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## **Evaluation of acrylate-sunflower oil copolymer as viscosity index improvers for lube oils**

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### **ABSTRACT**

*Copolymers of sunflower oil with methyl methacrylate and decyl acrylate were synthesized and characterized. Intrinsic viscosity and viscometric molecular weight were determined by using Huggins and Mark- Houwink equation respectively. Viscosity index (VI) of the additive doped base oils were evaluated and compared with that of the mineral base oils. VI values of the additive doped base oils depend on the nature of mineral base oils used and the type and concentration of VI improvers. For a comparison, respective homopolymers e.g. polymer of sunflower oil, poly(methyl methacrylate) and poly(decyl acrylate) were also prepared, characterized and evaluated in the similar fashion.*

**Keywords:** Viscosity index, Base oils, Blended oils, VI Improver.

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### **INTRODUCTION**

The development of modern engine and transmission technologies would be impossible without lubricant additive. From its conception in the early 1900s, the lubricant additive industry has worked in partnership with the oil and the automotive industries to enhance durability and performance of engine and drive line systems through lubricant design [1]. Additives are synthetic chemicals that can improve or add performances of lubricants. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life. One of the important types of additive is Viscosity Index Improvers (VII) commonly known as viscosity modifier [2].

The viscosity index is an indicator of the change in viscosity as the temperature is changed. The higher the viscosity index (VI), the less the viscosity of an oil changes for a given temperature change [3]. Viscosity index improvers are used to limit the rate of change of viscosity with temperature. These improvers have little effect on oil viscosity at low temperatures. However, when heated the improvers enable the oil viscosity to increase within the limited range permitted by the type and concentration of the additive. This quality is most apparent in the application of multi grade motor oils.

Viscosity index improvers function by increasing the relative viscosity of oil more at high temperatures than at low temperatures [4-5]. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is believed that the polymer molecule in solution exists as a random coil, which is swollen by the lube oil solvent. The volume of this molecule determines the viscosity increase. In cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules, having greater volume and the oil produces a proportionally greater thickening effect which in turn raises the VI of the oil.

An ideal lubricant for most purposes would possess the same viscosity at all temperatures. Viscosity index improvers (VII) are added to lubricating oils to make them conform more closely to the ideal lubricant. Although a few non-polymeric substances such as metallic soaps exhibit VI improving properties [6], all commercially important VI improvers today are oil-soluble organic polymers. Suitable polymers exert a greater thickening effect (percent increase in viscosity of the base oil for unit weight of polymer) on oil at higher temperatures than they do at lower temperatures [7] and thus improve the VI of lube oil. However, the recent demand for eco-friendly technology prompted the researchers to develop environmentally benign additives for the lubricant formulation.

The use of biodegradable vegetable oils was known for a long time. Today, due to growing environmental concern these oils are again finding their application into lubricants for transportation as well as for industrial applications. They can offer significant environmental advantages with respect to fuel consumption, biodegradability and displaying satisfactory performances in their field application. They are also reported to show excellent tribological properties when used as base stocks or as additives [8]. But the major limitations are their high cost, thermal and oxidative instability. Keeping these in mind and in continuation of our studies towards the development of chemical additives for lubricating and crude oils, in the present investigation an attempt has been made to incorporate the sunflower moiety into the acrylate skeleton through the process of copolymerization in an anticipation of getting an ideal blend of performance as well as eco-friendly chemistry. The present investigation comprises the homo and copolymerization of sunflower oil with different mass fraction of methyl methacrylate and decyl acrylate (DA), characterizations and their evaluations as a viscosity index improver in base oils.

## EXPERIMENTAL SECTION

### Esterification and polymerization

Esterification of acrylic acid with different alcohols, purification of the prepared esters and subsequent polymerization (homo and copolymerization) were carried out following the procedure as reported in our earlier publications [9, 10].

### Characterization

All the polymers were characterized on the basis of spectral analysis (IR, NMR), thermo gravimetric analysis (TGA) and by viscometric method as reported in our earlier paper [10].

### Determination of intrinsic viscosity and viscometric molecular weight

Intrinsic viscosity and viscometric molecular weight (Table 1) were determined by using the experimental viscosity of the polymer solutions in Huggins (eq.1) and Mark Houwink equation (eq.2) respectively [9, 10]

$$\text{Huggins equation: } \frac{\eta_{sp}}{C} = [\eta]_h + k_h [\eta]_h^2 C \quad (1)$$

Where, C is mass concentration.

$\eta_{sp} = \eta_r - 1$ , specific viscosity

$\eta_r = t/t_0$ , relative viscosity or viscosity ratio (where t is time flow of solution and  $t_0$  is time flow of pure solvent).

$[\eta]_h$  = intrinsic viscosity, respective to Huggins equation,  $k_h$ , Huggins coefficients

According to Mark Houwink – Sukurda (eq. 2), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = KM^a \quad (2)$$

Where  $[\eta]$ , the intrinsic viscosity, can be calculate by using Huggins equation, parameter ‘K’ and ‘a’ depends on the type of polymer, solvent, and temperature. For the viscosity – average molecular weight determination, the constants  $K = 0.00387$  dl/g and  $a = 0.725$  were employed in Mark Houwink – Sukurda relation [10].

### Determination of Viscometric Properties

Viscometric properties were determined at 40°C in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least eight different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer.

### Determination of Viscosity Index

The prepared polymers were tested for their effectiveness as viscosity index improvers in two different base oils (BO1 and BO2) according to ASTM D-7042 method and by using viscosity index calculation [11,12]. In this respect, the kinematic viscosity of the oil, doped with different concentrations of the tested additives was determined at 40°C and 100°C.

Different concentrations, ranging between 1 - 5 % (w/w), were used to study the effect of concentration on VI of the lube oil.

**Table 1 Intrinsic viscosity and viscometric molecular weight values of all polymeric samples. S-1 poly(methyl methacrylate), S-2 poly(decyl acrylate), S-3 polymer of sun flower oil, S-4 copolymer of sun flower oil+ 5% MMA, S-5 copolymer of sun flower oil+ 5% DA**

Samples	$[\eta]_h$	$M_h$
S-1	7.69	35400
S-2	4.34	16051
S-3	6.10	25735
S-4	5.00	19561
S-5	4.20	15365

**Table 2. Base oil properties**

properties	Base oils	
	BO1	BO2
Viscosity at 40 <sup>0</sup> C in cSt	6.700	24.229
Viscosity at 100 <sup>0</sup> C in cSt	2.00	4.390
Cloud point, <sup>0</sup> C	-8	-10
Pour point, <sup>0</sup> C	-3	-6

**Table 3. Viscosity temperature characteristics of poly(methyl methacrylate) (S-1) – BO1 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	7.809	2.512	166
4.0	7.772	2.270	100
3.0	7.789	2.203	81
2.0	7.567	2.118	88
0.0	6.700	2.000	80

**Table 4. Viscosity temperature characteristics of poly(decyl acrylate)(S-2) – BO1 blends**

Additives (w%)	Viscosity <sup>0</sup> C		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	8.279	2.561	151
4.0	7.881	2.264	93
3.0	7.767	2.243	93
2.0	7.267	2.143	91
0.0	6.700	2.000	80

**Table 5. Viscosity temperature characteristics of polymer sunflower oil(S-3) – BO1 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	7.829	2.542	173
4.0	7.984	2.389	121
3.0	7.889	2.321	107
2.0	7.632	2.218	93
0.0	6.700	2.000	80

**Table 6. Viscosity temperature characteristics of copolymer of sunflower oil with MMA(S-4) – BO1 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	8.406	2.862	226
4.0	8.058	2.697	203
3.0	7.762	2.555	182
2.0	7.3735	2.343	144
0.0	6.700	2.000	80

**Table 7. Viscosity temperature characteristics of copolymer of sunflower oil with DA(S-5) – BO1 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	8.586	3.043	262
4.0	8.381	2.873	230
3.0	8.172	2.657	184
2.0	7.964	2.342	109
0.0	6.700	2.000	80

**Table 8. Viscosity temperature characteristics of poly(methyl methacrylate) (S-1) – BO2 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	27.676	6.412	197
4.0	26.485	5.350	139
3.0	25.705	4.916	116
2.0	25.180	4.645	100
0.0	24.229	4.390	89

**Table 9. Viscosity temperature characteristics of poly(decyl acrylate) (S-2) – BO2 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	27.626	6.394	197
4.0	26.815	5.303	133
3.0	25.807	4.936	116
2.0	25.083	4.745	108
0.0	24.229	4.390	89

**Table 10. Viscosity temperature characteristics of polymer of Sunflower oil (S-3) – BO2 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	27.975	6.705	212
4.0	26.532	5.345	139
3.0	26.110	5.131	127
2.0	25.156	4.487	89
0.0	24.229	4.390	89

**Table 11. Viscosity temperature characteristics of copolymer of sunflower oil with MMA (S-4) – BO2 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	28.575	6.785	210
4.0	26.927	5.309	133
3.0	26.117	5.026	120
2.0	25.176	4.576	95
0.0	24.229	4.390	89

**Table 12. Viscosity temperature characteristics of copolymer of sunflower oil with DA (S-5) – BO2 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	29.396	7.025	215
4.0	28.349	5.269	118
3.0	26.940	4.952	108
2.0	24.802	4.545	97
0.0	24.229	4.390	89

**Table 13. Viscosity temperature characteristics of poly(methyl methacrylate) (S-1) – BO3 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	89.152	13.147	148
4.0	87.953	11.013	113
3.0	86.713	10.654	108
2.0	85.889	9.987	96
0.0	84.714	9.918	96

**Table 14. Viscosity temperature characteristics of polymer of DA(S-2) – BO3 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	90.152	13.045	145
4.0	87.983	11.048	113
3.0	87.312	10.854	111
2.0	85.789	10.221	101
0.0	84.714	9.918	96

**Table 15. Viscosity temperature characteristics of polymer of sunflower oil (S-3) - BO3 blends**

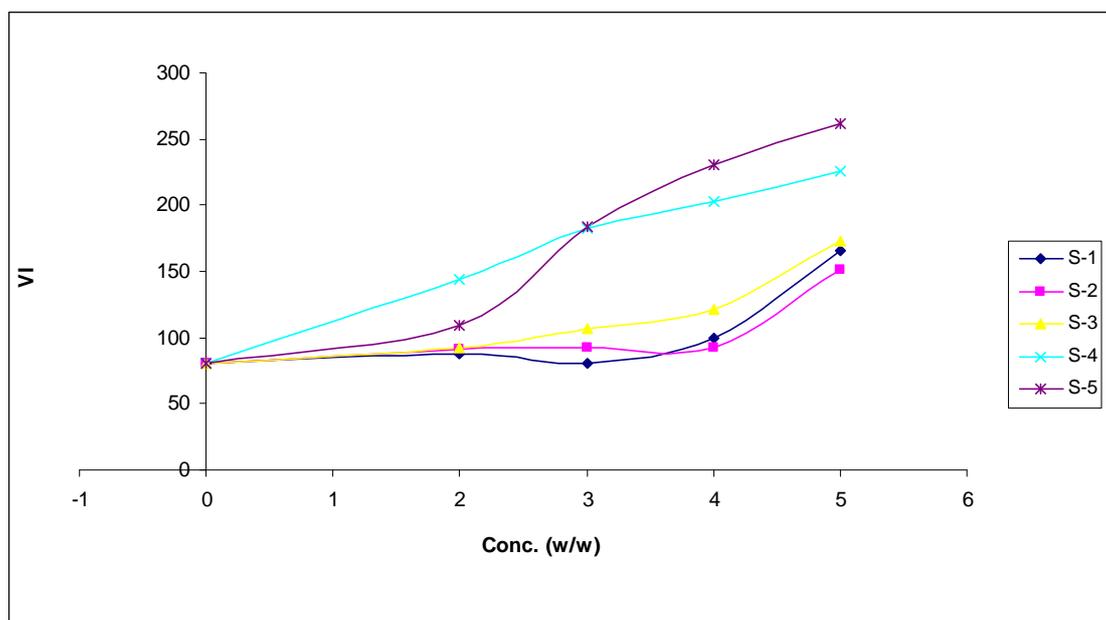
Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	90.252	13.405	152
4.0	88.398	11.548	122
3.0	88.301	11.085	113
2.0	84.889	10.121	100
0.0	84.714	9.918	96

**Table 16. Viscosity temperature characteristics of copolymer of sunflower oil with MMA(S-4) – BO3 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	89.112	13.104	148
4.0	88.748	11.048	112
3.0	88.312	10.854	109
2.0	86.789	10.321	101
0.0	84.714	9.918	96

**Table 17. Viscosity temperature characteristics of copolymer of sunflower oil with DA (S-4) – BO3 blends**

Additives (w %)	Viscosity		Viscosity index
	40 <sup>0</sup> C	100 <sup>0</sup> C	
5.0	90.552	12.645	137
4.0	87.831	11.480	121
3.0	86.312	10.952	114
2.0	85.769	10.102	98
0.0	84.714	9.918	96

**Figure 1. Plot of viscosity index (VI) vs polymer concentration in BO1 Where S-1 poly(methyl methacrylate), S-2 poly(decylacrylate), S-3 polymer sunflower oil, S-4 copolymer of MMA+ sunflower oil and S-5 copolymer of DA+ sunflower oil.**

## RESULTS AND DISCUSSION

Intrinsic viscosity and viscometric molecular weight of prepared sample is tabulated in Table 1. It is observed that intrinsic viscosity and molecular weight of the homopolymers [except poly(decyl acrylate)] is greater than the copolymers.

Physical properties of the base oils used in the present investigation are presented in Table 2, below.

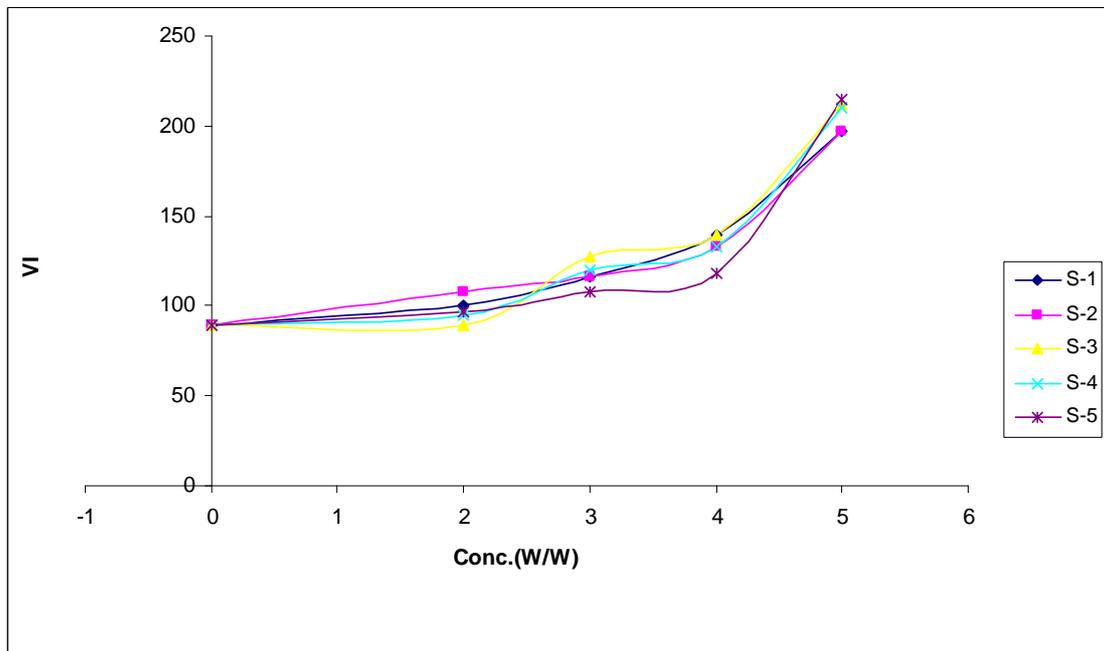


Figure 2. Plot of Viscosity index (VI) vs polymer concentration in BO2. Where S-1 poly(methyl methacrylate), S-2 poly(decyl acrylate), S-3 polymer sunflower oil, S-4 copolymer of MMA+ sunflower oil and S-5 copolymer of DA+ sunflower oil.

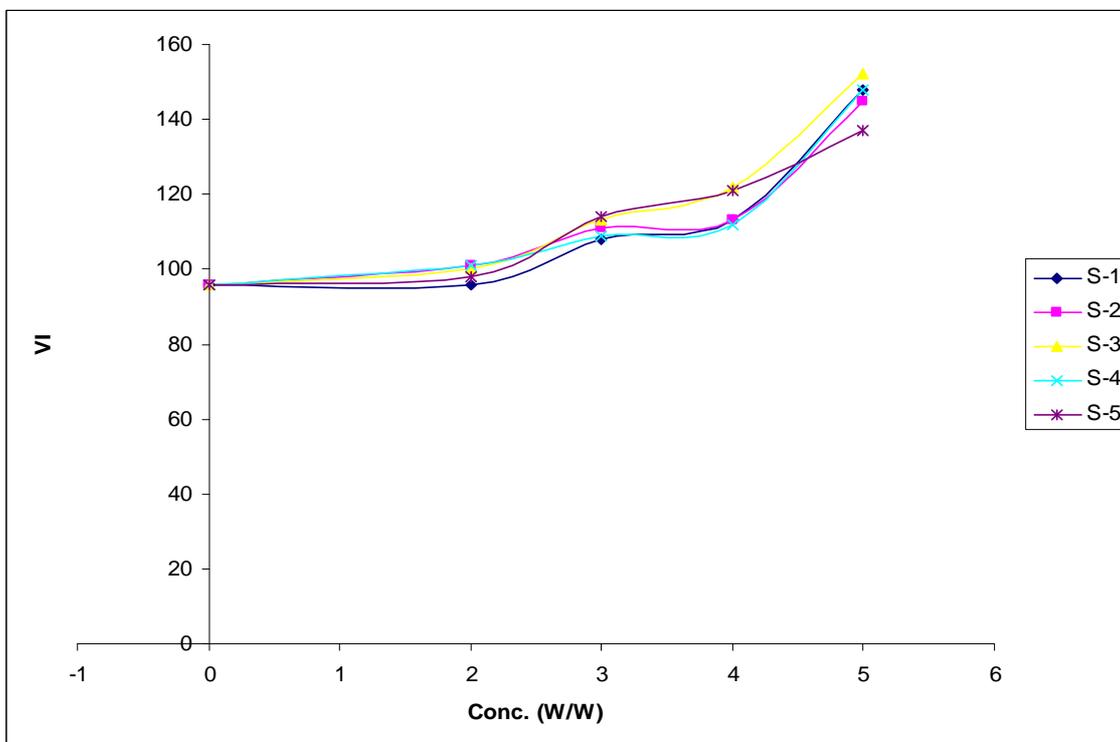


Figure 3. Plot of concentration (W/W) vs Viscosity index (VI) in BO3. . Where S-1 poly(methyl methacrylate), S-2 poly(decyl acrylate), S-3 polymer sunflower oil, S-4 copolymer of MMA+ sunflower oil and S-5 copolymer of DA+ sunflower oil.

The prepared copolymers were tested for their effectiveness as viscosity index improvers in base oils (BO1, BO2 and BO3) and the results are expressed in terms of VI. Kinematic viscosity of the different concentrations of additives doped base oils was determined at 40<sup>o</sup>C and 100<sup>o</sup>C. The concentration range investigated was from 0 to 5 % (w/w). The effect of additive concentration on the VI is studied and the results are tabulated (Table 3 – Table 16) as well as plotted (VI vs conc.) in Figure 1, 2 and 3.

Analysis of the experimental data as given in Table 3 – Table 16 and the plots (Figure 1-3), indicated that the values of viscosity index (VI) increases with the increase in concentration of the additives in solution and the VI values of the copolymer (S-4 and S-5) doped base oils are slightly higher in comparison to the homopolymers (S-1, S-2 and S-3) doped base oils. A possible explanation may be, as the temperature is raised, the lube oil viscosity gets decreased and as a result of that the polymer molecules get expanded due to the increase in the salvation power and the size of the micelle. This increase in micelle size counterbalanced the reduction of the viscosity of the lube oil and, hence, decreases the change of viscosity with temperature of the mixture [13, 14]. The increase in concentration of polymer leads to an increase in the total volume of the polymer micelles in the oil solutions. Consequently, higher concentration of additive will impart higher viscosity index [15].

### CONCLUSION

In general, viscosity index (VI) of the additive (both for homo and copolymer) doped base oil increases with the increase in concentration of the additives in solution irrespective of the nature of the base oils. Again the VI values of the copolymer (S-4 and S-5) doped base oils are slightly higher in comparison to the homopolymers (S-1, S-2 and S-3) doped base oils and the prediction is not dependent on the nature of the base oils.

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