Synthesis and Characterization of Novel Pour Point Depressants Based on Maleic Anhydride-Alkyl Acrylates Terpolymers

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ABSTRACT: The (Docosanyl acrylate-*co*-(octadecyl or hexadecyl acrylate)-*co*-maleic anhydride) terpolymers were prepared using different compositions of the used alkyl acrylates (namely, 90 : 10, 70 : 30, 50 : 50, 30 : 70, and 10 : 90) (DCA-ODA)/(MA) or (DCA-HDA)/(MA). The efficiency of these terpolymers as pour point depressants was discussed. Two western desert waxy crude oils with different wax content were used for evaluation. Correlation between pour point depression efficiency and rheological properties were performed. Rheological parameters were also computed and discussed. It was observed that the syn-thesized terpolymers showed non-Newtonian pseudoplastic relationships at different concentrations of synthesized ter-polymeres with monomer feed ratios of (DCA-ODA (1 : 1))/(MA) or (DCA-HDA (1 : 1))/(MA) = 90/10 mole %. This ratio showed a good ability to disperse wax crystals and improve the flow behaviors of tested two crude oils even at low temperatures below their pour points. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 72–78, 2010

Key words: terpolymerization; pour point depressant; flow improver; rheology

INTRODUCTION

Free radical multicomponent polymerization has been met with growing interest by both polymer industry and academic research. The synthesis of multicomponent polymers is of significant economic importance because of the great diversity of polymer grades that can be produced by variation of the number and relative concentrations of the monomers in the reaction mixture. This enhanced flexibility can lead to the production of polymers with desired physical, chemical, and mechanical properties.[1–4]

Some terpolymers that incorporate hydrophobic groups may be effective in viscosity enhancement because of intermolecular association of hydrophobic parts. Also, this would make them useful in various applications as in sewage treatment, flocculation, and oil recovery process. Another prospective application area of terpolymers is their use as pour point depressants (PPDs) for oil.[5] PPDs are designed to cost-effectively improve the cold-flow properties of crude and other fuel oils. PPDs modify size and shape of crystals and inhibit formation of large wax crystal lattices. However, flow improvers are proposed to cause wax dispersion through co-crystalli-zation mechanism.[6,7] The number of carbon atoms constituting *n*-paraffins or waxes in crude oil ranges from 16 to 60 carbons with different distribution. On the other hand, all PPDs are structured[8–13] so that part of the molecule is like the paraffins wax provid-ing nucleation and co-crystallization sites. The other part of the PPDs is often a polar component typi-cally acrylates or acetates at limits the degree of co-crystallization and counteract the self-crystallization. Acrylic and methacrylic ester copolymers are among the additives that can be used in this purpose because they show very good efficiency as crude oil flow modifiers and wax deposition inhibitors.[14,15]

In the present work, synthesis of terpolymers con-taining MA as the polar component, DCA as a main long-chain wax like alkyl acrylate and ODA or HDA as shorter chain alkyl acrylates. The synthesized ter-polymers were evaluated as PPDs for two different waxy crude oils through pour point depression and rheology improvement. Yield point and/or plastic viscosity values were correlated to pour point results.

EXPERIMENTAL

Materials

Acrylic acid (AA), docosanol (DC), octadecanol (OD), hexadecanol (HD), benzoyl peroxide, hydro-quinone, and methyl ethyl ketone (mek) were obtained as analytical reagents from Aldrich Chem.

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TABLE I
Physicochemical Properties of Tested Osores and Khalda Crude Oils

Test	Method	Crude oils	
		Osories	Khalda
API gravity at 60°F	ASTM D-1298	35	39
Wax content (wt %)	UOP 46/64	10	12
Asphaltene content (wt %)	IP 143/84	8	5
Water content (vol %)	IP 74/70	0.4	0.3
Kinematic viscosity (CSt) at			
50°C	ASTM D445	12	10
60°C		10.5	8

Co., Germany. Xylene was obtained from Adweic Chem. Co., Egypt. Two western deserts waxy crude oils namely Osores and Khalda were used to evaluate the synthesized additives. The physicochemical properties of both oils are listed in Table I. The n-paraffin distribution of the isolated waxes was determined by gas chromatographic analysis (auto system XL gas chromatograph, PerkinElmer, Wellesley, MA) according ASTMD2887 standards.

Synthesis of alkyl acrylate monomers

The reaction was carried out in four-neck reaction flask fitted with mechanical stirrer, reflux condenser, thermometer and a Dean-Stark trap. A solution of 66-mmol acrylic acid and 66 mmol of each alkyl acrylate were refluxed in 100 mL toluene in the presence 0.4 g of p-toluene sulfonic acid as a catalyst, and 0.25 g of hydroquinone as a polymerization inhibitor. The reaction was carried out at reflux temperature until the theoretical amount of water was collected azeotropically. The synthesized monomers were washed out with water to remove the catalyst, inhibitor, and any unreacted materials. The solvent was distilled off using cuprous chloride to inhibit polymerization. The chemical structure of the prepared monomer was confirmed by ^{1}HNMR spectroscopic analysis.

Terpolymerization

The terpolymerization of MA with [docosanyl acrylate (DCA) and octadecyl aclyate (ODA)] or [DCA and hexadecyl acrylate (HDA)] using various monomer feed ratios were carried out in 100 mL methyl ethyl keton at 70°C in presence of 0.1 weight % of benzoyl peroxide as initiator at constant under N_2 atmosphere in a standard three-necked round-bottom glass reactor equipped with a reverse cooler, a nitrogen inlet tube, a magnetic stirrer, and a thermometer was used. The solution was then heated. The time of the reaction was 8 h and the terpolymerization temperature increased from 70°C to 80°C during the course of the reaction. The monomer feed

ratios of (DCA-ODA (1 : 1))/(MA) or (DCA-HDA (1 : 1))/(MA) were 90/10, 70/30, 50/50, 30/70, and 10/90 mol %. Terpolymers were precipitated in excess ethanol with stirring. The obtained precipitate was filtered and dried under vacuum at 60°C.

Characterization

The prepared alkyl acrylates monomers were analyzed by FTIR (Mattson-infinity series bench tab 961, PerkinElmer Spectrum GX) as a spectroscopic technique for elucidating the structure. The structure of the synthesized polymeric additives were followed up by ^{1}HNMR spectra using a 300 MHz Varion NMR 300 spectrometer using $CDCl_3$ as a solvent. The average molecular weight (M_n) of the polymers was determined by GPC Waters model 510 using polystyrene standard, Ultrastyragel column, and tetrahydrofuran as an eluent.

Evaluation testes

The effect of the prepared polymers as flow improvers for the two Egyptian waxy crude oils was evaluated through pour point depression and rheological parameters.

Pour point was measured according to ASTM D97 test procedure at different concentrations of the prepared polymers namely, 250, 500, 1000, and 2000 ppm with Khalda crude oil and 2000, 2500, 3000, and 5000 ppm for Osores crude oil.

Rheological measurements were conducted using a coaxial rotational viscometer (Rheotest 2.1) equipped with thermostated cooling system with temperature control.

RESULTS AND DISCUSSION

The PPDs are specially designed substances having hydrophobic moieties to change the rheology of crude oil and to ease the flow problems in pipelines affected by deposition of wax.[16] In this respect, long-chain alkyl acrylate monomers were prepared by reacting docosanol (DC) or octadecanol (OD) or hexadecanol (HD) with acrylic acid. The structure of the prepared alkyl acrylates monomers were confirmed by FTIR spectroscopy analysis. The three synthesized alkyl acrylates afforded the same absorption bands. The FTIR spectrum (not represented here for brevity) of DCA as an example shows characteristic absorption bands at 2926 cm^{-1} (assigned for stretching vibration of the aliphatic C—H bond), 1750 cm^{-1} (assigned for stretching vibration of the C=O), 1620 cm^{-1} (assigned for stretching vibration of the C=C), 1143 cm^{-1} (assigned for stretching of C—O), and 900–650 cm^{-1} (out of plane rotational vibration of aromatic C—H). The disappearance of a band at

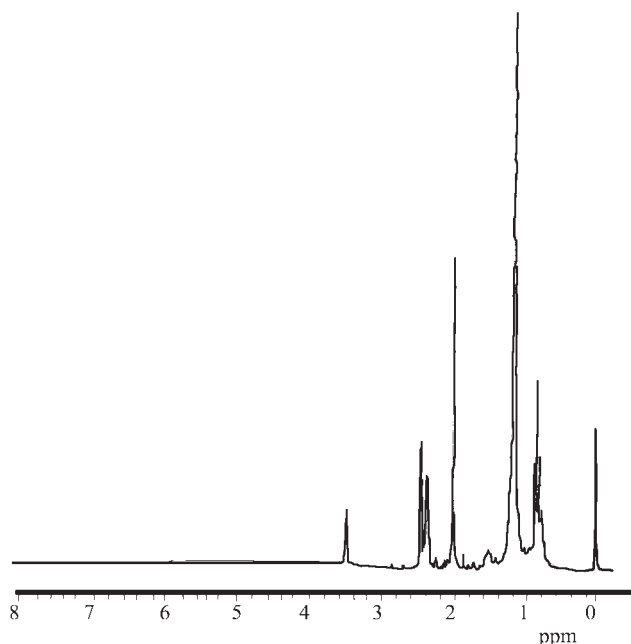**Figure 1** ^{1}HNMR Spectrum of (DCA-ODA)/(MA) terpolymer with molar ratio 90/10 mol %.

3200–3500 cm^{−1} confirms the completion of the esterification reaction between OH of each alkyl acrylates and acrylic acid.[17,18]

(DCA-ODA)/(MA) or (DCA-HDA)/(MA) terpolymers have been synthesized by free radical terpolymerization with different feed ratios of either monomers as described in experimental section. Terpolymers structure was determined by ^{1}HNMR spectroscopy using integral area of certain peaks as a quantitative analysis. Figure 1, represents ^{1}HNMR spectrum of the synthesized terpolymer (DCA-ODA)/(MA) at molar ratio 90/10 mol % using CDCl$_3$ as a solvent and TMS as an internal reference. This figure shows chemical shifts at 0.9 ppm for methyl protons in the terpolymer backbone, 1.2 ppm for long-chain methylene protons CH$_3$—(CH$_2$)$_n$- CH$_2$ in the alkyl chains moieties and 3.5 ppm for (CH$_2$)—O protons. The appearance of bands at 2.4 ppm for methylene protons adjacent to C=O in maleic anhydride moiety and 2.0 ppm for methylene protons adjacent to C=O in alkyl chain moiety together with the disappearance of vinyl protons in the alkyl and maleic group at 5.6–6.2 ppm indicate the incorporation of MA and alkyl acrylates in the terpolymer backbone.[17,18]

Gel permeation chromatography in organic solvents is generally very useful for the determination of molecular size distributions and size averages. In this respect, the data obtained from GPC, molecular weight of terpolymers, were represented in Table II. The data indicated that, the M_n values were varied from 9,000 to 50,000 g/mol depending on the

TABLE II
The Average Molecular Weights of the Synthesized Terpolymer at Different Compostions

Terpolymer compositions	Average molecular weight (M_n)	
	(DCA-HDA)/(MA)	(DCA-ODA)/(MA))
90/10	15×10^3	50×10^3
70/30	13×10^3	45×10^3
50/50	12×10^3	38×10^3
30/70	11×10^3	33×10^3
10/90	9×10^3	25×10^3

terpolymer composition. Careful inspection of data indicated that the molecular weight values increased with increasing of alkyl acrylate content. In case of (DCA-ODA)/(MA) terpolymer with different terpolymer compositions shows higher M_n values than those of [DCA-HDA)/(MA)] terpolymers.

Pour point measurements for crude oil and crude oil/terpolymers additives

The phase stability of crude oils is dependent on a multitude of factors, including temperature, pressure, and component fractions, especially long-chain paraffin and polar asphalting fractions.[19] Paraffin's precipitate out of the crude oil during pipeline transportation because of limited solubility forming paraffin-oil deposition on the pipe walls. To overcome
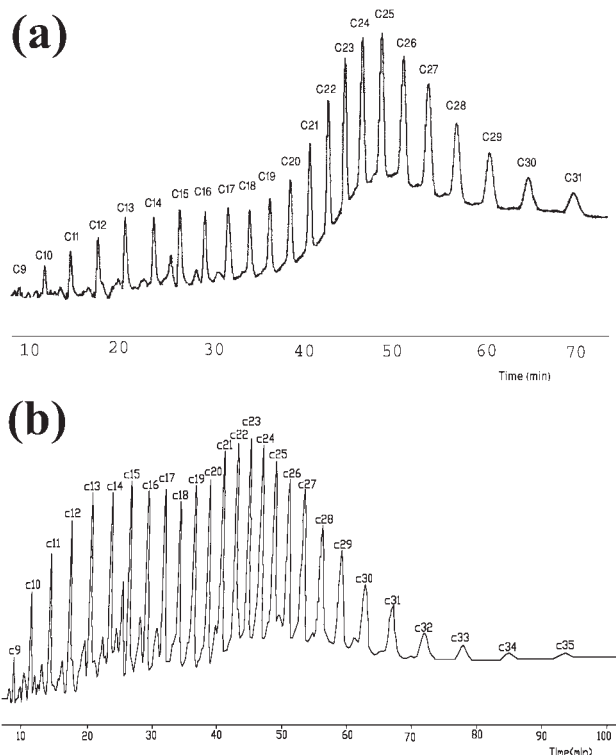

Figure 2 a) Chromatograms for extracted wax from Khalda crude oil. (b) Chromatograms for extracted wax from Osores crude oil.

TABLE III
The Influence of Different Concentrations of (DCA-ODA)/(MA) Terpolymer Additives on Khalda Crude Oil Pour Point

Terpolymer compositions	Pour point (°C) at concentration (ppm)				
	NIL	250	500	1000	2000
90/10	30	9	9	12	15
70/30	30	12	15	15	18
50/50	30	12	15	18	21
30/70	30	15	18	24	27
10/90	30	15	18	27	30

TABLE V
The Influence of Different Concentrations of (DCA-ODA)/(MA) Terpolymer Additives on Osories Crude Oil Pour Point

Terpolymer compositions	Pour point (°C) at concentration (ppm)				
	NIL	1000	2000	3000	5000
90/10	27	12	12	12	9
70/30	27	18	15	12	12
50/50	27	21	18	15	12
30/70	27	24	21	18	15
10/90	27	27	24	21	18

this problem of different concentrations of wax-control additives were added to the tested crude oils. The typical concentration of PPDs additives depends on crude oil characteristics and varies between 50 and 5000 ppm. The interaction between the PPD and paraffin in the crude oil is crucial, and the additives work well when they are matched to the paraffin distribution in the crud oil.[20]

In the present study, two waxy crude oils (from Egyptian Khalda Petroleum Company) were used for evaluating the performance of the prepared terpolymers. Their physico-chemical characteristics are given in Table I. In addition, the paraffinic contents of the tested crude oils were analyzed using gas-liquid chromatographic analysis for determining the average molecular weight distribution of paraffins. The variation of the effective depressants' concentration for both tested crude oils is ascribed to the difference in wax constitution of both. Figure 2(a,b) paraffinic chromatograms for Khalda and Osores oils, respectively, indicate that Osores oil has high average carbon number and *n*-paraffins ratio but contains low isoparaffins and naphthenes compared with Khalda one. It is well known that *n*-paraffins have relatively high melting points and their presence permit strong wax crystal structure. On the other hand, isoparaffins have low melting points and greater solubility in oil and thus remain dissolved until low temperatures. Also, when isoparaffins deposit their configuration dose not permit strong wax crystal structure. To investigate the usefulness of the prepared terpolymers, they were

added to crude oil in amounts of 250–2000 ppm for Khalda and 1000–5000 ppm for Osores crude oils. The influence of terpolymer concentration on pour point of the two tested crude oils is summarized in Tables III–VI. Regarding the effect of alkyl acrylates/maleic anhydride molar ratio, it is obvious that (DCA-ODA)/(MA) and (DCA-HDA)/(MA) terpolymer with molar ratio 90/10 mol % are more efficient in reducing Khalda crude pour point to a significant extent than other molar ratios Tables III, IV. This may be explained well matching long-chain alkyl acrylate moieties in terpolymer backbone with the average carbon number of oil wax. In addition, it has previously been reported[21] that during solidification of polymeric additive structures having pendant moieties less than C_{18} in length no crystalline packing of the polymers occurs that matches crystalline packing of oil waxes during growth, and thus that no interaction takes place. On the other hand, the effectiveness of the polymeric structure with high molar content of DCA-ODA or DCA–HAD moieties as PPDs was evaluated for Khalda crude oil at different concentrations ranging from 250 to 2000 ppm. It can be observed that a direct correlation between concentration of additives. The pour point of tested Khalda crude oil with high molar ratio 90/10 of (DCA-ODA)/MA or (DCA–HAD)/MA achieve good performance as PPDs at low concentration (250 ppm). This means that, at this concentration the additive co-crystallizes with paraffins and modifying their crystals. The loss of efficiency observed at high concentration may be ascribed to precipitation of the

TABLE IV
The Influence of Different Concentrations of (DCA-HDA)/(MA) Terpolymer Additives on Khalda Crude Oil Pour Point

Terpolymer compositions	Pour point (°C) at concentration (ppm)				
	NIL	250	500	1000	2000
90/10	30	12	15	15	18
70/30	30	12	15	18	21
50/50	30	15	18	21	15
30/70	30	18	21	24	27
10/90	30	18	21	27	30

TABLE VI
The Influence of Different Concentration of (DCA-HDA)/MA) Terpolymer Additivies on Osories Crude Oil Pour Point

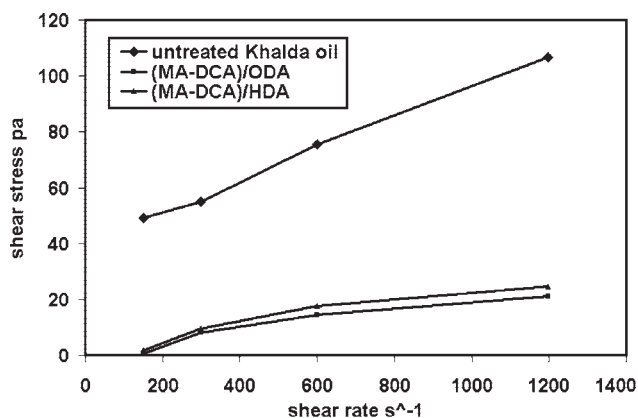| Terpolymer compositions	Pour point (°C) at concentration (ppm)				
	NIL	1000	2000	3000	5000
90/10	27	15	15	12	12
70/30	27	18	15	15	12
50/50	27	21	18	18	15
30/70	27	24	24	21	18
10/90	27	27	27	24	18

Figure 3 Rheogram of untreated and treated khalda crude oil with 250 ppm of 90/10 mol % of (DCA-ODA)/(MA) and (DCA-HDA)/(MA) terpolymers at 15°C.

pure terpolymer, or being crystallization itself a nucleating agent.

The pour point results for untreated and treated Osores crude oil containing different concentrations of synthesized inhibitors (DCA-ODA)/(MA) or (DCA-HDA)/(MA) are listed in Table V, VI, respectively. The data show that the synthesized terpolymers with molar ratio 90/10 mol % are also more effective PPDs. It is also apparent that (DCA-ODA)/(MA) teropolymers reduce the pour point of Osores crude oil to some extent more than that of (DCA-HDA)/(MA) terpolymer in all molar ratios. This may be attributed again to the presence long alkyl side chains (C18) that making them more efficient additives. There long alkyl side chains afford favorable adsorption sites for wax crystals, while keep them separated from each other by MA polar center. The same behavior for Osores crude oil in depressing pour point is observed at different terpolymers concentrations, except about the optimum concentration. The optimum concentration achieved the best performance is 5000 ppm for all molar ratios. This
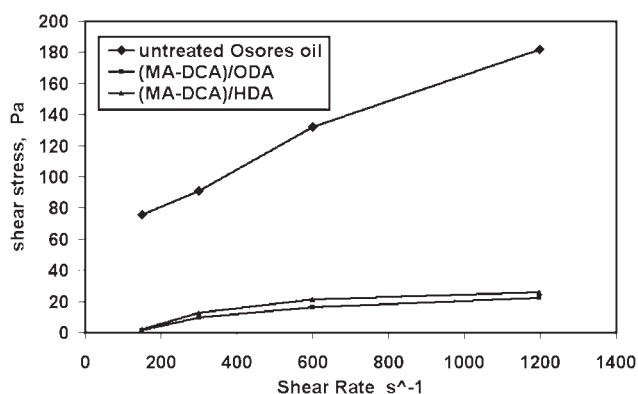

Figure 4 Rheogram of untreated and treated osores crude oil with 5000 ppm of 90/10 mol % of (DCA-ODA)/(MA) and (DCA-HDA)/(MA) terpolymers at 15°C.

TABLE VII
Rheological Parameters of Untreated and Treated Khalda Crude Oil Using 250 ppm of Selected Pour Point Depressants at Different Temperature

Oil sample	$T°C$	Yield stress (Pa)	Plastic viscosity (Pa s)
Untreated	15	40.20	2.590
	30	18.55	1.375
	45	12.50	0.546
(DCA-HDA)/(MA)	15	0.0183	0.9240
	30	0.0140	0.0942
	45	0.0128	0.0469
(DCA-ODA)/(MA)	15	0.0181	0.5570
	30	0.0128	0.0484
	45	0.0090	0.0271

may be due to higher asphaltene content in Osores crude oil in Khalda one Tables III–VI. This high asphaltenes constitute nucleation centers for paraffin crystallization.[22] Thus, interferes flowing enhancement by the tested additives.

Rheological measurements of crude oil and crude oil/terpolymers additives

The rheological behaviors of effective PPDs (DCA-ODA)/(MA) and (DCA-HDA)/(MA) terpolymers with molar ratio 90/10 mol % for the optimum concentrations 250 ppm for the Khalda and 5000 ppm for Osores crude oils were evaluated. The tests were performed for untreated and treated crude oils at temperatures below and above their pour points (15, 30, and 45°C).

Figures 3 and 4 represent shear stress versus shear rate plots for untreated and treated crude oils of the selected terpolymes ratio at 15°C. The data reveals that the untreated crude oils follow a non-Newtonian yield-pseudo plastic rheological behavior. Regarding the treated samples for both crude oils, the rheograms show the additivies changes the behavior of both oils into yield stress fluids with very low yield value or even zero value. Tables VII and VIII show yield stress values for the treated samples of both crude oils at 15, 30, 45°C. A remarkable decrease in yield values on increasing the temperature to 45°C (a temperature that is higher than the pour point of both Khalda and Osores crude oils) is observed. At 30°C (a temperature that is more than or equal to the pour point of both oils) yield stress values drop significantly to near zero. A higher drop is observed upon using (DCA-HAD)/(MA) in both cases. This behavior is ascribed to shorter chain length of HAD incorporated in the additive structure than that of ODA. Plastic viscosities for selected terpolymers with ratio 90/10 mol % and optimum concentrations at 15, 30, and 45°C are shown in Tables VII and VIII. A logical decrease in

Oil sample	$T°C$	Yield stress (Pa)	Plastic viscosity (Pa s)
Untreated	15	62.907	0.1101
	30	18.680	0.0184
	45	13.860	0.0140
(DCA -HDA)/(MA)	15	3.808	0.0295
	30	4.000	0.01610
	45	0.235	0.01320
(DCA-ODA)/(MA)	15	3.55	0.0242
	30	1.568	0.0112
	45	0.156	0.0075

crude oils using the selected terpolymes ratio 250 ppm for Khalda and 5000 ppm for Osores, respectively, at 15°C. At this temperature paraffin's 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 terpolymers show non-Newtonian pseudoplastic relationships at selected concentration (250 ppm for Khalda and 5000 ppm for Osores). This indicates that these terpolymers have the ability to disperse wax crystals and improve the flow behaviors of the tested crude oils.

Finally, from pour point and rheological measurements, it can be concluded that a good correlation was attained between pour point results and rheological measurements.

plastic viscosity values is observed with increasing temperature from 15 to 45°C. This temperature was selected (below pour point of both oils) to show the effect of temperature on the viscosity of the crude oil. Both untreated and treated oils show a non-Newtonian shear thinning behavior, but with a significant decrease in crude oil viscosity on using the additives. (DCA-ODA)/(MA) provoke a higher depression in the apparent viscosity of both crude oils than (DCA-HAD)/(MA).

Figures 5 and 6 represent the recorded apparent viscosity versus shear rate for untreated and treated

Correlation between viscosity and pour point results

Good interaction between additives and wax crystals makes it easy to destroy any wax aggregates when the oil is submitted to shearing. In the present work, when the optimum concentrations of both selected additives were applied they precipitate together with the wax crystals modifying the crystals morphology and inhibiting their aggregation causing depression in oil pour point. This behavior is reflected in the significant drop of yield values into approximately nil upon applying additives.
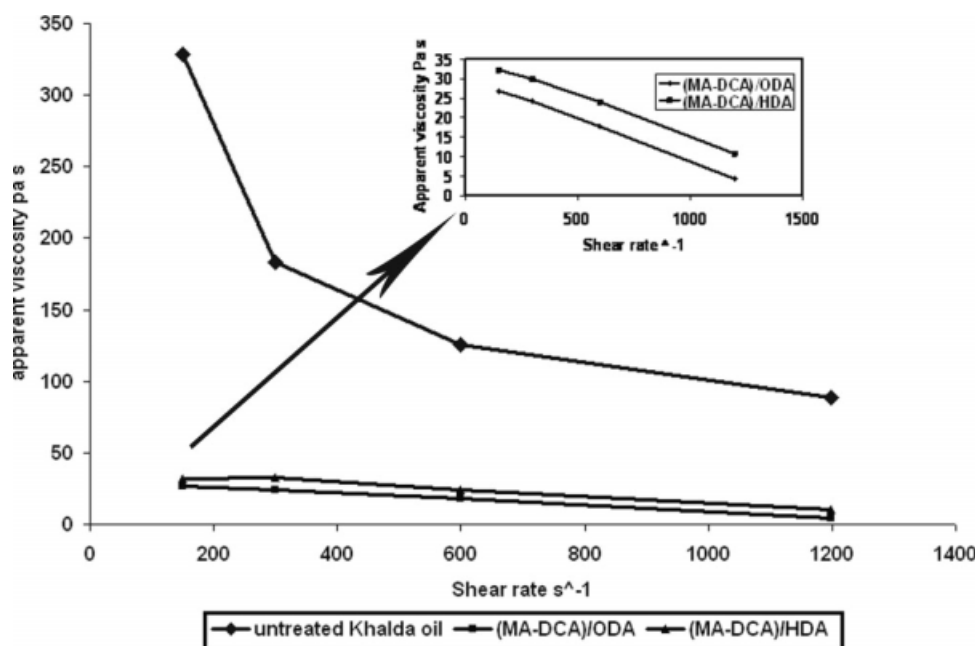

Figure 5 Effect of shear rate on apparent viscosity of untreated and treated khalda crude oil with 250 ppm of 90/10 mol % (DCA- ODA)/(MA) and (DCA-HDA)/(MA) terpolymers at 15°C.
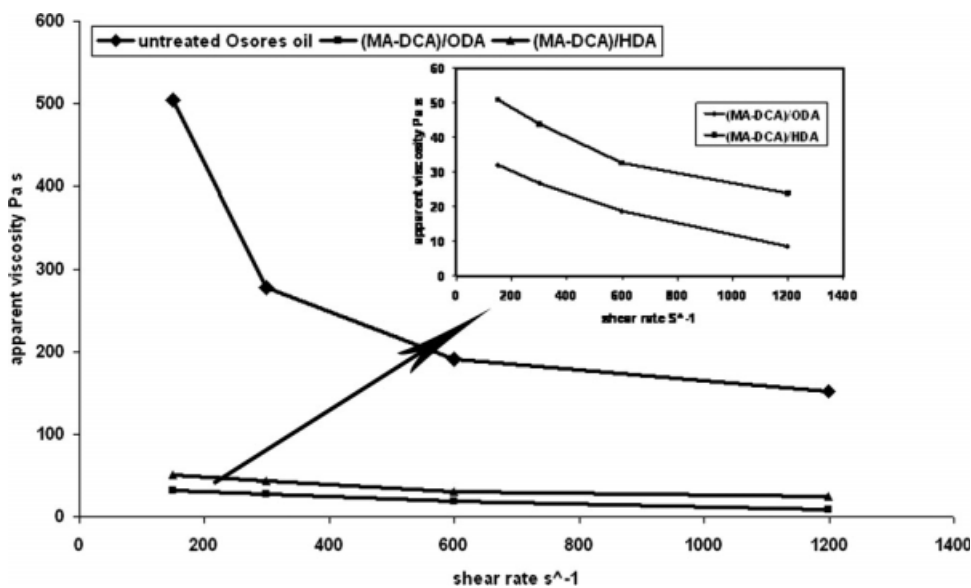
Figure 6 Effect of shear rate on apparent viscosity of untreated and treated osores crude oil with 5000 ppm of 90/10 mol % (DCA- ODA)/(MA) and (DCA-HDA)/(MA) terpolymers at 15°C.

CONCLUSIONS

- Increased ODA ratio in the prepared terpolymers backbone show high average molecular weights.
- The most effective PPD are (DCA-ODA)/(MA) and (DCA-HDA)/(MA) terpolymers with molar ratio 90/10 mol %.
- (DCA-ODA)/(MA) terpolymer is more efficient as PPD than (DCA-HDA)/(MA) terpolymers in all concentrations and compositions.
- The effective concentration for pour point depression of 90/10 mol % synthesized terpolymers ratio is 250 ppm for Khalda crude oil and 5000 ppm for Osores crude oil.
- The pour point depression efficiency depends on the variation of wax constitution in crude oil.
- The selected synthesized terpolymers show non-Newtonian pseudoplastic relationships at different temperatures (15, 30, and 45°C).

References

1. Rzaev, Z. M. O. Chem Abstr 1985, 102, 11410w.
2. Rzaev, Z. M. O. Prog Polym Sci 2000, 9, 163.
3. Yang, L.; Zhang, L.; Liu, G.; Gao, J.; Yang, S.; Yang, M.; Jin, R. J. J Appl Polym Sci 2001, 79, 1067.
4. Ham, G. E. J J Macromol Sci Chem 2001, 28, 733.
5. El-Gamal, S. J Appl Polym Sci 1996, 61, 1265.
6. Tiedje, J. L.; Holyday, W. C. Hydrocarbon Process 1961, 40, 111.
7. Holder, G. A.; Winkler, J. J Inst Pet 1965, 51, 228.
8. El-Gamal, I. M.; Gad, E. A. M.; Farmaui, S.; Gobiel, S. J Chem Technol Biotechnol 1992, 123,
9. Wang, S. L.; Flamberg, A.; Kikabhai, T. Hydrocarbon Process 1999, 78, 59.
10. Zhang, F.; Xie, H.; Donge, L. Proc SPE Int Symp Oilfield Chem 2001; 637.
11. Chanda, D.; Sarmah, A.; Borthakur, A.; Rao, K. V.; Subrahmanyam, B.; Das, H. C. Fuel 1998, 77, 1163.
12. Duffy, D. M.; Rodger, P. M. J Am Chem Soc 2002, 124, 5206.
13. Didukh, A. G.; Koizhaiganova, R. B.; Bimendina, L. A.; Kudaibergenve, S. E. J Polym Sci 2004, 92, 1042.
14. Dellyo, A.; Elizabete, F. L. Pet Sci Technol 2000, 18, 195.
15. Ante, J.; Marko, R.; Zvonimir, J. Eur Polym J 2006, 42, 1105.
16. Ashbaugh, H. S.; Fetters, L. J.; Admson, D. H.; Prud Home, R. K. J Rheol 2002, 46, 763.
17. Organic Spectroscopy, 2nd ed.; William Kamp, ELBS: Hong Kong, 1987; Chapter 1, p 2.
18. Pasto, D. J.; Johnson, C. R. Organic Structural Determination; Prentice- Hall, Inc.: Englewood Cliffs, NJ, 1969; Chapter 4, p 5.
19. Yen, T. F.; Chilinaring, G. V. Asphaltenes and Asphalts; Elsevier: New York, 1994; Chapter 1, p 476.
20. Manka, J. S.; Ziegler, K. L. World Oil 2001, 222.
21. Jordon, E. F.; Feldessen, D. W.; Wrigly, A. J Polym Sci A 1971, 1, 1835.
22. Garcia, M. C. Fuels 2000, 41, 1043.