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Studies on the Influence of Long Chain Acrylic Esters Co-Polymers Grafted With Vinyl Acetate as Flow Improver Additives of Crude Oils

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ABSTRACT

A variety of techniques have been employed in order to reduce problems caused by the crystallization of paraffin during the production and/or transportation of waxy crude oil. Flow improvers are used extensively to increase the mobility of crude oil. In this study, the influence of the PEAA graft co-polymer (PEAA- g-VA), as flow improver, on the viscosity and pour point of some Egyptian waxy crude oils. The produced purified and characterized by FT-IR and ^{1}*HNMR and rheological measurements. The shear rate-shear stress and shear rate-apparent viscosity were measured at different concentration (from 500 to 3000 ppm) and temperatures below and equal the pour point temperature. The copolymer leads to a large reduction in the pour point of samples of Khalda Petroleum Co. (KhPC) crude oils. The polymeric additives were diluted with xylene and added by different doses ranged from 500 to 3000 ppm to crude oil to reduce its pour point. The pour point measurements show good reduction of pour point temperature depending on the composition and location of Khalda crude oil. Thus establishing the large efficiency of the products synthesized in this work.*

Keywords: Waxy crudes, Pour point depressants, Flow improvers.

INTRODUCTION

Polymers such as vinyl acetate copolymer, acrylate copolymer and their derivatives **[1, 2]** are the main additives used to improve the flowability of very waxy crude oil, diesel fuel and other base oils at low temperature. It should be noted that polymer additives are not equally effective with the various crude oils, nor are they necessarily effective at all **[3].** It is presumed that effective additives have a good match between the polymer and crude 7, such as structure, composition and content. However, how the polymer flow improver works is not clear. Usually, more attention has been paid to the interaction of the polymer flow improver with wax **[5-8]**.

Inhibition of wax crystallization is considered to occur in the presence of polymer by nucleation, co-crystallization or adsorption **[7, 8]**. It is reported that resin and asphaltene are natural pour point depressants **[9]**. Recently, **Ei-Gamal et al**. pointed out that the combination of polymer flow improver with asphaltene is highly efficient in improving the flowability of waxy crude **[5]**. The rheological behaviour of a crude oil is highly influenced by its chemical composition, temperature and the current, as well as previous thermal history. High waxy crudes exhibit a non-Newtonian character, often with a yield stress at and below their pour point temperature. At a sufficiently high temperature the crude oil, although chemically very complex, is a simple Newtonian liquid **[10]**. If the waxy crude oil is allowed to cool, wax will crystallize, agglomerate and entrap the oil into its structure. This phenomenon often happens if the ambient temperature of the place is below the pour point of the crude oil. Pretreatment of the crude oil is necessary for transportation of these waxy crudes through the pipeline. Pretreatment of the crude oil with flow improver is one method by which the rheological character of the gelled waxy crude is changed for easier transportation **[10]**.

The present work, aims to synthesis of co-polymers from PEAA and grafted with vinyl acetate by reaction of PEAA with fatty alcohol or amine then graft by vinyl acetate in presence of benzoyl peroxide as initiator, and investigates the obtained graft co-polymers as pour point depressants and flow improvers for waxy crude oil.

MATERIALS AND METHODS

2.1. Materials

Poly Ethylene acrylic acid (PEAA) collected from waste material. Hexadecyl alcohol (HDA), Hexadecyl amine (HDM), Vinyl acetate (VA), Benzoyl peroxide (BzPO) and P-Toluene sulfunic acid monohydrate (PTSA) are from Aldrich Chemicals. Egyptian waxy crude oil, Khalda Petroleum Co. (KhPC), was used for evaluating the performance of the synthesized polymeric additives.

2.2. Synthesis of Graft copolymers

PEAA-HDA and HDM copolymers were prepared by reacting PEAA waste with HDA or HDM under N_2 gas at 140 ^{o}C in o-xylene in the presence of 1% PTSA (wt % based on total weight of reactants). The reaction was carried out in a four-neck glass flask equipped with a stirrer, thermometer, nitrogen gas inlet and a reflux condenser. The water of the reaction was removed throughout the course of the reaction using Dean and Stark separator. The PEAA copolymer was first dissolved in refluxing o-xylene, and then PTSA catalyst and HDA or HDM were added to reaction medium. The product was grafted with vinyl acetate (ratio of reactants are 65% co-polymer to 35% vinyl acetate) in the presence of benzoyl peroxide as initiator for 6h to produced four samples as the fowling types (PEAA-C_{16}OH, PEAA-$C_{16}NH_2$, PEAA-C_{16}OHVA and PEAA-$C_{16}NH_2$VA).

2.3. Pour point measurement

The tested crude oils (50 ml) were heated up to 60 ^{o}C and the PPD additives were added at different concentration. The solution was transferred to bottle test tube in water bath cooled at 48 ^{o}C. The tube was transferred to another cooling bath cooled down to 24 ^{o}C. The tube was transferred to cooling bath cooled down to 0 ^{o}C, then the pour point temperature was measured at temperature 48 ^{o}C, **ASTM D 97-93**.

2.4. Rheological measurements

A Haake viscometer model Rotovisco RV12 was utilized to measure the dynamic viscosity for untreated and treated crude oil with some selected pour point depressants at different concentrations (from 500 to 3000 ppm) and at different temperatures above and below pour point of crude oils ranging from 36 to 15 °C. Yield point, and apparent viscosity values were determined **[11].**

RESULTS AND DISCUSSION

3.1. Characterization of Graft Co-polymers

The present work aims to prepare graft co-polymers soluble in petroleum crude oil to be evaluated for improving flow properties of waxy crude oil. All graft co-polymers have to be purified before characterization. The purified copolymers were analyzed by FTIR spectroscopy. In this respect, increasing of peak intensity at 1735 cm^{-1} and decreasing of peak intensity at 1700 cm^{-1}, which represent C=O stretching of ester group and carboxylic groups, indicates the conversion of carboxylic acid groups into ester groups. Furthermore, the appearance of strong peak at 1100 cm^{-1} in all spectra, C-O vibration, indicates the formation of ester grafts for PEAA copolymers. On the other hand, the disappearance of the broad peak at 3450-2800 cm^{-1} (–OH stretching of COOH group) can be attributed to the formation of ester groups for all grafts. A strong absorption of bending vibration at 721cm^{-1} can be attributed to the presence of C-$(CH2)_n$-C as long alkyl chain moiety of the ester graft. On the other hand appearance of peak at 3010 cm^{-1} (CH stretching of aromatic) indicates the ester groups produced onto PEAA backbone as side chain.

To analyses co-polymer containing > 20-40 mol% VA, the absorption bands at 1372 cm^{-1} (rocking CH_3 in acetate groups) and at 2925 cm^{-1} (stretching CH_3 in ethylene units) **[12, 13]** were used.

The new signals at 1.97, 4.9-5.3 and 3.8 ppm in all spectra of PEAA grafts which attributed to $COOCH_3$, $COOCH_2$ and CHCO of VA, indicate that VA was grafted onto PEAA chains. On the other hand, the signals at 1.188 and 1.42 ppm are observed in all spectra and can be attributed to CH_2 of ethylene and VA, respectively. The presence of singlet and triplet signals at 0.812, 1.2 ppm (CH_3) in spectra of all samples were studied indicate that COOH group of PEAA were esterified with alcohols and amides.

On the other hand, the signals at δ= 1.25 ppm of the methylene protons in the PE backbone and δ= 3.65 ppm of the grafts copolymers are observed in all spectra and indicate that the ester and amide groups were formed from PEAA with alcohols and amides.

3.2. Pour point measurement

3.2.1. Effect of Additives on Pour Point of the Tested Crude Oils

The high wax crude oils are characterized by high pour point, high viscosity, high gel strength, and abundant wax deposits. It is well known that, as the paraffin wax content increases in crude oil, this leads to difficult solubility of wax in oil, in some cases forming a separate solid phase.

Chemical additives, referred as pour point depressants, flow improvers, paraffin inhibitors or wax crystal modifiers, are widely used for overcoming the problem worldwide. These additives have received the greatest acceptance due to its simplicity and economy. These additives function by one or more several postulated mechanisms, viz. nucleation, adsorption, co-crystallization and improved waxy solubility, which result in the formation of smaller wax crystals with more regular shape **[14]**.

Polymers such as vinyl acetate copolymer, acrylate copolymer and their derivatives **[14]** are the main additives used to improve the flowability of very waxy crude oil, diesel fuel and other base oils at low temperature.

The relations between ΔP and additive concentrations for crude oils without and with additives (PEAA-C_{16}OH, PEAA-$C_{16}NH_2$, PEAA-C_{16}OHVA and PEAA-$C_{16}NH_2$VA) are shown in **Figures (1-5).** The pour point reduction was calculated by the following equation:

$$\text{Pour point reduction } (\Delta P) = PP_{pure} - PP_{add}$$

Where, PP_{pure} is the pour point of the pure crude oil and PP_{add} is the pour point of the crude oil containing additives.

These figures show that the ΔP value increased with increasing of additive concentrations from 500 ppm to 5000 ppm for KhPC crude oil. On the other hand, the **figures (1-5)** indicate that the prepared graft co-polymers can be used as pure point depressant depending on the composition of crude oils.

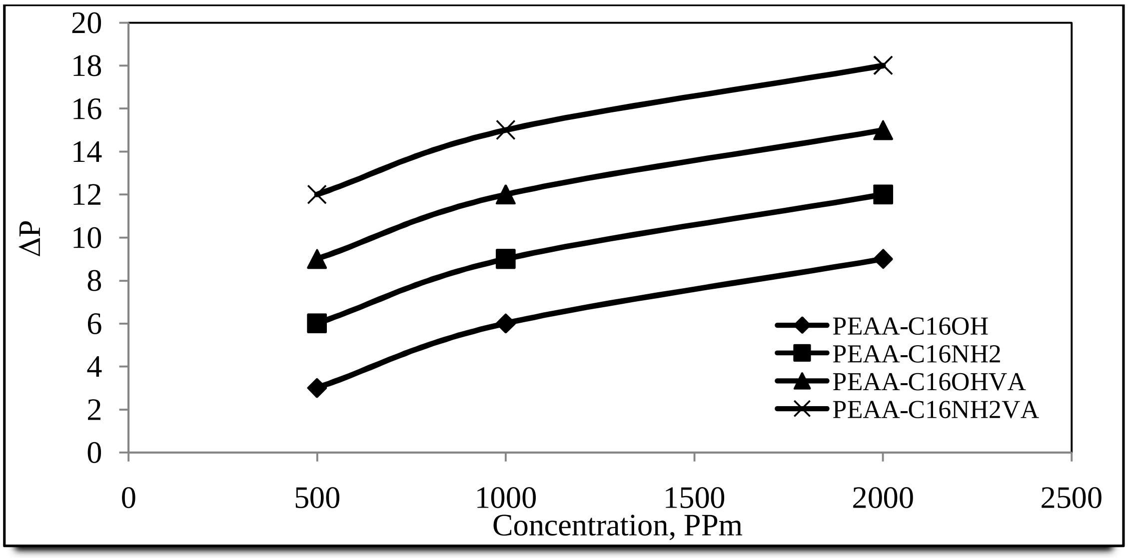

Figure 1: Relation between ΔP and concentration of the graft co-polymers on Oum Baraka crude oil.

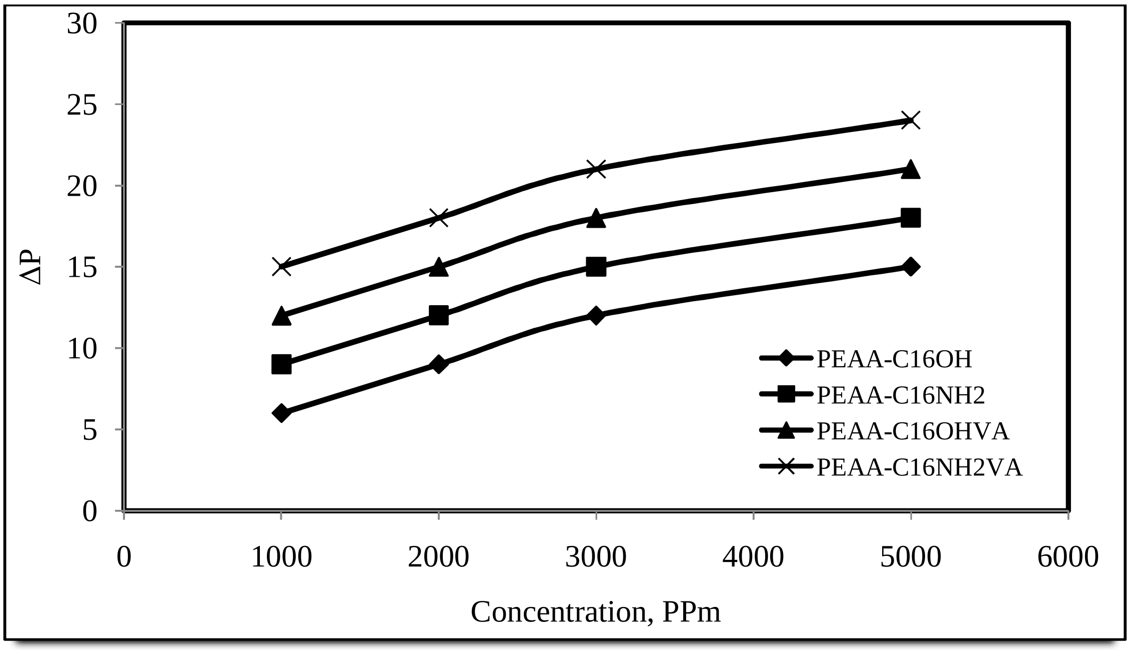

Figure 2: Relation between ΔP and concentration of the graft co-polymers on Khepr crude oil.

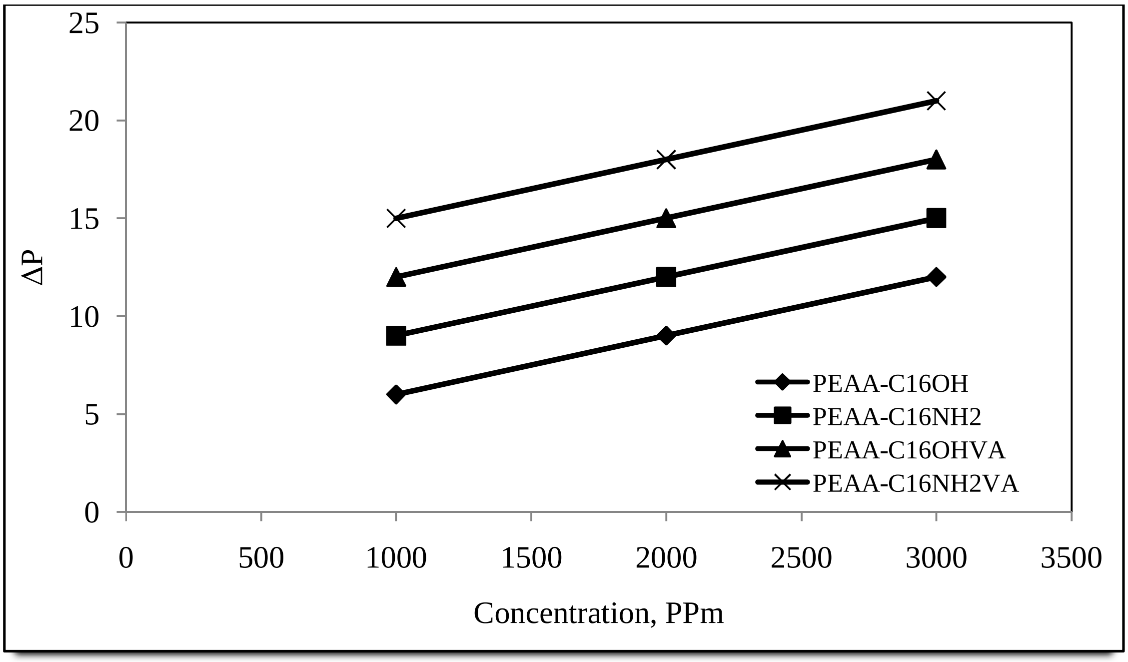

Figure 3: Relation between ΔP and concentration of the graft co-polymers on Sumpetco crude oil.

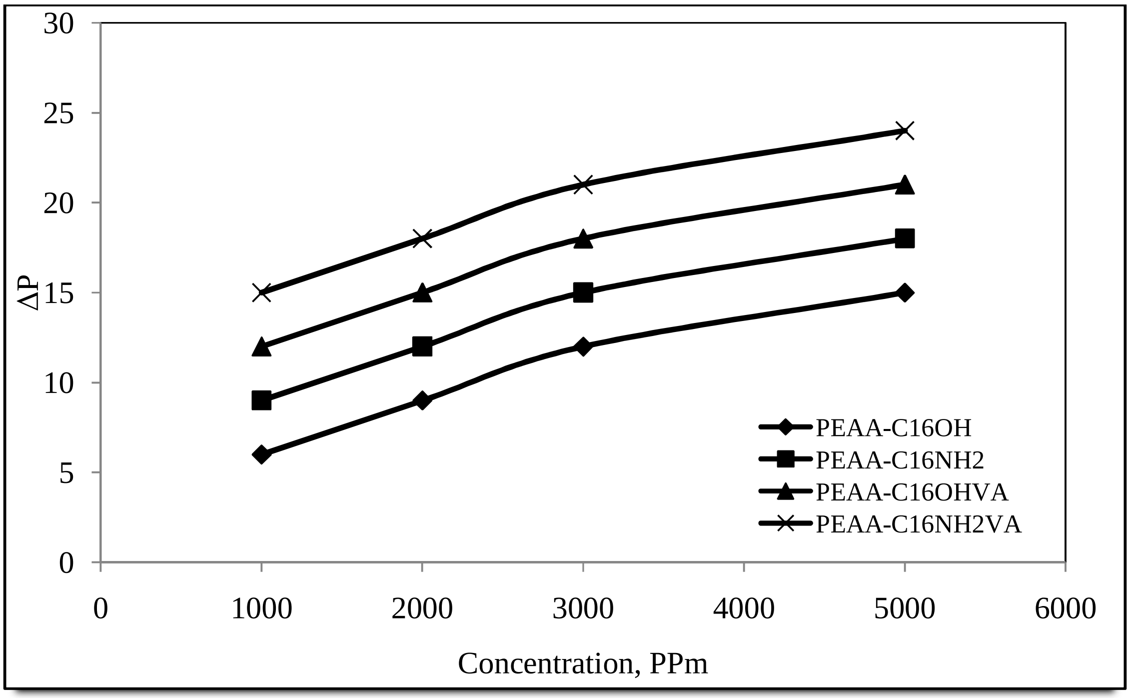

Figure 4: Relation between ΔP and concentration of the graft co-polymers on Salam Base crude oil.

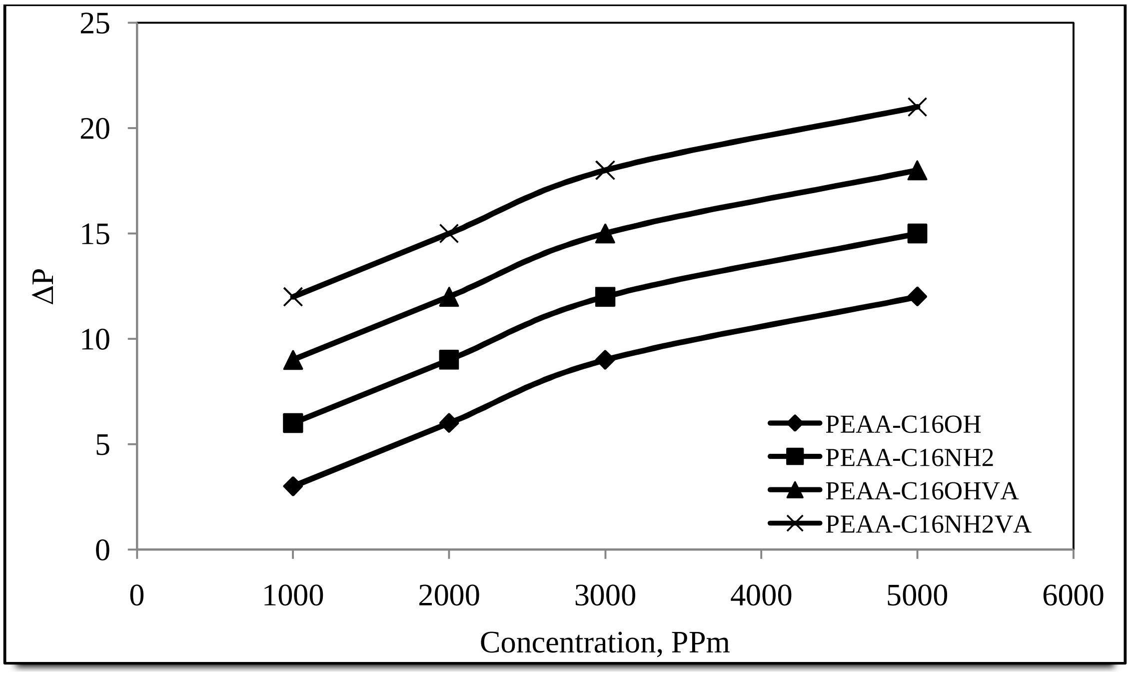

Figure 5: Relation between ΔP and concentration of the graft co-polymers on Khalda crude oil.

Figures (1-5) illustrate the results obtained from the pour point measurements for KhPC crude oil. Pour point values reduction higher than 21 ^{o}C (ΔP values) were achieved by adding 500 and

5000 ppm of graft PEAA copolymers to the crude oil. This means that, in this concentration range, the additive co-crystallizes with the paraffin, modifying their crystals.

3.3. Rheological Measurements:

3.3.1. Evaluation of PEAA Grafts as Flow Improver

PEAA graft co-polymers were evaluated for their performance as flow improvers for the tested crude oils through rheological measurements at concentration from 500 to 5000 ppm. Measurements of the shear stress – shear rate relationship were carried out at different temperatures ranging from 36 °C to 15 °C. The apparent viscosity – shear rate relationships for the untreated and treated crude oils at the selected concentration (3000 ppm) of PEAA graft copolymers are plotted in **Figures (6-8)** as flow improvers at different temperatures.

It was observed that the PEAA graft co-polymers having alkyl side chains are efficient additives as flow improver. On the other hand, the apparent viscosity – shear rate relationships show non-Newtonian pseudoplastic behaviors at different low concentrations and temperatures (equal or below their pour point) but their yield stress and viscosity values were decreased as compared with untreated crude oils even at low temperatures. However, the dynamic viscosity decreases with increasing the shear rate reaching a limiting value at high shear rate. This infinite shear rate viscosity is known as the apparent viscosity **[15].**

These data indicate that PEAA co-polymeric additives have the ability to disperse asphaltene particles around the wax crystals and improve the flow behavior of the tested crude oils. The behavior of decreasing rheological parameters after addition of the prepared co-polymers can thus be attributed to their chemical structure. The high polarity of oxygen in the ester group along the co-polymer chain played a role in preventing the agglomeration of wax crystals in crude oil **[16].**

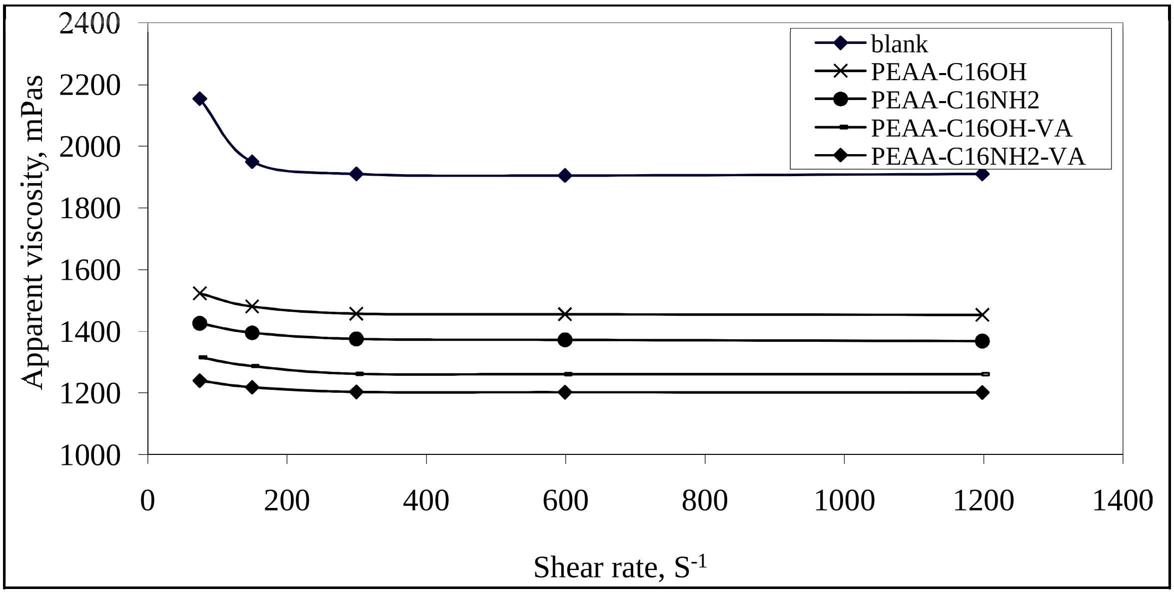

Figure 6: Relation between shear rate and apparent viscosity of Khalda Crude oil with PEAA graft co-polymers at 3000 ppm and at 15 °C.

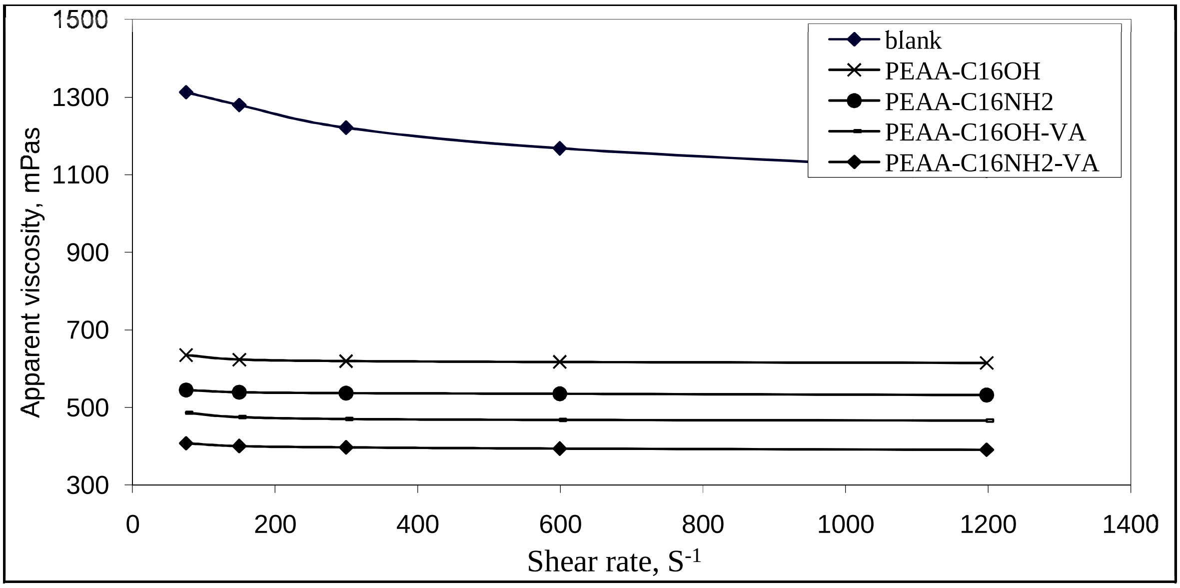

Figure 7: Relation between shear rate and apparent viscosity of Khalda Crude oil with PEAA graft co-polymers at 3000 ppm and at 27 °C.

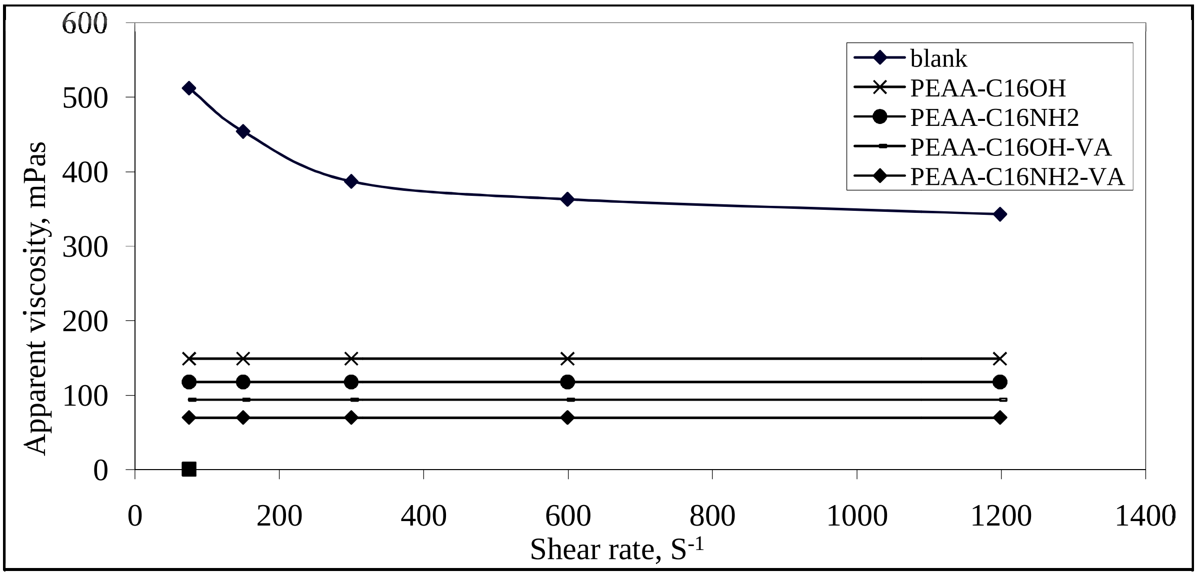

Figure 8: Relation between shear rate and apparent viscosity of Khalda Crude oil with PEAA graft co-polymers at 3000 ppm and at 36 °C.

3.3.2. Effect of temperatures and shear on the Rheological behavior of Untreated and Treated Crude Oils

The shear and thermal history play an essential role in identifying this flow behavior. The lowering of temperature of crude oils increasing pour point, yield stress, viscosity and progressive wax deposition **[17]**.

To supplement a realistic low temperature flow behavior of the tested crudes, rheological measurements have to be evaluated. Hence, these additives were evaluated for their performance as flow improvers for the tested crude through rheological measurements at concentration of 500-5000 ppm. Measurements of the shear stress – shear rate relationship were carried out at different temperatures ranging from 15 ^{o}C to 36 ^{o}C.

The shear stress – shear rate relationships for the untreated and treated crude oils at different concentrations of PEAA-DcA are plotted in **Figures (7-10)** at different temperatures. These figures illustrate the fitted experimental data of both shear stress and shear rate measurements according to the Bingham plastic model. The obtained data of $\eta_{p,}$ τ_y and correlation coefficient were determined for all tested crude oils at different temperatures and are listed in **Tables (1-4)**. However, the linear plots of the shear rate-shear stress curves can be extrapolated to zero shear rates and the intercept with the y axis is the Bingham yield value ($\tau\beta$). The Bingham yield value is defined as the shear stress required for initiating flow and it is important because it measures the ability of fluid to restart its flow after shutdown **[18].**

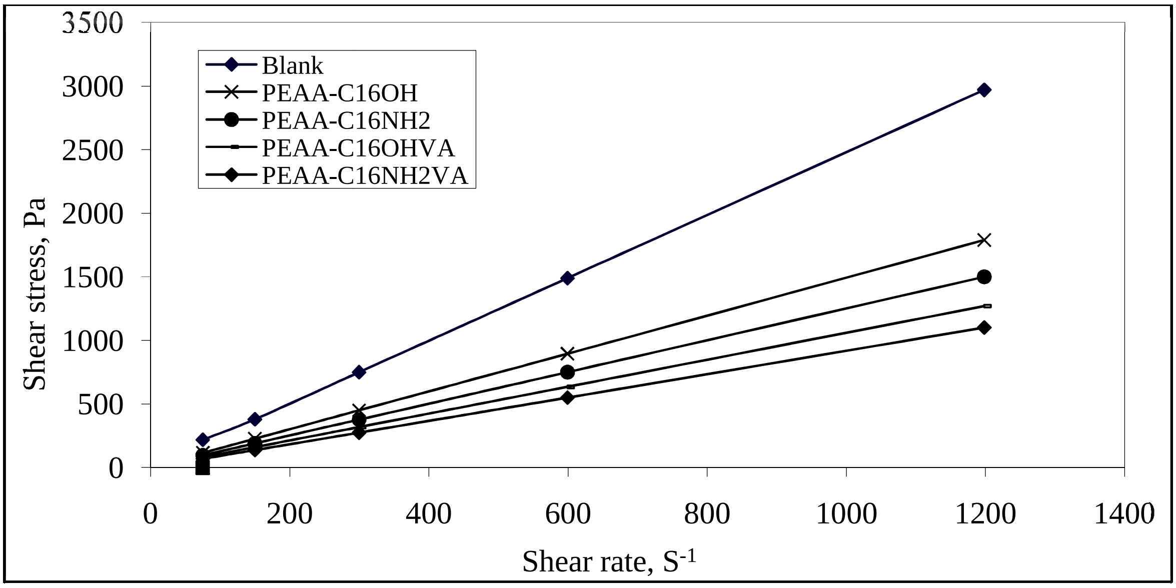

Figure 9: Relation between shear rate - shear stress of Khalda Crude oil with PEAA graft co-polymers at 3000 ppm and at 15 ^{o}C.

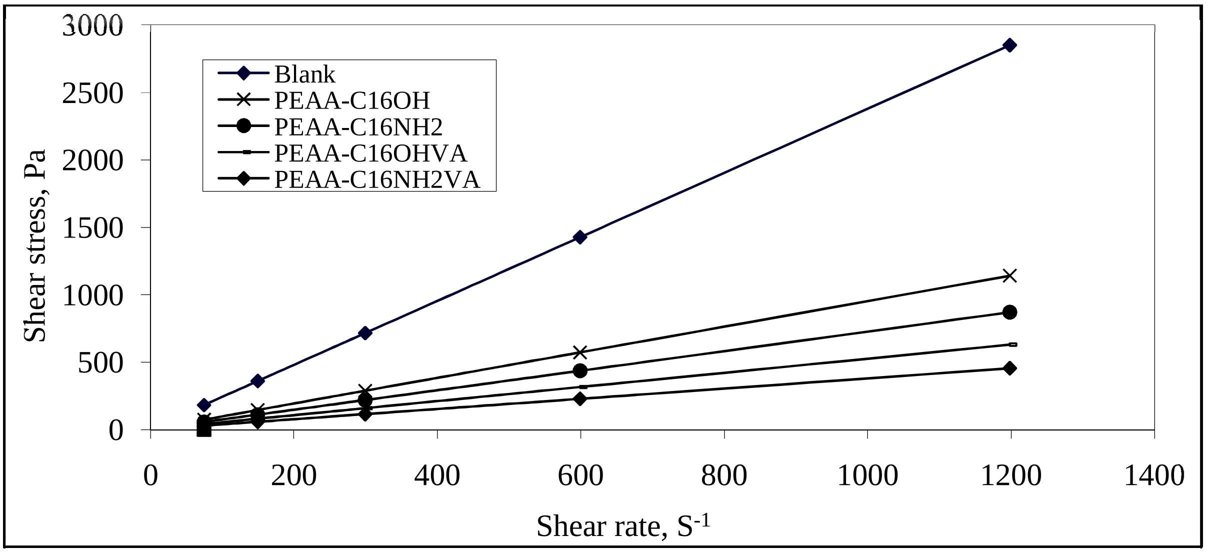

Figure 10: Relation between shear rate - shear stress of Khalda Crude oil with PEAA graft co-polymers at 3000 ppm and at 27 °C.

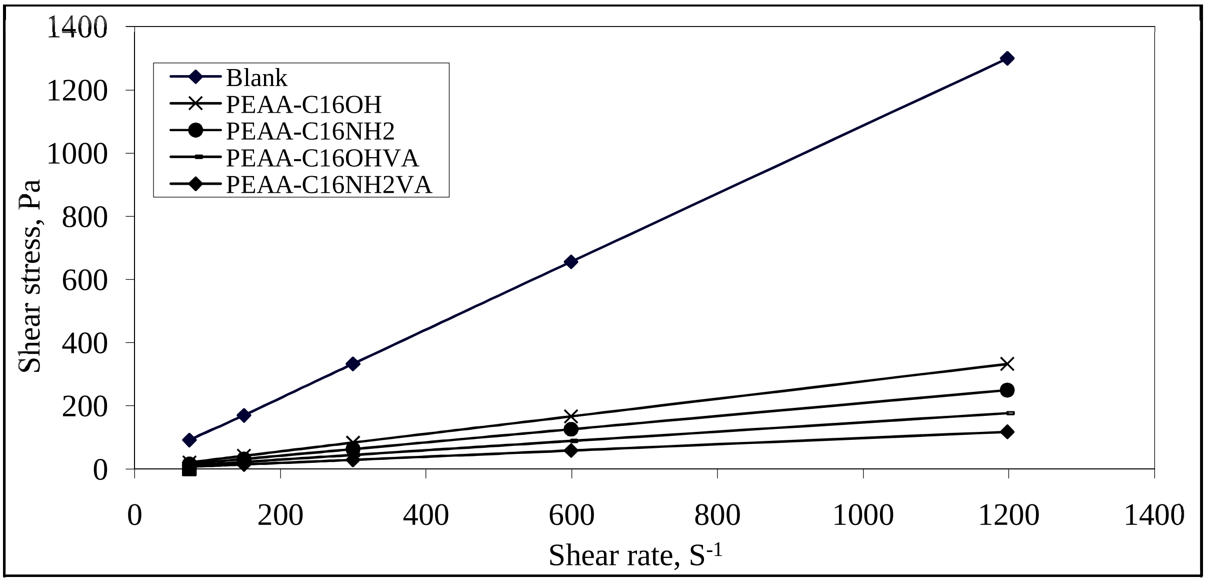

Figure 11: Relation between shear rate - shear stress of Khalda Crude oil with PEAA graft co-polymers at 3000 ppm and at 36 °C.

On the other hand, the apparent viscosities (mPaS) of the untreated and also treated crude oil with PEAA graft co-polymers were determined at different temperatures to evaluate the effect of the polymers on the viscosities of the crude oil. The data indicate that the viscometric behaviors of the treated crude oil depend on the crude oil compositions and the structure of the prepared PEAA co-polymeric additive. In this respect, the values of the plastic viscosity (mPaS) and yield values (Pa) are found to decrease by the addition of PEAA graft co-polymeric additives even at low concentrations (500 ppm). It is obvious that the plastic viscosity and yield stress values decreased significantly with increasing the concentration of the additives with crude oil up to

5000 ppm. **Figures (9-11)** illustrate the fitted experimental shear stress-shear rate measurements according to the Bingham plastic model for the selected samples. They show that the minimum yield stress was attained at 5000 ppm concentration for the additives with crude oil. This can be attributed to the interactions between the additives and crude oil constituents. Eventually, the final activity of the polymeric additives as flow improver for petroleum crude oil is judged by the degree of interaction of the two structures, and by relating the physicochemical properties of the polymers with wax, resin and asphaltene composition of crude oil **[17]**. The synthesized PEAA graft co-polymers were tested for improving the cold flow properties of the tested crude oils in term of the rheological parameters of yield point and plastic viscosity.

The data listed in **Tables (1-4)** for treated crude oils indicate that the length of side chain of C_{16} decreases the plastic viscosity and yield stress for the crude. This may be explained by the lack of interaction between the alkyl chain moieties with the n-paraffines in the wax constituent of the crude oils. In our system, the mechanism for improving the crude oil viscosity by using additives can be referred to its ability to disperse asphaltene molecules. The additives disperse the asphaltenes and concentrate them on wax crystals to impede the formation of large crystals. Therefore, the size of the wax crystals is in a reduced form to lower the viscosity of crude oils. The crystal growth rate of these waxes is slower than that of the normal wax crystal without PPD. The viscosity reduction was obtained with the C_{16} alkyl substituent when added to crude oil **[15]**.

Table 1: Rheological measurement data of Khalda crude oil without and with 1000 ppm from PEAA-$C_{16}NH_2VA$ graft co-polymer at different temperatures.

Temperatures	Additive Concentrations (PPM)	Plastic Viscosity	Yield Value	Correlation Coefficient
15 °C	**Blank**	19.97	2.46	0.999
	1000	5.14	2.05	1
	2000	2.98	1.76	1
	3000	2.61	1.54	1
	5000	1.19	1.38	1
27 °C	**Blank**	10.36	2.38	0.999
	1000	2.98	1.42	1
	2000	3.65	1.21	1
	3000	1.36	1.05	1
	5000	1.28	0.93	1
36 °C	**Blank**	4.43	1.08	0.999
	1000	3.16	0.66	1
	2000	3.33	0.63	1
	3000	1.49	0.58	1
	5000	0.79	0.51	1

Table 2: Rheological measurement data of Khalda crude oil without and with 2000 ppm from PEAA-$C_{16}NH_2VA$ graft co-polymer at different temperatures.

Temperatures	Additive Concentrations (PPM)	Plastic Viscosity, Cp	Yield Value, Pa	Correlation Coefficient
15 °C	**Blank**	19.97	2.46	0.999
	1000	6.90	1.79	1
	2000	2.82	1.56	1
	3000	2.65	1.32	1
	5000	1.78	1.16	1
27 °C	**Blank**	10.36	2.38	0.999
	1000	2.28	1.13	1
	2000	1.28	0.93	1
	3000	1.07	0.76	1
	5000	0.86	0.64	1
36 °C	**Blank**	4.43	1.08	0.999
	1000	1.44	0.47	1
	2000	1.08	0.36	1
	3000	0.69	0.29	1
	5000	0.46	0.21	1

Table 3: Rheological measurement data of Khalda crude oil without and with 3000 ppm from PEAA-$C_{16}NH_2VA$ graft co-polymer at different temperatures.

Temperatures	Additive Concentrations (PPM)	Plastic Viscosity, Cp	Yield Value, Pa	Correlation Coefficient
15 °C	**Blank**	19.97	2.46	0.999
	1000	2.86	1.49	1
	2000	2.44	1.25	1
	3000	1.28	1.06	1
	5000	0.70	0.92	1
27 °C	**Blank**	10.36	2.38	0.999
	1000	2.78	0.95	1
	2000	1.28	0.72	1
	3000	0.79	0.53	1
	5000	0.71	0.38	1
36 °C	**Blank**	4.43	1.08	0.999
	1000	0.73	0.28	1
	2000	0.54	0.21	1
	3000	0.59	0.15	1
	5000	0.11	0.10	1

Table 4: Rheological measurement data of Khalda crude oil without and with 5000 ppm from PEAA-$C_{16}NH_2VA$ graft co-polymer at different temperatures.

Temperatures	Additive Concentrations (PPM)	Plastic Viscosity, Cp	Yield Value, Pa	Correlation Coefficient
15 °C	**Blank**	19.97	2.46	0.999
	1000	3.53	1.29	1
	2000	3.07	1.07	1
	3000	1.45	0.91	1
	5000	1.28	0.80	1
27 °C	**Blank**	10.36	2.38	0.999
	1000	2.07	0.73	1
	2000	0.57	0.53	1
	3000	0.99	0.35	1
	5000	0.58	0.24	1
36 °C	**Blank**	4.43	1.08	0.999
	1000	0.00	0.14	1
	2000	0.00	0.10	1
	3000	0.00	0.07	1
	5000	0.00	0.04	1

CONCLUSION

1-In the pour point tests that were conducted with various samples of PEAA graft co-polymer, we noted that for a given size of dependant hydrocarbon group, an increase in the proportion of these groups increases the performance of the additive. Also, for a given co-polymer composition, increasing the length of the alkyl group improves the performance of the additive.
2-For the Khalda crude oils, the best performance as pour point depressant was obtained by PEAA-g-VA with amine and the optimum dosage was 3000 ppm.
3-The prepared material show a good results as pour point depressant and as flow improver for the tested KhPC crude oils at concentration 5000 ppm.
4-The rheological measurements indicate that the viscometric behaviors of the treated crude oils depend on the crude oil compositions and the structure of the prepared PEAA co-polymeric additives.
5- The values of the plastic viscosity (mPaS) and yield values (Pa) are found to decrease by the addition of PEAA graft co-polymeric additives even at low concentrations (500 ppm).
6- PEAA graft co-polymeric additives show non-Newtonian pseudoplastic behaviors at different low concentrations and temperatures (equal or below their pour point) but their yield stress and viscosity values were decreased as compared with untreated crude oils even at low temperatures.

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