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Synergistic effect of liquid crystals on the additive performance of poly acrylate in lubricating oil

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ARTICLE INFORMATION

ABSTRACT

Multifunctional additive performance of the poly acrylate at the presence of the selective liquid crystal structures was evaluated using the standard ASTM methods. Homopolymer of the mixed acrylate (octyl, decyl and dodecyl) was synthesised and characterized by thermo gravimetric, spectroscopy and viscometric analysis. Additive performances of the polymer were evaluated as the viscosity modifier (VM), thickening agent (TA), pour point depressant (PPD) and antiwear (AW) additive. Physical blend of the polymer with six different types of liquid crystals (LC) were also made, and their performance was evaluated. The results indicated that all the LC-blended samples acted as a better VM, PPD, along with excellent AW and thickening performance compared with the pure polymer sample.

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Graphical Abstract
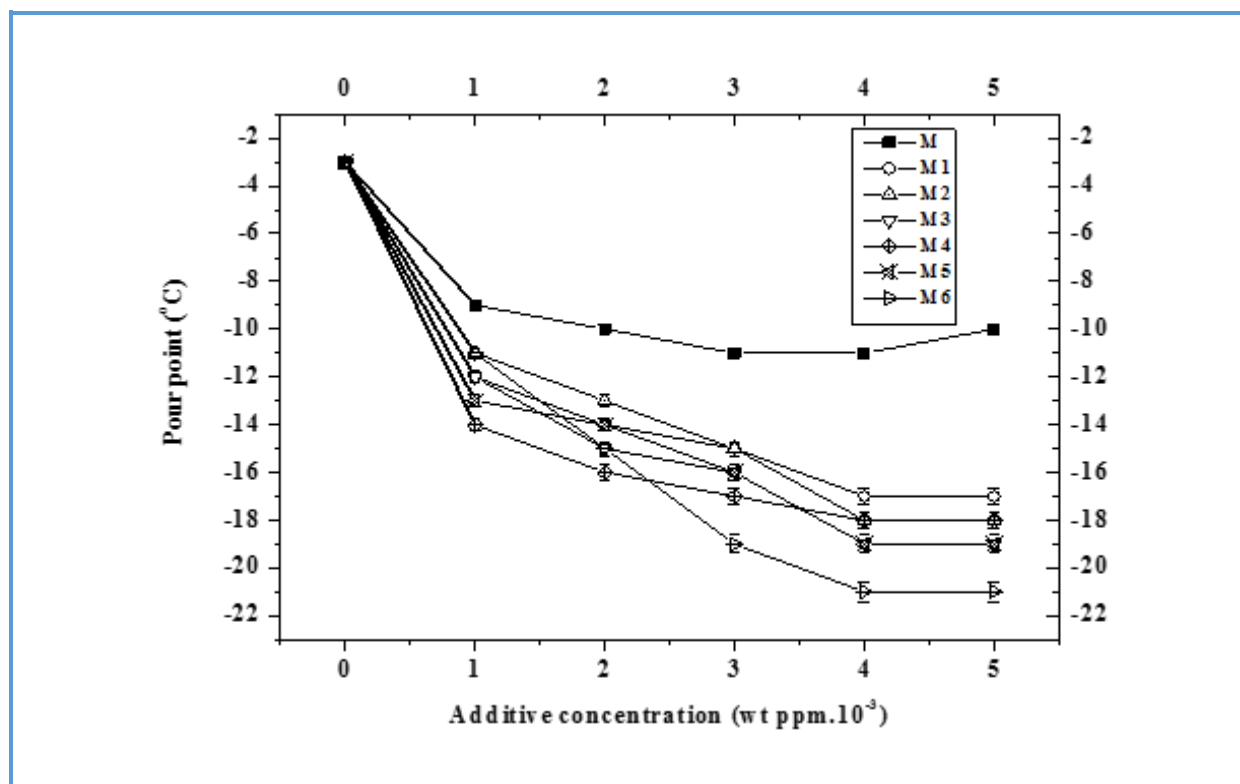
Introduction

Lubricating oil, known as base oil, is the basic lubricant for an engine. A lubricant should have different qualities including, flow ability at very low temperature, less variation of viscosity at high temperature, tribological activity, and fuel economy. However, most of the times, the base oils fail to achieve so many criteria. To improve the performance, different chemicals have been doped in the base oils to induce specific performance.

Acrylate and methacrylates are well known as viscosity modifier (VM) and pour point depressant (PPD) [1–4] for base oils. Polymers of the mixed acrylate found better in performance compare with that of the respective homo poly acrylates [5]. In the present research study, we have prepared a mixed acrylate using three homologous alcohols and acrylic acid, in an anticipation of better performance than any of the poly alkyl acrylate itself. Liquid crystals are also popular anti wear additives for base oils [6–8]. However reports of induction of LC in acrylate system are very few. In our previous work [9] we blended liquid crystals in homo poly decyl acrylate which result in multifunctional additive performance. In continuation, here we have introduced LC in a mixed acrylate system in order to achieve further better performance.

The average molecular weight (Mn and Mw) of the mixed acrylate was determined by gel permeation chromatography. Physical characterization was carried out using TGA (thermal gravimetric analysis) and spectroscopic (IR, NMR) method. Performance was evaluated as VM, PPD, AW and thickening agent using standard ASTM methods.
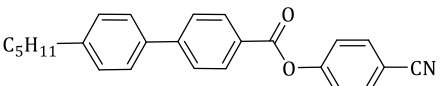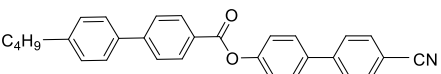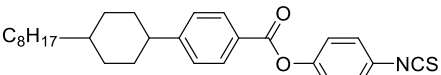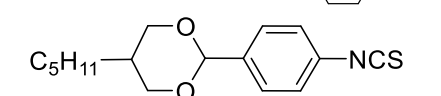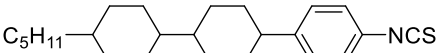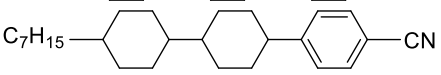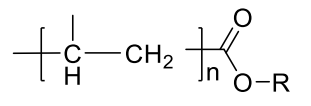
Experimental

Materials and methods

Details of the reagents used and their specification are shown in Table 1. LC samples (I to VI) were procured from the Department of Physics, University of North Bengal. Their chemical structures are tabulated in Table 2. Two different base oils (BO1 and BO2) were collected from IOCL, Kolkata and their physical properties are presented in Table 3.

Table 1. Specification of chemicals

Chemical name	Source	Mole fraction purity
Toluene	Merck Specialities Pvt. Ltd.	0.991
Hydroquinone	Merck Specialities Pvt. Ltd.	0.988
Benzoyl Peroxide	Merck Specialities Pvt. Ltd.	0.979
H_2SO_4	Sigma-Aldrich Pvt. Ltd.	-
Acrylic Acid	Thomas Baker Pvt. Ltd.	0.988
1-octanol	Sigma-Aldrich Pvt. Ltd.	0.993
1-decanol	Sigma-Aldrich Pvt. Ltd	0.989
1-dodecanol	Sigma-Aldrich Pvt. Ltd	0.977
Hexane	Thomas Baker Pvt. Ltd.	0.949
1-Decene	Sigma-Aldrich Pvt. Ltd.	0.947
Methanol	Thomas Baker Pvt. Ltd.	0.979

Table 2. Details of liquid crystals/ additives used

Sample no.	Chemical structure	Commercial name	Source	Mole fraction purity
I		5CPB	ACL[a]	0.991
II		4CBB	ACL	0.992
III		8TPCHB	ACL	0.988
IV		5DBT	ACL	0.994
V		5TPBCH	ACL	0.989
VI		6CPBCH	ACL	0.990
M		-	-	-

I to VI: liquid crystals used
M: polymer of mixed acrylate
ACLa is abbreviation of AWAT Co. Ltd., Warsaw, Poland, all the liquid crystals were used as received

Table 3. Base oil properties

Properties	Base Oils	
	BO1	BO2
density (kg·m^{-3}) at 313 K	839.98	918.68
viscosity (m^2·s^{-1}) at 313 K	6.70×10^{-6}	24.22×10^{-6}
viscosity (m^2·s^{-1}) at 373 K	1.96×10^{-6}	4.32×10^{-6}
cloud point/°C	-10	-8
pour point/°C	-3	-6
Chemical composition		
saturated/%	65-80	90-95
aromatic/%	15-20	5-7
sulphur/ppm	300-2500	5-300

Synthesis of monomer by esterification

The mixed acrylate was prepared using *n*-octanol, *n*-decanol, *n*-dodecanol and acrylic acid in a molar ratio of 1:1:2:4. The reaction was carried out under nitrogen atmosphere at the presence of the catalytic amount of the concentrated sulphuric acid in toluene media in a resin kettle. Hydroquinone (0.25%) was used to inhibit the polymerization. The reactants were heated gradually from room temperature to 403 K using a thermostat. Amount of the liberated water was measured to check the extent of reaction to produce ester of mixed alcohols.

Purification

For purification at first, a desired amount of the charcoal was added to the ester, followed by reflux for 3 h and filtration. The filtrate was then repeatedly washed with 0.5 N sodium hydroxide solution to ensure complete removal of unreacted acid. The purified ester was then washed several times with the distilled water to remove the traces of sodium hydroxide. The ester was then left overnight on calcium chloride and recollected by distillation under reduced pressure. This purified ester wasused in the polymerization process.

Polymerization

The polymerization was carried out in a four-necked round bottom flask equipped with a stirrer, condenser, thermometer, and an inlet for the introduction of nitrogen. Desired mass of prepared ester and initiator (BZP) were placed in the flask in presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. After that the reaction mixture was poured into the methanol and stirred to terminate the polymerization and to precipitate the polymer (M). The polymer (M) was further purified by the repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K.

Preparation of polymer-lliquid crystal blends

Physical blend of the polymer (M) with LCs were prepared by mixing M with desired amount of LC (100 wt ppm with respect to the polymer) in a mechanical stirrer at 60 °C for 1hour. The blended samples named as M1 (for M + I), M2 (for M + II), M3 (for M+III), M4 (for M+IV), M5 (for M+V) and M6 (for M + VI).
Five different concentrations ($1 \cdot 10^3$ wt ppm to 5×10^3 wt ppm) of additive doped base oils solutions were prepared with all the above samples including M. The final composition of the mixture of base oil and additive may be presented as, base oil:M:LC=10^6**:**a x10^4**:**a, where

a varies from 1 to 5 depending upon additive concentration.

Measurements

Spectroscopic study

IR spectra of the prepared polymer (M) was recorded on a Shimudzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the range 400 cm^{-1} to 4000 cm^{-1}. Brucker Avance 300 MHz FT-NMR was employed to record the ^{1}H and ^{13}C NMR in a 5mm BBO probe. CDCl$_3$ was used as solvent and TMS as reference material.

Thermal gravimetric analysis (TGA)

The thermograms in air of the samples were obtained on a Mettler TA–3000 system, at a heating rate of 10 K min^{-1}. 0.5 g of each samples were taken in platinum crucible at room temperature and atmospheric pressure and heated gradually.

Molecular weight determination by GPC

The weight average and number average molecular weights (M$_W$ and M$_N$) and the polydispersity of M were measured using the Water's gel permeation chromatography equipment with the polystyrene standards for calibration in THF phase. The M$_n$, M$_w$ and poly dispersity index were found to be 90000, 182000, and 2.02, respectively.

Performance evaluation as viscosity modifier

Viscometric properties of the prepared samples were determined in two base oils (BO1 and BO2), using an Ubbelohde OB viscometer, thoroughly cleaned, dried and calibrated at the experimental temperatures (313 K and 373 K) with triply distilled, degassed water and purified methanol [10, 11]. It was then filled with experimental liquid and placed vertically in a glass sided thermostat. After reaching the thermal equilibrium, the time flow of liquids was recorded with a digital stopwatch. In all determinations an average of three measurements was taken into account and precautions were taken to minimize losses due to evaporation. The kinematic viscosity (ν) of the sample solutions, which is useful to calculate viscosity index (VI), was determined at 313 K and 373 K, using the following equation [12].

$$\nu = (Kt - L/t)\, \rho \qquad (1)$$

Where K and L are the viscometric constants and t and ρ are time flow and density of experimental solution respectively.

The densities were measured using a vibrating-tube density meter (Anton paar, DMA 4500M). Before measurements the density meter was calibrated with distilled and degassed water and dry air at experimental temperature and atmospheric pressure. VI was calculated using the Eequation (2) [12, 13].

$$VI = 3.63\,(60 - 10^n) \qquad (2)$$

Where n is given by,

$$n = (\ln \nu_1 - \ln k)/\ln \nu_2 \qquad (3)$$

where ν_1 is the kinematic viscosity at lower temperature, ν_2 is the kinematic viscosity at higher temperature, k is a function of temperature only and n is a constant characteristic for each oil [12].

Five different concentrations (1×10^3 wt ppm to 5×10^3 wt ppm) of the sample solutions were used to investigate the effect of concentration on VI.

Performance evaluation as thickening agent

Thickening agents, or thickeners, are the substances which can increase the viscosity of a solution or liquid/solid mixture. Thickening power of the samples was determined by

evaluating the percent increase in kinematic viscosity of the base stocks by the addition of unit amount of additive, which may be expressed as follows

% Thickening = [(ν of additive doped base oil - ν of base oil) / ν of base oil] x 100   (4)

Thickening also determines the extent of polymer-base oil interaction, which is directly proportional with thickening [14]. Here also five different concentrations(1×10^3 wt ppm to 5×10^3 wt ppm) of additive doped base oils were used in the measurements.

Performance evaluations as pour point depressant (PPD)

Evaluations of the PPD properties of the prepared samples were performed in two base oils (BO1 and BO2) using the pour point test according to the ASTM D 97 method on a Cloud and Pour Point Tester model WIL-471 (India). To evaluate the effect of the additive concentration on the pour point, five different doping concentrations (1×10^3 wt ppm to 5×10^3 wt ppm) from each sample were considered. An average of three experimental data taken under the identical condition was recorded.

Performance evaluations as anti -wear additive

Anti-wear properties were studied in sliding contact by means of a four–ball wear tester as per ASTM D-4172 method, using 196 N and 392 N load conditions. In addition, effect of additive concentration on anti-wear performance was also studied. To investigate the AW performance wear scar diameter (WSD) was measured for all the samples in two base oils (BO1 and BO2). All the WSD data mentioned were noted taking the average of three experimental results.
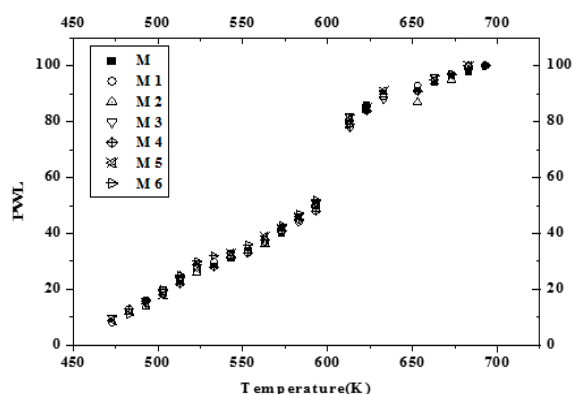
Results and Discussion

Spectroscopic analysis

In its IR spectra the homopolymer of the mixed acrylate showed following peaks: ν_{max}/cm^{-1} 1737 (CO), 1168 (C-O strch.), 996 (C-H bend.). The NMR spectra had the following peaks: δ_H 4.03(-OCH$_2$), δ_C 174 (-CO). Absence of peak within the range δ_H 5 to 6 indicated that olefinic double bond was absent in the polymer sample, which was further supported by absence of peak at δ_C 130-150 (sp^2 C).

Thermal gravimetric analysis

Comparison between the experimental TGA data for M and the blended samples (M1 to M6) showed similar thermal stability for all the samples. The graphical presentation is shown in Figure 1.

Figure 1. Plot of PWL vs decomposition temperature (K), where PWL is the percent weight loss of the polymer. The symbols signify: ■, M; ○, M1; △, M2; ▽, M3; ⬦, M4; ⋇, M5; ⬠, M6

Performance evaluation - viscosity modifier

The prepared samples were tested for their effectiveness as viscosity modifier by measuring the VI of the respective additive doped base oils from the kinematic viscosity values at 313 K and 373 K. The kinematic

viscosity and the corresponding VI are presented in Table 4 and Table 5 respectively for BO1. Accordingly, Table 6 and Table 7 represent the results for BO2.

Table 4. Kinematic viscosity (ν) of the additives doped base oil (BO1) with additive concentration at temperature (313 and 373) K

Conc. (wt ppm. 10^{-3})	Temp. (K)	ν ($\cdot 10^{-6}$ /m$^2\cdot$s^{-1}) in presence of						
		M	M1	M2	M3	M4	M5	M6
0	313	6.70	6.70	6.70	6.70	6.70	6.70	6.70
	373	1.96	1.96	1.96	1.96	1.96	1.96	1.96
1	313	11.72	12.30	11.99	11.92	12.10	12.04	12.12
	373	2.71	2.86	2.80	2.78	2.83	2.77	2.79
2	313	12.04	12.90	12.43	12.39	12.34	12.40	12.43
	373	2.80	3.00	2.94	2.92	2.94	2.96	2.90
3	313	12.57	13.43	13.14	12.94	12.81	12.87	12.87
	373	2.91	3.18	3.09	3.12	3.04	3.13	3.00
4	313	12.99	13.93	13.72	13.32	13.21	13.19	13.38
	373	3.08	3.37	3.24	3.24	3.17	3.24	3.13
5	313	13.47	14.46	14.39	13.87	13.69	13.76	13.78
	373	3.21	3.50	3.36	3.33	3.31	3.35	3.26

ν=kinematic viscosity
M=polymer of mixed acrylate
M1=M +I; M2=M+II; M3=M+III; M4=M+IV; M5=M+V; M6=M+VI
The uncertainties in measurement of ν was within the range 0.26%

Table 5. Viscosity index values (VI) of the additive doped in base oil (BO1) with additive concentration

Conc. (wt ppm. 10^{-3})	VI in presence of						
	M	M1	M2	M3	M4	M5	M6
0	85	85	85	85	85	85	85
1	112	118	117	117	119	113	114
2	116	122	124	123	126	127	120
3	119	130	127	132	128	134	123
4	128	137	131	136	132	137	127
5	132	139	131	136	136	138	132

M=polymer of mixed acrylate
M1=M +I; M2=M+II; M3=M+III; M4=M+IV; M5=M+V; M6=M+VI
The uncertainty in determining the viscosity index was within the range ± 0.33 %

Table 6. Kinematic viscosity (ν) of the additives doped base oil (BO2) with additive concentration at temperature (313 and 373) K

Conc. (wt ppm. 10^{-3})	Temp. (K)	ν ($\cdot 10^{-6}$ / m²·s⁻¹) in presence of						
		M	M1	M2	M3	M4	M5	M6
0	313	24.22	24.22	24.22	24.22	24.22	24.22	24.22
	373	4.32	4.32	4.32	4.32	4.32	4.32	4.32
1	313	31.15	32.66	32.83	32.65	32.52	32.10	32.82
	373	5.36	5.70	5.62	5.76	5.70	5.80	5.81
2	313	31.85	33.46	33.43	33.48	33.24	33.16	33.59
	373	5.52	5.88	5.80	6.01	5.91	6.04	5.93
3	313	32.76	34.99	34.68	34.37	34.13	34.43	34.55
	373	5.96	6.08	6.47	6.30	6.18	6.32	6.17
4	313	35.48	35.35	35.94	35.23	34.90	35.42	35.65
	373	6.16	6.52	7.20	6.63	6.54	6.63	6.42
5	313	38.72	40.24	38.92	35.71	35.63	35.68	36.31
	373	6.66	7.28	7.72	6.96	6.94	7.07	6.98

ν=kinematic viscosity
M=polymer of mixed acrylate
M1=M +I; M2=M+II; M3=M+III; M4=M+IV; M5=M+V; M6=M+VI
The uncertainties in measurement of ν was within the range 0.26%

Table 7. Viscosity index values (VI) of the additive doped in base oil (BO2) with additive concentration

Conc. (wt ppm. 10^{-3})	VI in presence of						
	M	M1	M2	M3	M4	M5	M6
0	104	104	104	104	104	104	104
1	115	120	117	122	121	125	123
2	117	123	120	126	124	128	124
3	120	125	133	131	129	131	127
4	123	132	144	135	134	135	130
5	126	135	145	140	140	142	139

M=polymer of mixed acrylate
M1=M +I; M2=M+II; M3=M+III; M4=M+IV; M5=M+V; M6=M+VI
The uncertainty in determining the viscosity index was within the range ± 0.33

Effect of additive concentration on VI

The results revealed that, the kinematic viscosity and VI of the additive doped base oils increased with increasing the additive additives concentration, irrespective of the nature of the base oils. At higher temperature the long chain high molecular weight VI improvers increases the relative viscosity of the oil to a great extent.

This may be because of the change of the physical configuration of the VI improvers at a higher temperature of the system [15].
At low temperature the polymer molecules adopt a coiled form. With the rise in temperature the polymer molecules tend to straighten out and make an effective interaction with the base oils (Figure 2). Thus at a higher temperature there will be a drop in the

reduction of viscosity of the base oil due to the presence of VM additives. Again increase in

concentration of the additives causes increase in the total volume of polymer in the oil solution and thus exerting greater thickening effect and VI as well [15, 16].
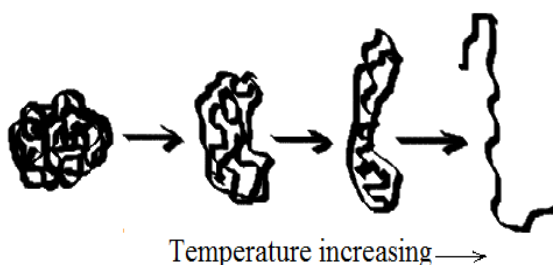

Figure 2. Schematic diagram of temperature dependence behaviour of viscosity modifier, conversion from coiled form to chain like structure

Effect of liquid crystal on VI

VI values of all the LC blended samples (M1 to M6) are better compare to M in every concentration level and in both the base oils (BO1 and BO2). The presence of LC samples in the polymer-oil blend favoured the process of polymer–oil interaction towards their performance as a better VI improver [17]. Uniform alignment of LC molecules present in the polymer-LC blend is playing the key role to increase the molecular mobility of the additive and hence the performance of the blend as a whole [6].

Performance evaluation -thickening agent

The thickening percentages were measured from the kinematic viscosity data of the base oils (BO1 and BO2) and additive doped base oils at 373 K, to understand the affectivity of the samples at higher temperature range [14]. The results are shown in Figure 3.
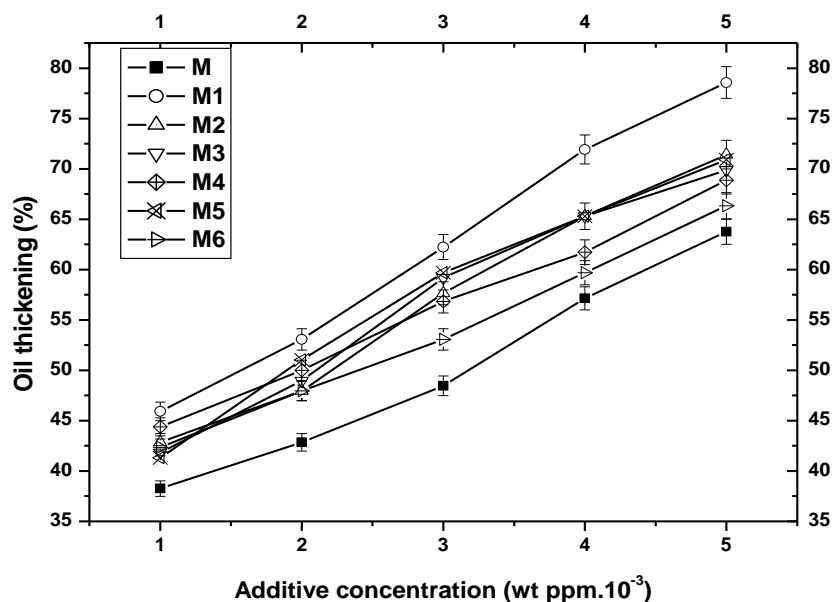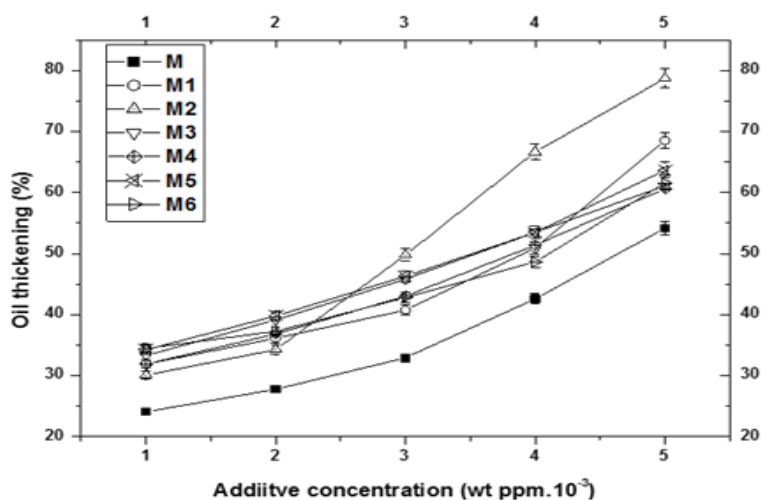

Figure 3. a) Plot of oil thickening (%) vs additive concentration at 373 K in BO1. The symbols signify: ■, M; ○, M1; △, M2; ▽, M3; ◈, M4; ✖, M5; ➤, M6

Figure 3. b) Plot of oil thickening (%) vs additive concentration at 373K in BO2. The symbols signify: ■, M; ○, M1; △, M2; ▽, M3; ✦, M4; ✕, M5; ▷, M6

Effect of additive concentration on thickening property

The results indicate a gradual increase of thickening with increasing concentration for all the samples in both the base oils. The reason is same as explained in case of effect of additive concentration on VI [14–16].

Effect of liquid crystal on thickening property

Liquid crystal doped samples (M1 to M6) are better thickener than the homopolymer (M) at every concentration level. The explanations are same as in case of VI property. Presence of liquid crystals favours the formation of suitable alignment of the polymer in base oils, resulting higher polymer- base oil interaction and thereby greater thickening effect [6–17].

Performance evaluation - pour point depressant

Pour points of additive doped base oils (BO1 and BO2) were measured (Figure 4).

Figure 4. a) Plot of pour point (ºC) of the additive doped base oil vs additive concentration in BO1. The symbols signify: ■, M; ○, M1; △, M2; ▽, M3; ✦, M4; ✕, M5; ▷, M6
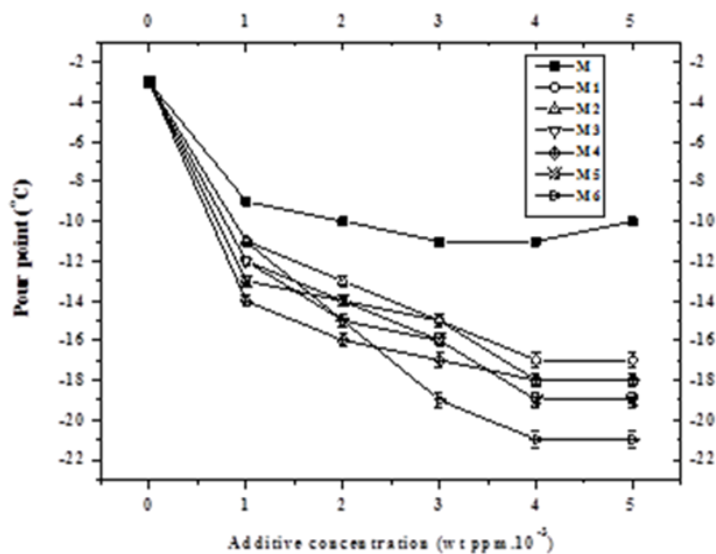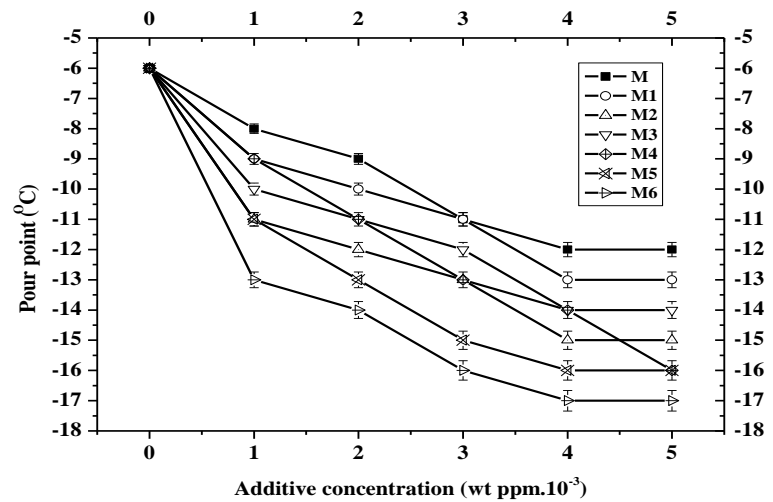
Figure 4. b) Plot of pour point (ᵒC) of the additive doped base oil vs additive concentration in BO2. The symbols signify: ■, M; ○, M1; △, M2; ▽, M3; ◈, M4; ✕, M5; ⬦, M6

Effect of additive concentration on pour point

The results showed that, the pour points of the additive doped base oils decreased with increasing the additive concentration (up to a certain limit). This was due to the effective polymer-oil interaction at higher concentration of polymer and the increased hydrodynamic volume of the additive resulting in the depression of pour point [18].

Effect of liquid crystal on pour point

Comparison between M and the blended samples (M1 to M6), indicate that the latter are better in PPD performance in most of the cases. This can again be explained on the basis of more effective polymer-oil interaction in presence of LC [6–17].

Performance evaluation-antiwear additive

AW performances of the additives were evaluated on the basis of wear scar diameter (WSD) in BO1 and BO2 at two load condition (196 N and 392 N).The lower the WSD, the better is the AW performance. The results are shown in Figure 5.

Figure 5. a) Plot of wear scar diameter (WSD) vs additive concentration at 196 N in BO1. The symbols signify: ○, M; △, M1; ▽, M2; ✕, M3; ◁, M4; ▷, M5; ⬗, M6
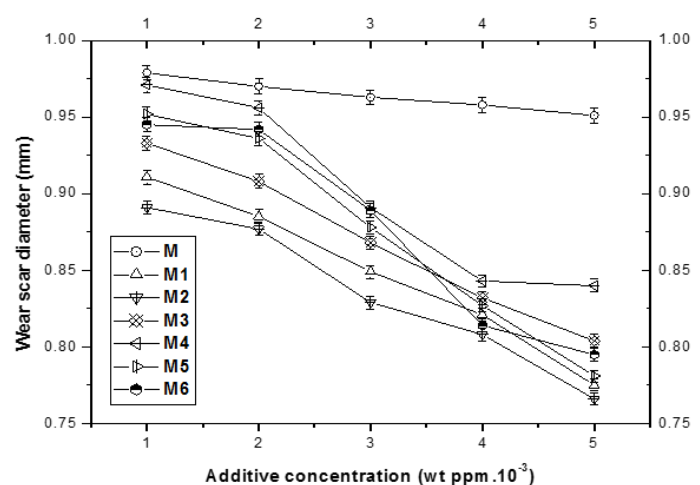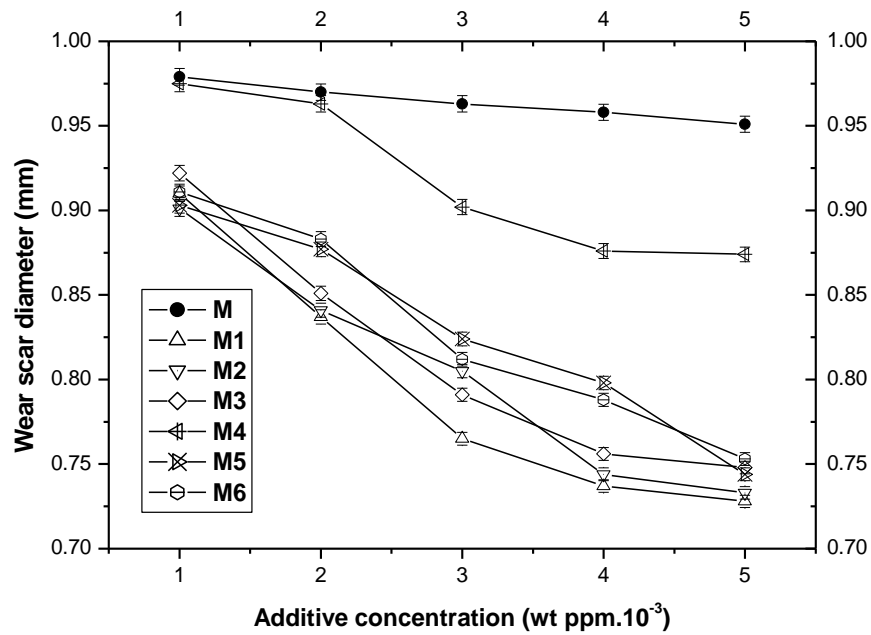
Figure 5. b) Plot of wear scar diameter (WSD) vs additive concentration at 392 N in BO1. The symbols signify: ●, M; △, M1; ▽, M2; ◇, M3; ◁, M4; ✳, M5; ⊖, M6
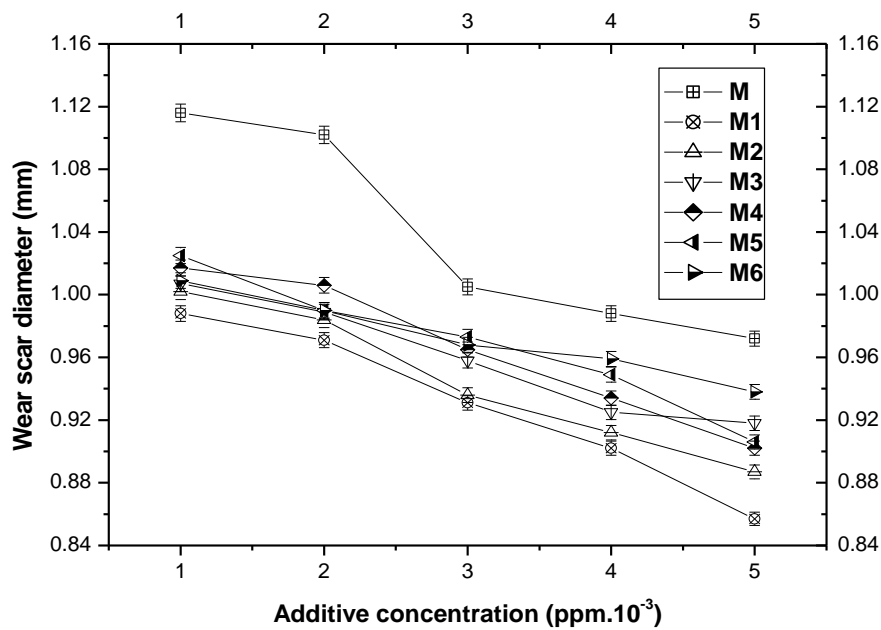

Figure 5. c) Plot of wear scar diameter (WSD) vs additive concentration at 196 N in BO2. The symbols signify: ⊞, M; ⊗, M1; △, M2; ⊥, M3; ◆, M4; ◀, M5; ▶, M6
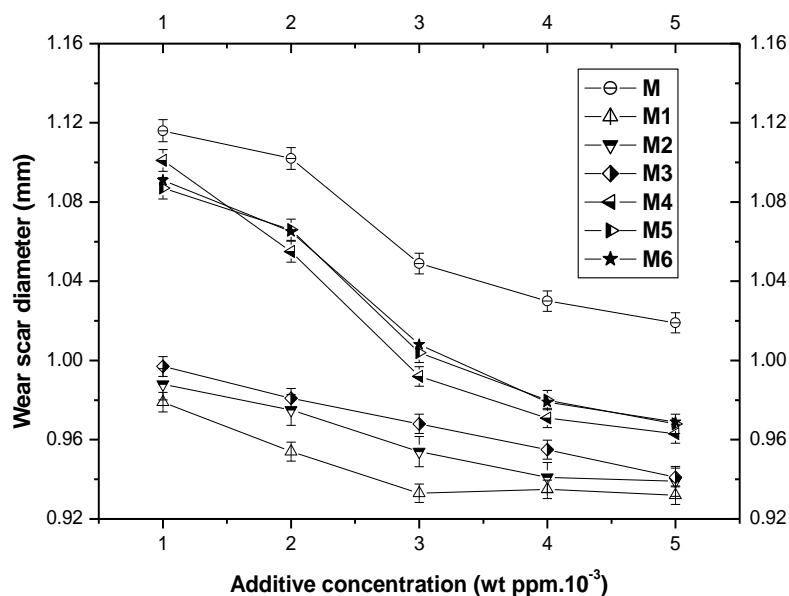
Figure 5 d). Plot of wear scar diameter (WSD) vs additive concentration at 392 N in BO2. The symbols signify: ⊖, M; ⌒, M1; ▽, M2; ◆, M3; ◀, M4; ▶, M5; ★, M6

Effect of additive concentration on anti-wear

In BO1, for both the load conditions, the blended samples are acting as better AW additive at higher concentration level. But the reverse is true for BO2. In BO2, relatively lower WSD (better AW performance) were found at lower additive concentration.

Effect of liquid crystal on anti-wear

LC blended samples (M1 to M6) showed better AW performance (lower WSD) compared to M in both the base oils at every concentration. It is also observed that in most of the cases, samples (M1, M2, and M3) containing LCs with more aromatic rings [19] and ester (-COO) functionality [20, 21] in their structure (I, II, III) showed much better AW performances compared to the others. This is in agreement with our earlier observation [9].

In most of the cases, sample M4 has shown worst performance among the blended samples.

However, M5 and M6 have similar performance. This may be due to the similar kinds of chemical structure of the liquid crystals (V, VI) present in them.

Conclusions

The liquid crystal blended mixed acrylate (M1 to M6) showe the best additive for the base oils compared to M. Addition of very little amount (100 wt ppm) of liquid crystal in acrylate system is introducing the AW performance to a great extent, along with enhancement of already existing additive performance *viz.*VM and PPD of the mixed acrylates (M). This has made the derived polyacrylate samples to act as potential multifunctional additive for the lubricating oil.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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