Studies of poly ethylene acrylic acid derivatives as pour point depressants of waxy crude oils

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ABSTRACT

This study aims to prepare some compounds based on PEAA co-polymer. PEAA was reacted with alcohols and amines then grafted with vinyl acetate in the presence of PTSA as catalyst and xylene as solvent to produce graft co-polymers. The influence of PEAA graft co-polymer (PEAA- g-VA), as flow improver, on the viscosity and pour point of some Egyptian waxy crude oils were studied. The produced gravt co polymer was purified and characterized by FTIR and ^{1}HNMR. The rheological behaviors were measured at different concentration (from 1000 to 5000 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. These reductions of pour point temperature were depending on the composition and location of Khalda crude oil. Thus establishing the large efficiency of the products synthesized in this work.
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INTRODUCTION

Crude oil containing high amount of wax exhibit high pour point and non-Newtonian viscosity behavior below the cloud point. The pour point of the crude oil is the temperature at which the crude is just capable to flow under specified condition of testing. To overcome such problem pour point depressants (PPD) have been used which contain oil soluble long chain alkyl group and a polar moiety in the molecular structure. The long chain alkyl group insert into wax crystal and polar moiety exist on the wax surface and reduces wax crystal size[1,2]. Thus, chemical products known as flow improvers, crystal modifiers and pour point reducers need

to be used to reduce the apparent viscosity, the flow limit and the pour point of oils[3-5]. During production, these additives minimize problems related to the deposition of paraffin waxes min the production equipment. Thus, the development of new additives that can solve or minimize such problems is of great interest for the petroleum industry in the whole world. According to Kumar's investigation on pour point depressants[6], an efficient polymeric additive for paraffin oils should be a linear polymer or copolymer that has pendant hydrocarbon chain groups and/or presents hydrocarbon chains in the polymeric backbone. In order to synthesize a polymer that can perform as an agent to reduce the pour point, the following characteristics should be

considered: a sufficient number of pendant alkyl groups; alkyl groups with sufficiently long chains; a convenient distance between the hydrocarbon pendant chains; a medium molar mass; in the case of a copolymer, a suitable ratio between the co-monomers, a high stability of the additive and, the amorphous or crystalline nature of the additive[3,4,7-9]. The most extensively used flow improver for fuel oils are ethylene-vinyl acetate copolymer[10-14], alkyl ester of unsaturated carboxylic acid-olefin copolymer[10,15], maleic anhydride alkyl ester of unsaturated carboxylic acid copolymer[16,17].

This paper describes the synthesis, characterization and evaluation of the performance of various PEAA graft co-polymers as pour point depressant and flow improver additives for some Egyptian waxy crude oils (Khalda crude).

EXPERIMENTAL

Materials

Poly Ethylene acrylic acid (PEAA) is waste material. Fatty alcohols and amines, 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.

Synthesis of graft copolymers

PEAA copolymers were prepared by reacting PEAA waste with Fatty alcohols and amines under N_2 gas at 140 °C in o-xylene in the presence of 1% PTSA (wt % based on total weight of reactants). The reaction was carrie 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 alcohol or amine 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 (PEAA-C_{18}-OH, PEAA-C_{18}-NH_2, PEAA-C_{18}-OH-g- VA, and PEAA-C_{18}-OH-g-VA).

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[18].

Pour point measurement

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

RESULTS & DISCUSSION

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-$(CH_2)_n$-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.

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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)[19,20] 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 co-polymers are observed in all spectra and indicate that the ester and amide groups were formed from PEAA with alcohols and amides.

Pour point measurement

Effect of additives on pour point of the tested crude oils

The additives are 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[21]. Polymers such as vinyl acetate co-polymer, acrylate copolymer and their derivatives are the main additives used to improve the flowability of very waxy crude oil, diesel fuel and other base oils at low temperature[21].

The pour point temperatures (PPT) values of un-treated and treated of the tested crude oils with concentration of additives were calculated listed in TABLES 1-5. These tables indicate that the PPT values decreased with increasing of additive concentrations from 500 ppm to 5000 ppm for different crude oils. On the other hand, the TABLE 1-5 indicate that the prepared graft co-polymers can be used as pure point depressant depending on the composition of crude oils.

TABLE 1-5 illustrate the results obtained from the pour point measurements for the crude oils. Pour point values reduction higher than 21 °C (ΔP values) were achieved by adding 500 and 5000 ppm of graft PEAA copolymers to the crude oils. This means that, in this

TABLE 1 : Pour point measurements for graft copolymers (PPD) at UMB mix crude oil

Dosage, ppm	Pour Point Temperature (PPT), °C			
	PEAA-C$_{18}$OH	PEAA-C$_{18}$NH$_2$	PEAA-C$_{18}$OH-VA	PEAA-C$_{18}$NH$_2$-VA
Blank	21	21	21	21
1000	12	9	6	6
2000	9	6	3	3
3000	6	6	3	3

TABLE 2 : Pour point measurements for graft copolymers (PPD) at Khip mix.crude oil

Dosage, ppm	Pour Point Temperature (PPT), °C			
	PEAA-C$_{18}$OH	PEAA-C$_{18}$NH$_2$	PEAA-C$_{18}$OH-VA	PEAA-C$_{18}$NH$_2$-VA
Blank	27	27	27	27
1000	18	15	12	12
2000	15	12	9	9
3000	12	9	6	6

TABLE 3 : Pour point measurements for graft copolymers (PPD) at SUMPECTO mix crude oil

Dosage, ppm	Pour Point Temperature (PPT), °C			
	PEAA-C$_{18}$OH	PEAA-C$_{18}$NH$_2$	PEAA-C$_{18}$OH-VA	PEAA-C$_{18}$NH$_2$-VA
Blank	33	33	33	33
1000	30	30	30	30
2000	27	24	24	21
3000	21	18	15	15
5000	15	12	12	9

TABLE 4 : Pour point measurements for graft copolymers (PPD) at SALAM BASE mix crude oil

Dosage, ppm	Pour Point Temperature (PPT), °C			
	PEAA-C$_{18}$OH	PEAA-C$_{18}$NH$_2$	PEAA-C$_{18}$OH-VA	PEAA-C$_{18}$NH$_2$-VA
Blank	30	30	30	30
1000	24	24	21	21
2000	15	15	12	12
3000	12	12	9	9
5000	9	9	6	6

concentration range, the additive co-crystallizes with the paraffin, modifying their crystals.

Rheological measurements

Evaluation of PEAA grafts as flow improver

PEAA graft co-polymers were evaluated for their performance as flow improvers for the tested crude oils

TABLE 5 : Pour point measurements for graft copolymers (PPD) at KHALDA mix (all crude oil for KhPC)
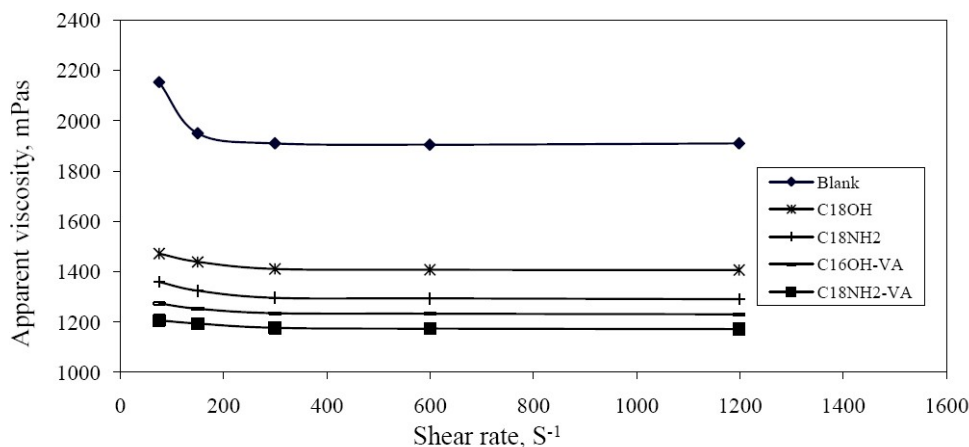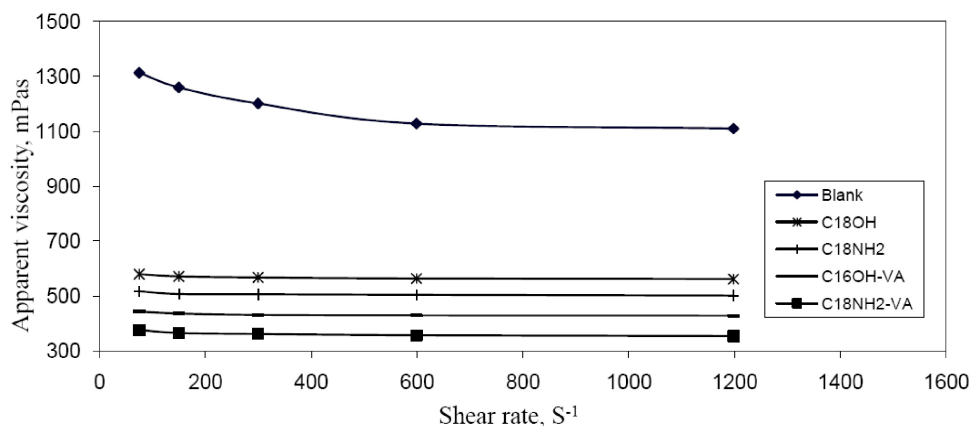
Dosage, ppm	Pour Point Temperature (PPT), °C			
	PEAA-C_{18}OH	PEAA-C_{18}NH$_2$	PEAA-C_{18}OH-VA	PEAA-C_{18}NH$_2$-VA
Blank	27	27	27	27
1000	21	18	18	18
2000	15	15	12	12
3000	12	12	9	9
5000	9	9	6	6

through rheological measurements at concentration from 500 to 5000 ppm. Measurements of the viscosity – 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 1-3 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[22].

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

Figure 1 : Relation between shear rate and apparent viscosity of Khalda crude oil with PEAA graft co-polymers at 3000 ppm and at 15 °C

Figure 2 : Relation between shear rate and apparent viscosity of Khalda crude oil with PEAA graft co-polymers at 3000 ppm and at 27 °C
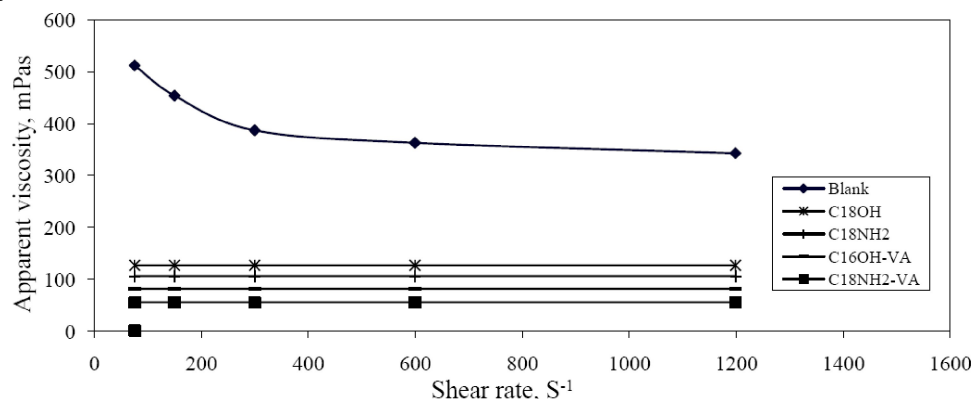
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Figure 3 : Relation between shear rate and apparent viscosity of Khalda crude oil with PEAA graft co-polymers at 3000 ppm and at 36 °C

the agglomeration of wax crystals in crude oil[23].

Effect of temperatures and shear on the rheological behavior of untreated and treated crude oils

Chemical 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 °C to 36 °C.

The obtained data of ηp, τy and correlation coefficient were determined for all tested crude oils at different temperatures. The selected additives from prepared additives are listed in TABLE 6. 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 (τβ). 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[24].

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 and evaluate the effect of polymers on the crude oil viscosities. 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.

The minimum yield stress was attained at 3000 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[25-27].

The data listed in TABLE 6 for tested crude oils indicate that the length of side chain decreases the plastic viscosity and yield stress for the crude. This may be

TABLE 6 : Rheological measurement data of Khalda crude oil without and with PEAA-$C_{18}NH_2$-VA graft co-polymer at different temperatures

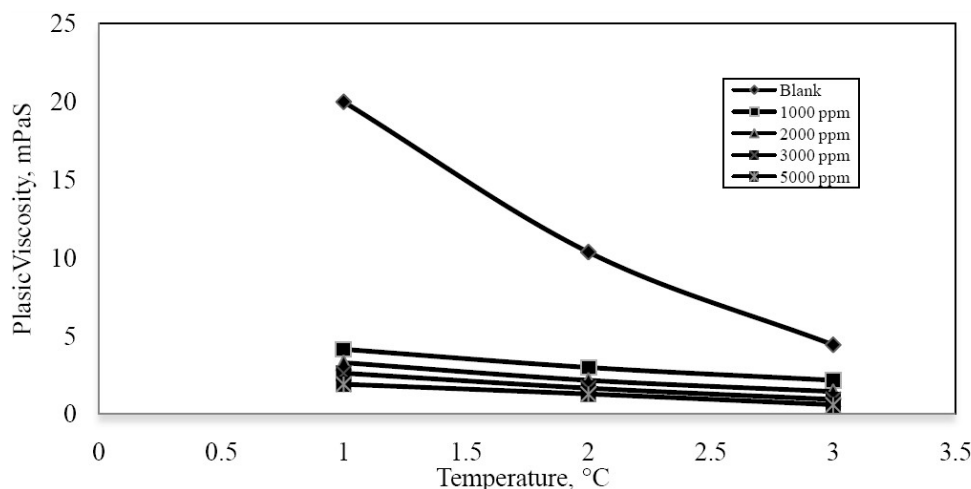| Temperatures	Additive Concentrations (PPM)	Plastic Viscosity	Yield Value	Correlation Coefficient
15 °C	Blank	19.97	3.46	0.994
	1000	4.14	2.05	0.996
	2000	3.28	1.76	0.998
	3000	2.61	1.58	0.998
	5000	1.91	1.38	0.999
27 °C	Blank	10.36	1.78	0.996
	1000	2.98	1.42	0.999
	2000	2.15	1.21	1.0
	3000	1.66	1.05	1.0
	5000	1.28	0.87	1.0
36 °C	Blank	4.43	1.08	0.999
	1000	2.16	0.86	1.0
	2000	1.43	0.63	1.0
	3000	0.94	0.48	1.0
	5000	0.59	0.31	1.0

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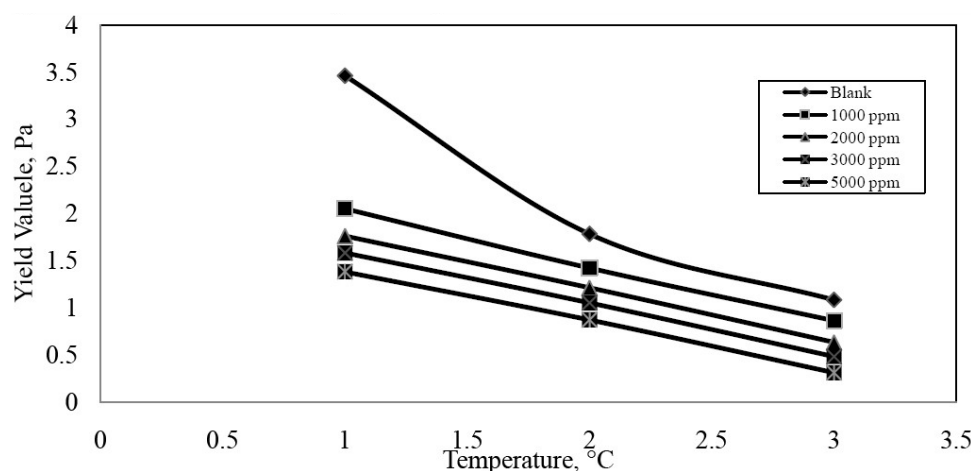**Figure 4 : Plot of plastic viscosity vs temperature at different concentrations**

Figure 5 : Plot of yield value vs temperature at different concentrations

explained by the lack of interaction between the alkyl chain moieties with the n-paraffins 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[22].

Figures 4 and 5 shows that the plots of plastic viscosity Vs temperature and yield value Vs temperature for different dosages of synthesized additives for KhPC crude oil. All these plots (with additives) are linear and show a decreasing slope as the temperature is increased, up to the pour point of crude oil. The decreasing slope of plots indicates the transition of non-Newtonian to Newtonian behavior of KhPC crude oil with increasing

temperature and concentration from 1000 ppm to 5000 ppm.

CONCLUSION

1   For synthesis of PEAA graft co-polymer, we noted that 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 3000 ppm.

4   The rheological measurements indicate that the viscometric behaviors of the treated crude oils depend on the crude oil compositions and the struc-

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ture 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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