Final progress report for UGC Major Research Project entitled

Polymeric Flow Improvers for Indian Crude Petroleum

April 2013 – March 2017

Submitted By

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FINAL PROGRESS REPORT

Polymeric Flow Improvers for Indian Crude Petroleum

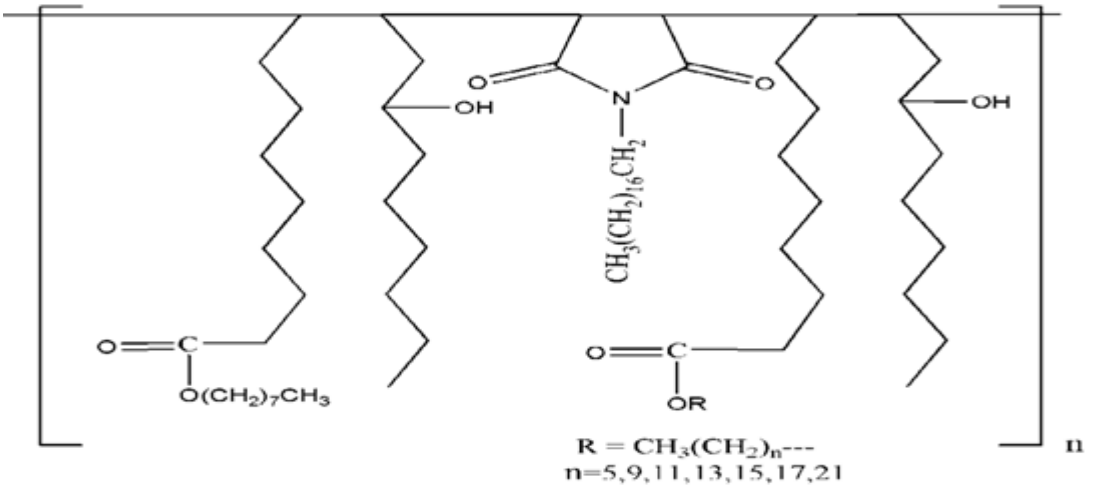
OBJECTIVE OF PROJECT: Two main objective of the present investigation are

[A] Synthesis of new polymeric flow improvers for the crude oils from different location of India and evaluating their effects on rheological properties of crude oil.

[B] To find correlation of the extent of pour point depression, viscosity and yield value with that of the molecular structure of basic polymeric unit.

SUMMARY OF PROJECT: Deposition of Wax in oil production forms a critical and difficult to control problem, in terms of production and operation cost, going from reservoir to surface facilities. In order to find suitable flow improvers for Kosamba-47, Kosamba-33 & Bombay High Crude oil, twenty eight new polymers were synthesized, possessing aliphatic and aromatic units as pendant chains with polar Nitrogen functional groups in their structure. The synthesized additives have dual behavior of flow improver and good pour point depressants. The additives can be categorized into four different classes based on basic polymeric unit and length of pendant alkyl chains. The structural formulas of synthesized four classes are shown as follows,

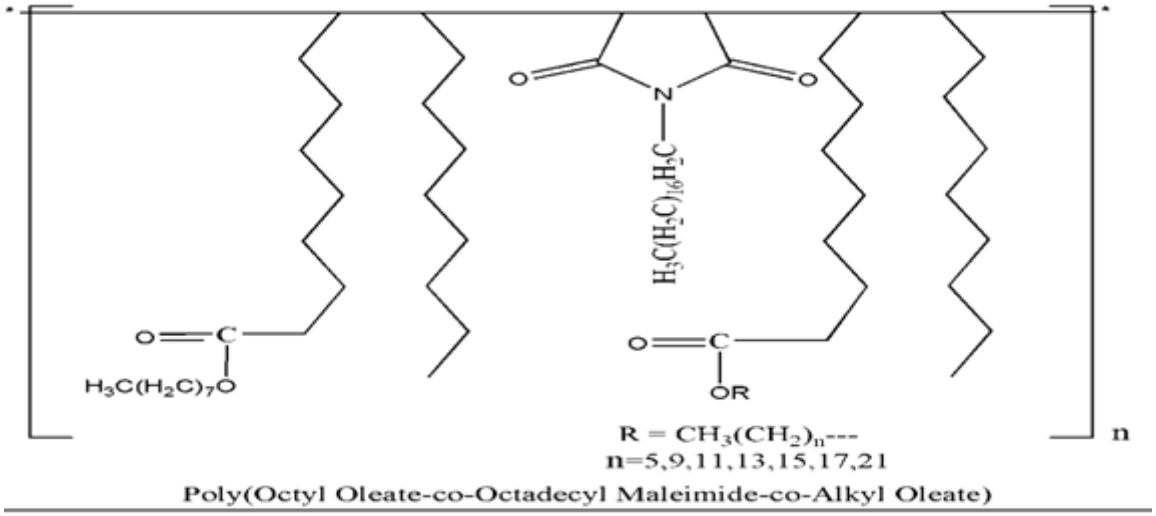
Class I



$R = CH_3(CH_2)_n$---
n=5,9,11,13,15,17,21

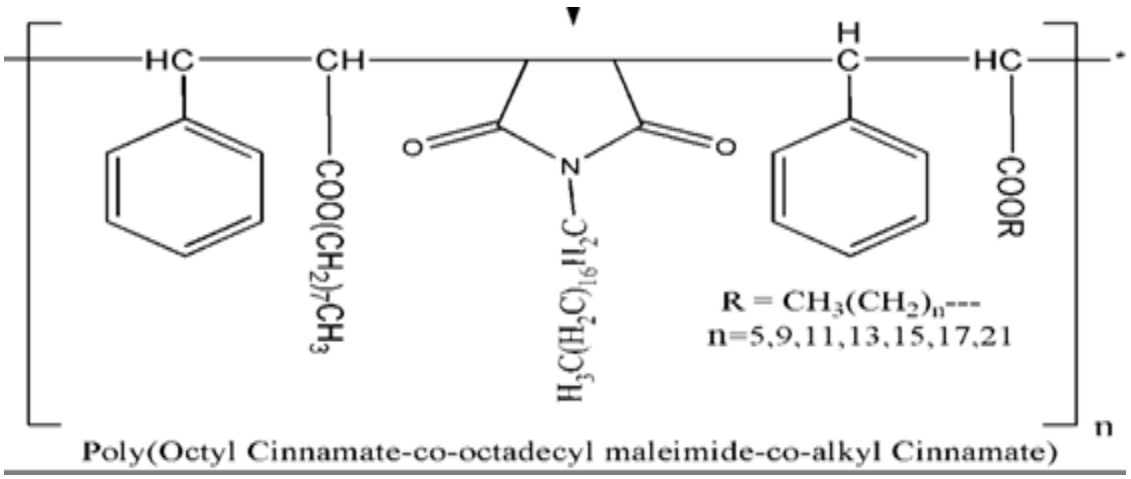
Poly(Octyl Ricinoleate-co-Octadecyl Maleimide-co-Alkyl Ricinoleate)

Class II



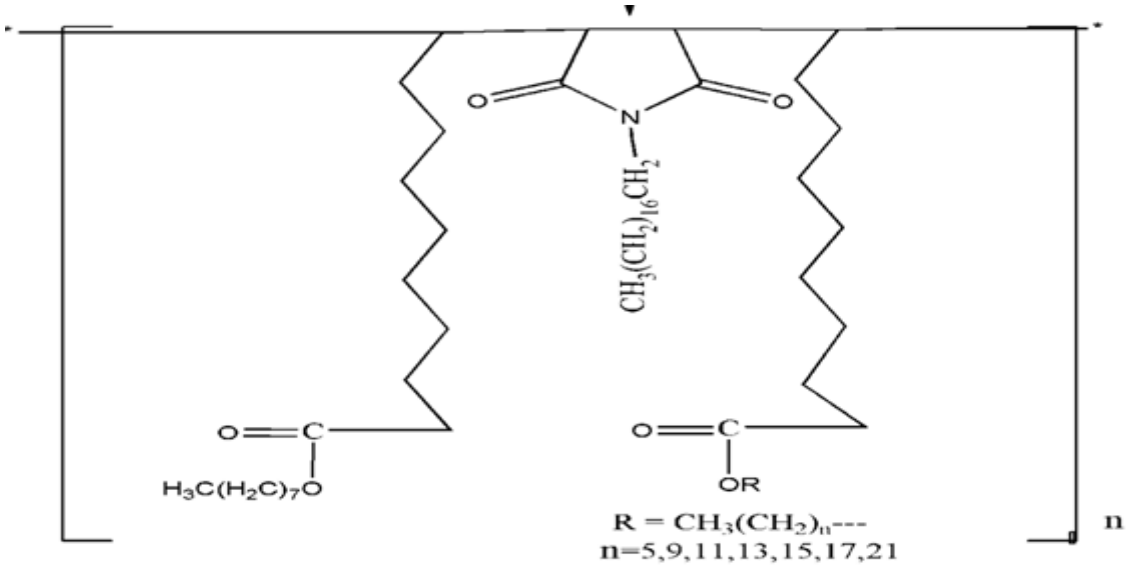
Poly(Octyl Oleate-co-Octadecyl Maleimide-co-Alkyl Oleate)

Class III



Poly(Octyl Cinnamate-co-octadecyl maleimide-co-alkyl Cinnamate)

Class IV



Poly(Octyl Undecylineate-co-Octadecyl Maleimide-co-Alkyl Undecylineate)

The synthesis of polymeric additives by process of esterification, terpolymerization by free radical polymerization and insertion of polar Nitrogen group in the synthesized polymer are the different stages of the synthesis route. The structural elucidation was done by FTIR and GPC used for molecular weight determination.

Testing the efficiency of prepared additives in terms of pour point depression and to study the effects of additives on rheological properties of Kosamba-33, Kosamba-47 and Bombay High crude oil was done. As the determination of the pour point proceeded, there was a growing realization of a probable correlation with molecular geometry of the copolymer indicating basic changes in polymeric pendant chains and structures. Not all the experimentally tested additives showed encouraging result. Therefore the results of some additives have been recorded and discussed. Some of these additives showed brilliant pour point depression property while others can be considered as good. Yield stress and viscosity of the crude oil at different temperatures and concentrations of additives were evaluated by zero friction advanced rheometer AR 1500 ex of TA instruments. The rheological data indicates selected crude oil have Bingham plastic nature. The synthesized four classes of polymeric flow improver showed variable results with respect to pour point depression and low temperature performance of the selected crude oils. Most additives could perform satisfactorily well.

Polymeric flow improvers possess an oil soluble long chain alkyl group and a polar structure in the molecular set up. The long chain alkyl group can insert into the wax crystal from the crude oil and polar part exists on the surface of the wax crystal, thus inhibiting crystal lattice formation and decreasing wax crystal size. The prepared nitrogen containing one component polymeric structure exhibits dual function of pour point depression and flow improver simultaneously. They possess the advantage of inevitable compatibility in one compound. The depressing effect mainly depends on polar effect of nitrogen/oxygen containing functional groups incorporated in the terpolymers moiety. On the other hand flow ability depends on well matching of pendant alkyl chain of terpolymers with average carbon number of paraffin content present in crude oil. The higher the paraffin contents in the crude oil the lower the response to flow improvement.

WHETHER OBJECTIVES WERE ACHIEVED: YES

Synthesis of new polymeric flow improvers for the crude oils and evaluating their effects on rheological properties were done successfully.

Also the correlation of the extent of pour point depression, viscosity and yield value with that of the molecular structure of basic polymeric unit was successfully established.

ACHEIVEMENTS FROM THE PROJECT:

The synthesized four classes of polymeric flow improver showed variable results with respect to pour point depression and low temperature performance of the selected crude oils. Most additives could perform satisfactorily well.

Additives having C_{11} to C_{20} pendant alkyl chains are more efficient PPD for **Kosamba-47 crude oil**. Additives 8-16UA18N & 8-14OA18N brought significant reduction in viscosity & Yield value of Kosamba-47 crude oil.

For **Kosamba-33 crude oil** additives 8-12UA18N, 8-16UA18N, 8-6CA18N, 8-14CA18N, 8-12RA18N, 8-14RA18N, 8-6OA18N and 8-16OA18N showed good efficiency as pour point depressants. Additives having effective PPD behavior were found to have C_{13} to C_{20} pendant alkyl chain length. Also the presence of aromatic ring made molecule more bulky which helped in improving its pour point depressing tendency.

For **Bombay High crude oil** additives 8-6UA18N, 8-14UA18N, 8-14CA18N, 8-16CA18N, 8-14RA18N, 8-16RA18N, 8-14OA18N and 8-16OA18N showed good efficiency as pour point depressants.

SUMMARY OF THE FINDINGS:

Deposition of Wax in oil production forms a critical and difficult to control problem, in terms of production and operation cost, going from reservoir to surface facilities. In order to find suitable flow improvers for Kosamba-47, Kosamba-33 & Bombay High Crude oil, twenty eight new polymers were synthesized, possessing aliphatic and aromatic units as pendant chains with polar Nitrogen functional groups in their structure. The synthesized additives have dual behavior of flow improver and good pour point depressants. The additives can be categorized into four different classes based on basic polymeric unit and length of pendant alkyl chains.

It was found that additives from any of the five series behaves differently with crude oils of different oil field. Not a single additive is equally effective on all the crude oils under study. Additives having C_{11} to C_{20} pendant alkyl chains are more efficient PPD for Kosamba-47 crude oil. C_{22} and above pendant alkyl chain makes polymeric chain bulky decreasing their efficiency. Additives 8-16UA18N & 8-14OA18N brought significant reduction in viscosity & Yield value of Kosamba-47 crude oil. Reverse results were shown by 8-14UA18N, 8-6CA18N, 8-18CA18N, 8-14RA18N, 8-16RA18N and 8-16OA18N with increase in concentration of additive and pendant alkyl chain length.

For Kosamba-33 crude oil additives 8-12UA18N, 8-16UA18N, 8-6CA18N, 8-14CA18N, 8-12RA18N, 8-14RA18N, 8-6OA18N and 8-16OA18N showed good efficiency as pour point depressants. Additives having effective PPD behavior were found to have C_{13} to C_{20} pendant alkyl chain length. Also the presence of aromatic ring made molecule more bulky which helped in improving its pour point depressing tendency. The result obtained clearly indicates that additives like 8-16UA18N, 8-14RA18N brought reasonably good reduction in viscosity of Kosamba-33 crude oil. Decrease in viscosity of crude oil decreased the yield stress also. The additives 8-12UA18N, 8-6CA18N, 8-14CA18N, 8-12RA18N, 8-6OA18N and 8-16OA18N showed reverse results of increasing viscosity of Kosamaba-33 crude oil. It was observed that with increase in concentration of additive, viscosity and yield stress increases. Flow behavior is affected. Hence these additives were not suitable for Kosamba-33 crude oil.

For Bombay High crude oil additives 8-6UA18N, 8-14UA18N, 8-14CA18N, 8-16CA18N, 8-14RA18N, 8-16RA18N, 8-14OA18N and 8-16OA18N showed good efficiency as pour point depressants. Possible reason for good efficiency of these additives can be matching of carbon number of the wax present in Bombay High crude oil with pendant chain. Additives having

effective PPD behavior were found to have C_{13} to C_{20} pendant alkyl chain length. Also the presence of aromatic ring made molecule more bulky which helped in improving its pour point depressing tendency. Additives like 8-14CA18N, 8-16CA18N & 8-16OA18N brought significant reduction in viscosity of Bombay High crude oil. As viscosity of crude oil decreases then the yield stress needed to start flow also decreases and so it is possible to keep crude oil in flowing condition even at low temperature. Other additives coded 8-6UA18N, 8-14UA18N, 8-14RA18N, 8-16RA18N and 8-14OA18N have given reverse results that is increased the viscosity of Bombay High crude oil. The reason for such high values of rheological parameters may be such that the polymer additive becomes insoluble in crude oil and forms aggregates, which precipitate out from the crude along with wax crystal without being properly adsorbed on the surface. Due to this they cannot make a change in the crystal structure but instead, the pendant chains of polymers interlock into one another like a zipper. Now the polymer molecules cannot slide over one another which results in an increase in viscosity and yield value of the crude oil.

Polymeric flow improvers possess an oil soluble long chain alkyl group and a polar structure in the molecular set up. The long chain alkyl group can insert into the wax crystal from the crude oil and polar part exists on the surface of the wax crystal, thus inhibiting crystal lattice formation and decreasing wax crystal size. The prepared nitrogen containing one component polymeric structure exhibits dual function of pour point depression and flow improver simultaneously. They possess the advantage of inevitable compatibility in one compound. The depressing effect mainly depends on polar effect of nitrogen/oxygen containing functional groups incorporated in the terpolymer moiety. On the other hand flow ability depends on well matching of pendant alkyl chain of terpolymer with average carbon number of paraffin content present in crude oil. The higher the paraffin contents in the crude oil the lower the response to flow improvement.

CONTRIBUTION TO THE SOCIETY:

The aim of the project is to solve the problem of choking of oil pipelines due to crystallization of wax molecules in the crude oil. Pipelines are the most efficient and cost effective means of oil transportation. Use of pour point depressants will put an end to the need of separate solution for separate oil types thus bringing the cost of transportation significantly low level. The savings in cost and time can be diverted to areas such as digging, purifying and so on.

PHD ENROLLED AND PRODUCED OUT OF THE PROJECT:

Name: Chitte Pranav S.

PhD degree awarded in March-2018

NO. OF PUBLICATIONS OUT OF THE PROJECT: one

DETAILS OF THE PUBLICATIONS:

Oleic acid based polymeric flow improvers for Langhnaj (North Gujarat, India) crude oil

Mayur R. Patel, Pranav S. Chitte, D.P. Bharambe

Egyptian Journal of Petroleum (2017) 26, 895–903

http://dx.doi.org/10.1016/j.ejpe.2015.04.006

Copy of publication attached with this report.

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FULL LENGTH ARTICLE

Oleic acid based polymeric flow improvers for Langhnaj (North Gujarat, India) crude oil

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KEYWORDS

Polymeric flow improvers;
Pour point;
Plastic viscosity;
Apparent viscosity;
Yield value

Abstract This research article investigates the effect of polymeric flow improvers (FI) as pour point depressants (PPD) and rheological property improvers of waxy crude oil in Langhnaj, North Gujarat (India), since application of FI is a more economically viable option for crude oil transportation. Three new comb-shaped copolymers of maleic anhydride and n-alkyl oleate were synthesized by free radical solution polymerization, which were consequently reacted with hexadecyl amine to get poly (hexyl oleate-co-hexadecyl maleimide-co-n-alkyl oleate). Synthesized polymers were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Gel Permeation Chromatography (GPC). These FIs were further evaluated for their pour point depression property and rheology modifier with and without additive using Fann Viscometer. The prepared FIs act as effective pour point depressants as well as viscosity index improvers.

1. Introduction

Crude oil and its many downstream derivatives have a complex & wide range of hydrocarbon components leading to variation in physical properties. Paraffin waxes have been a major component representing up to 20 wt.% of the total mixture of hydrocarbon.

In today's world global economy heavily depends on the cost of crude oil. Major factor governing crude oil cost is transportation through pipelines underground or below the sea. In subsea pipelines n-paraffin waxes separate out below the wax appearance temperature (WAT). At temperatures near pour point wax crystallizes out in 'house-of-card' type structures having orthorhombic wax crystals which overlap & combine to give three dimensional networks. The rate of crystallization is faster near the inner wall of pipeline & slower at center of pipeline due to temperature difference. A further decrease in temperature leads to gelation, hardening & blocking of pipelines as a result rheological behavior of crude oil shifts from Newtonian to non-Newtonian. Transportation of such crude oil consumes high energy [1].

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Possible solutions available are preheating of crude oil or pipelines, special heating–cooling cycles for wax crystal modification, controlled thermal conditioning for better pour point effect of resin and asphaltene which are natural pour point depressants. Application of microwave and ultrasound irradiation, use of magnetic field, addition of precious light distillates to crude oil before pumping, lining & coating pipelines with fiber reinforced plastics decreasing wettability of paraffin with walls and use of polypropylene on the inner wall of transportation lines to inhibit wax deposition are other possible solutions. However, each solution has its own limitation. Use of oil-soluble surfactants or polymeric chemical additives (before pumping) is the most economical and suitable solution for the problem [2].

Most widely used polymeric additives are of linear or comb-shaped type polymers. Linear polymers include crystallizable domains in the polymeric backbone such as ethylene–vinyl acetate co-polymers (EVA) and Ethylene–Butene (PE-PEB) co-polymers while the comb-shaped polymers generally have long alkyl chains (crystallizable appendages) appended to the backbone of polymers such as alkyl acrylate homopolymers, alkyl esters of styrene-maleic anhydride copolymers, alkyl fumarate-vinyl acetate co-polymers, unsaturated carboxylic ethers-maleic anhydride derivative, maleic anhydride-alkyl acrylate terpolymers, etc. [3].

Structurally, flow improvers (FI) are made up of a part similar to paraffin waxes that provides nucleation sites to co-crystallize with paraffin waxes while dissimilar part blocks the extensive growth of wax network. Hence the bulk stream remains flowable and filterable [4,5].

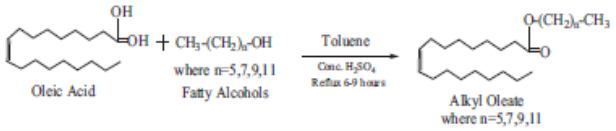
The aim of successful polymeric PPD is to decrease congealing temperature, inhibit the wax separation of crude oil and reduce the yield strength [6].

In the present work, alkyl oleate-maleic anhydride-hexadecyl amine terpolymers with a range of molecular weights were prepared. The efficiency of terpolymers as PPD and viscosity improvers was evaluated on Langhnaj crude oil (North Gujarat, India).

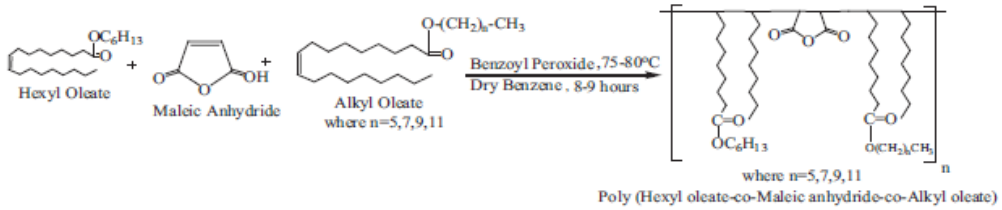
2. Experimental details

2.1. Synthesis of n-alkyl oleates

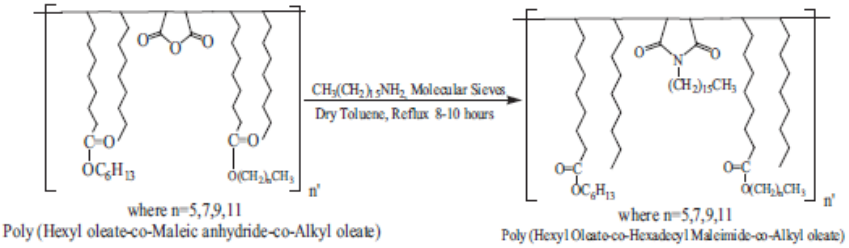
Esters of Oleic acid with different fatty alcohols were synthesized by acid catalyzed esterification using sulfuric acid as catalyst and toluene as solvent. Azeotropic distillation was carried out using Dean–Stark apparatus where completion of the reaction was decided by collection of theoretically calculated amount of water from Dean–Stark Apparatus. Oleic acid and different fatty alcohols were taken in 1:1 mol ratio with a catalytic amount of sulfuric acid in toluene as solvent for azeotropic distillation. Completion of reaction ranged from 6 to 9 h and depends on fatty alcohol used. After completion of the reaction the crude ester obtained was neutralized by washing with 10% aqueous sodium bicarbonate and subsequently dried on anhydrous sodium sulfate. Crude esters were



Scheme 1 Synthesis of n-alkyl oleates.



Scheme 2 Synthesis of terpolymers.



Scheme 3 Synthesis of polymeric additives.

obtained by distillation of toluene under vacuum (see Scheme 1).

2.2. Synthesis of terpolymers (hexyl oleate-co-maleic anhydride-co-alkyl oleate)

Different terpolymers were synthesized by free radical solution polymerization. Hexyl oleate, maleic anhydride and alkyl oleate $R = CH_3(CH_2)_n-$ where n = 7, 9, 11 were taken in 1:1:1 mol ratio in dry benzene. The reaction was carried out in four necked round bottom flask where inert atmosphere was maintained during reaction by purging of nitrogen. The addition of peroxide acting as initiator was done at 75 °C in 30 min. Duration of reaction was 8–9 h with reaction temperature maintained between 75 and 80 °C. On completion of reaction benzene was distilled off & the crude terpolymers obtained were purified by solvent non-solvent method. Traces of solvent were removed by drying under reduced pressure at 50 °C/25 mmHg for 12 h. Polymers prepared were code named as O-8, O-10, and O-12 (see Scheme 2).

2.3. Synthesis of polymer additives (hexyl oleate-co–hexadecyl maleimide-co-alkyl oleate)

Above synthesized terpolymers were reacted with a hexadecyl amine in 1:1 mol ratio using dry toluene & molecular sieves to trap water molecules. Refluxed for 8–10 h the crude product obtained was purified using solvent-nonsolvent method. Additives prepared were code named as MPO8, MPO10 & MPO12 (see Scheme 3).

2.4. Characterization

2.4.1. Characterization of n-alkyl oleates

The structures of synthesized esters were confirmed by Infrared Spectroscopy using a Shimadzu FTIR-8400S spectrophotometer. The IR spectrum shows absorption bands at 1735 cm^{-1}, 1639 cm^{-1}, 2924 & 2854 cm^{-1} for C═O stretch, C═C stretch, and C—H stretching —CH_3— and —CH_2— respectively (see Fig. 1).

2.4.2. Characterization of terpolymers

2.4.2.1. FTIR spectrum of terpolymers. The IR spectrum shows absorption bands at 1737 cm^{-1}, 1855 & 1778 cm^{-1}, 2935 & 2854 $cm^{-1}$for C═O stretching of ester, C═O stretching of anhydride, and C—H stretching of —CH_3– and —CH_2– respectively (see Fig. 2).

2.4.2.2. GPC characterization of terpolymers. The synthesized terpolymers were characterized for their molecular weight and Polydispersity index using Gel Permeation Chromatography against polystyrene molecular standard weight. The

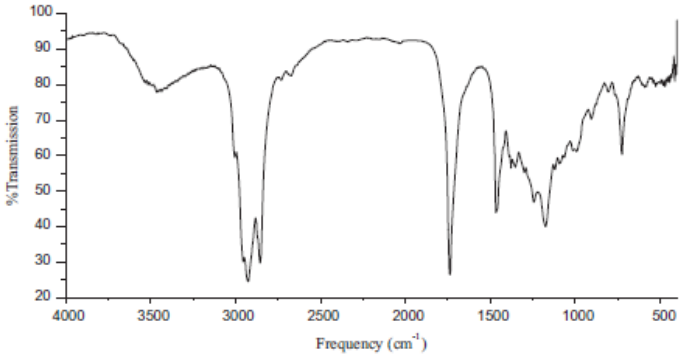


Figure 1 FTIR spectrum of the alkyl oleate.

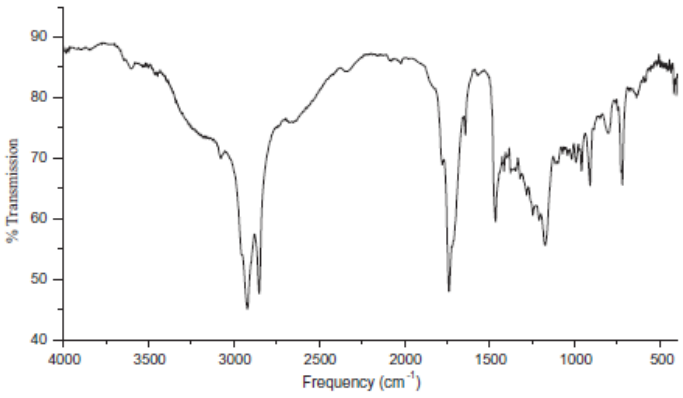


Figure 2 FTIR spectrum of terpolymers.

measurements were carried out by GPC (Waters Model-515) with an HPLC grade THF solvent, stayragel HR4 column and 1 ml/min flow rate at 25 °C. Molecular weights obtained are as follows (see Table 1):

Table 1 Molecular weight of terpolymers.

S. No.	Polymer code	Weight average molecular weight (M_w)	Number average molecular weight (M_n)	Polydispersity (M_w/M_n)
1	O-8	34,092	25,350	1.345
2	O-10	30,556	22,491	1.359
3	O-12	28,093	21,794	1.289

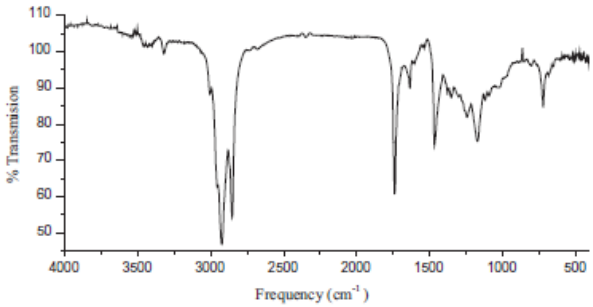


Figure 3 FTIR spectrum of polymeric additives.

Table 2 Physico-chemical properties of Langhnaj crude oil.

Physico-chemical properties	Langhnaj crude oil
Density	0.79 g/cc at 32 °C and 0.84 g/cc at 15 °C
Specific gravity	0.8252 g/cc
API gravity (degree)	44.2
Pour point	22 °C
Wax content (wt.%)	22.37%
Resin content (wt.%)	6.82%
Asphaltene (wt.%)	0.18%
IBP	57 °C

Table 3 Distillation characteristics of Langhnaj crude oil.

Temperature (°C)	Volume (ml)
75	5
100	11
125	16
150	22
175	28
200	33
225	39
250	51
275	58
300	71

2.4.3. Characterization of polymer additives

The IR spectra show absorption bands at 1737 cm^{-1}, 1695 cm^{-1}, 2852 & 2924 cm^{-1} for C═O stretching of ester, C═O stretching of imide, and C─H stretching of ─CH_3─ and ─CH_2─ respectively (see Fig. 3).

2.5. Physical testing and analysis of crude oil

2.5.1. Characterization of crude oil

Physico-chemical properties and distillation characteristics of Langhnaj crude oil is as shown below (see Tables 2 and 3):

2.5.2. Evaluation test of pour point

Pour point depends on the wax content of the crude oil while viscosity depends on naphthalene content, hence the pour point is either waxy pour or viscosity pour. Naphthenic crude oils have generally a lower pour point compared to paraffinic crude oils [7]. The pour point determination was done by ASTM D97 IP-15 [8].

The results of pour point at different concentration are as shown in Table 4. All the additives were efficient to show a decrease in pour point of Langhnaj crude oil. At 1000 ppm the decrease in pour point in all the additives reported to be maximum as MPO8 shows 3 °C, MPO10 and MPO12 show a 6 °C drop in pour point.

2.5.3. Rheological testing of additives [9]

The rheological testing of virgin and additive doped crude oil was studied using rotational Fann Viscometer Model 35 SA with the additional SR-12 gearbox. The virgin crude oil was heated up to 50–70 °C, under stirring for half an hour and cooled overnight without disturbing (12 h). Viscosity measurement at 3 °C intervals and 6 °C below the pour point were done at different speeds starting from 600 rpm to 3 rpm. The value of each shear rate was read when the dial pointer was steady. Apparent viscosity, plastic viscosity and yield value were calculated at desired temperature using the standard formula for the Fann Viscometer (see Tables 5–7).

$$\text{Apparent Viscosity} = \frac{\text{Dial reading at 600 rpm}}{2}\text{cPs}$$

$$\text{Plastic Viscosity} = (\text{Dial reading at 600 rpm} - \text{Dial reading at 300 rpm})\text{cPs}$$

$$\text{Yield Value} = (\text{Dial reading at 300 rpm} - \text{Plastic Viscocity})\text{lb}/100\text{ft}^2$$

2.6. Results and discussion

2.6.1. Apparent viscosity

All the three FIs MPO8, MPO10 & MPO12 were capable of reducing apparent viscosity to a great extent as compared to virgin crude oil. Apparent viscosity data of all three additives show that with an increase in concentration of additive the apparent viscosity increases, but is less than the apparent viscosity of virgin crude oil.

Table 4 Pour points of additive treated Langhnaj crude oil.

Additive code	Pour point (°C)	Pour point of treated crude oil					Maximum change in pour point (°C)	Extent of pour point depression (°C)
		100 ppm	200 ppm	400 ppm	500 ppm	1000 ppm		
MPO 8	22	22	22	22	22	19	19	3
MPO 10	22	22	19	19	19	16	16	6
MPO 12	22	19	19	19	19	16	16	6

Table 5 Apparent viscosity of Langhnaj crude oil by Fann Viscometer.

Concentration of additives	Sample code	Apparent viscosity (cPs) at different temperatures		
		16 (°C)	19 (°C)	22 (°C)
0 ppm	Virgin crude oil	148.5	145.0	141.5
100 ppm	MPO8	51.5	45.0	23.5
	MPO10	23.0	21.5	19
	MPO12	20.0	19.0	17.5
200 ppm	MPO8	63.5	46.0	36.0
	MPO10	35.0	33.5	32.5
	MPO12	36.0	34.5	33.0
400 ppm	MPO8	62.5	56.5	64.0
	MPO10	45.0	42.5	41.0
	MPO12	46.0	44.5	42.5
500 ppm	MPO8	69.5	67.5	65.0
	MPO10	48.5	47.5	46.5
	MPO12	52.5	50.5	47.0
1000 ppm	MPO8	67.5	62.5	58.0
	MPO10	48.0	45.0	43.0
	MPO12	65.0	59.5	55.0

Table 6 Plastic viscosity of Langhnaj crude oil by Fann Viscometer.

Concentration of additives	Sample code	Plastic viscosity (cPs) at different temperatures		
		16 (°C)	19 (°C)	22 (°C)
0 ppm	Virgin crude oil	87	85	83
100 ppm	MPO8	42	38	21
	MPO10	21	20	18
	MPO12	17	17	16
200 ppm	MPO8	52	38	27
	MPO10	32	31	31
	MPO12	31	30	29
400 ppm	MPO8	52	46	54
	MPO10	37	35	33
	MPO12	38	37	36
500 ppm	MPO8	61	59	56
	MPO10	41	36	35
	MPO12	37	36	35
1000 ppm	MPO8	60	57	54
	MPO10	40	39	38
	MPO12	45	41	48

The above trend is clear as apparent viscosity of MPO8, MPO10 & MPO12 added crude oil at 16 °C, 100 ppm concentration is 51.5, 23.0, 20.0 cPs respectively which increased to 67.5, 48.0 & 65.0 cPs at 1000 ppm concentration (see Fig. 4).

At 19 °C, 100 ppm concentration MPO8, MPO10 & MPO12 show 45.0, 21.5 & 19.0 cPs respectively which increased to 62.5, 45.0 & 59.5 cPs respectively (see Fig. 5).

Finally, at 22 °C, 100 ppm concentration MPO8, MPO10 & MPO12 show 23.5, 19.0 & 17.5 cPs respectively, which further increased to 58.0, 43.0 & 55.0 cPs respectively (see Fig. 6).

2.6.2. Plastic viscosity

Additives MPO8, MPO10 & MPO12 found to decrease plastic viscosity to a significant lower value as compared to that of virgin crude oil.

At 16 °C, 100 ppm concentration plastic viscosity observed for MPO8, MPO10 & MPO12 treated crude oil is 42.0, 21.0 & 17.0 cPs respectively, which increased to 60.0, 40.0 & 45.0 cPs at 1000 ppm. At 19 °C, 100 ppm concentration 38.0, 20.0 & 17.0 cPs observed for MPO8, MPO10 & MPO12 additive that increased to 57.0, 39.0 & 41.0 cPs respectively at 1000 ppm. Also at 22 °C, 100 ppm concentration MPO8, MPO10 & MPO12 values obtained was 21.0, 18.0 & 16.0 cPs that increased to 54.0, 38.0 & 48.0 cPs respectively.

Table 7 Yield value of Langhnaj crude oil by Fann Viscometer.

Concentration of additives	Sample code	Yield value (lb/100 ft^2) at different temperatures		
		16 (°C)	19 (°C)	22 (°C)
0 ppm	Virgin crude oil	123	120	117
100 ppm	MPO8	19	14	5
	MPO10	4	3	2
	MPO12	6	4	3
200 ppm	MPO8	23	16	6
	MPO10	2	6	5
	MPO12	10	9	8
400 ppm	MPO8	21	21	20
	MPO10	16	15	16
	MPO12	16	15	13
500 ppm	MPO8	17	17	18
	MPO10	15	23	23
	MPO12	31	29	24
1000 ppm	MPO8	15	11	8
	MPO10	16	12	10
	MPO12	40	37	34

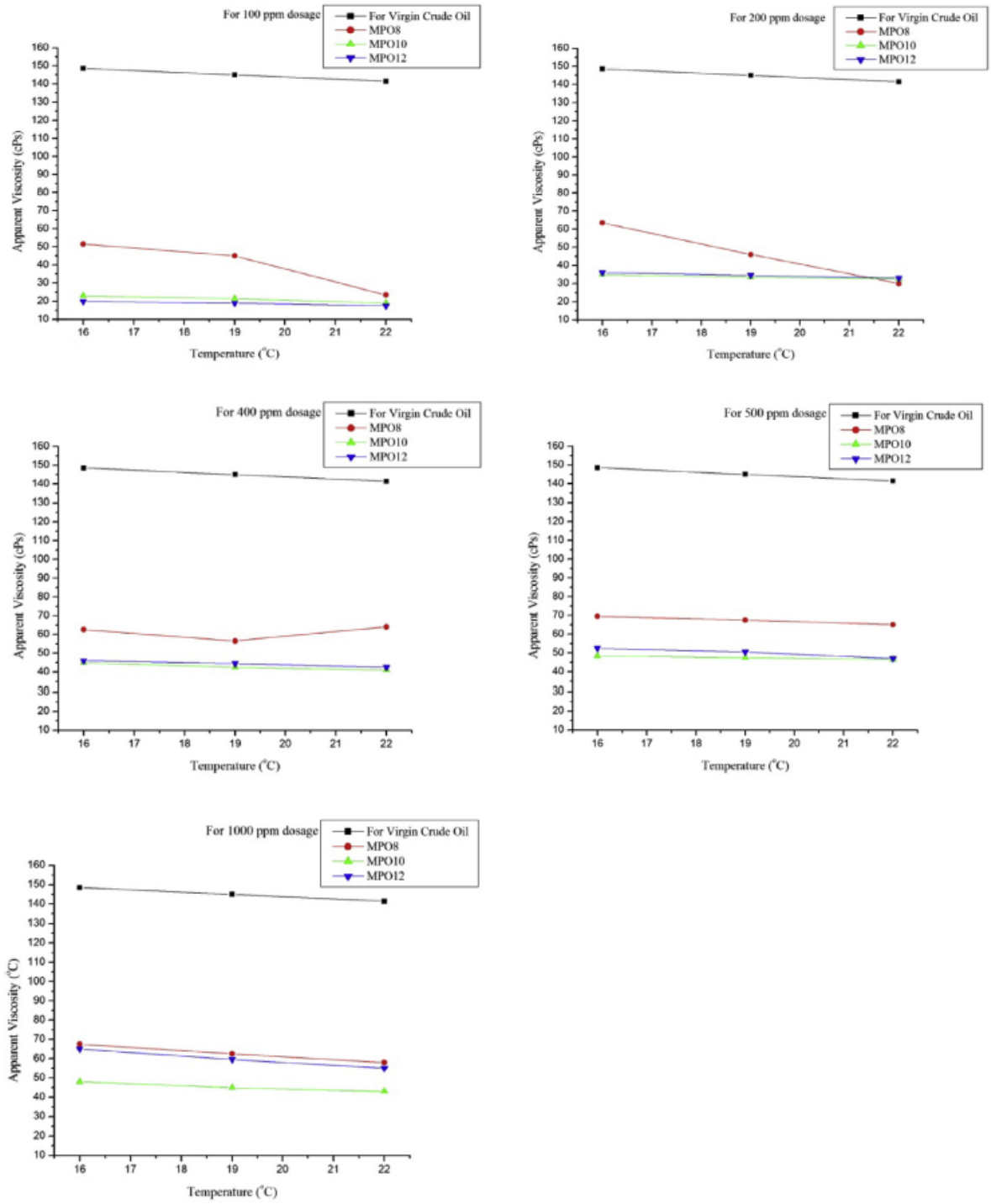


Figure 4 Plot of apparent viscosity versus temperature at different concentration.

2.6.3. Yield value

Finally, yield value clearly showed that with an increase in concentration of additives from 100 ppm to 1000 ppm, a significant increase in yield values was observed although compared to virgin crude oil the yield value observed is quite low.

Now at 100 ppm additive concentration of MPO8, MPO10 & MPO12 best results of apparent viscosity, plastic viscosity

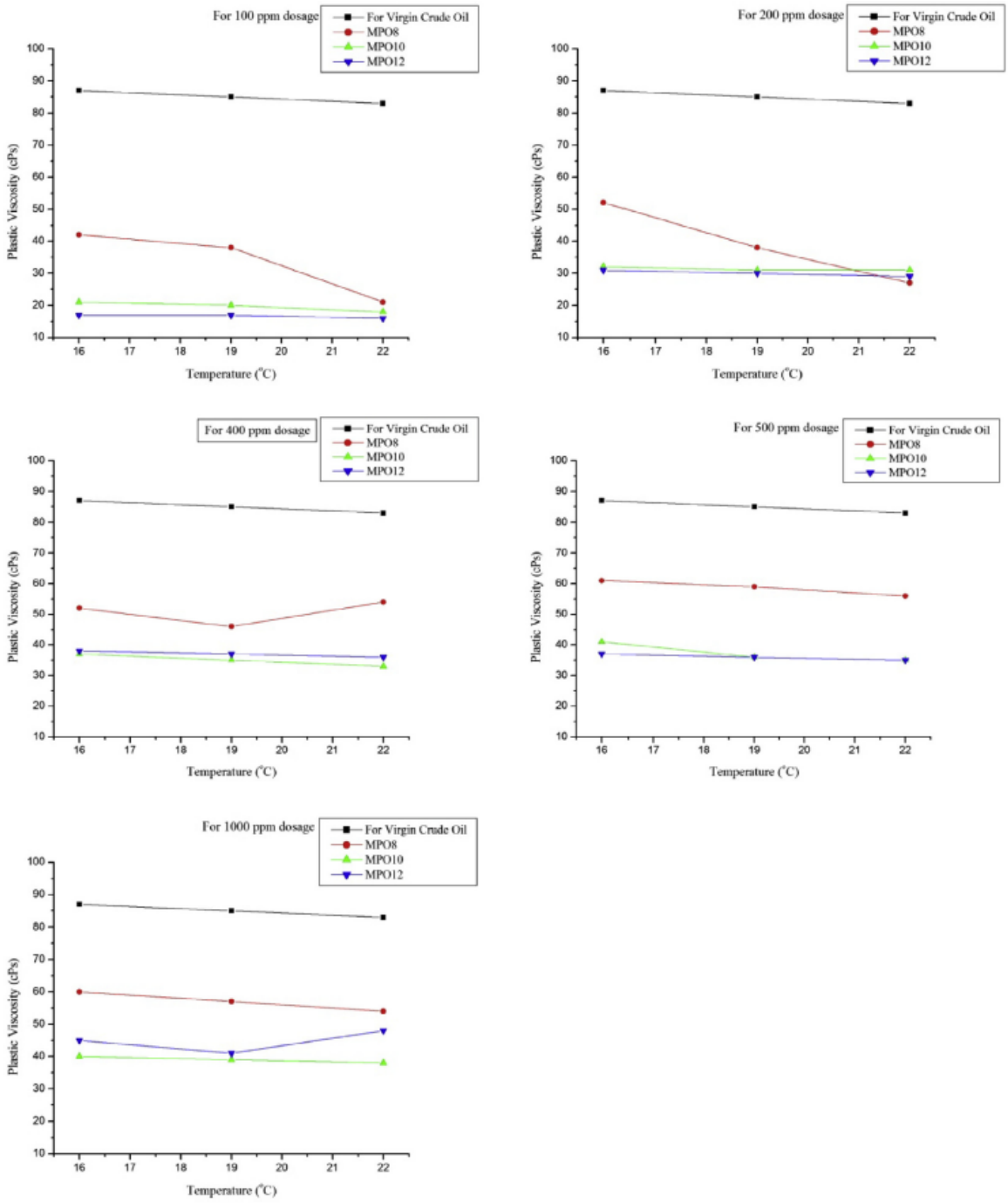


Figure 5 Plot of plastic viscosity versus temperature at different concentration.

& yield value were found. It was observed that with the increase in alkyl chain length from MPO8 to MPO12 the viscosity values as well as yield values decreased considerably. Hence the efficiency of additives to decrease viscosity increases with an increase in alkyl chain length. But at higher concentration of additive such trend was not observed. The above results show that with an increase in chain length of additive, non-polar part of FI co-crystallize with that of paraffin waxes while polar part blocks network growth leading to lowering of viscosity.

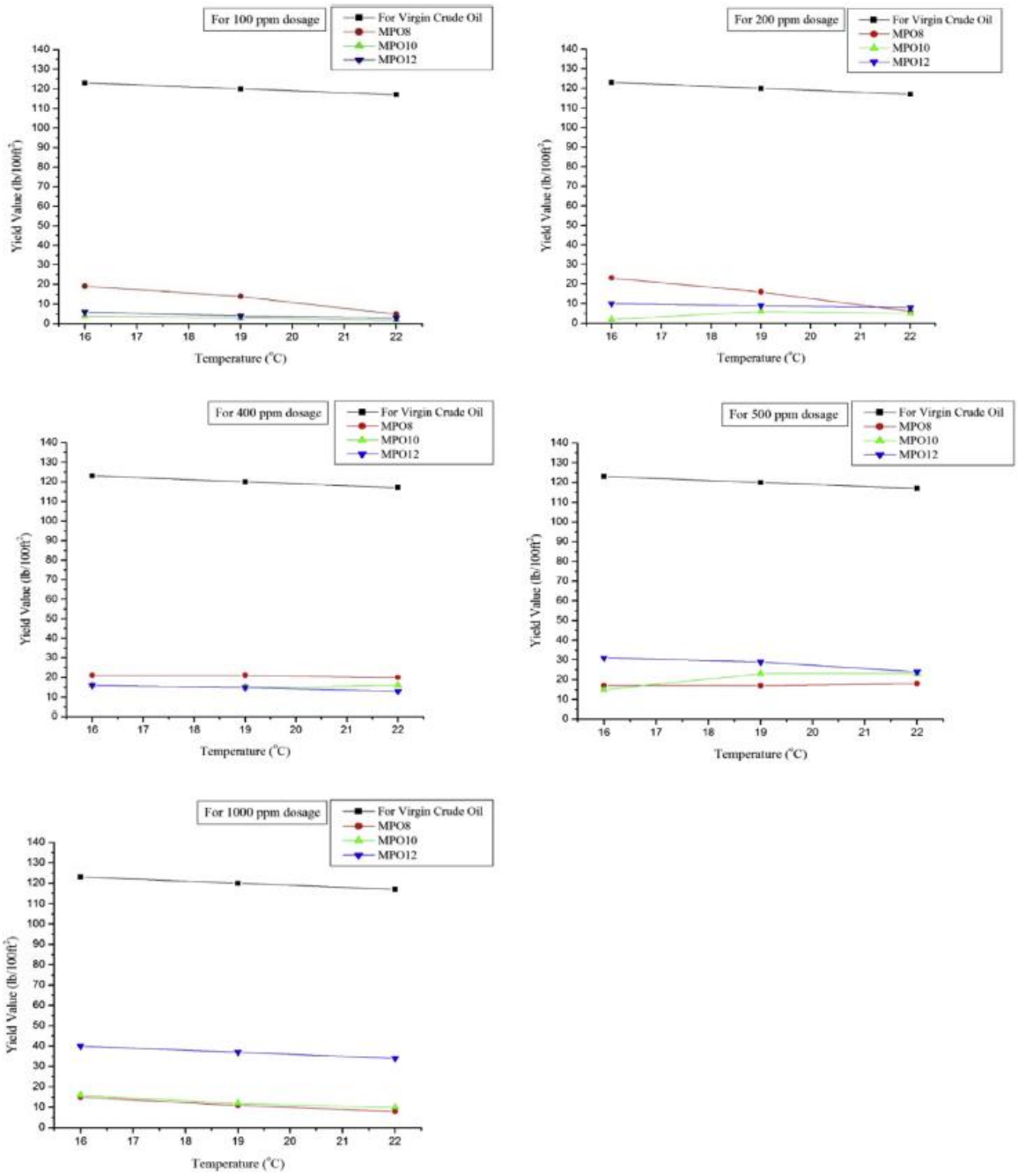


Figure 6 Plot of yield value versus temperature at different concentration.

2.7. *Conclusions*

The following conclusions are made from the study:

(1) The synthesized FI acts as effective pour point depressant at higher concentrations.

(2) All synthesized FIs effectively reduced the apparent viscosity, plastic viscosity & yield value of virgin crude oil to significantly lower values.

(3) At a higher concentration FI performed the dual function of wax inhibitor and viscosity index improvers.

(4) At lower concentrations of additives, crude oil showed low viscosity which increases at a higher concentration. Hence, these additives can be effectively used as viscosity index improvers.

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References

[1] P. Singh, V. Ramachandran, H.S. Fogler, N.R. Nagrajan, J. AlChE. 47 (2001) 6–18.

[2] H.P. Soni, Kiranbala, D.P. Bharambe, Energy Fuels 22 (2008) 3930–3938.

[3] Y. Wu, G. Ni, F. Yang, C. Li, G. Dong, Energy Fuels 26 (2012) 995–1001.

[4] W. Chen, Z. Zhao, C. Yin, Fuel 89 (2010) 1127–1132.

[5] N. Miskolezi, R. Sagei, L. Bartha, L. Forcek, J. Fuel Chem. & Tech. 37 (3) (2009) 302–310.

[6] D.S. Schuster, J.H. Magill, in: D. Schulz et al. (Eds.), Polymers as Rheology Modifiers, ACS Symposium Series, Washington DC, 1991, pp. 301–310.

[7] R.A. Vora, D.P. Bharambe, Indian J. Tech. 31 (23) (1993) 633–635.

[8] Annual book of ASTM standards, Standard methods of test for pour point of petroleum oils, 1974. ASTM D 97-66, Part 17, pp.81-84.

[9] H.P. Soni, D.P. Bharambe, A. Nagar, Kiranbala, Synthesis of chemical additives and their effect on Akholjuni crude oil, Ind. J. Chem. Tech. 12 (2005) 55–61.