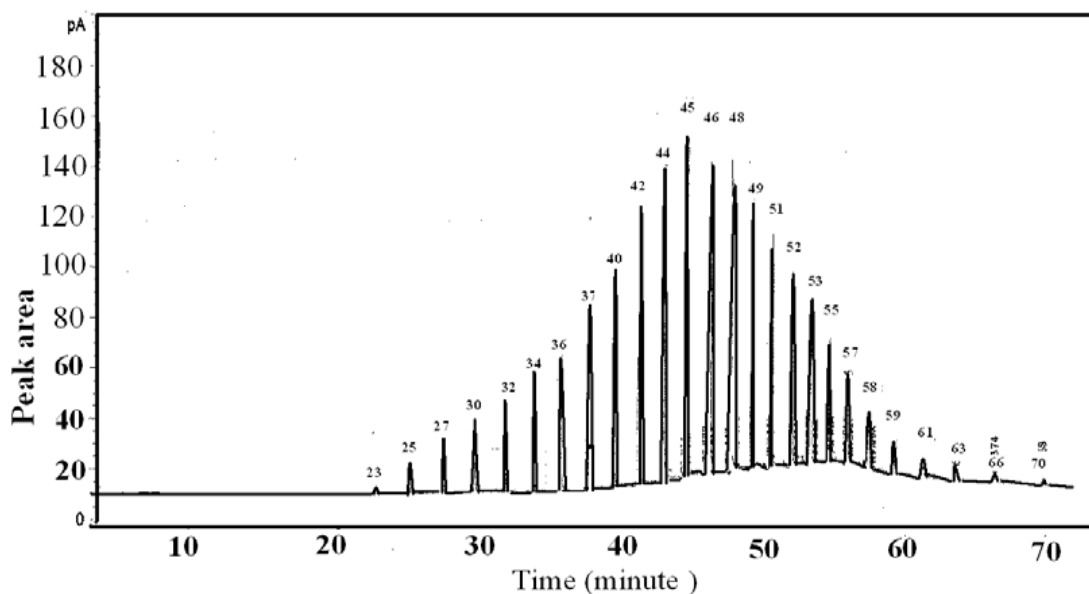


Figure 2 : Chromatogram for wax from Norpetco crude oil

The performance of PPD depends on the characteristics of crude oil including total wax content, the chain length and shape (linear or branched), quantity and type of wax present in crude^{9,20} The mechanism of pour point depression has been well explained,^{9, 21} the PPD in crude oil changes the wax crystal shapes from extensively interlocking plates to more compact crystals by co-crystallizing with the wax. The more similar the polymer structure to wax components, the better is its performance and the better its ability to attach to wax components and create a

barrier for networking of wax particles¹. The efficiency of these copolymers as PPD was evaluated through the pour point test procedure. The six prepared additives were tested for reduction of pour point at different concentrations namely 1000, 2000, 3000, 4000, 5000 ppm. The pour point depression results for stearyl methacrylate-co-vinyl acetate (CoVASMA) were measured and listed in **Table 3** Also the results of behenyl methacrylate-co-vinyl acetate (CoVABMA) are listed in **Table 4**.

Table 3 : The pour point of untreated crude oil and treated crude oil with CoVASMA

Copolymer composition	Pour point temperature (°C) at concentrations (ppm)					
	Nil	1000	2000	3000	4000	5000
CoVASMA (1:1)	30	27	15	15	12	12
CoVASMA (1:2)	30	15	15	15	15	12
CoVASMA (2:1)	30	15	12	12	12	12

Table 4 : The pour point of untreated crude oil and treated crude oil with CoVABMA

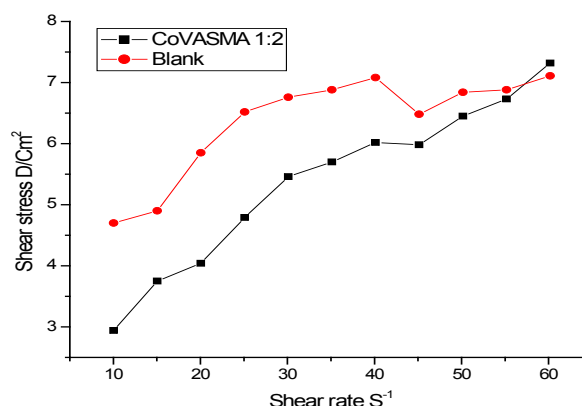
Copolymer composition	Pour point temperature (°C) at concentrations (ppm)					
	Nil	1000	2000	3000	4000	5000
CoVABMA (1:1)	0	30	27	27	27	27
CoVABMA (1:2)	0	27	27	27	27	24
CoVABMA (2:1)	0	30	30	27	27	24

The pour point data given in **Tables 3** and **4** shows the most effective copolymers for depression of pour point of this crude oil was the CoVASMA with mole ratio (2:1). It was able to reduce the pour point to about 12°C at concentration of 2000 ppm. 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 good dispersing action through interacting with the wax crystal and impeding the growth of wax crystals, and the long 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 inhibit 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. On the other hand the poor efficiency of behenyl esters for this crude oil can be explained by the increased chain length which affects the interactions between wax crystals and polymeric additives. This effect result in, not only, poor interaction between the polymeric additive and the paraffins in crude oil which make it less efficient but also may introduce adverse effect and assist wax nucleation and deposition.

c) The influence of additive on rheology of crude oil

The rheological parameters for untreated and treated crude oil with 2000 ppm concentration of CoVASMA (2:1) were determined at different temperatures namely 12°C, 15°C, and 21°C. **Figures 3,**

4, and **5** represent shear stress against shear rate relationships and **Figures 6, 7, and 8** represent the relationship between viscosity and shear rate. The yield values of of neat crude oil and crude oil in presence of 2000 ppm concentration of CoVASMA (2:1) are displayed in **Table 5**. Investigation of the previous data shows that the CoVASMA (2:1) was able to modify the flow and rheological behavior of the treated crude oil by decrease the yield shear stress value. The decrease in yield shear stress values increase with increasing the temperature. The higher efficiency of CoVASMA with mole ratio (2:1) in lowering the yield shear stress value of crude oil may be attributed to the fact that the polar groups present in the polymeric backbone of the additives were able to form some type of physical attraction with polar moieties of resins and asphaltenes present in the crude oil such as hydrogen bond. The high polarity of this additive may be rationalized by presence of polar ester groups in the polymer in addition to polar acetate groups from vinyl acetate.

**Figure 3 :** Rheogram of untreated and treated crude oil with 2000 ppm of CoVASMA (1:2) at 12 °C

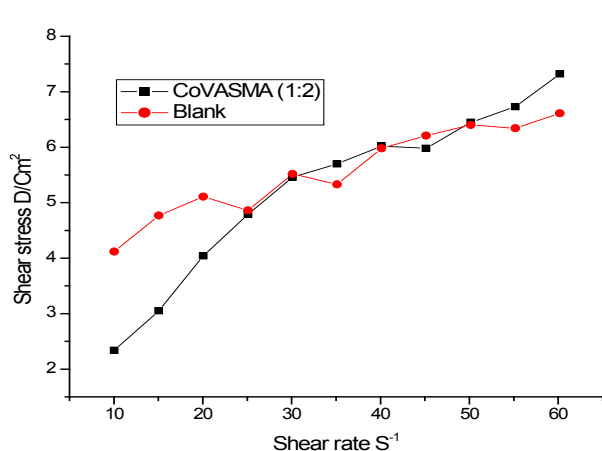


Figure 4 : Rheogram of untreated and treated crude oil with 2000 ppm of CoVASMA (1:2) at 15 °C

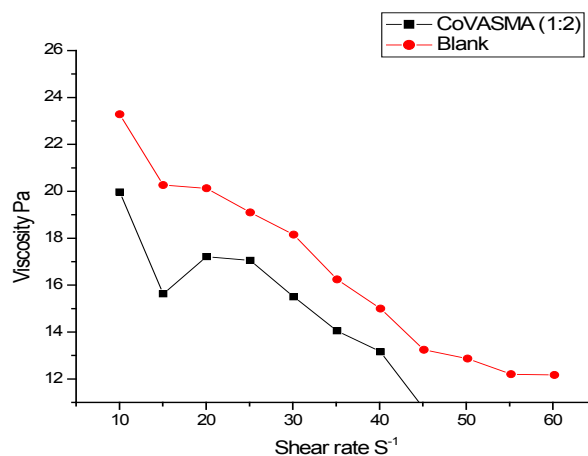


Figure 6 : Effect of shear rate on viscosity of untreated and treated crude oil with 2000 ppm of CoVASMA (2:1) at 12 °C

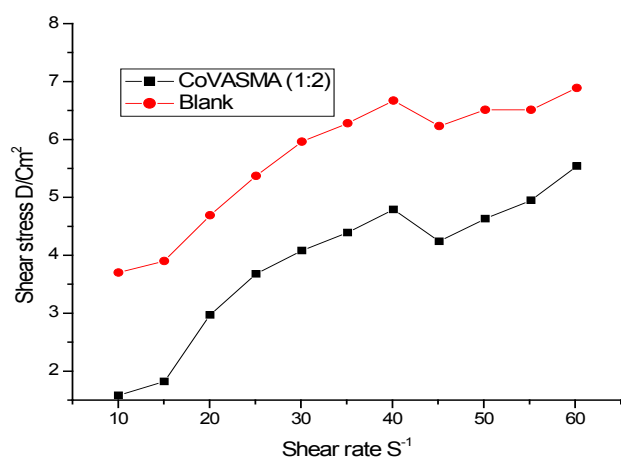


Figure 5 : Rheogram of untreated and treated crude oil with 2000 ppm of CoVASMA (1:2) at 21 °C

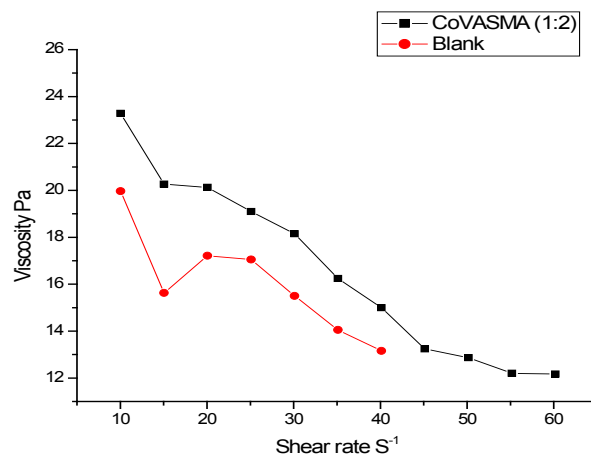


Figure 7 : Effect of shear rate on viscosity of untreated and treated crude oil with 2000 ppm of CoVASMA (2:1) at 15 °C

Table 5 : Yield value of untreated and treated crude oil with 2000 ppm Concentration of CoVASMA (2:1)

Oil sample	T °C	Yield value (D/cm²)
Untreated	12	4.89
	15	3.93
	21	3.52
CoVASMA (2:1)	12	2.63
	15	2.09
	21	1.39

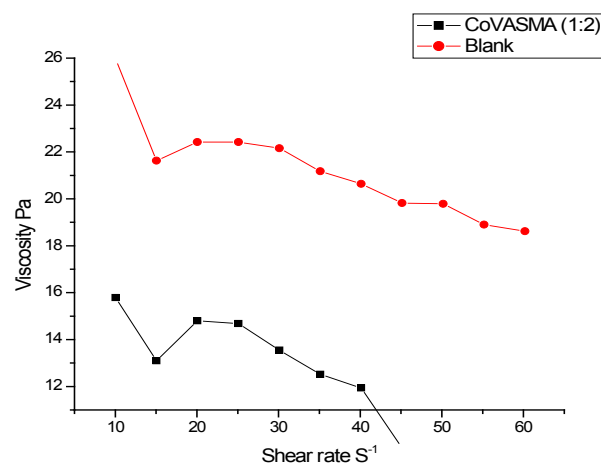


Figure 8 : Effect of shear rate on viscosity of untreated and treated crude oil with 2000 ppm of CoVASMA (2:1) at 21 °C

The obtained results for pour point and viscosity showed good correlation. This may be explained in terms of the ability of CoVASMA (2:1) to introduce strong interaction with the wax crystals modifying their crystal structure and forming small crystals. This in turn inhibits the probability of wax crystals to agglomerate and thereby depress the pour point. In case of rheological measurements the task of the additive was relatively easier since the rheology testing involves shearing that assist to break probable aggregations of wax producing particles whose size and shape are easier to disperse by the additive and the net results is decrease in the yield shear stress and viscosity of crude oil that correlate well with the results of pour point depression.

IV. CONCLUSION

In this work six polymeric additives with different composition were synthesized and evaluated as pour point depressants and flow improvers for Egyptian crude oil. The copolymers of CoVASMA, particularly the copolymer with monomer feed ratio (2:1), were satisfactorily able to act as pour point depressants (PPD's) and flow improvers. They were able significantly to improve the viscosity of the tested crude oil in as well as decrease in the crude oil pour point. In this study it was clear the effect of the length of alkyl side chain of the polymeric additive in the response of the crude oil to the additive introduced.

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