ISSN : 0974 - 7486 Volume 10 Issue 9

Materials Science

An Indian Journal

Full Paper

MSAIJ, 10(9), 2014 [355-362]

Effect of hetero atoms on crystal wax structures modification for Egyptian waxy crude oils

Enas A.Ismail[1], Hussin I.Al-Shafey[1]*, R.S.Abdel Hameed[2,3], O.E.El Azabawy[1]

[1]Egyptian Petroleum Research Institute, Petroleum Application Department, Nasr City, 11727, Cairo, (EGYPT)

[2]Chemistry Department, Faculty of Science, Alazhar Univrsty, 11884, Cairo, (EGYPT)

[3]Chemistry Department, College of Science, Hail University, Hail 1560, (KSA)

ABSTRACT

Hetero Atoms compounds can prepare by direct reaction between acid and alcohol to form esters or acid and amine to form amides. Ethylene acrylic acid copolymer, PEAA, was esterified with Hexadecyl alcohol, HDA, and amidation with Hexadecyl amine, HDM, to produced ester and amide respectively. The produced ester and amide were characterized by FTIR and ^{1}HNMR. The copolymer leads to a large reduction in the pour point of samples of Norpetco Petroleum Co. (NPC) crude oils. The polymeric additives were diluted with xylene by 10%, 20% 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 from 27 to 3 ^{o}C depending on the composition and location of Norpetco crude oil. Thus establishing the large efficiency of the products synthesized in this work.

KEYWORDS

Waxy crudes;
Pour point depressants;
Flow improvers.

INTRODUCTION

The complex nature of crude oil creates many problems during its transportation through long distance pipelines. At lower temperature crystallization of waxes creates problem in restart ability of crude oil after shutdown of the pipeline. The waxes generally crystallize as an interlocking network of fine sheets, thereby entrapping the remaining oil in cage-like structures[1-3] and cause the blockage of pipeline.

The rheological behavior 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. 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[4].

Flow improver (FI) additive, alternatively known as pour point depressant (PPD)/wax crystal modifier, can reduce the growth of the wax crystal and forms smaller crystals of a higher volume to surface ratio. Owing to this change in crystal shape the ability of wax crystals to intergrowth and interlock is greatly diminished. The combination of these two effects lowers the pour point, viscosity and yield stress appreciably, and it becomes easier for the transportation of waxy crude oil[5,6]. But wax is not the only component in a crude oil. Other constituents in the crude oil i.e. asphaltenes, resins, lighter distillates, polar aromatics etc. should also be considered as important factors while ascertaining the flow behavior of a crude oil. Asphaltenes are very large heterogeneous molecules with condensed aromatic nuclei[7], which may associate to form colloidal sized particles that strongly influence the viscosity of the oil medium and affect the crystallization of the wax[8-10].

All pour point depressants are structured so that part of the molecules is like the paraffin wax crystals, this part functions by providing nucleation sites and co-crystallizing with the paraffin waxes, while the other part of the structure, dissimilar to the wax crystals, blocks the extensive growth of the wax matrices. This enables the bulk stream to remain pumpable, pourable and filterable. Oil composition, particularly n-paraffins, plays an important role in defining the response of untreated and treated oils to flow improvement[11,12].

These additives were a combination of the conventional flow improvers and wax dispersants. The structure and composition of wax dispersants is similar to conventional flow improver in some feature, but different in others. They often possess highly polar functional groups. This polarity may reach a surfactant character, which is considered as the basic prerequisite for the dispersant potential. Polar hetero atom containing polymers can function as wax dispersants and flow improvers simultaneously in one component additive[13-17].

So, to find out efficient flow improvers for oil a series of hetero atom containing polymers were prepared and characterized, and the influence of the structure of the polymer as pour point depressant was mainly investigated in this paper.

EXPERIMENTAL

Materials

Poly ethylene acrylic acid (PEAA) as waste material. Hexadecyl alcohol (HDA), Hexadecyl amine (HDM) and P-Toluene sulfunic acid monohydrate (PTSA) are from Aldrich Chemicals.

Egyptian waxy crude oil, Norpetco Petroleum Co. (NPC), was used for evaluating the performance of the synthesized polymeric additives. Their physico-chemical characteristics are given in TABLE (1).

Synthesis of PEAA-HDA and HDM copolymers

TABLE 1 : Physico-chemical characteristics of all crude oils are used.

Test	Method	Norpetco Crude Oil
API Gravity at 60 ^{o}F	ASTMD-1298	42.1
Specific Gravity at 60/60 ^{o}F	ASTM D-1298	0.820
Wax content, (Wt %)	UOP 46/64	12.5
Asphaltene content, (Wt %)	IP 143/84	3
Water content, vol. %	IP 74/70	30
Pour Point, ^{o}C	ASTM D-97	27

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 esterification 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.

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 shacked for 3 minutes and the temperature was kept constant to 5 minutes according to NPC procedure. 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. The pour point temperature was measured at temperature 48 ^{o}C, ASTM D 97-93 .

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 12 °C. Yield point, and apparent viscosity values were determined[18]. Shear-rate, shear-stress, and viscosity can be calculated by the following equations:

Shear-rate (D)

$$D = M \times n\,(S\,1) \qquad (1)$$

Where; M is shear –rate factor, depending on sensor system, and n is actual test speed. The actual test speed is calculated as following:

$$n = \frac{\text{Set test speed}}{\text{Reduction factor "R"}} \qquad (2)$$

Shear-stress (τ):

$$\tau = A \times S \text{ (Pascal [Pa])} \qquad (3)$$

Where; A is shear –stress factor, depending on time of measuring drive unit and sensor system, and S is measuring value (scale grade).

Apparent Viscosity (η):

$$\eta = (G \times S)/n \text{ (mPa.S)} \qquad (4)$$

Where; G is "instrument factor", depending on the type of measuring drive unit and sensor system.

Characterization of the products

All reagents and products for reactions performed in this investigation were analyzed by Fourier Transform Infrared Spectrometry (FTIR) in a BIORAD-Excalibur Series FTS 3500GX system. The method of analysis varied according to the characteristics of the products, however, all of them were performed with 20 scans/min and resolution of 4 cm $^{-1}$. The copolymer and graft copolymer were analyzed as molten films between KBr cells.

The analyses by hydrogen nuclear magnetic resonance (^{1}H NMR) were recorded by a BRUKER-Avance 400 (400 MHz) spectrometer operating at 9.4 T, observing hydrogen at 400.13 MHz, in deutered chloroform solution (CDC13) and TMS as internal reference to NMR chemical shifts.

RESULTS & DISCUSSION

Synthesis of PEAA-HDA and HDM copolymers

The present work aims to prepare ester copolymers soluble in petroleum crude oil to be evaluated for improving flow properties of petroleum crude oil. In this respect, PEAA was esterified with HDA and HDM in presence of PTSA as catalyst at 140 °C for 6h to produce PEAA-HDA and PEAA-HDM copolymers.

The copolymers have been utilized by esterification with using the carboxylic acid groups of ethylene acrylic acid copolymer as reactive sites in reactions with ROH and RNH_2. The carboxylic acid groups of PEAA are intermolecular hydrogen bonded, and this fact, in addition to the effects of the crystalline morphology of the polymer, makes a true solution difficult to obtain. In this respect, esterification of HDA and HDM with –COOH groups of PEAA was completed separately to produce esters having one type of ester groups and to determine the reactivity of each group towards PEAA.

All prepared of PEAA esters were soluble in xylene and have to be purified before characterization.

The purified copolymers were analyzed by FTIR spectroscopy. Spectra of the purified ester copolymer (PEAA-HDA) sample are shown in Figure (1). 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 for PEAA copolymer. 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 group for the ester. Copolymer composition was determined by means of IR spectroscopy.

The chemical structure of PEAA-HDM can be confirmed by ^{1}HNMR analysis. The signals in ^{1}HNMR spectra of the studied copolymer were assigned according to published data[19]. In this respect, ^{1}HNMR spectra of PEAA-HDM are presented in Figures (2).

The new signals at 3.8 ppm in spectra of PEAA-HDM, which attributed to CONH, of HDM, indicate that HDM was amidation onto PEAA chains. On the other hand, the signals at 1.188 ppm are observed in all spectra and can be attributed to CH_2 of ethylene. The presence of singlet and triplet signals at 0.812, 1.2 ppm (CH_3) in spectra of PEAA-HDM indicates that COOH group of PEAA were amidation with HDM.

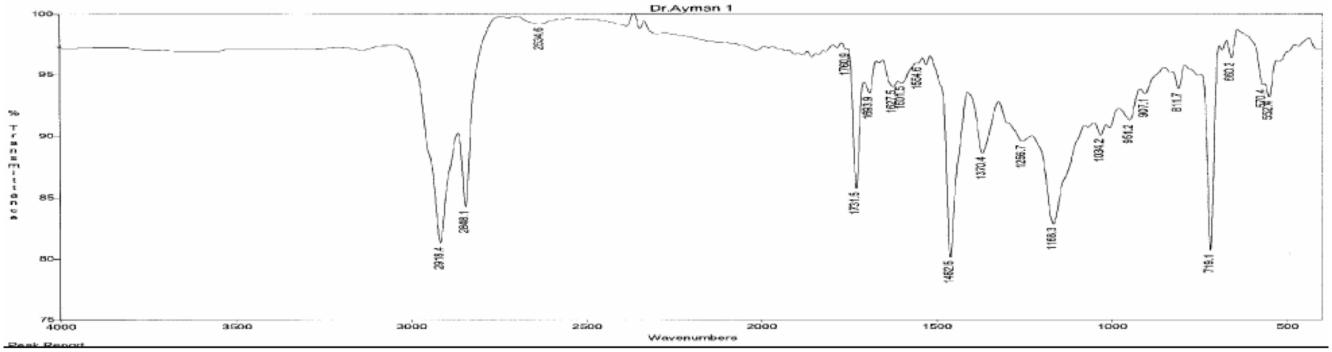

Figure 1 : IR Spectrum for PEAA-HDA.

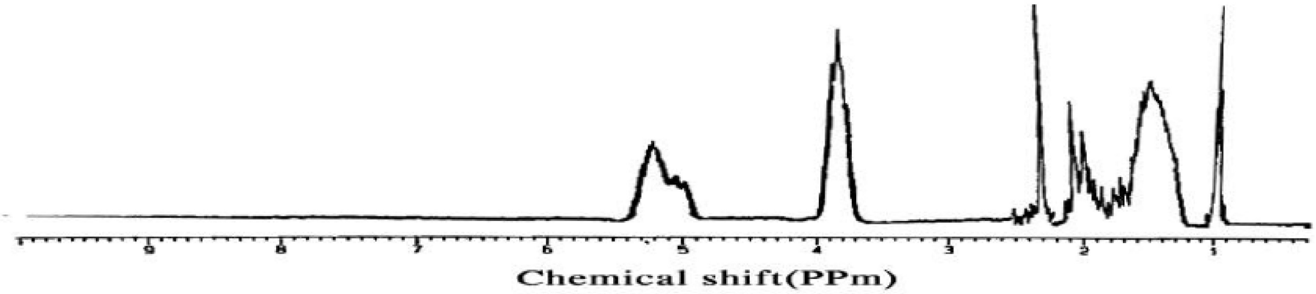

Figure 2 : ^{1}HNMR Spectrum for PEAA-HDM.

Pour point

Norpetco field is located in the Egyptian western desert and as almost of the producing fields in western desert, Norpetco field produces paraffinic crude with a relatively medial pour point but the paraffinic chains are completely different.

The results are presented as pour point reduction in relation to the pour point of the pure crude oil[8]. The pour point reduction was calculated by:

Pour point reduction (ΔP) = $PP_{pure} - PP_{padd}$ (5)

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

The pour point results and pour point reduction (ΔP) for pure crude oils and for the crude oil containing additive (PEAA-HDA and PEAA-HDM) are shown in TABLES (2, 3).

The 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 function by one or more several postulated mechanisms, viz. nucleation, adsorption, co-crystallization and improved wax solubility that result in the formation of smaller wax crystals with more regular shape.

The date in TABLES (2, 3), show the pour point of treated and untreated crude oils for Norpetco-mix and Ferdaus-mix. In this respect, crude oils which have PPD

TABLE 2 : Pour point data of treated Norpetco-mix crude oil with PEAA-HDA and PEAA-HDM

Crude oils	Dose	PEAA-HDA				PEAA-HDM			
		10%		20%		10%		20%	
		PP, °C	ΔP	PP, °C	ΔP	PP, °C	ΔP	PP, °C	ΔP
Norpetco-mix	Blank	27	0	27	0	27	0	27	0
	500	24	3	18	9	18	9	15	12
	1000	18	9	15	12	12	15	9	18
	2000	15	12	12	15	9	18	6	21
	3000	12	15	9	18	6	21	3	24

TABLE 3: Pour point data of treated Ferdaus-mix crude oil with PEAA-HDA and PEAA-HDM

Crude oils	Dose	PEAA-HDA				PEAA-HDM			
		10%		20%		10%		20%	
		PP, °C	ΔP	PP, °C	ΔP	PP, °C	ΔP	PP, °C	ΔP
Ferdaus-mix	Blank	24	0	24	0	24	0	24	0
	500	21	3	18	6	18	6	12	12
	1000	15	9	15	9	12	12	9	15
	2000	15	9	12	12	9	15	6	18
	3000	12	12	9	15	6	18	3	21

are exhibiting a lower pour point more than that without PPD at different doses ranging from 500 to 3000 ppm. The additives were more efficient in reducing the pour point of the oil obtained from the Norpetco fields.

For all the fields, the additives presented the following performance order: PEAA-HDA < PEAA-HDM. These behaviors can be correlated to the structure of PEAA amides that possess HDA and HDM moieties and its interaction with crude oil. However, it does not precipitate the sufficient amount that would be necessary to significantly modify the wax crystals[4].

The effectiveness of a pour point depressant depends on the chemical composition and structural characteristics of the polymer and the length of the alkyl

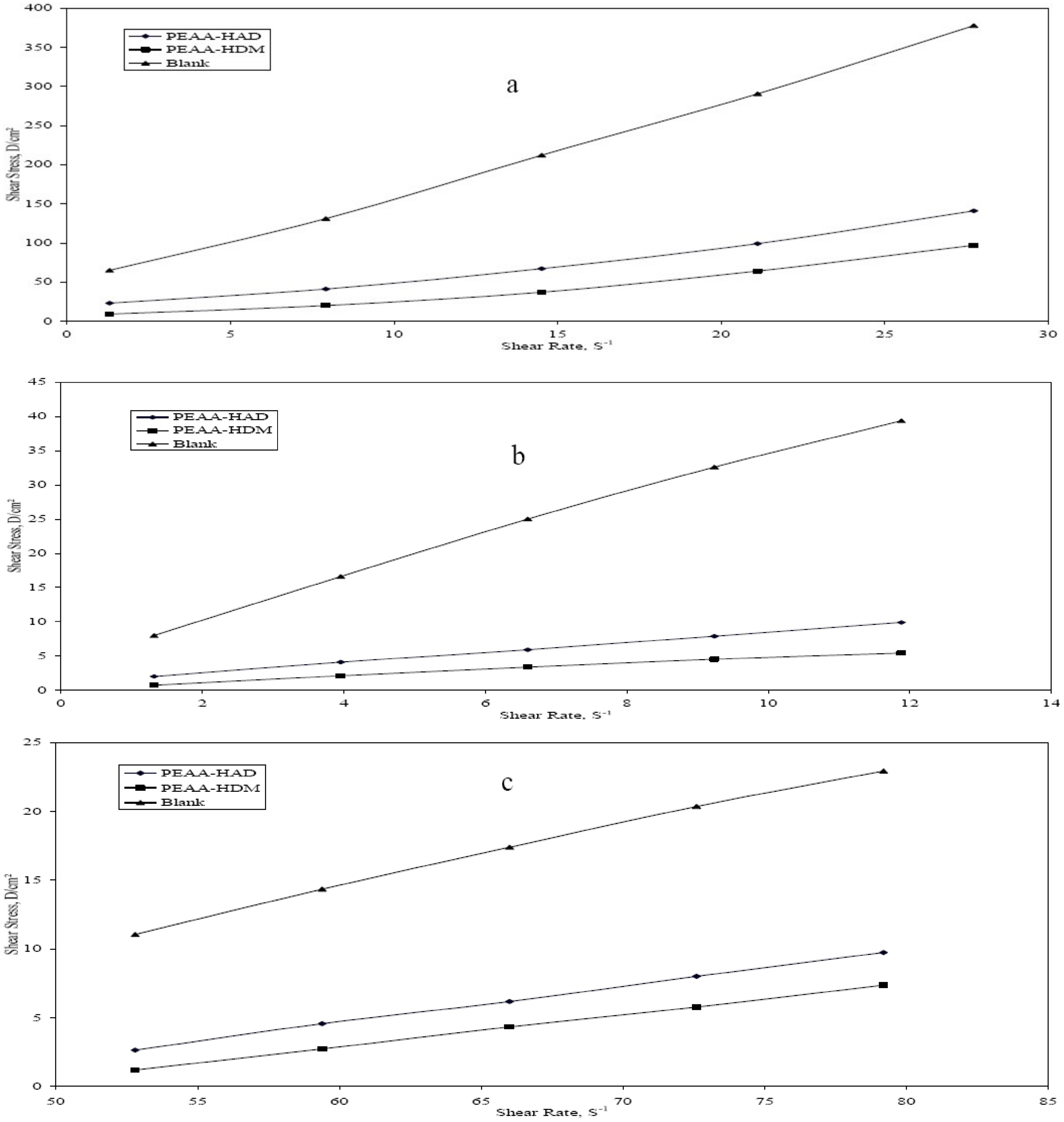

Figure 3: Relation between shear rate and shear stress of Norpetco-mix Crude with 3000 ppm of PEAA-HDM at Temperatures at a) 12 °C, b) 27 °C and c) 36 °C.

side chain.

Effect of additives on rheology of crude oils

The rheological behavior of 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 shear stress at and below their pour point temperature[20]. The flow properties of waxy crude oil depend strongly on the shear rate, temperature, rate of cooling, time of shearing, and composition of the crude oil[21].

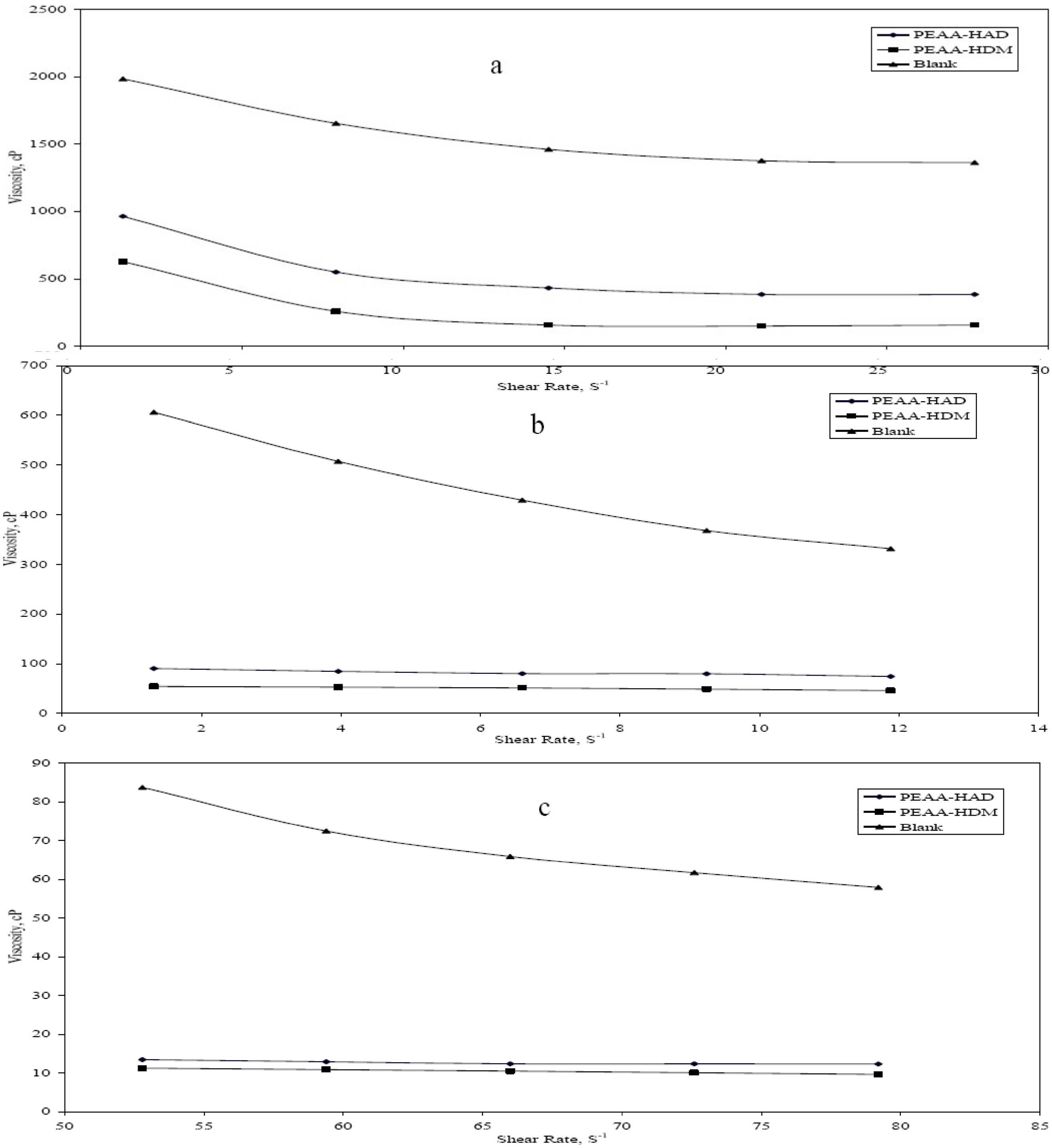

Figure 4 : Relation between shear rate and apparent viscosity of Norpetco-mix Crud with 3000 ppm of PEAA-HDM at Temperatures at a) 12 °C, b) 27 °C and c) 36 °C.

Hence, copolymer additives were evaluated for their performance as flow improvers in the two tested crude oils through rheological measurements at concentration of 500-3000 ppm. Measurements of the shear stress–shear rate and viscosity- shear rate relationships were carried out at different temperatures ranging from 36 °C to 12 °C. Shear stress – shear rate relationships for the untreated and treated crude oils with PEAA-HAD and PEAA-HDM at different concentrations and temperatures 36 and 12 °C were plotted in Figure 3. This figure illustrates the fitted experimental data of both shear stress and shear rate measurements according to the Bingham plastic model[20].

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[21]. On the other hand, the relation between the shear rate and the dynamic viscosity for a representative example is shown in Figure 4. 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.

This behavior may be explained by the following reasons; at temperatures around the pour point of the waxy crude oils at low shear rate, the energy exerted by shear and dissipated energy in the matrix tends to break down the wax crystals partially. But by increasing the shear rate, the dissipated energy is high enough to overcome the yield stress and start flow[22]. Upon increasing the shear rate, the size of the agglomerates decreases and this process releases some of the continuous phase originally immobilized within the agglomerates. As a result, the effective dispersed phase concentration decreases, and leads to decreasing the viscosity. The viscosity decreases with increasing the shear rate until the agglomerates are completely broken into the basic particles. So the waxy oil system shows non-Newtonian characteristic.

The behavior of decreasing the rheological parameters after addition of the prepared copolymers can thus be attributed to their chemical structure. The high polarity of hetero atom in the copolymer additives was playing a role in preventing the agglomeration of wax crystals in crude oil. In addition, the interaction of the alkyl branch with the paraffin fraction in the oil occur through well matching of the alkyl chain length and as discussed before, as the alkyl chain length increases a better mach occurs[17].

CONCLUSION

- In using the polymer additives obtained in this investigation, a reduction in the pour point of a sample of crude oils, thus demonstrating the efficiency of the products synthesized in this study.
- For the crude oils of Norpetco-mix, the best performance as pour point depressant was obtained in the order PEAA- HDM <PEAA- HDM.
- The prepared materials show good results as pour point depressant and as flow improver for the tested NPC crude oils at concentration 3000 ppm.
- The data of 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 copolymeric additives.
- There is an apparent disagreement between the pour point reduction and the rheological results obtained for the PEAA copolymers. This difference has been ascribed to the different wax particles behavior in the static pour point test and in the measurements involving shearing.

REFERENCES

[1] R.Malcolm, Q.Davidson, Dzuy Nguyen, Hans Petter Rønningsen; Restart model for a multi-plug gelled waxy oil pipeline, J.Petrol.Sci.and Engin., **59**, 1 **(2007)**.

[2] H.P.Rønningsen, B.Bjørndal, A.B.Hansen, W.B.Pedersen; Wax precipitation from North Sea crude oils:Crystallization and dissolution temperatures, Newtonian and non-Newtonian flow properties, Energy Fuels, **5(6)**, 895 **(1991)**.

[3] H.I.Al-Shafey, A.I.Hashem, R.S.Abdel Hameed, E.A.Dawood; Studies on the Influence of Long Chain Acrylic Esters Co-Polymers Grafted With Vinyl Acetate as Flow Improver Additives of Crude Oils, Advances in Applied Science Research, **2(5)**, 476-489 **(2011)**.

[4] Ayman M.Atta, H.I.Al-Shafey, E.A.Ismail; Influ-

ence of Ethylene Acrylic Alkyl Ester Copolymer Wax Dispersants on the Rheological Behavior of Egyptian Crude Oil, J Dispersion Science Technology, **32**, 1296-1305 **(2011)**.

[5] M.C.Garcia, L.Carbognani, A.Urbina, M.Orea; Paraffin depositon in oil production.Oil composition and paraffin inhibitors activity, J.Petrol.Sci.Technol., **16(9)**, 1001 **(1998)**.

[6] J.Denis, J.P.Durand; Modification of wax crystallization in petroleum products.Rev.Inst.Fr.Pet.Ann., **46**, 637 **(1991)**.

[7] Rafael A.Soldi, Angelo R.S.Oliveira, Ronilson V.Barbosa, A.F.Maria; Ce´sar-Oliveira J.European Polymer, **43**, 3671 **(2007)**.

[8] L.C.Andre, A.B.Machado, F.Elizabete, A.Lucas, B.Gaspar Gonza´lez; J.Petrol.Sci.and Eng., **32**, 159 **(2001)**.

[9] D.Chandaa, A.Sarmaha, A.Borthakura, K.V.Raoa, B.Subrahmanyama, H.C.Dash; Fuel, **77(11)**, 1163 **(1998)**.

[10] L.T.Wardhaugh; Ph.D.Thesis, University of Melbourne, **(1990)**.

[11] K.M.Agrawal, R.C.Purohit, G.C.Joshi; J.Fuel Sci.Technol.Int., **12**, 1245 **(1994)**.

[12] K.S.Wang, C.H.Wu, J.L.Creek, P.T.Shuler, V.Tang; J.Pet.Sci.Technol., **21**, 359 **(2003)**.

[13] H.I.Al-Shafey, A.M.Atta, E.A.Ismail, R.S.Abdel Hameed; New Polymeric Additives as Pour Point Depressants for Egyptian Waxy Crude Oils, J Petroleum Science and Technology, onlin, **(2013)**.

[14] Y.Song, T.Ren, X.Fu, X.Xu; J.Fuel Process. Technol., **86**, 641 **(2005)**.

[15] D.P.Srushti Deshmukh, Bharambe; Fule Processing Technology, **89**, 227 **(2008)**.

[16] Y.Songa, T.Rena, X.Fub, X.Xu; Study on the relationship between the structure and activities of alkyl methacrylate-maleic anhydride polymers as cold flow improvers in diesel fuels, Fuel Process.Technol., **86(6)**, 641 **(2005)**.

[17] A.M.Al-Sabagh, M.R.Noor El-Din, R.E.Morsi, M.Z.Elsabee; J.Petrol.Sci.and Engin.8 **(2009)**.

[18] R.B.Bird, R.C.Armstrong, O.Hassager; Dynamics of Polymeric Liquids.John Wiley and Sons, New York.**(1987)**.

[19] V.Barboiu, A.Natansohn, D.Blum, Rev.roum.chim.**25**, 933 **(1980)**.

[20] H.I.AL-Shafey; Ph.D.Thesis, AL-Azhar University, Cairo, Egypt, **(2007)**.

[21] A.K.Chatterjee, S.D.Phtak, P.S.Murthy, G.C.Joshi; Comb-type polymers and their interaction with wax crystals in waxy hydrocarbon fluids: wide-angle X-ray diffraction studies.J.Appl.Polym.Sci.**52(7)**, 887 **(1994)**.

[22] C.Li, X.Pan, C.Hua, J.Su, H.Tian; Synthesis of novel copoly (styrene-maleic anhydride) materials and their luminescent properties.J.Eur.Polym.**39(6)**, 1091 **(2003)**.