FULL LENGTH ARTICLE

Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties

A.M. Al-Sabagh [a,*], M.W. Sabaa [b], G.R. Saad [b], T.T. Khidr [a], T.M. Khalil [b]

[a] Department of Petroleum Applications Egyptian Petroleum Research institute (EPRI), 1 Ahmed El-Zomor St., Nasr City, 11727 Cairo, Egypt
[b] Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

Abstract Modification of the wax crystal habit practical interest during transportation processing of lube oil at low temperature. Various pour point depressant (PPD) additives can facilitate this modification by different mechanisms. Comb shaped polymer additives are known to depress the pour point of lube oil by providing different nucleation sites for the precipitation of wax. This paper describes performance based design, synthesis, characterization and evaluation of comb shaped polymeric additives. Alkyl itaconates were prepared by the esterification of itaconic acid with different saturated alcohols C_{16}/C_{18}/NAFOL 20 + A (C_{av} = 20)/NAFOL 1822 B (C_{av} = 22). The four synthesized monomers were characterized and copolymerized with styrene in different molar ratios. All the products were characterized by infra-red (FTIR), Nuclear Magnetic Resonance (NMR) Spectroscopy and Gel permeation chromatography (GPC). Rheological properties of lube oil (with and without additives) were studied by Brookfield viscometer. In this study the additives based on itaconic acid were evaluated as good PPD and rheology modifiers.

1. Introduction

Lube oil and diesel are complex processes and highly depend on chain length distribution of *n*-alkanes along with their solubilities in the medium. This solubility factor has many variables, it is a summation property of individual types of molecules, for example iso-alkane, naphthenic and aromatics [1–2]. Lube oil having wax content causes many problems during production, storage and transportation. At low temperature, waxes separate out from the lube oil and deposit on the wall of pipelines or tankers. Due to this, the effective diameter

* Corresponding author.
E-mail address: alsabaghh@gmail.com (A.M. Al-Sabagh).

for flow of the lube oil through pipeline becomes less [3–6]. Therefore pressure drop between the two ends of the pipeline increases. This results in the reduction of flow and extra burden on the pumping system. Another major problem during the handling of the lube oil is the reusing of the pipeline after prolonged shut down period; the cooled oil slowly develops gel structure which results in a high yield stress [7–10]. Wax crystal modifier additives can minimize these problems. The designing of better additives requires a good understanding of the crystallization behavior of the paraffin molecules in hydrocarbon fluids. Any additive which is as effective as PPD may be ineffective to reduce viscosity and yield stress and enhance the flow. The following factors play an important role in the efficiency of flow improvers and pour point depressants [11–16]. The number of pendant alkyl side chains and the length and distance between them are important factors; the solubility of the additives (which are generally polymers) in lube oil depends on their average molecular weights. If the additive is a copolymer, then monomer to monomer ratio should be taken into consideration. Amorphous and crystalline parts of the additive are very important in determining its efficiency and its physical and chemical stability [17–20].

Flow improvers are generally ashless polymeric materials which when added to lube oil show excellent function for lowering the pour point. Many different types of pour point depressants have been used to overcome this problem e.g. condensation products of chlorinated paraffins and naphthalene polyacrylates, polymethacrylate, copolymers of ethylene and vinyl esters, copolymers of fumarates/maleates and vinyl acetate, copolymers of α-olefins and maleates and poly-α-olefin [21] All pour point depressants are structures so that a 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-paraffin's, plays an important role in defining the response of untreated and treated oils to flow improvers [22,23].

For evaluation of the improved operability of the treated lube oil, determination of flow parameter via cloud point and pour point tests are the most widely adopted methods. Photo analysis is used also as a fast and simple supplementary screening tool confirming other laboratory tests for evaluating the cold flow properties of untreated/treated lube oil [24,25].

In the present work, polymeric additives based on itaconic acid were synthesized in the laboratory and evaluated as pour point depressants and flow improvers for lube oil. The rheological properties of lube oil (with and without additives) were studied in terms of shear rate, shear stress and viscosity.

2. Experimental

2.1. Materials

The following chemicals were used, itaconic acid, hexadecyl alcohol, Octadecyl alcohol, two linear saturated long chain alcohol blends NAFOL 20 + A and NAFOL 1822 B were supplied from Condeu Chemical Company, the typical analysis is listed in Table 1. P-toluene sulfonic acid, dibenzoyl peroxide, styrene, toluene and other common chemicals used were of laboratory grade reagents.

Table 1 Typical analysis of linear long-chain alcohol blends (NAFOL).

Properties	NAFOL 20 + A	NAFOL 1822 B
Composition, wt%		
C16—OH	0.9	0.2
C18—OH	24.3	15.0
C20—OH	24.4	14.8
C22—OH	38.2	69.8
C24—OH	9.9	0.2
C26—OH	2.3	–
Average carbon number (calculated)	$C_{av} = 20$	$C_{av} = 22$
Density g/cm^3 at 70 °C	0.803	0.802
Solidification point, °C	56–60	63–65
Ester no. mg KOH/g	9.9	0.16
Acid no. mg KOH/g	0.05	0.01
Water, wt%	0.06	0.04
Flash point, °C	208	204
Iodine no. mgL/100 mg	8.2	0.23

Table 2 Physicochemical properties of investigated lube oil.

Test	Method	Result
Density@15 °C Kg/L	ASTM D1298	0.9083
Color	ASTM D1500	5.5
Pour point °C	ASTM D97	15
Flash point °C (PMC)	ASTM D93	203
Kinematic viscosity@ 40 °C CST	ASTM D445	243.59
Kinematic viscosity@ 100 °C CST	ASTM D445	18.94
Viscosity index	ASTM D445	87
Saybolt viscosity@ 100 °F SUS	ASTM D445	96.8
X-ray (sulfur) wt%	ASTM D4294	1.084
n-paraffins, wt%	GLC	62.27
Iso-paraffin, wt%	GLC	4.12
Total paraffins content, wt%	Urea adduct	66.39
Average carbon number (n)	GLC	28.56

2.2. Lube oil composition

Lubrication oil is submitted from Suez Oil Processing Company (SOPC). The general physicochemical characteristics of lube oil were shown in Table 2. The lube oil was used for evaluating the performance of the synthesized polymeric additives. The n-paraffin content of lube composition is determined by urea adduction [26]. The lube oil and its n-paraffin fraction were then subjected to gas chromatographic analysis for determination of the average molecular weight expressed in terms of average carbon number on the basis of carbon number distribution as illustrated in Fig. 1.

2.3. Synthesis of n-alkyl itaconate

Itaconic acid (0.3 mol), was esterified with a series of n-alkanols which having increasing number of carbon atoms (hexadecyl alcohol C_{16}, octadecyl alcohol C_{18}, blend of alcohol NAFOL 20 + A ($C_{av} = 20$) and NAFOL 1822 B ($C_{av} = 22$) (0.2 mol) in a round bottomed flask equipped with a Dean and Stark trap to remove the water of reaction azeotropically as it is formed. The reaction was conducted in the presence of toluene (100 ml) as a solvent, at reflux temperature. P-toluene
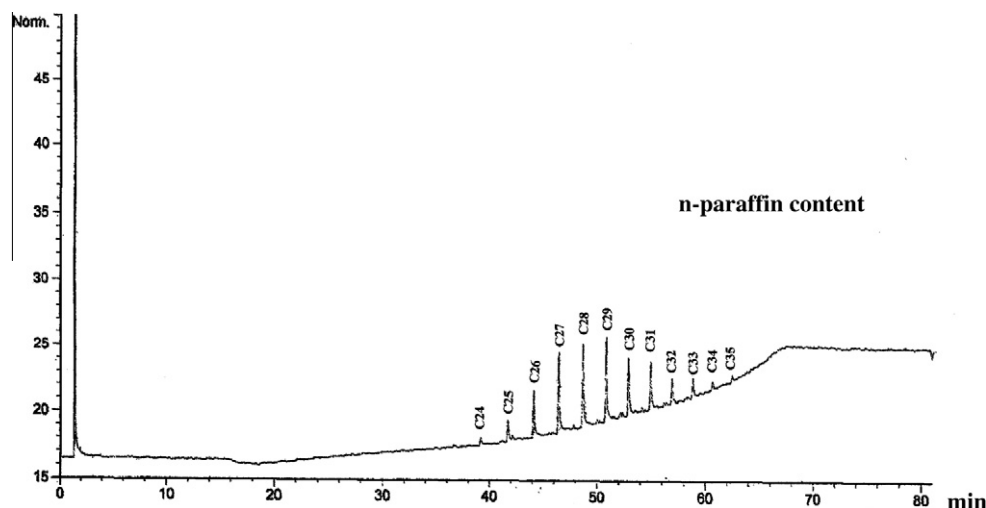
Figure 1 Carbon number distribution of *n*-paraffin content of lube oil.

sulfonic acid was used as a catalyst and hydroquinone as a polymerization inhibitor. The four prepared monomers (hexadecyl itaconate, octadecyl itaconate, NAFOL 20 + A itaconate, and NAFOL 1822 B itaconate) were then purified by distilling off the solvent at the end of esterification at reduced pressure. The reaction mixture was then extracted with *n*-hexane, washed with distilled water to remove the catalyst and any unreacted acid until the washing becomes neutral, then separation of organic layer comes out.

2.4. Copolymerization of n-alkyl itaconate monomers and styrene

Free radical solution copolymerization of each of the four hexadecyl/octadecyl/NAFOL 20 + A/NAFOL 1822 B itaconate monomers and styrene in different molar ratios (25%:75%), (50%:50%) and (75%:25%) was carried out in a four-necked round bottomed flask fitted with a mechanical stirrer, a condenser, a temperature controller and a nitrogen controlled inlet valve. Toluene was used as a solvent. Dibenzoyl peroxide (0.5 wt%), as an initiator, was dissolved in toluene then added to the reaction mixture in equal metered portions every 0.5 h during the course of the reaction. At the

beginning of polymerization, the reaction mixture was subjected to nitrogen flushing for twenty minutes then heated gradually to reflux temperature, under nitrogen blanket, while adding the first portion of initiator and applying vigorous stirring. The reaction was continued for 6h. The twelve prepared copolymers designated as PPD1–PPD12 are illustrated In Table 3. They were purified by precipitation in an excess volume of methanol then filtered. Further purification was carried out by dissolution in toluene and reprecipitation with methanol, filtration and vacuum drying at 40 °C.

2.5. Characterization of copolymers

The structures of the prepared mono-esters alkyl itaconate and copolymers with styrene were confirmed by using Infrared (IR) spectroscopic analysis in technology laboratory, petrochemical department. Egyptian petroleum Research Institute (EPRI). The infrared spectra were measured by using model Genesis series (USA) infrared spectro-photometer adopting KBr technique. The structure of the prepared mono-esters alkyl itaconate, and copolymers with styrene was also confirmed by using Nuclear Magnetic Resonance Spectroscopic analysis at the Chemistry Department, Faculty of Science (Cairo Univer-

Table 3 Characteristization of the synthesized polymeric additives.

Additive designation	Composition	Molar ratio alkyl itaconate-styrene (%)	Average side carbon length (C_{av})	M.wt.	Poly dispersity index
PPD 1	Poly (hexadecyl itaconate-styrene)	25:75	16	40313	1.68
PPD 2		50:50		45411	1.70
PPD 3		75:25		38513	1.50
PPD 4	Poly (octadecyl itaconate-styrene)	25:75	18	40933	1.70
PPD 5		50:50		48415	1.72
PPD 6		75:25		41513	1.62
PPD 7	Poly (NAFOL 20 + A itaconate- styrene)	25:75	20	58298	1.57
PPD 8		50:50		35026	1.50
PPD 9		75:25		28858	1.31
PPD 10	Poly (NAFOL 1822 B itaconate styrene)	25:75	22	60096	1.58
PPD 11		50:50		37710	1.55
PPD 12		75:25		30512	1.20
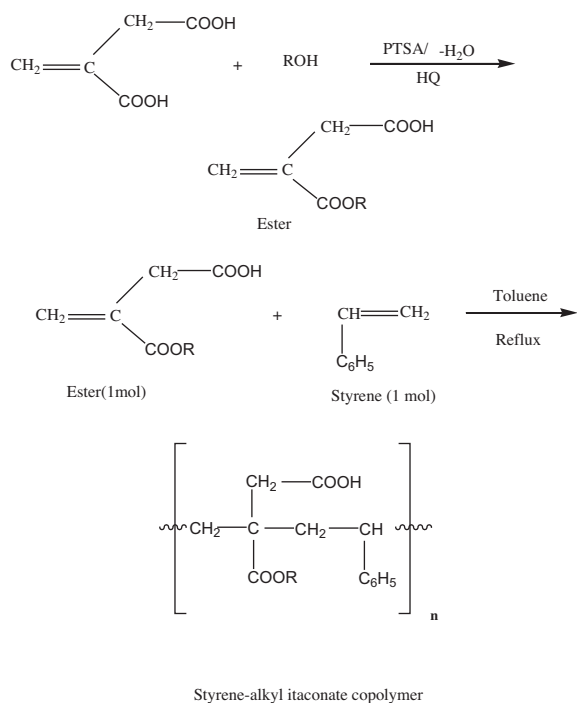
Scheme 1 Synthesis of alkyl itaconate monomer, and alkyl itaconate styrene copolymer.

sity). The ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer (USA) ^{1}H NMR spectra were run at 300 MHz in deuterated chloroform (CDCl$_3$).

The copolymers of different alkyl itaconate with styrene were abbreviated as PPD1–PPD3 (C$_{16}$), PPD4–PPD6 (C$_{18}$), PPD7–PPD9 (C$_{20}$), PPD10–PPD12 (C$_{22}$). The esterification and copolymerization are shown in Scheme 1. The characterization of the prepared copolymers is illustrated in Table 3. The molecular weight was determined using Gel permeation chromatography (GPC) in technology laboratory, petrochemical department, Egyptian petroleum Research Institute (EPRI) includes Waters 515 HPLC pump, Waters temperature control module and 2410 refractive index detector from Water company. And further supplement using viscosity (Brookfield viscometer, USA).

2.6. Evaluation tests

2.6.1. Pour point measurement (ASTM D 97-96) [27]
Solutions of oil soluble samples PPD1–PPD12 in toluene contain 10% active material, are prepared according to ASTM, D97–96 method. Different concentrations (250,500,1000, 1500,2000 and 3000 ppm) of PPD solutions were injected into the lube oil and tested as pour point depressants. The pour point is set at 2.8 °C above the temperature at which the oil becomes solid [28], the location of pour point instrument is Suez Oil Processing Company (SOPC).

2.6.2. Dynamic viscosity measurements

The dynamic viscosity using (Brookfield viscometer USA), (DVII) at the Chemistry Department, Faculty of Science (Cairo University) for untreated and treated lube oil with some selected pour point depressants PPD2, PPD5, PPD8 and PPD11 at concentration 2000 ppm and different temperatures (10, 15 and 20 °C) have been studied. In addition, the common flow modes that reasonably identify the non- Newtonian rheological flow properties of lube oil at temperatures around and lower than the pour point have been also studied. The rheology parameters were obtained from the following equations [29]:

SHEAR RATE

$(\sec^{-1}): \quad S' = \frac{\omega}{\sin\theta}$

SHEAR STRESS

$(\text{dynes/cm}^2): \quad F' = \frac{M}{\frac{2}{3}\pi r^3}$

VISCOSITY

Definitions : ω = angular velocity of spindle $\frac{F'}{S'}$

(rad/sec)

$\left[= \left(\frac{2\pi}{60}\right)N\right], \ N = \text{RPM}$

M = torque input by instrument

θ = cone angle(degrees)

r = cone radius (cm)

The Bingham yield value (τ_B) can be obtained from the intercept of the graph relation between shear rate and shear stress. On the other hand, the linear line from the relation between shear rate and viscosity gives us the dynamic viscosity.

2.7. Photo micrographic analysis

The photomicrographs showing wax crystallization behavior of the untreated and treated lube oil (LO) sample with the synthesized additives at different concentrations have been recorded. An Olympus polarizing microscope model BHSP fitted with an automatic camera with a 35 mm format was used for photo micrographic analysis. The light source was a helium lamp. The temperature of the tested lube oil sample was controlled on the microscope slide by an attached cooling thermostat. All photos were taken at 0 °C. The adopted magnification was 100×.

3. Results and discussion

3.1. Chemical structure and characterization of the prepared copolymers

3.1.1. Ester monomers
The chemical structure was studied by Infrared spectral analysis which showed similar patterns for the four esters. A representative IR pattern for octadecyl itaconate monomer is shown in Fig. 2a which illustrates the O—H stretching band of mono carboxylic group absorbed small broad band at 3443 cm^{-1} due to partial esterification reaction. The C—H stretching vibration of CH$_3$ and CH$_2$ groups absorbed strongly at 2913–2845 cm^{-1}, the ester C=O appeared as a strong absorption band at 1707 cm^{-1} and the presence of the ester functionality was further supported by appearance of a C—O stretching vibration at 1154–1188 cm^{-1}. The characteristic C=C stretching band appeared at 1636 cm^{-1}, whereas the CH in plane deformation vibrations of itaconate ester monomers appeared at 1323 cm^{-1}. A strong absorption of the bending vibration of
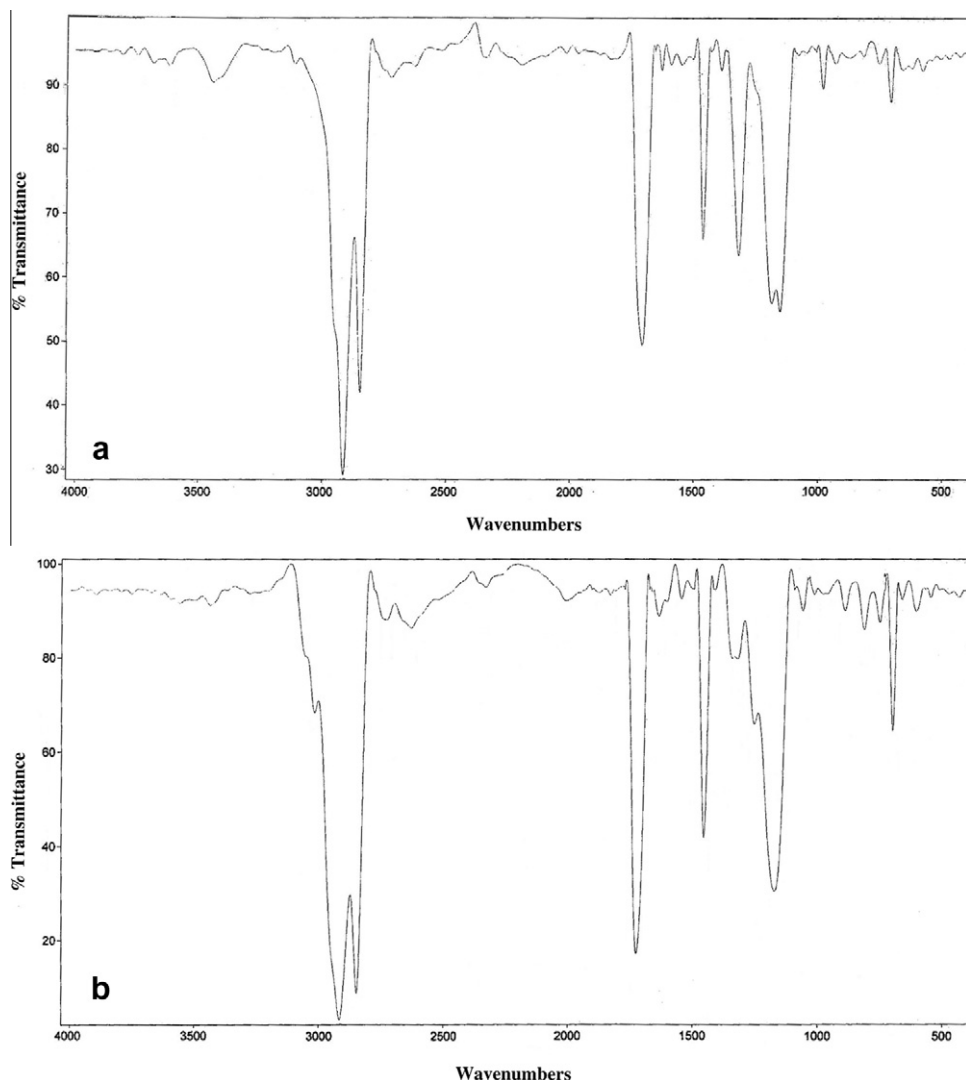
Figure 2   IR spectra of (a) octadecyl itaconate (b) octadecyl itaconate-styrene copolymer (50%:50%).

C—(CH$_2$)—C of long alkyl chain of the ester appeared at 713 cm^{-1}.

The chemical structure was further studied by ^{1}H Nuclear Magnetic Resonance Spectroscopy which showed similar patterns for the four esters. A representative ^{1}H NMR pattern for octadecyl itaconate monomer is shown in Fig. 3i which illustrates the signal at 0.9 ppm which is assigned to C—CH$_3$ group, the signal at 1.3 ppm which is assigned to C—CH$_2$—C group, the signal at 3.3 ppm which is assigned to CH$_2$—C=O group, the signal at 4.1 which is assigned to CH$_2$O group (ester linkage), and the signals at 5.7 and 6.3 assigned to C=CH group.

3.1.2. Copolymers

The synthesized copolymers were characterized through average molecular weight and polydispersity using gel permeation chromatographic analysis as listed in Table 3. The chemical structure of the prepared copolymers was further studied through infrared spectral analysis that showed similar patterns. A representative example is illustrated in Fig. 2b for octadecyl itaconate-styrene copolymer which showed strong absorption bands at 1726 cm^{-1}, 1454 cm^{-1} and 1173 cm^{-1}, assigned to stretching vibration C=O, C—H bending vibration

of aromatic and C—O stretching vibration, respectively. The characteristic C=C stretching absorbed at 1637 cm^{-1} due to conjugated aromatic ring and aromatic C—H absorption of the bending vibration appeared at 713 cm^{-1}.

The chemical structure of the synthesized copolymers was also studied by ^{1}H NMR spectroscopy which showed similar patterns. A representative example is illustrated in Fig. 3ii for octadecyl itaconate-styrene copolymer which illustrates the signal at 0.9 ppm which is assigned to C—CH$_3$ group, the signal at 1.3 ppm which is assigned to C—CH$_2$—C group, the signal at 3.3 ppm which is assigned to CH$_2$—C=O group, the signal at 4.1 which is assigned to CH$_2$O group (ester linkage), and the signal at 7.1 ppm which is assigned to Ph-H group (Aromatic Ring).

3.2. Influence of pendant chain length of the various copolymers on their effectiveness in terms of pour point depression

The effectiveness of the different alkyl chain lengths on the pour point depression of lube oil follows the order PPD1–3   C$_{16}$ > PPD4–6   C$_{18}$ > PPD7–9   C$_{20}$ > PPD10–12   C$_{22}$. From the demonstrated results in Table 4, it is obvious that
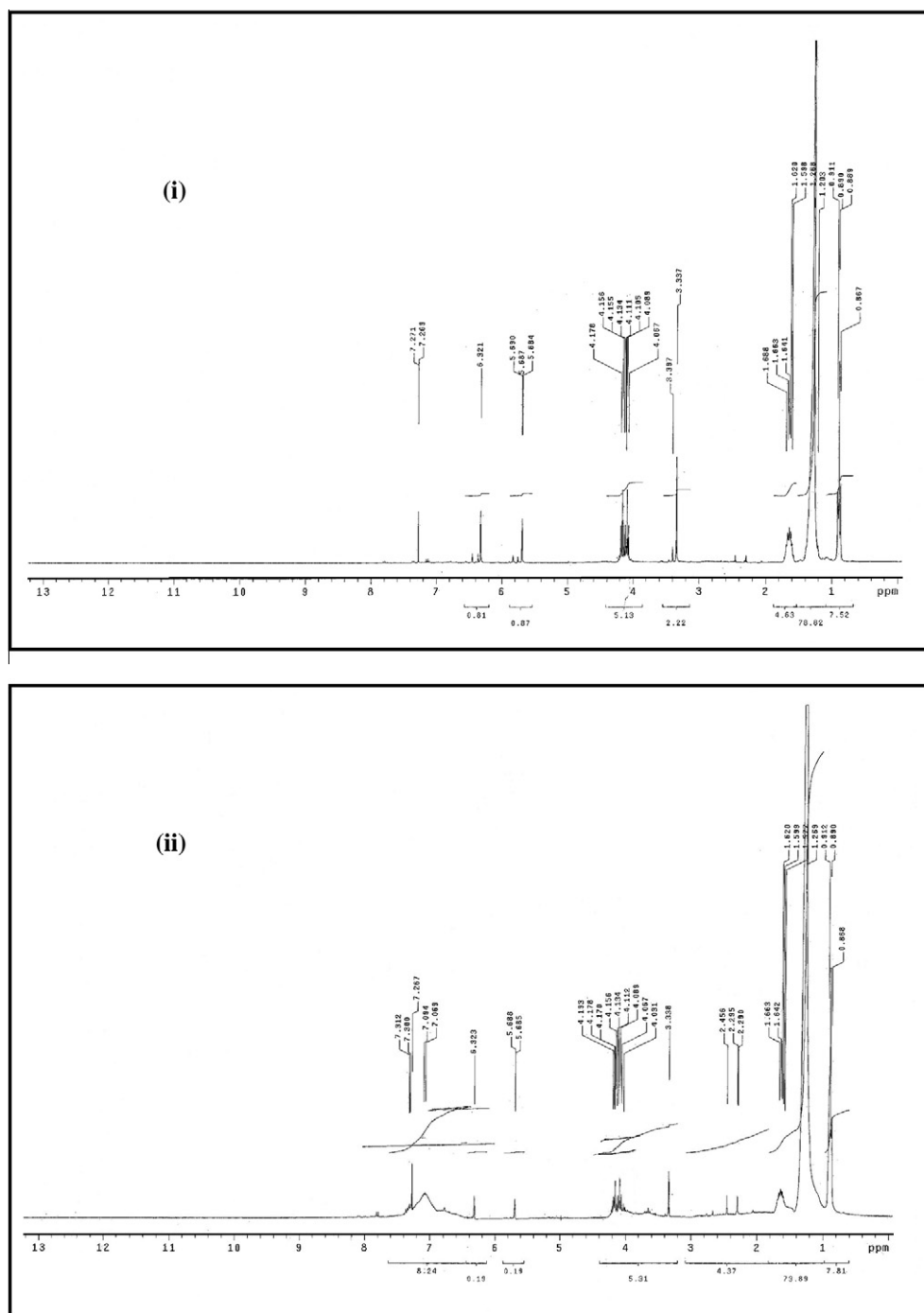
Figure 3 ¹H-NMR spectra of (i) octadecyl itaconate ester, (ii) Copolymer of octadecyl itaconate-styrene (50%:50%).

depressant efficiency decreases with increasing the alkyl chain length from C_{16} to C_{22}. On the other hand, (C_{16} itaconate-styrene) at molar ratio 50%:50% (PPD2) has achieved the optimum flow improver to the extent of $PP_{2000\ ppm} = -15\ °C$. It seems that decreasing the alkyl chain length C_{22} to C_{16} increases the interaction between the alkyl chain of the copolymer and the paraffin in the lube oil. Thus inhibition of the wax crystal formation should be obtained. The ester functionalities are preferably of short alkyl chain length to enhance steric hindrance. Long alkyl chain length makes the copolymer bulky and less soluble making the copolymer less effective [30,31]. Accordingly, the degree of the

improvement of the flow of the oil depends primarily on the alkyl chain that matches with the paraffin content in the lube oil.

3.3. Influence of the average molecular weights of the various investigated copolymers on their effectiveness in terms as pour point depression

The twelve synthesized polymers (PPD1–PPD12) were assessed as PPD/FI at 2000 ppm concentration in lube oil in terms of pour point depression. Their average molecular

Table 4 Effect of the polymeric additives on the flowability of lube oil.

Lube oil

| Additive design	Additive concentration, ppm												
	Nil	250		500		1000		1500		2000		3000	
		pp	Δpp	pp	Δpp	pp	Δpp	pp	Δpp	pp	Δpp	pp	Δpp
PPD 1	15	12	3	12	3	0	15	−3	18	−9	24	−12	27
PPD 2	15	12	3	3	12	0	15	−9	24	−18	33	−18	33
PPD 3	15	12	3	12	3	3	12	0	15	−6	21	−9	24
PPD 4	15	12	3	12	3	0	15	−6	21	−9	24	−12	27
PPD 5	15	12	3	0	15	−3	18	−9	24	−15	30	−15	30
PPD 6	15	12	3	12	3	6	9	0	15	−6	21	−9	24
PPD 7	15	12	3	12	3	6	9	0	15	−6	21	−9	24
PPD 8	15	12	3	9	6	3	12	−3	18	−12	27	−12	27
PPD 9	15	12	3	9	6	6	9	3	12	0	15	−6	21
PPD 10	15	15	0	12	3	3	12	−3	18	−6	21	−9	24
PPD 11	15	15	0	12	3	3	12	−3	18	−6	21	−9	24
PPD 12	15	15	0	12	3	9	6	6	9	0	15	−3	18
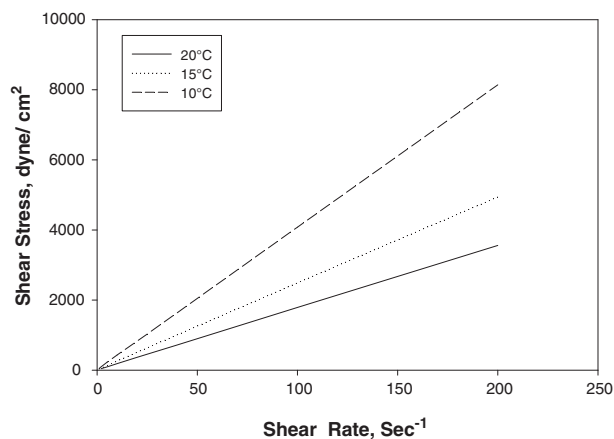
Figure 4a Relation between shear rate and shear stress for untreated lube oil.
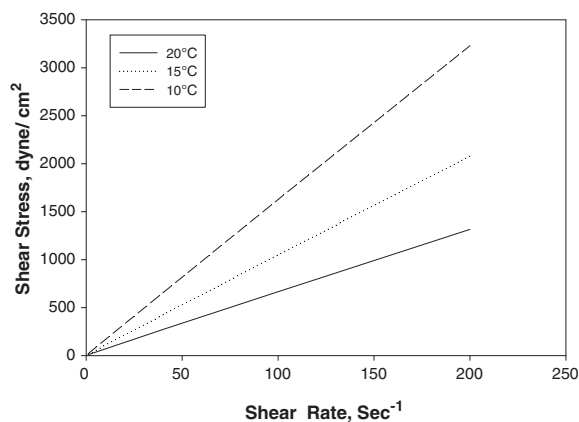

Figure 5a Relation between shear rate and shear stress for lube oil treated with 2000 ppm C16(50%) and styrene (50%).
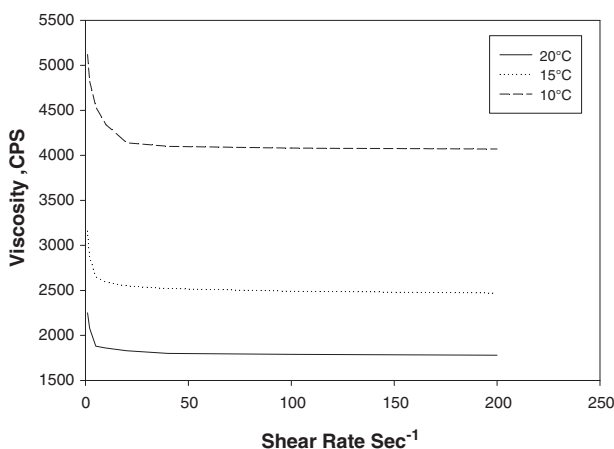

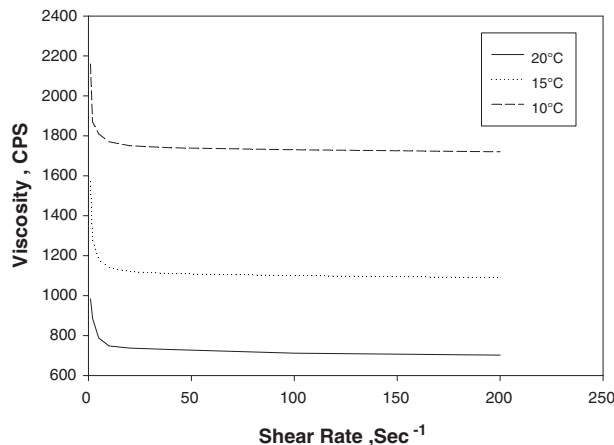**Figure 4b** Relation between shear rate and viscosity for untreated lube oil.

Figure 5b Relation between shear rate and viscosity for lube oil treated with 2000 ppm C16 (50%) and styrene (50%).

weights and polydispersity were determined by GPC analysis. Results are listed in Table 3. The data obtained showed that the prepared polymeric additives have different molecular weights varying from 28,858 to 60,096 and that the optimum effectiveness is achieved at the range of 40,313 to 48,415 (PPD1, PPD2, PPD4, PPD5, PPD6). Moreover, the results

in Table 3 showed that PPD2 and PPD5, with the highest poly dispersity index (1.70 and 1.72). respectively accomplished the optimum pour point depression with respect to the other copolymers. Whereas, copolymers PPD9 and PPD12, with the lowest polydispersity (1.31 and 1.20), respectively, achieved the least depression. The results also indicate that the performance of these copolymers is almost improved with increasing the polydispersity index. This result confirmed our preceding publication in this respect [32]. Thus it is concluded that average molecular weights and polydispersity index are substantial parameters controlling the effectiveness of the used polymeric additives.

3.4. Influence of the concentration of the various investigated copolymers on their efficiency in terms of pour point depression

With increasing the concentration of the additives, an increase in their activity was obtained and as a result, a great depression of pour point was achieved [32]. From the demonstrated results in Table 4, it was observed that the pour point values regularly depressed as the additive concentration increased up to 2000 ppm. This means that at this concentration range, the additive may co-crystallize with the paraffin and modify their

crystals. In general, at lower additive concentrations, side way growth of the crystal faces may be slightly restricted and accordingly, the crystal grows is relatively slower, however crystallization may still be able to form. At higher concentrations of the additives, the side way growth becomes so much more difficult for the wax crystals [33].

3.5. Influence of the molar ratios of the various investigated copolymers on their effectiveness in terms of pour point depression

The effectiveness of the pour point depression is related to molar ratio of alkyl itaconate and styrene, the effectiveness of copolymers increases in the order (50%:50%) > (25%:75%) > (75%:25%). Copolymer (50%:50%) alkyl itaconate styrene is the highest efficient as pour point depressant for Lube oil. This can be found in PPD2, PPD5, PPD8, and PPD11, due to this molar ratio has moderate polarity. This result is correlated with that reported in the literature [34] which denotes that slight polar groups are needed in the flow improver structure rather than non polar or highly polar to improve interaction with the precipitating paraffin.
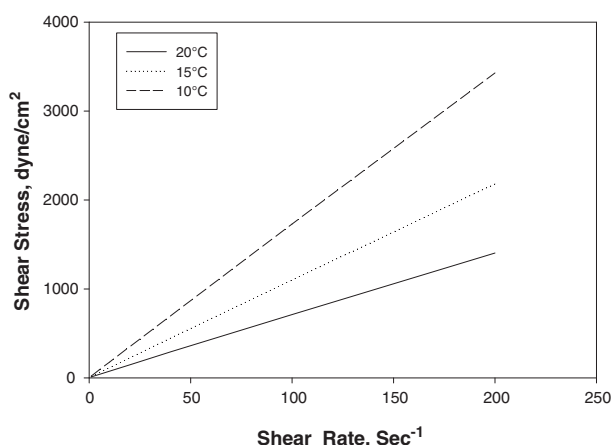

Figure 6a   Relation between shear rate and shear stress for lube oil treated with 2000 ppm C18 (50%) and styrene (50%).
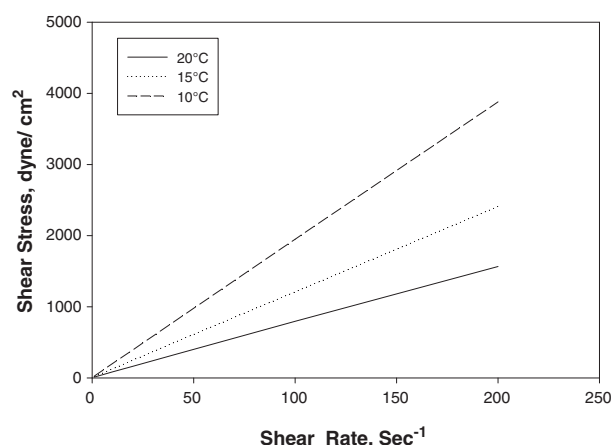

Figure 7a   Relation between shear rate and shear stress for lube oil treated with 2000 ppm C20 (50%) and styrene (50%).
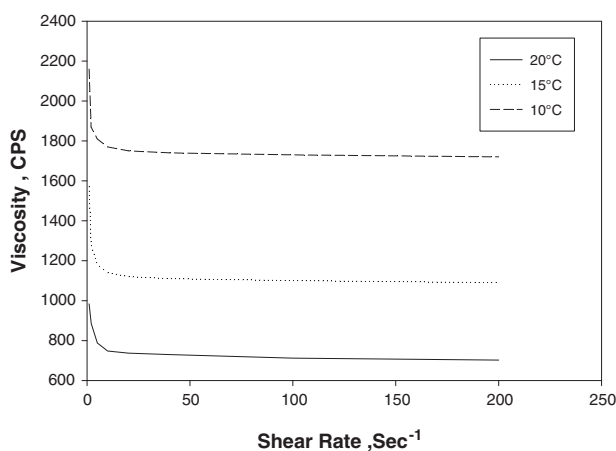

Figure 6b   Relation between shear rate and viscosity for lube oil treated with 2000 ppm C18 (50%) and styrene (50%).
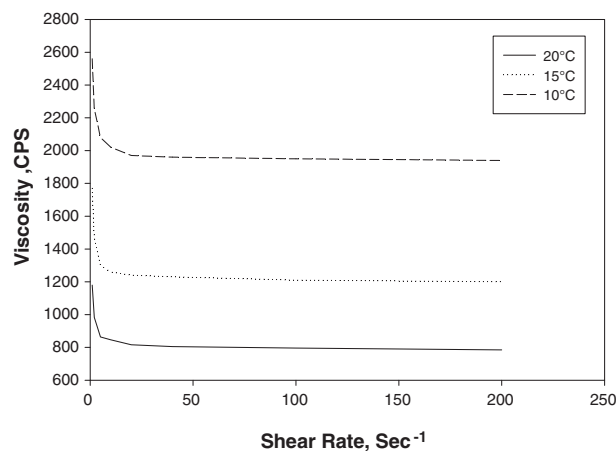

Figure 7b   Relation between shear rate and viscosity for lube oil treated with 2000 ppm C20 (50%) and styrene (50%).

3.6. Rheological properties and flow behavior

If the oil is cooled during transportation the wax crystals tend to deposit on the cold pipe wall. If these deposits get too thick, they can reduce the capacity of the pipeline transportation and cause problems during pigging. Wax deposition in process equipment may lead to more frequent shutdowns and operational problems. In extreme cases, wax crystals may also cause oil to gel and lead to problems of restarting the pipeline.

A thorough understanding of the rheology of the lube oil is therefore necessary for tackling these problems particularly at low temperatures. The nature, the type and the quantity of wax, as well as its crystallization habits influence flow properties to a large extent. The flow properties of the lube oil depend strongly on the shear rate, temperature, rate of cooling, time of shearing and composition of the lube oil [35].

Rheological behavior of the untreated and treated lube oil using PPD2, PPD5, PPD8 and PPD11 samples have been determined in the most efficient concentration (2000 ppm) via dynamic viscosity measurements at 20, 15 and 10°C. From the representative examples in Figs. 4a–8a, it can be noticed that the shear noticed stress increases with increase in the shear rate at all temperatures. In general, Bingham model showed a regular increase of parameters with the decrease of temperature as shown in Table 5. For the untreated lube oil, shear stress increases sharply with increasing shear rate in such a way that the cold flow pattern follows a non newtonian yield pseudo plastic rheological behavior as shown in Fig. 4a.The rheological data in Figs. 5b–8b are in a scale as shear rate versus viscosity from which it is noticed that the viscosity decreases approximately linearly with the increase of the shear rate at all test temperatures and the rate of decrease was lowered at higher shear rates, as at high shear rates the viscosity reached a constant value. Here also PPD2 and PPD5 were found to be superior. This behavior may be explained by the following reasons: At temperature around the pour point and 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. 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 re-
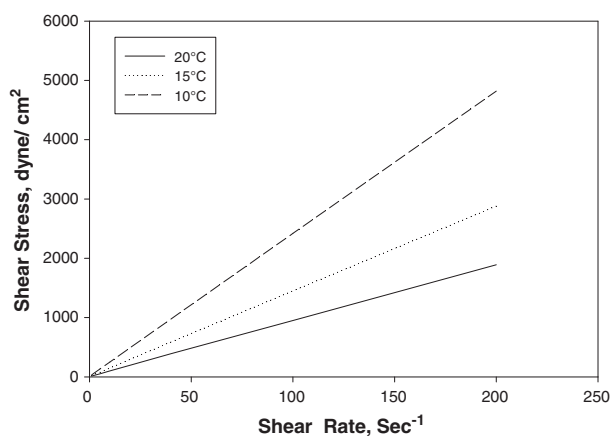
Table 5 Rheological parameters for untreated and treated lube oil at 2000 ppm of different pour point depressants.

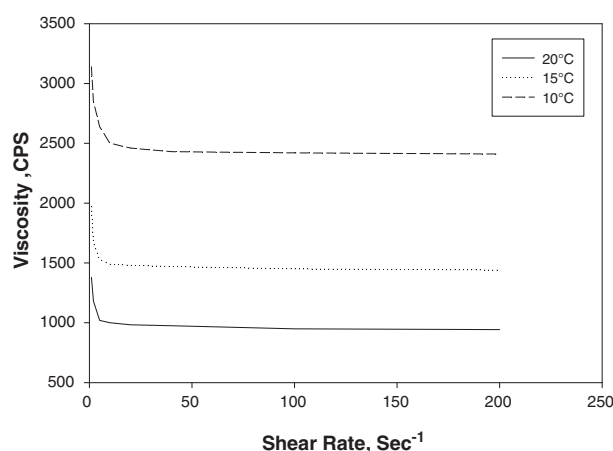| Flow improver	Temperature (°C)	Bingham yield value (dyne/cm^2)
Untreated lube oil	20	7.57
	15	12.91
	10	18.32
PPD 11	20	6.58
	15	7.03
	10	10.22
PPD 8	20	6.27
	15	6.61
	10	7.64
PPD 5	20	5.93
	15	6.17
	10	6.69
PPD 2	20	4.25
	15	5.24
	10	5.83

Figure 8b Relation between shear rate and viscosity for lube oil treated with 2000 ppm C22 (50%) and styrene (50%).

sult, the effective dispersed phase concentration decreases and leads to decrease of viscosity. The viscosity decreases with increasing the shear rate until the agglomerates are completely broken down into the basic particles. So the waxy oil system shows non-newtonian characteristics [36].The behavior of decreasing the rheological parameters after addition of the prepared polymers can thus be attributed to their chemical structures. The slight polarity of the benzene ring in the polymer backbone and the presence of high polarity of oxygen in the acid and ester groups along polymer chain play a role in preventing the agglomeration of wax crystals in lube oil. In addition, the interaction of the alkyl chain with the paraffin fraction in the oil occurs through a good match of the alkyl chain length and as discussed before, as the alkyl chain length decreases a better match occurs.

3.7. Effect of flow improver and pour point depressant type on wax crystal modification

Photo analysis confirms other standard flow tests that evaluate the cold flow properties of untreated/treated lube oil through

Figure 8a Relation between shear rate and shear stress for lube oil treated with 2000 ppm C22 (50%) and styrene (50%).

wax crystallization behavior. It is applied herein for assessing the action of the previously prepared bifunctional flow additives as wax inhibitor/pour point depressant through wax modification according to their type, concentration and molar ratios of the copolymer.

3.7.1. Type of additive and wax modification

Photomicrographs illustrated in Plate 1a–d have showed variant wax morphology changes according to the type of additive. Plate 1a of the untreated lube oil showed large cyclic like crystals (PP = 15 °C) of approximate size of 100 μm which on treatment with PPD5 $PP_{2000 \, ppm}$ = −15 °C Plate 1b have lead to significant reduction of wax crystal size and formation of abundant number of fine dispersed crystals. When using the

PPD8 $PP_{2000 \, ppm}$ = −12 °C additives a higher wax modification degree was observed and fine dispersed wax crystals started to appear Plate 1c. On treatment of 2000 ppm of PPD11, small cyclic wax crystals were observed $PP_{2000 \, ppm}$ = −6 °C. Concerning the correspondent flow parameter measurements, it is revealed that with the increase of additive activity in terms of ΔPP, the induced wax modification is increased to a higher degree in the order PPD5 > PPD8 > PPD11 i.e., there is a good correlation between wax modification and measured flow parameter.

3.7.2. Concentration of additive and wax modification

The effect of the concentration of the most efficient PPD5 additive was assessed through photographic analysis on wax
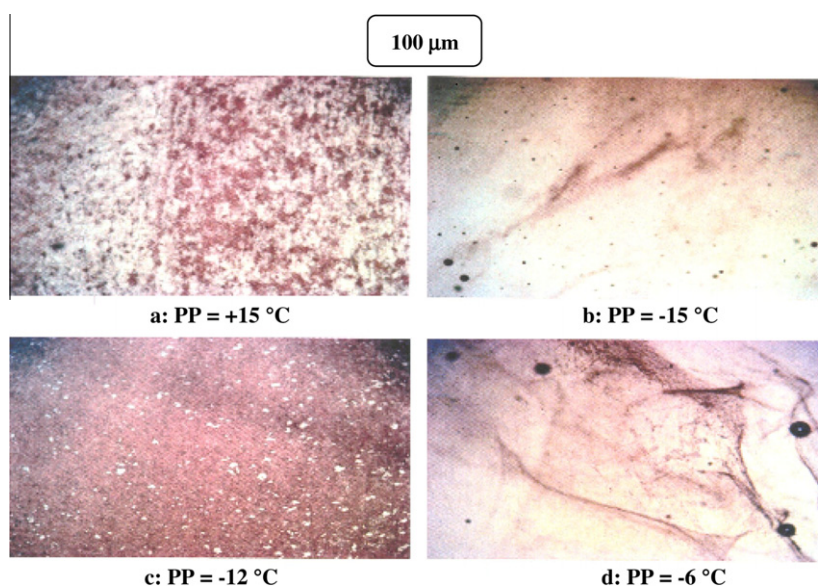

100 μm

a: PP = +15 °C   b: PP = -15 °C

c: PP = -12 °C   d: PP = -6 °C

Plate 1 Photomicrographs of (a) LO untreated, (b) LO + PPD5, (c) LO + PPD8 and (d) LO + PPD11 at 2000 ppm.

100 μm

a: PP = +15°C   b: PP = +12°C
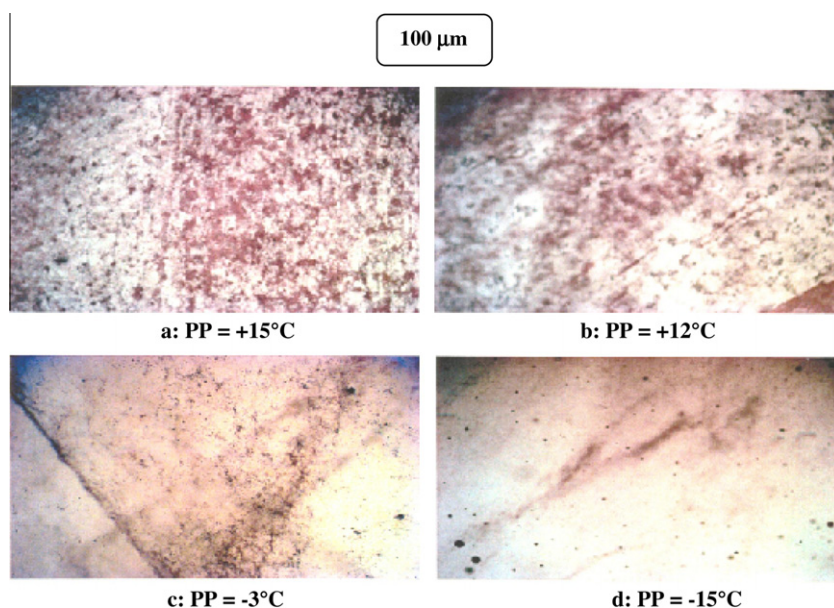
c: PP = -3°C   d: PP = -15°C

Plate 2 Photomicrographs of (a) LO untreated, (b) LO + 250 ppm PPD5), (C) LO + 1000 ppm PPD5 and (d) LO + 2000 ppm PPD5).
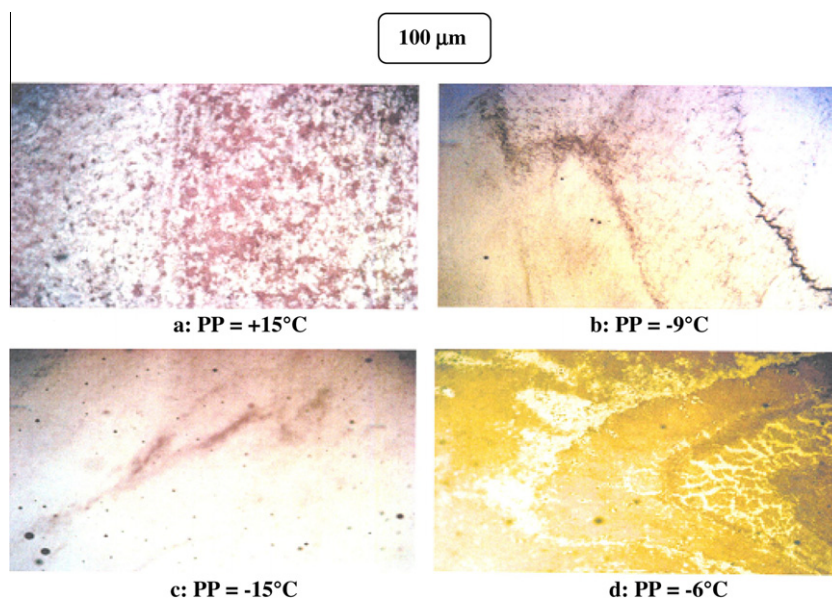
Plate 3   Photomicrographs of (a) LO untreated, (b) LO + PPD4, (c) LO + PPD5, and (d) LO + PPD6 at 2000 ppm.

modification at 250, 1000 and 2000 ppm successively. Results are illustrated in Plate 2a–d from which it is obvious that with the increase of additive concentration, the wax crystal size is significantly decreased from large cyclic like crystal (Plate 2a) passing through Plates 2b and c to abundant number of very small dots dispersed in the oil phase of the lube oil Plate 2d. It is also noted that the extent of wax modification induced by the increase of additive concentration is well correlated with the improved pour point flow parameter.

3.7.3. Molar ratio of copolymer and wax modification

Photomicrography of lube oil without treatment showed large cyclic like crystals (PP = 15 °C) Plate 3a. Lube oil was doped with the flow improver PPD 4 (Poly octadecyl itaconate-styrene) 25%: 75% ratio PPD4 Plate 3b, further crystal modification has been achieved leading to the formation of fine dispersed wax crystal $PP_{2000\ ppm} = -9$ °C. By treatment of lube oil with poly octadecyl itaconate-styrene at molar ratio (50%:50%) PPD5, $PP_{2000\ ppm} = -15$ °C, further crystal size reduction with the formation of very fine dispersed crystals was achieved as indicated in Plate 3c. Plate 3d illustrates the lube oil treated with polyoctadecyl itaconate copolymer molar ratio 75%:25% PPD6. A remarkable modification of wax crystal size has been achieved as a result of the break down of the cyclic form of crystals by this additive $PP_{2000\ ppm} = -6$ °C.

4. Conclusion

- Twelve alkyl itaconate-styrene copolymer additives with different alkyl groups from C_{16} to C_{22} and different molar ratios were prepared, purified and characterized by FTIR, ^{1}H NMR and GPC and their effect on pour point and rheological properties of the lube oil was investigated.
- Both average molecular weights, polydispersity index of additive drastically affect the performance of pour point depressants/ flow improvers.

- The effect of the different alkyl chain lengths on the pour point depression follows in the order PPD1-3 C_{16} > PPD4–6 C_{18} > PPD7–9 C_{20} > PPD10–12 C_{22}.
- With increasing the concentration of the additives, an increase of their activity was obtained and as a result, a great depression of pour point was achieved.
- The prepared copolymers were tested as pour point depressants for lube oil and it was found that the maximum depression was obtained by the sample that has short alkyl chain (C_{16} itaconate-styrene) at molar ratio 50%:50% (PPD2) from 15 °C to −18 °C ($\Delta PP = 33$ °C at 2000 ppm) while the minimum depression was exhibited by long alkyl chain length (C_{22} itaconate-styrene) at molar ratio 75%:25% PPD12 from 15 °C to 0 °C ($\Delta PP = 15$ °C at 2000 ppm under the same conditions.
- The effect of these copolymers on the rheology and flow properties of lube oil was investigated.
- The photo analysis has showed that a wax modification caused by the effective pour point depressant on crystal growth generally alters the irregular large size crystals to form fine depressant wax crystals further enhancement of flow ability and depressions of pour point were obtained.

References

[1] S.S. Ray, N.K. Pandey, A.k. Chatterjee, Fuel 88 (2009) 1629.
[2] D. Petijean, J.F. Schmitt, V. Laine, M. Bouroukba, C. Cunat, M. Dirand, Energy & Fuels 22 (2008) 697.
[3] H.P. Soni, K.S. Kiranbala, A. Agrawal, D. Nagar, P. Bharambe, Fuel Processing Technology 91 (2010) 997.
[4] A.M. Al-Sabagh, M.R. Noor El-Din, R.E. Morsi, M.Z. Elsabee, Journal of Petroleum Science & Engineering 65 (2009) 139.
[5] V. Ramchandran, J.A. Ostlund, H. Chawla, P. Wattana, N. Magnus, H.S. Fogler, Energy & Fuels 17 (2003) 1630.
[6] J.Y. Zuo, D. Zhang, Energy & Fuels 22 (2008) 2390.
[7] J.F. Tinsley, R.K. Prud'homme, Journal of Petroleum Science and Engineering 27 (2010) 166.

[8] T.T. Khidr, E.M.S. Azz, S.S. Mutawaa, A.M.A. Omar, Industrial Lubrication and Tribology 57 (2) (2007) 64.

[9] H.P. Soni, D.P. Bharambe, Polymer journal 15 (12) (2006) 943.

[10] S. Han, P. Wang, Y. Wang, Y. Song, T. Ren, Process Safety and Environmental Protection 88 (2010) 41.

[11] S. Misra, S. Baraah, K. Sinyl, Society of Petroleum Engineers 28181 (1995) 50.

[12] A.M. Al-Sabagh, A.F. El-Kafrawy, T.T. Khidr, R.A. El-Ghazawy, M.R. Mishrif, Journal of Dispersion Science and Technology 28 (6) (2007) 976.

[13] A.E. Kuzmic, M. Radosevic, G. Bagdanic, V. Srica, R. Vukovic, Fuel 87 (2008) 2943.

[14] J.F. Tinsley, J.P. Jahnke, D.H. Adamson, X. Guo, D. Amin, R. Kriel, R. Saini, H.D. DEttman, R.K. Prud'homme, Energy & Fuels 23 (2009) 2065.

[15] A.M. Al-Sabagh, T.T. Khidr, A.M. Atta, Journal of Petroleum Science and Technology 20 (7&8) (2002) 693.

[16] I.M. El-Gamal, E.A.M. Gad, Institut Francais Du Petrol 52 (3) (1997) 370.

[17] I.M. El-Gamal, A.M. Atta, A.M. Al-Sabagh, Fuel 76 (14–15) (1997) 1471.

[18] A.M. El-Gamal, T.T. Khidr, F.M. Guiba, Fuel 77 (5) (1998) 375.

[19] S. Deshmukh, D.P. Bharambe, Fuel Processing Technology 89 (2008) 227.

[20] C. Wu, J. Zhang, W. Li, Y. Wang, H. Cao, Fuel Processing Technology 87 (2006) 585.

[21] I.M. El-Gamal, S. Gobiel, Journal of Applied Polymer Science 61 (1996) 1265.

[22] W. Chen, Z. Zhao, C.Y. Yin, Fuel 89 (2010) 1127.

[23] N. Miskolczi, R. Sagei, L. Bartha, L. Forcek, Journal of Fuel Chemistry and Technology 37 (3) (2009) 302.

[24] T.T. Khidr, Journal of Petroleum Science and technology 25 (5) (2007) 671.

[25] T.T. Khidr, A.M.A. Omar, Egypt. Journal of Petroleum (EPRI) 13 (1) (2003) 21.

[26] J.R. Marquat, G.B. Dellow, E.R. Freitas, Analytical Chemistry 40 (11) (1968) 1633.

[27] J.G. Speight, Handbook of Petroleum Analysis, John wiley and Sons Inc., USA, 2001.

[28] J.S. Manka, K.L. Zieglers, Society of Petroleum Engineers International Symposium, SPE, 67326 (2001).

[29] J.R. Van Wazer, J.W. Lyons, K.Y. Kim, R.E. Colwell, Viscosity and Flow Measurement, Interscience Publishers, New York, 1963.

[30] G.A. Holder, J.J. Winkler, Journal of the Institute of Petroleum 51 (499) (1965) 235.

[31] H. Wirtz, P.V. Halasz, M. Feustel, J. Balzer, United States Patent, Patent number 5, 349, 019 sep. 20 (1994).

[32] I.M. El-Gamal, E.A.M. Gad, S. Faramui, S.J. Gobeil, Chemical Technology and Biotechnology 55 (1992) 123.

[33] A.L. Machado, E.F. Lucas, G. Conzalez, Journal of Petroleum Science & Engineering 32 (2–4) (2001) 159.

[34] R. Berkhof, H.J. Kwekkboom, Reprint, 3rd Servo Oil Field Chemicals Symposium, Moscow, USSR, October, 1985.

[35] H. Li, J. Zhany, Fuel 82 (11) (2003) 1387.

[36] A.K. Chatterjee, S.D. Phtak, P.S. Murthy, G.C. Joshi, J. Appl. Polymer. Sci. 52 (7) (1994) 887.