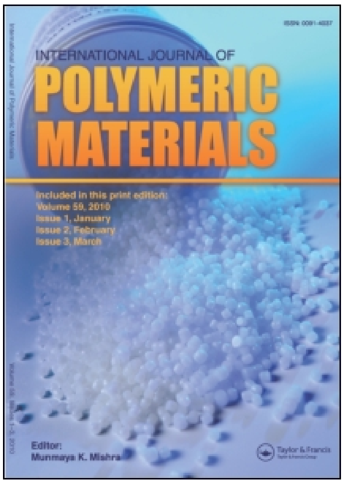

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Poly(Cinnamoyloxy Ethyl Methacrylate-Co-Octadecyl Acrylate) as Flow Improver for Egyptian Waxy Crude Oils

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Poly(Cinnamoyloxy Ethyl Methacrylate-Co-Octadecyl Acrylate) as Flow Improver for Egyptian Waxy Crude Oils

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The octadecyl acrylate–cinnamoyloxy ethyl methacrylate linear copolymers (CEMA-ODA) were designed to be applied as pour point depressants. The preparation scheme involved synthesis of cinnamoyloxy ethyl methacrylate (CEMA) monomer and then copolymerization with octadecyl acrylate (ODA) at different molar ratios in the feedstock. The efficiency of these copolymers to depress pour points and rheological characteristics for waxy crude oils using different concentrations of CEMA-ODA additives were studied. It was observed that the synthesized copolymers showed nonNewtonian pseudoplastic relationships at different concentrations of synthesized additives. CEMA-ODA copolymer with molar ratio 1:3 has good ability to disperse wax crystals and improve the flow behavior of tested crude oils even at temperatures below their pour points. The results showed that there is a good correlation between viscosity measurements and pour point characteristics.

Keywords: flow improver, pour point depressant, rheology, viscosity

INTRODUCTION

Some crude oils contain large amounts of wax, and have high pour points. As the temperature of crude oil is dropped, the wax will crystallize and accumulate, increasing the viscosity of the crude oil and making it more difficult to flow in pipelines at a given velocity. It was found that only 2–4% precipitated wax is sufficient to cause oil gelling [1–3]. Wax crystallization depends on crude oil composition, temperature and pressure conditions. The temperature at which the first crystal appears—Wax Appearance Temperature (WAT)—is an important

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parameter for the flow ability of the crude oil [4]. Several techniques have been developed to minimize the problems caused by wax crystals deposition/aggregation. Chemical methods using polymeric additives are considered a pioneering choice.

Pour point depressants (PPDs) are used as chemical additives to transport crude oils at temperatures below their wax appearance points. PPDs are polymeric compounds formed mainly of hydrocarbon chains which interact with wax crystals to modify wax morphology so as to inhibit the aggregation stage. For this reason such inhibitors are known as *wax crystal modifiers*. There are many kinds of polymers that can be used as wax crystal modifiers to influence the behavior of the wax crystallites formation [5–9]. Acrylic and methacrylic ester copolymers are among the additives that can be used for this purpose, since they show very good efficiency as crude oil flow modifiers and wax deposition inhibitors [10,11]. This work aims to synthesize linear cinnamoyloxyethylmethacrylate- octadecylacrylate, CEMA-ODA, copolymers as wax inhibitors for two waxy Egyptian crude oils. The effects of the prepared copolymers on PPDs and rheology of the treated crude oils at different temperatures are computed and discussed.

EXPERIMENTAL

Materials

Cinnamoyl chloride, 2-hydroxyethyl methacrylate (HEMA), octadecyl acrylate (ODA), benzoyl peroxide, tetrahydrofuran (THF), triethylamine (TEA) and benzene were obtained as analytical reagents from Aldrich Chem. Co., Germany. Xylene was obtained from Adweic Chem. Co., Egypt and used as received. Petroleum crude oils were obtained from Khalda and Qaron (Karama) petroleum companies, Egypt, with specifications listed in Table 1.

TABLE 1 Specification of the Tested Karama and Khalda Crude Oils

		Crude oils	
Test	Method	Karama	Khalda
API gravity at 60°F	ASTM D-1298	41.1	39
Wax content (wt%)	UOP 46/64	16	12
Asphaltene content (wt%)	IP 143/84	3	5
Water content (vol%)	IP 74/70	0.23	0.3
Kinematic viscosity (CSt) at	ASTM D445		
50°C		7	10
60°C		4.3	8

Synthesis of Cinnamoyloxy Ethyl Methacrylate Monomer (CEMA)

A solution of 66 mmol of HEMA and 66 mmol of TEA was refluxed in 100 ml of THF for 2 h in nitrogen atmosphere, and then the clear solution was cooled to 0°C in an ice bath. Then, 79 mmol of cinnamoyl chloride was added dropwise with vigorous stirring for 2 h at 0°C and then for 4 h at room temperature. The formed triethylamine hydrochloride salt was filtered out and the filtrate was concentrated in a rotary evaporator. The concentrated solution was slowly added to 500 ml of n-hexane. The precipitate was filtered off and the solvent was distilled off using cuprous chloride to inhibit polymerization.

Synthesis of Linear CEMA-ODA Copolymers

A mixture of CEMA and ODA at molar ratios 1:1, 1:2, 1:3, 2:1, 3:1 of CEMA:ODA mol% was dissolved in 100 ml benzene and the solution was poured into a round-bottom flask under N_2 atmosphere. The solution was then heated at 70°C in the presence of 0.1 wt% benzoyl peroxide as an initiator. The time of the reaction was 4 h and the polymerization temperature increased from 70°C to 80°C during the course of the reaction. The purification was carried out by cooling the reaction mixture and precipitating in excess methanol with stirring. The obtained precipitate was filtered and dried in vacuum at 30°C for 4 h.

Characterization of the Prepared Copolymers

The compositions of the prepared copolymers were established from ^{1}HNMR spectroscopy data. ^{1}HNMR spectra of CEMA-ODA linear copolymers having different molar ratios were obtained at 300 MHz on a Varion NMR 300 spectrometer using $CDCl_3$ as a solvent. The structure of copolymers was confirmed by FTIR (Mottson-infinity series bench tab961). The average molecular weight was measured for the prepared copolymers using gel permeation chromatography (GPC). The molecular weight (Mn) of CEMA-ODA linear copolymers was measured in toluene using linear polystyrene as standards. The molecular weight was measured by GPC (Waters model 510) using Ultrastyragel column 500, 1000, 10.000 and 100.000 Å.

Crude Oils Composition

The tested crude oils (Khalda and Karama crude oils) have a complex composition, comprising wax, resins and asphaltenes that drastically affect their cold flow properties. Asphaltenes were isolated by the IP 143 procedure using n-heptane. The deasphalted crude oil was treated with activated silica gel at 50°C, allowed to settle overnight, and filtered. The silica gel containing the resins was twicely washed with hot n-heptane to remove the wax portion and subsequently extracted with hot benzene-methanol mixture (9:1). The resins were isolated by evaporating the solvent from the benzene-methanol extract. The filtrate was treated with concentrated sulfuric acid and allowed to settle overnight. The supernatant liquid was mixed with methyl ethyl ketone (1:1), cooled to 0°C and filtered. The ketone was evaporated from the precipitate to give the wax, which was weighed. It was then analyzed by gas chromatographic analysis to determine the distribution of n-paraffins.

POUR POINT MEASUREMENT

Pour point was measured according to the ASTM D97 test procedure at different concentrations of the additives, namely 250, 500, 1000 and 2000 ppm, using Khalda crude oil. The concentrations of additives were 2000, 2500, 3000 and 5000 ppm for Karama crude oil.

Rheology Measurements

Rheology measurements were conducted using a coaxial rotational viscometer (Rheotest2.1) equipped with thermostated cooling system with temperature control. To make accurate rheological measurements with constant results, the crude oil samples were heated at 80°C with stirring followed by quiescent cooling at room temperature for 48 h before testing. Tests were started by heating the preconditioned untreated crude oil to 60°C, then loading it into the viscometer preheated to the temperature; meanwhile the cooling thermostat was adjusted to the test temperatures (15, 30 or 45°C). The rheological measurements were begun by applying a very low shear rate until the temperature of the sample decreased to the test temperature mentioned above.

RESULTS AND DISCUSSION

It is well known that petroleum additives should have hydrophobic character in order to interact with crude oil. In previous works [12,13], CEMA monomer based on hydrophobic moieties such as alkyl or phenyl groups was prepared to be applied as oil sorbers. It is well-established that HEMA monomer contains both hydrophilic and hydrophobic moieties. So, it is important to convert it to hydrophobic monomers by reaction of its hydroxyl group. This was carried out by reaction of HEMA with cinnamoyl chloride, as described in the Experimental section, to add a phenyl moiety as a hydrophobic group. The chemical structure of the obtained monomer, CEMA, was evaluated from IR and ^{1}HNMR analyses (IR and HNMR spectra are not shows here for brevity). The IR spectrum of CEMA shows characteristic absorption bands at 2926 cm^{-1} (assigned to stretching vibration of the aliphatic C−H bond), 1730 cm^{-1} (assigned to stretching vibration of the C=O), 1620 cm^{-1} (assigned to stretching vibration of the C=C), 1149 cm^{-1} (assigned to stretching of C−O), and 900–650 cm^{-1} (out of plane rotational vibration of aromatic C−H). The disappearance of a band at 3200–3500 cm^{-1} confirms the completion of the esterification reaction between −OH of HEMA and cinnamoyl chloride. In the ^{1}HNMR spectrum, the peaks of CEMA indicated aromatic protons at 7.2–7.8 ppm, vinyl protons at 5.6–6.6 ppm, and methyl protons at 1.9 ppm.

In the present study, CEMA monomer has been copolymerized with ODA in the presence of benzene at 70°C using the procedure described in the experimental section. The structure of the prepared linear copolymers was confirmed by ^{1}HNMR analysis. The ^{1}HNMR spectrum of CEMA-ODA copolymer with molar ratio 1:1 is represented in Figure 1. The ^{1}HNMR spectroscopic analysis of the synthesized copolymers afforded similar spectra, which show bands at 1.1, 7.2–7.8, and 5.6–6.2 ppm that represent methyl protons in the polymer backbone, aromatic protons of CEMA and vinyl proton in the cinnamoyl moiety,

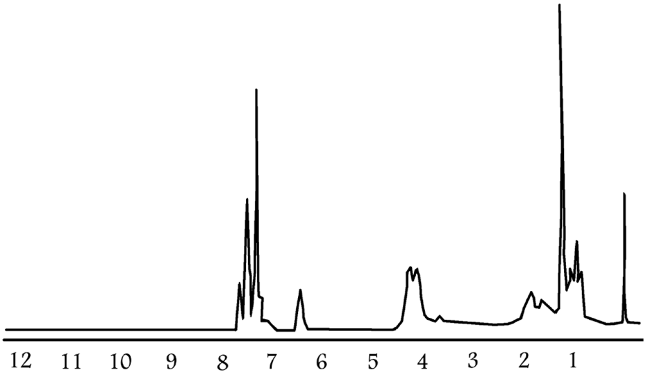

FIGURE 1 ^{1}HNMR Spectrum of CEMA-ODA copolymer with molar ratio 1:1.

TABLE 2 Characterization of the Prepared CEMA-ODA Copolymer at Different Concentrations, of CEMA:ODA Monomer

Copolymer number	Copolymer composition mol %	Average molecular weight (Mn)
1	1:3	125×10^3
2	1:2	70×10^3
3	1:1	50×10^3
4	2:1	37×10^3
5	3:1	20×10^3

respectively. The appearance of the methylene protons band at 1.9 ppm, together with the disappearance of vinyl protons in the acryloyl group at 5.6–6.2 ppm, indicates the incorporation of ODA and CEMA in the copolymer backbone.

Gel permeation chromatography in organic solvents is generally very useful for the determination of molecular size distributions and size averages. The molecular weight data obtained from GPC, are represented in Table 2. The data indicate that the M_n values varied from 20,000 to 125,000 g/mol depending on the copolymer composition. Careful inspection of data indicates that the molecular weight values increased with increasing ODA content.

Effect of Additives on Pour Point of Tested Crude Oils

Two waxy crude oils (from Egyptian Qaron (Karama) and Khalda Petroleum Companies) were used for evaluating the performance of the CEMA-ODA copolymers. Their physico-chemical characteristics are given in Table 1. In addition, the paraffin content of the tested crude oils was determined using gas-liquid chromatographic analysis for determinating the average molecular weight distribution of paraffins. For example, Figure 2 presents the paraffin content of Khalda crude oil. The activity of the prepared CEMA-ODA copolymers as wax dispersants was evaluated on the basis of their chemical structures. The prepared products were tested to improve the flow properties of the investigated crude oils in terms of pour point depression at different copolymer concentrations. The pour point, PP, values were measured and listed in Tables 3 and 4. In general, it was observed that increasing concentrations of additives up to 5000 ppm decreases PP values. These additives' function can be explained by one of several postulated mechanisms, namely, nucleation adsorption, co-crystallization and improved wax solubility [14,15]. The pour point results for

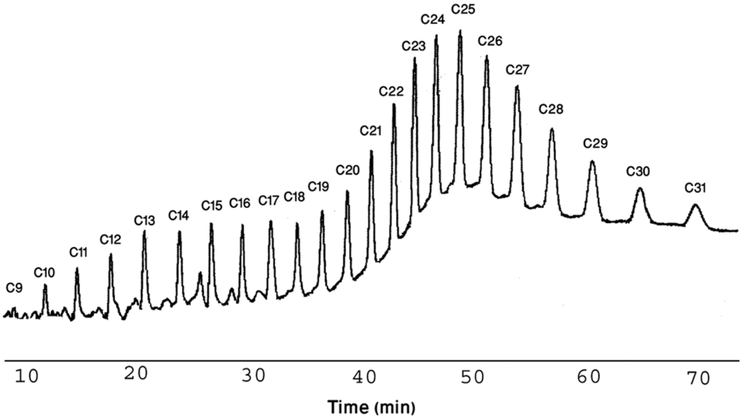

FIGURE 2 Chromatogram of paraffins extracted from Khalda crude oil field.

untreated and treated Khalda crude oil with different concentrations of synthesized inhibitors (250, 500, 1000 and 2000 ppm) are shown in Table 3. It is obvious that CEMA-ODA copolymer with molar ratio 3:1 had no effect on the pour point of Khalda crude oil, whereas CEMA-ODA copolymer with molar ratio 1:3 is more efficient for reducing the pour point to a significant extent. This may be explained by the lack of interaction between the alkyl chain moieties of the CEMA monomer in the structure of CEMA-ODA copolymer with the average carbon number of the n-paraffin of the wax component. On the other hand, ODA in CEMA-ODA copolymer shows a good match of alkyl chain lengths with the average carbon number of the wax. In addition, it has previously been reported [16] that during the solidification of polymeric additive structures with pendent moieties less than C_{18} in

TABLE 3 The Influence of the Different Concentrations of CEMA-ODA Copolymer Inhibitor on the Pour Point of Khalda Crude Oil

	Pour point (°C) at concentration (ppm)					
Copolymer composition	NIL	250	500	1000	2000	Δpp_{250}
1:3	30	9	9	12	15	21
1:2	30	12	15	18	21	18
1:1	30	15	21	24	24	15
2:1	30	21	24	27	27	09
3:1	30	24	27	30	30	06

TABLE 4 The Influence of the Different Concentrations of CEMA-ODA Copolymer Inhibitor on the Pour Point of Karama Crude Oil

	Pour point (°C) at concentration (ppm)					
Copolymer composition	NIL	2000	2500	3000	5000	Δpp_{5000}
1:3	24	12	12	9	6	18
1:2	24	15	12	12	9	15
1:1	24	18	18	15	12	12
2:1	24	21	18	18	15	9
3:1	24	24	21	21	18	6

length, as in the case of CEMA comonomer, no crystalline packing of the polymers occurs that matches the crystalline packing of the waxes during growth so that no interaction takes place. It is obvious that higher pour point depression is observed with additives of melting point around that of the wax constituent. Whereas the effectiveness decreases significantly with additives having greatly different melting points from that of wax. This may be attributed to the fact that interaction of the additive with wax (adsorption or co-crystallization) takes place in the solid phase. Consequently, for complete interaction, their melting point must be close to each other. The effectiveness of the polymeric structure with high molar content of ODA as PPDs was then evaluated in Khalda crude oil at different concentrations ranging from 250 to 2000 ppm. The results are given in Table 3, from which one can observe the direct correlation between the concentration of the additives and the pour point. CEMA-ODA copolymers with high molar ratio of ODA achieve the best performance as pour point depressants at low concentration (250 ppm). This means that at this concentration the additive co-crystallizes with the paraffins and modifies their crystals. The loss of efficiency observed at high concentration may be ascribed to precipitation of the pure copolymer, or to wax crystallization with copolymer-induced nucleation.

The pour point results for untreated and treated Karama crude oil containing different concentrations of synthesized inhibitors (2000, 2500, 3000 or 5000 ppm) are listed in Table 4. The data show that CEMA-ODA copolymer with molar ratio 3:1, 2:1 had no effect on the pour point of Karama crude oil, whereas CEMA-ODA copolymer with molar ratio 1:3 is more effective to a significant extent. It is also apparent that CEMA-ODA copolymer with molar ratio 1:2 and 1:1 reduces the pour point of Karama crude oil to some extent. This may be attributed to the presence of both alkyl side chains (C18) and aromatic side chains making them more efficient additives. It can be seen that the copolymer exhibits maximum effectiveness of pour point depression which is attributed to the adsorption of the additive on the surface of the wax crystals keeping them separated from each other. Thus, the size of these fine wax crystals falls at the upper limit of the category of colloidal particles. This explains the amelioration of anti-settling characteristics in addition to improved flow ability [17]. From Table 4 one can observe that as the concentration of copolymer increases from 2000 to 5000 ppm, the pour point reduction increases. Accordingly, the data listed in Tables 3 and 4 indicate that the pour point depression depends on the type of crude oil. It was noted that Khalda crude oil shows greater reduction in pour point than Karama crude at low concentration. The observed difference in the flow behavior of these crude oils may be accounted for by a difference in composition such as their wax and asphaltene content.

The Effect of the Prepared Additives on Rheology of the Crude Oils

The rheological behavior of crude oil is highly influenced by its chemical composition and temperature as well as thermal history. High wax crude oils exhibit a non-Newtonian character often with a yield stress at and below their pour point temperature. Polymeric additives are usually used in treating crude oils in the oil industry as flow improvers, wax inhibitors etc. Pour point depressants (PPDs) are necessary for transportation of these crudes through pipeline and have received the greater acceptance due to their simplicity and economy [1,18]. In the present work, the more effective pour point depressant CEMA-ODA copolymer with molar ratio 1:3 of CEMA to ODA was selected and evaluated for its performance as a flow improver in the two tested crude oils through rheological measurements. The rheological behavior of untreated and treated crude oils (Khalda and Karma) with different concentrations of additive at temperatures lower or above their pour points (15, 30 and 45°C) was measured by rotary viscometer as described in the Experimental section. Measurements of the shear stress-shear rate relationship were carried out at different temperatures (15, 30 and 45°C). Figures 3 and 4 represent the shear stress versus shear rates for untreated and treated Khalda crude oil with 250, 500, 1000, and 2000 ppm concentrations of the selected copolymer ratio at 15°C. It was observed that the untreated crude oil follows a non-Newtonian yield—pseudo plastic rheological behavior. Increasing shear rate, the shear stress increases in pseudoplastic flow behavior, approaching a dynamic equilibrium steady state which is reflected by the progressive tendency to stabilize the higher shear rates [19].

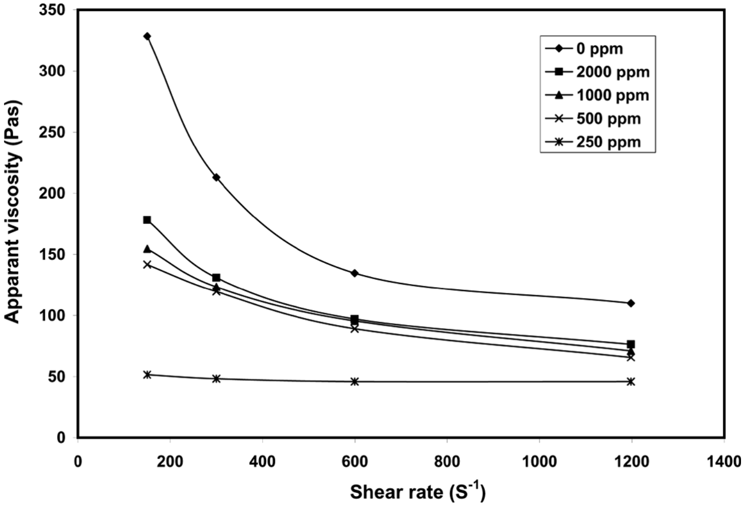

FIGURE 3 Apparent viscosities versus shear rate for untreated and treated Khalda crude oil with different concentrations of CEMA-ODA copolymer at molar ratio 1:3 at 15°C.

The effect of the selected synthesized copolymer ratio on rheology of tested crude oils is shown by a marked decrease in the obtained shear stress. The same behavior was also observed with the treated

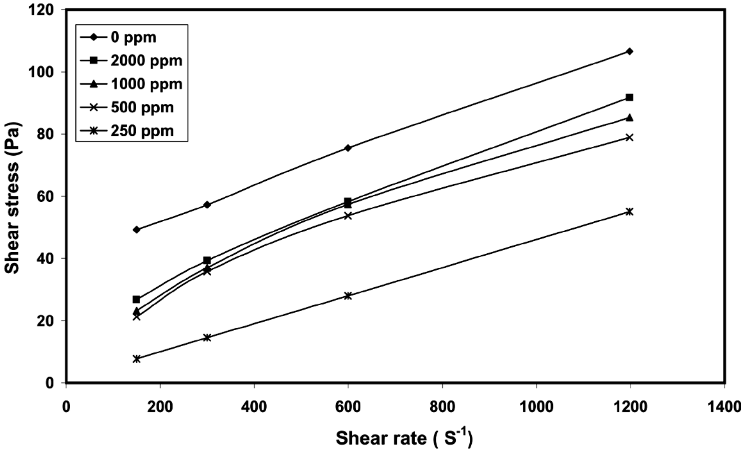

FIGURE 4 Shear stress versus shear rate for untreated and treated Khalda crude oil with different concentrations of CEMA-ODA copolymer at molar ratio 1:3 at 15°C.

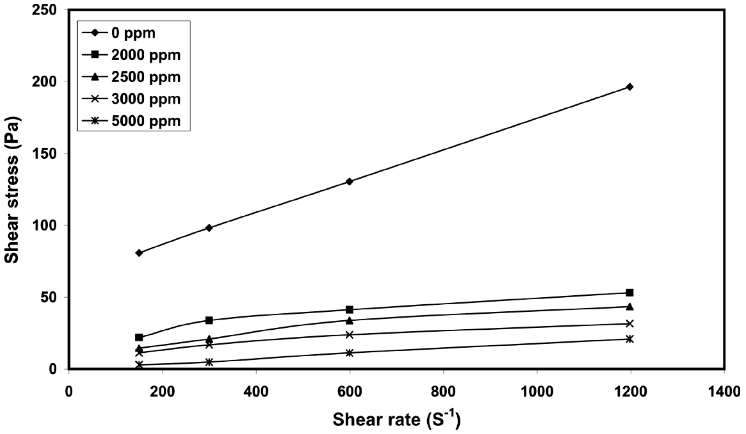

FIGURE 5 Shear stress versus shear rate for untreated and treated Karama crude oil with different concentrations of CEMA-ODA copolymer at molar ratio 1:3 at 15°C.

crude oil, but to a smaller extent. This may be due to a more rigid additive-wax structure that affords a higher energy of shear than the single wax structure in the untreated crude oil. The same behavior was found for both tested crude oils.

The influence of concentrations of 2000, 2500, 3000 and 5000 ppm, on Karama oil respectively at 15°C is illustrated in Figures 5 and 6. It is obvious that at high shear rates, the copolymer reduces the apparent viscosity of crude oil while at low shear rates decrease is more significant. At high shear rates the apparent viscosity reached a constant value at which equilibrium steady state is attained. For treated Khalda crude oil, it is noticeable that most of the rheological improvement is exerted by additive obtained at a concentration of 250 ppm. Further increase of concentrations ranging from 250 to 2000 ppm was accompanied by a slight decrease in shear stress as in Figure 4 or apparent viscosity as in Figure 3. For treated Karama crude oil, it is obvious that as concentration increases from 2000 to 5000 the apparent viscosity (Figure 6) and shear stress (Figure 5) decreased markedly. Most of the rheological improvement was exerted by additives at a concentration 5000 ppm for Karama crude oil. The experimental rheological data were fitted to the Casson flow model [20]. Tables 5 and 6 show all the rheological parameters (plastic viscosity and yield value) for untreated and treated Khalda and Karama crude oils with different concentrations of some selected copolymer ratios using different concentrations at variant temperatures (15, 30 and

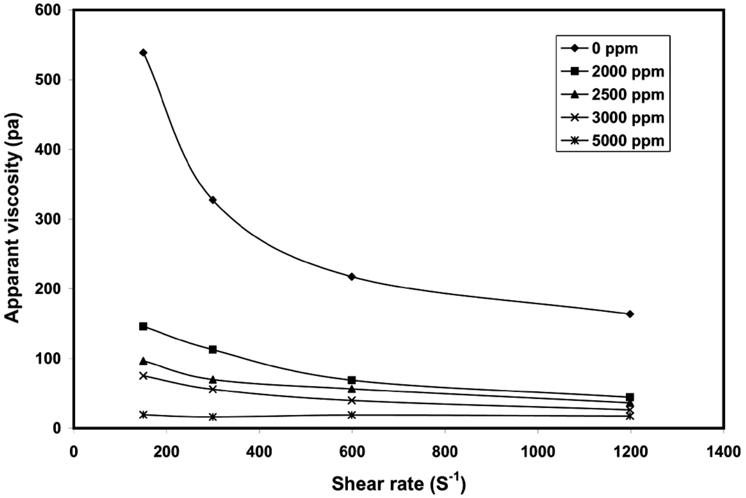

FIGURE 6 Shear rate versus apparent viscosity for untreated and treated Karama crude oil with different concentrations of CEMA-ODA copolymer at molar ratio 1:3 at 15°C.

45°C). It is clear that the plastic viscosity and yield shear stress values decreased significantly with the decreasing concentration of synthesized copolymer for Khalda crude oil (Table 5). It is also obvious that the plastic viscosity and yield shear stress values decreased significantly with the increasing concentration of synthesized copolymer for Karama crude oil, (Table 6). It is also clear from these tables that

TABLE 5 Effects of Additives on Fitted Rheological Parameters of Different Concentrations of CEMA-ODA Copolymer at Molar Ratio 1:3 at Different Temperatures Using Khalda Crude Oil

	Rheological parameter at 15°C		Rheological parameter at 30°C		Rheological parameter at 45°C	
Conc. (ppm)	Yield value (pa)	Plastic viscosity Pa s	Yield value (pa)	Plastic viscosity Pa s	Yield value (pa)	Plastic viscosity Pas
0	41.32	0.0609	18.55	0.0484	11.00	0.029
2000	19.75	0.0549	1.5	0.0239	1.73	0.009
1000	18.31	0.0577	0.787	0.012	0.797	0.0081
500	17.71	0.0529	0.787	0.012	0.797	0.0081
250	0.963	0.0452	0.686	0.0081	0.496	0.0049

TABLE 6 Effects of Additives on Fitted Rheological Parameters of Different Concentrations of CEMA-ODA Copolymer at Molar Ratio 1:3 at Different Temperatures Using Krama Crude Oil

	Rheological parameter at 15°C		Rheological parameter at 30°C		Rheological parameter at 45°C	
Conc. (ppm)	Yield value (pa)	Plastic viscosity Pa s	Yield value (pa)	Plastic viscosity Pa s	Yield value (pa)	Plastic viscosity Pa s
0	64.73	0.1099	17.71	0.0481	13.034	0.03
2000	22.288	0.0271	0.657	0.025	1.1204	0.012
2500	12.05	0.0271	0.5709	0.011	0.256	0.0053
3000	10.444	0.085	0.3427	0.0064	0.2617	0.0029
3000	0.154	0.0175	0.1570	0.0039	0.364	0.0015

the plastic viscosity and yield shear stress values decreased significantly with increasing the temperature from 15 to 45°C. It was also observed that the prepared CEMA-ODA copolymer with molar ratio 1:3 reduces the crude oil apparent viscosity at 15°C. At this temperature the paraffin crystals that have already formed in the liquid media and the rheological behavior of the oil is non-Newtonian. It is observed that the synthesized copolymer shows non-Newtonian pseudoplastic relationships at the three temperatures used (15, 30 and 45°C) and also at all the concentrations used. This indicates that CEMA-ODA copolymer has the ability to disperse wax crystals and improve the flow behavior of the tested crude oils. Finally, from pour point and rheological measurements it can be concluded that the prepared CEMA-ODA copolymer, with molar ratio 1:3, gives high pour point reduction for both tested crude oils and at all used concentrations, and reduces the viscosity of the tested crude oils. A good correlation was attained between pour point results and rheological parameters.

CONCLUSIONS

From the above results, it can be concluded that:

- Increment of ODA in the prepared CEMA-ODA copolymers increases the average molecular weight of the prepared copolymers.
- CEMA-ODA copolymer with 1:3 molar ratio of CEMA to ODA co-monomer is the most effective pour point depressant.
- It is observed that the synthesized copolymer shows non-Newtonian pseudoplastic relationships at the three temperatures (15, 30 and 45°C).

- CEMA-ODA copolymer with molar ratio 1:3 has the ability to disperse wax crystals and improve the flow behaviors of tested crude oils even at temperatures below their pour points.

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