

# Chapter III

Synergistic effect of liquid crystal on the  
additive properties of long chain alkyl  
acrylates in lube oil

### 1.2.1. Introduction

After the successful application of cholesteryl benzoate-polymer composite (which contain 100 ppm. of CB in polymer) as multifunctional additive the author has continued the search towards different kind of blended composites of CB with acrylate polymer of varying ppm level liquid crystal in polymer matrix. As we know mineral oils are commonly used as a lubricating medium. The possibility of enhancement in their lubricating properties is restricted and that is why one must use additives for the existing minerals oils to improve them. Nowadays, the used additives for lubricating oils are among others graphite and molybdenum disulfide. A mechanism of lubricant acting with these additives is based on formation of the surface-active film filling irregularities of a material surface. These additives increase lubricity of the oil base because they possess the stronger ability of adsorbing oil than metal, and their layered structure enables formation of a slip plane. Liquid crystalline compounds, which are characterized by an oriented arrangement of molecules as well as a sort of positional ordering, can play the same role. Applications of liquid crystals, being in a pure state and additives for mineral oils, as lubricants have been reported in the literature in the last few years.<sup>1-4</sup>

It is well reported that cholesteryl based liquid-crystal additives to lubricating oils improve their anti-wear and antiscoring properties.<sup>5-8</sup> Among the different kind of cholesteryl based compound like cholestery acetate, cholesteryl pelargonate, cholesteryl acrylate, cholesteryl benzoate; cholesteryl benzoate (CB) showed good film thickening property.<sup>9</sup> This is because of higher polarity of CB. Despite of the anti-wear property, these compounds are not so effective as every kind of additive performance. Again poly acrylates are known to act as pour point depressants and viscosity modifier additives<sup>10</sup> but as anti-wear additive these are not so effective.

<sup>11</sup> In this connection of developing multifunctional additives having VII, PPD and AW property,

we have already studied the additive performance of CB-poly acrylate blended composite.<sup>12-13</sup> The study indicated that the additives improved VI, PPD and AW property. In the continuation of this study the authors were made an attempt to investigate the additive performance of CB-homo poly decylacrylate composite having different ppm level of CB in the blended composites.

## **1.2.2. Experimental procedure**

### **1.2.2.1. Material and methods**

Decyl alcohol, and acrylic acid (stabilized with 0.02% hydroquinone monomethylether), toluene, hydroquinone and H<sub>2</sub>SO<sub>4</sub> were purchased from Merck Specialties Pvt. Ltd. Methanol and hexane were purchased from Thomas Baker (Chemicals) Pvt. Ltd. Benzoyl peroxide (BZP) was purchased from LOBA chemicals. The paraffinic base oil obtained from Indian oil corporation limited, Dhakuria, Kolkata, West Bengal, India which has a density of 0.94 g.cm<sup>-3</sup> at 40°C, kinematic viscosity of 24.229 cSt (40°C) and 4.39 cSt (100°C) and a VI of 89, was used as received for all lubricant formulations. The properties of base oil are also depicted in **table 1.5**.

### **1.2.2.2. Preparation of monomer (via esterification)**

Esterification reaction was carried out by usual method taking acrylic acid and decyl alcohol with mole ratio of 1.1:1, using a Dean Stark apparatus in the presence of concentrated sulfuric acid as a catalyst, 0.25% hydroquinone as a polymerization inhibitor for acrylic acid and toluene as a solvent in nitrogenous atmosphere as reported in a earlier publication.<sup>14</sup>

### **1.2.2.3. Purification of prepared monomer**

The decyl acrylate was purified according to the method reported in earlier publication.<sup>14</sup>

### **1.2.2.4. Preparation of homo polymer**

The polymerization of decyl acrylate was carried out by taking required amount of DA and radical initiator (BZP) and toluene as a solvent in a four-neck round bottom flask and according to the process as reported earlier.<sup>14</sup> The polymer obtained was then purified by frequent precipitation of its hexane solution using methanol followed by drying under vacuum at 313 K.

#### **1.2.2.5. Preparation of LC-polymer blend**

Required amount of polymer was taken in toluene; liquid crystal of cholesteryl benzoate was added to make a 100, 200, 300, 400, 500 ppm blend. They were heated at 40°C with stirring for 1 hour for homogeneous blending. The designation and composition of all the blended composites are given in **table 1.7**.

### **1.2.3. Measurements**

#### **1.2.3.1. Molecular weight determination**

Ubbelohde OB viscometer was used to study the viscometric properties of polymer at 313 K temperature. Toluene was used as solvent. The time flow of at least five different concentrations of the polymer solution was observed for experimental determination. The lowest value of solution concentration was selected for calculation in the single point measurement. For the viscosity – average molecular weight determination, the constants  $K = 0.00387 \text{ dl/g}$  and  $a = 0.725$  were employed in Mark Houwink–Sukurda relation.<sup>14</sup> The intrinsic viscosity was calculated from different equations as described in chapter II.

#### **1.2.3.2. Spectroscopic analysis**

IR spectra were recorded using 0.1 mm KBr cells on a Shimadzu FT-IR 8300 spectrometer at room temperature within the wave number range of  $400\text{--}4000 \text{ cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra

were recorded in Bruker Advance 300 MHz FT-NMR spectrometer using 5 mm BBO probe.  $\text{CDCl}_3$  was used as solvent and TMS (tetramethylsilane) was used as reference material.

#### **1.2.3.3. Thermo gravimetric analysis (TGA)**

The thermograms in air were determined on a Mettler TA-3000 system, at a heating rate of 10K/min. For D and the liquid crystal blended composites (L-1, L-2, L-3, L-4, L-5), 1g each was placed in the platinum crucible and heated gradually from room temperature to 850K.

#### **1.2.3.4. Evaluation of additives as viscosity index improver**

The prepared lubricant formulations were evaluated as viscosity modifiers or viscosity index improvers in base oils according to the ASTM D2270 method and by following the equations as reported in a publication.<sup>15</sup> The kinematic viscosity of the additives doped base oil was determined at 40°C and 100°C. Different concentration ranging from 1 wt% to 5 wt% was used to verify the effect of additive concentration on VI.

#### **1.2.3.5. Evaluation of additive as pour point depressant**

The evaluation of the lubricant formulations as pour point depressants (PPD) in base oil were performed according to the ASTM D97 method on a Cloud and Pour Point Tester model WIL-471 (India). Here also concentration varying from 1 wt% to 5 wt% was used.

#### **1.2.3.6. Evaluation of additive as anti-wear agent**

The anti-wear properties of the homo polymer and LC blended polymer in base oil were examined in sliding contact by means of a four-ball wear test machine as per ASTM D 4172 method employing 20 kg and 40 kg load.

### **1.2.4. Results and discussion**

#### **1.2.4.1. Spectroscopic analysis**

The main objective of this study is to investigate the lubricating performance of CB-polymer blended composites having different concentration (ppm) of CB. The homo poly decyl acrylate (D) was already characterized by spectroscopic method and same polymer was taken for this investigation.

#### **1.2.4.2. Molecular weight determination**

The molecular weight of homo polymer (D) was already determined by viscometric method as described in chapter II.

#### **1.2.4.3. Thermo gravimetric analysis**

The TGA data of homopolymer (D) and five different blended composites are represented in **figure 1.8**. From the figure, it is found that all the blended composites (L-1, L-2, L-3, L-4 and L-5) are comparatively more thermally stable than homopolymer (D) and the thermal stability is increases with increasing the concentration of CB in the polymer matrix. But this effect of CB in the polymer matrix is not so effective after L-3 composite. At 290°C temperature the percent of decomposition of the polymers from D to L-5 are 38.86, 31.23, 30.97, 29.12, 28.92, 28.86 respectively, whereas at 390°C temperature the percent weight loss of the polymers are 86.34, 78.23, 77.12, 76.17 and 76.13 respectively. That means beyond 300ppm level, the incorporation of CB in polymer matrix did not influence the thermal stability further.

#### **1.2.4.4. Efficiency of additive as viscosity index improver**

VI values were determined by dissolving the additives (D, L-1, L-2, L-3, L-4 and L-5) to the base oils at different concentrations ranging from 1 wt% to 5% wt%. The experimental results are reflected in **figure 1.10**. From the figure it is established that, VI values gradually increases with increasing the concentration of additives in base oil which is in accord with the earlier

study.<sup>16</sup> It is also observed that the VI values of the LC blended polymers doped base oil are comparatively better than the pure polymer (D) doped base oil. The long range order of CB molecules results the additional viscosity increase of blended composites. The VI values increases from L-1 to L-3 significantly, but after that there is no significance improvement of VI (L-4, L-5) values. This may be due to saturation effect of CB molecules in polymer matrix.

#### **1.2.4.5. Efficiency of additives as pour point depressant**

The pour point values of all the lubricant compositions prepared by dissolving the additives in base oil at different level of concentration varying from 1 to 5% (w/w) are represented in **figure 1.9**. All the compositions were exhibited good pour point depressant property and the efficiency increases with increasing the concentration of additives up to a certain limit (3% concentration). This indicates that at lower temperature the lubricant compositions interacts with the paraffinic wax in base oil and decreases their crystal size.<sup>17</sup> The L-1 composite has comparatively better efficiency as PPD among the six polymer compositions. The higher polarity effect of CB may influence the PPD properties. LC blended composites (L-1, L-2, L-3, L-4 and L-5) have lower pour point compared to D in every concentration level.

#### **1.2.4.6. Efficiency of additive as anti-wear agent**

The tribological properties (anti-wear) of the formulated lubricant compositions were determined by measuring wear scar diameter (WSD) by four ball wear test apparatus applying 20 kg and 40 kg load and the values are depicted in **Figure 1.11** and **1.12** respectively. For all additives doped base oil WSD increases with increasing load. That means at milder condition formulated additives working as better AW additives. Again, with increasing concentration of additives WSD decreases at both load condition which is in agreement with our earlier study.<sup>12</sup> The anti-wear performance of the base oil is significantly enhanced when the polymer (D) is blended with

CB and is reflected in lower WSD values of the formulated lubricants and the effect is more significant up to L-3, after this i.e, for L-4 and L-5 no significant lowering of WSD was observed compared to L-1, L-2 and D. The better performance of LC blended composites may be due to the highly polar character and layer structure of CB. With increasing concentration, more CB molecules are absorbed by solid metal surfaces and thicker film is formed. But no significant improvement of WSD at higher concentration may be due to over saturation at metal surfaces by CB molecules.

### **1.2.5. Conclusion**

From this study it was found that all the lubricant composition formulated with CB blended polymers (L-1, L-2, L-3, L-4 and L-5) showed excellent performance as PPD, VI and AW additives compared to homo polymer (D). It was also found that L-3 composites showed comparatively better performance than other blended composites. It implies that, there is a certain limit of significant performance of blended composites. This may be due to the over saturation of CB after certain concentration.

### **1.2.6. References**

References are given in BIBLIOGRAPHY under Chapter III of Part I (PP 158-159).

### 1.2.7. Tables and figures

**Table 1.5: Properties of base oil**

<i>Properties</i>	<i>Base oil</i>
Density (g.cm <sup>-3</sup> ) at 40°C	0.94
Viscosity at 40°C in cSt	24.229
Viscosity at 100°C in cSt	4.390
Cloud point (°C)	-8
Pour point (°C)	-6

**Table 1.6: Molecular weight of homo poly decyl acrylate (D) used in this investigation**

<i>Intrinsic viscosity</i>				<i>Viscosity average molecular weight</i>			
$\eta_h$	$\eta_k$	$\eta_m$	$\eta_{sb}$	$M_h$	$M_k$	$M_m$	$M_{sb}$
2.411	2.418	2.431	2.452	7152.53	7277.79	7234.55	7320.89

**Table 1.7: Designation and composition of LC-blended composites**

<i>Designation</i>	<i>Composition</i>	
	Polymer in g	LC (CB) in mg
D	4	0
L-1	4	0.4
L-2	4	0.8
L-3	4	1.2
L-4	4	1.6
L-5	4	2.0

Figure 1.8: TGA data of polymer (D) and blended composites (L-1, L-2, L-3, L-4 and L-5)

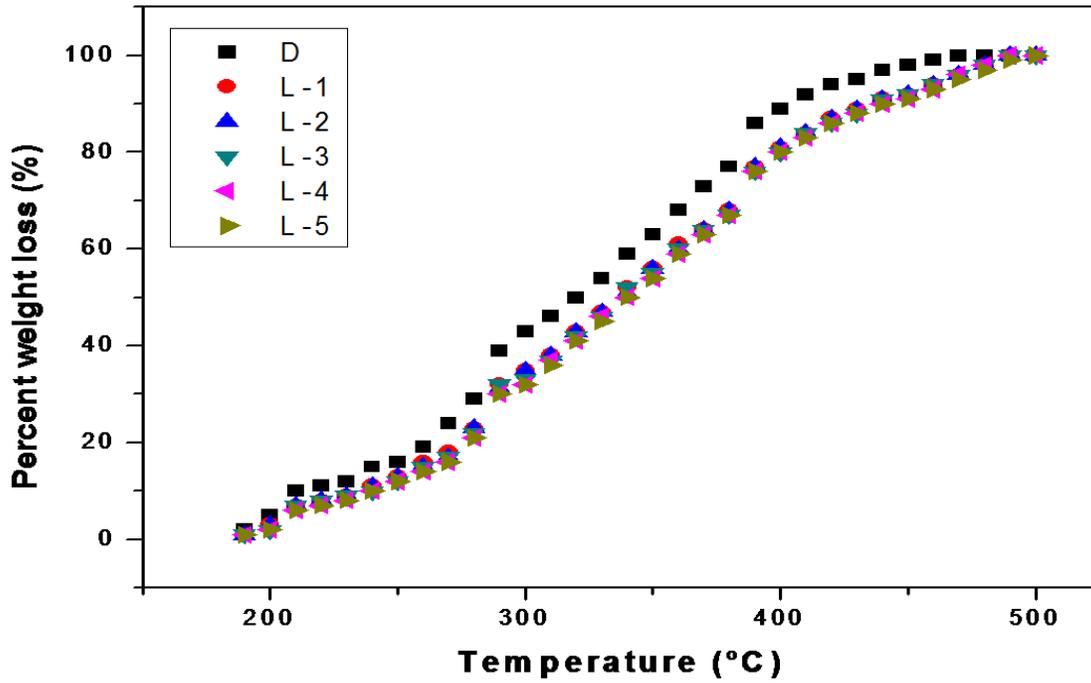


Figure 1.9: Plot of pour point of formulated lubricants as a function of additives concentration (w/w)

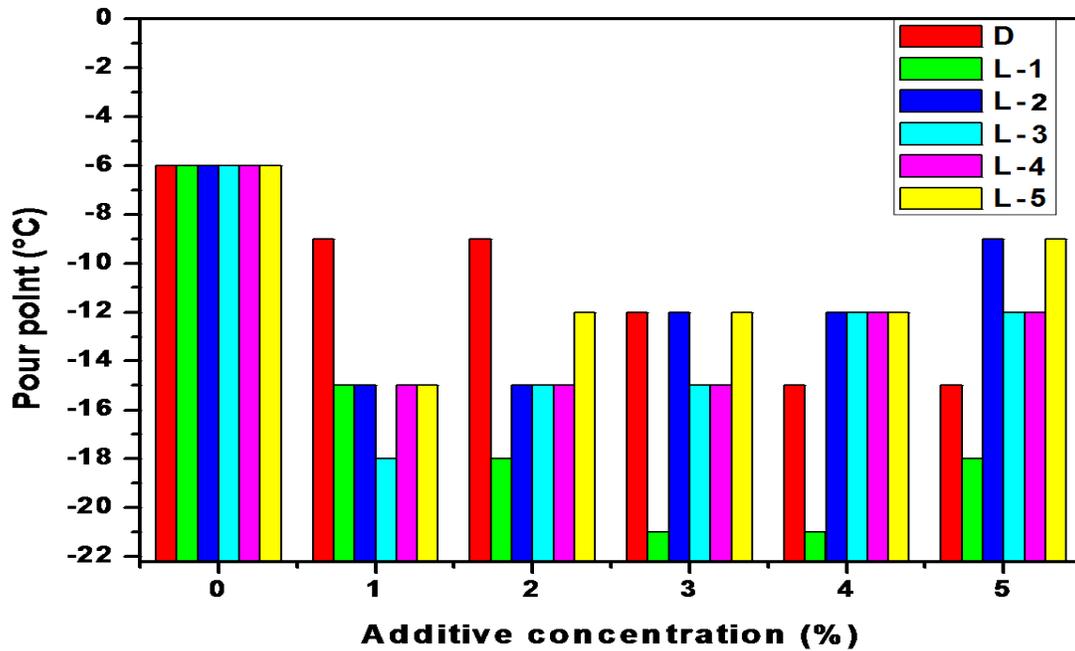


Figure 1.10: Plot of viscosity index of formulated lubricants as a function of additives concentration (w/w)

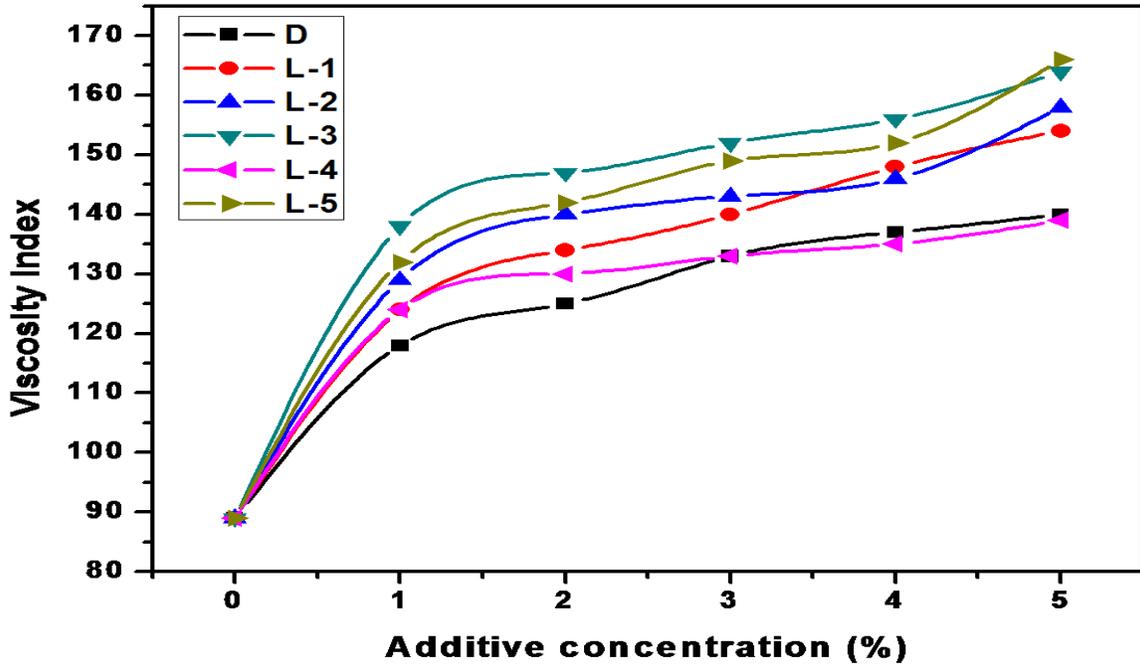


Figure 1.11: Wear scar diameter (mm) of formulated lubricants as a function of additives concentration (w/w) at 20 kg load condition

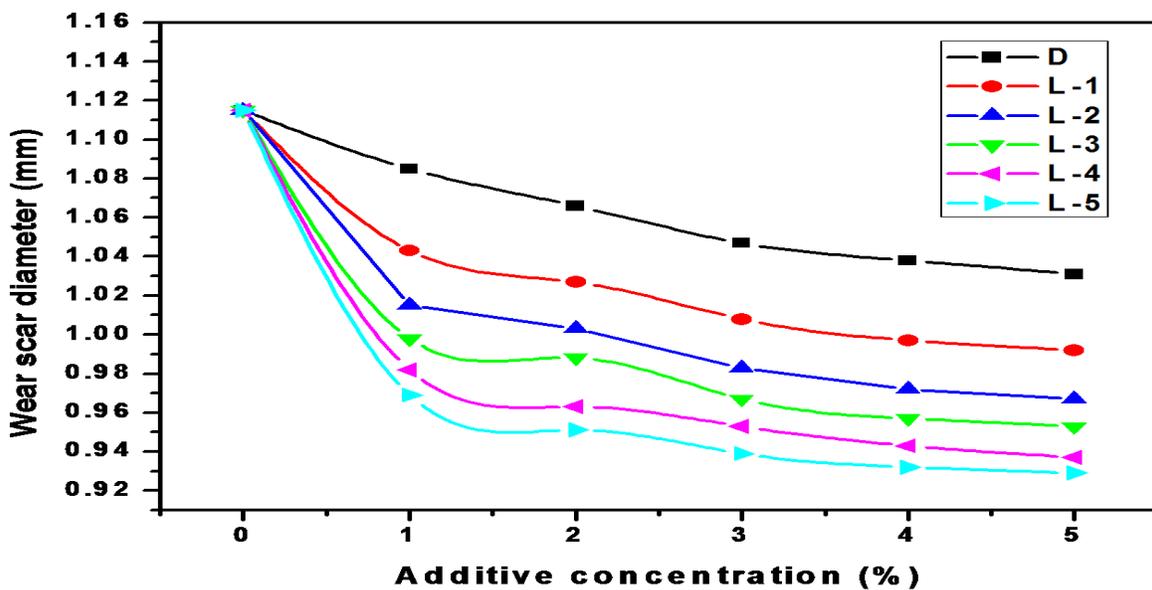


Figure 1.12: Wear scar diameter (mm) of formulated lubricants as a function of additives concentration (w/w) at 40 kg load condition

