Chapter III

Correlation of anti wear performance and shear stability with the chemistry of some commercial viscosity modifiers for lube oil

2.2.1. Introduction

Broadly two kinds of lube oil additives used extensively are surface active additive e.g. anti wear, corrosion inhibitor, friction modifier[1-3] and performance additive e.g. viscosity modifier (VM), pour point depressant (PPD),[4-5] detergent, dispersant etc. Under a particular kind two or more functions can be present in a single additive, e.g. those who is acting as anti wear additive can be a friction modifier too.[6] Similarly for performance additive multifunctional properties can be found in a system.[7] But a single system with both kinds of properties i.e. surface activity as well as performance property is not well known.

Viscosity modifiers are one of the most important kinds of performance additive. Viscosity modifiers (VM) are substances that resist the change of viscosity with temperature. They increase the lube oil viscosity at high temperature and minimise the increase of oil viscosity at low temperature, thus maintaining a favourable relation between viscosity and temperature.[8,9] Some commercially used popular VMs are poly methacrylate (PMA), olefin copolymer (OCP) and styrene-isoprene polymer (SIP).[7-10] As mentioned earlier these are popular performance additive, but their tribological functions are not well known. Reports regarding the correlation of surface activity with the chemistry of the viscosity modifier (VM) in multi grade oils are still scanty.[11-14] The matter is further complicated by variations in experimental conditions / apparatus chosen to ascertain in the wear properties. It was felt necessary to draw a correlation between nature of VM and anti wear properties. The study of the additive performance in regard to their chemistry, molecular size etc may provide a better understanding about the structure activity relationship of the additives. Keeping this view in mind a preliminary investigation has been carried out on the AW properties of three types of viscosity modifiers, i.e. PMA, OCP and SIP with different chemistry.

The shear stability of a viscosity modifier (VM) is also a very important parameter in the field application of engine oils and is given a strong consideration in the choice of a VM for

its use in multigrade lubricant formulations. It is a measure of polymers ability to withstand high shearing forces existent during engine operations. Shear stability of the VMs expressed in terms of shear stability index (SSI) and those of finished formulations by percent shear loss (PSL)[15] were measured and reported.

2.2.2. Experimental Procedure

2.2.2.1. Materials and methods

The three types of viscosity modifiers e.g. PMA, OCP and SIP were collected from the manufacturers. Their structures are shown in **figure 2.10**. The base oils were collected from IOCL, Kolkata and BPCL, Siliguri and their properties are tabulated in **table 2.5**.

Solutions of different sample concentration (1-6 wt %) in the base oils were made by dilution method from their respective 10% stock solutions at about 60-70^{0}C with continuous stirring until clear solutions were obtained. Viscosity modifier properties, anti wear performance and shear stability of the sample solutions were determined gradually by respective methods.

2.2.3. Measurements

2.2.3.1. Molecular weight determination by GPC

The weight average and number average molecular weights (M_w & M_n) and the poly dispersity of the polymers were measured in Water's gel permeation chromatography equipment using polystyrene standards for calibration in THF phase. The results are tabulated in **table 2.6**.

2.2.3.2. Thermo gravimetric analysis (TGA)

The thermo grams in air of the samples were obtained on a Mettler TA – 3000 system, at a heating rate of 10ºC min^{-1}. The samples were heated gradually from room temperature to 500ºC in a platinum crucible. Initial weights of the samples were 1g. The findings are compiled in **figure 2.11**.

2.2.3.3. Performance evaluations as Viscosity modifier

Viscosity index (VI) of the sample solutions (in base oils BO1 and BO2) were determined to measure the efficiency of the samples as viscosity modifier (VM). An Ubbelohde OB viscometer was used for this purpose at the experimental temperatures 313K and 373K, as already described in Chapter II of Part I.

Six different concentrations (1-6 wt %) of the sample solutions were used to investigate the effect of additive concentration on VI.

2.2.3.4. Performance evaluations as anti wear additive

Anti wear properties of mineral base stocks as well as polymer-oil blends were studied in sliding contact by means of a Four-Ball Wear Test Machine as per ASTM D-4172. The tests were carried out employing 20kg and 40kg load condition.

2.2.3.5. Determination of shear stability

Shear stability of the samples were expressed in terms of shear stability index (SSI) and those of finished formulations by percent shear loss (PSL). [15,16] The measurements were carried out at 100°C as per ASTM D-445 method as described in Chapter II earlier.

2.2.3.6. Evaluation of thickening properties

Thickening properties was determined in terms of thickening percentage using the formula mentioned in Chapter II earlier. Six different concentrations (1 to 6% wt/wt) of additive doped base oils were used in the measurements.

2.2.4. Results and discussion

2.2.4.1. Viscosity modifier properties

Efficiency of the samples as VM was measured in terms of viscosity index (VI). VI was calculated from the viscosity data of the sample-base oil solutions at 313K and 373K. **Figure 2.12** presents the viscosity index values of the additives doped base oils.

In general there was a gradual increase in VI values with the increase in additive concentration. The increase in polymer concentration leads to an increase in total volume of

polymer micelles in the oil solutions. Consequently, a high concentration of polymer will impart a high viscosity index rather than a low concentration of the same polymer.[5, 11]

From the data it was evident that the VI values of SIP doped base oils are higher than those of OCP and PMA doped base oils at every concentration level irrespective of base oil used.

2.2.4.2. Anti wear performance

Employing a Four Ball Wear Test Machine as per ASTM test conditions, the anti wear contributions of the samples was determined. Experiments were conducted first with pure base oils followed by polymer-oil blends. The efficiency was measured in terms of wear scar diameter (WSD), the smaller the WSD, the better is the performance. The results are presented in **figure 2.13**.

Decrease in WSD (mm) with increasing concentration of the additives was found in both the base stocks and the decrease was generally greater under 40 kg load condition, which indicated better AW performance of the samples under higher load (40 kg) condition. However, beyond 5% additive concentration no significant AW benefit was observed.

SIP containing polymer - oil blend always showed better AW performance in both the base oils followed by PMA and OCP type. This is due to the presence of aromatic ring in the sample structure, which increases the surface activity.[17,18] The AW performance of PMA sample may be explained on the basis of ester functionality present in it (**figure 2.14**)**.** It is believed that one of the oxygen atoms present in the ester group can form a donor–acceptor bond with the vacant orbital of iron atom using its lone pair of oxygen, thereby increasing tribological activity.[18,19] In case of OCP type of VM, none of the above effects are present and accordingly it showed poor AW performance.

2.2.4.3. Degradative stability in terms of shear stability index (SSI) and percent shear loss (PSL)

As per ASTM D-3945 method, shear stability index (SSI) and percent shear loss (PSL) of the samples were determined from the viscosity data at 100°C using equations mentioned earlier.

In general**,** SSI (**figure 2.15**) and PSL (**figure 2.16**) of all the samples were found to increase gradually with the increase in additive concentration. This is in consistent with the earlier observations reported by Suzuki et al.[20] Restricted chain mobility due to the enhanced viscosity in base stock and the poor solubility of the polymer samples leading to tight coiling of polymer chain have been explained by Alexander for their concentration / base stock dependent SSI variations.[21] Suzuki explained these behaviors based on the hydrodynamic volume acquired by the VM due to their molecular weight and their interaction with the base oil. Again the rise in PSL was relatively higher in the lower viscosity base oil (BO1) compared to the higher viscosity base stocks (BO2).

In case of SIP type of VM, both SSI and PSL values were found to be higher compare to OCP and PMA for a given concentration. Although hydrodynamic volume of a polymer has a significant role, apparently it is the restricted chain mobility and poor solubility of certain polymer segments in solution which give rise to a kind of "brittleness" causing chain scissions during high shearing. This is apparently the case with SIP type of VM where thickening increases sharply with concentration that can cause severe restriction on chain mobility. SIP type of polymers is also known to form aggregated structure in base stocks[22] which are not in a fully dissolved state and hence tight coiling of the chain is possible. Considering the above, a strong concentration dependence of SSI and PSL in SIP type of system is expected as observed in our investigation. The PMA systems having pendent long alkyl side chains have better oil solubility with increasing polymer concentration and most of its mass is in the side chain which contribute poorly to the thickening / viscosity of the oil and hence apparently more shear stable over the others. OCP type VMs displayed relatively lower

shear stability in the base stocks probably because of the absence of such effects as mentioned for PMA.

2.2.4.4. Thickening studies

Thickening percentage measured for the polymer samples in two base stocks with increasing polymer concentration up to 6% at 100^0C are shown in **figure 2.17.**

Thickening effect found to decrease with increasing additive concentration in both the base oils for every sample. At higher concentration polymer molecules assume a coil like aggregation which results decreased solubility and hence poor thickening. In comparison between the samples studied SIP was found to have highest thickening followed by PMA and OCP, which can be explained on the basis of above discussion.

2.2.5. Conclusion

On the basis of experimental results it is evident that better anti wear performance was obtained with higher additive concentration in both the base oils. Again SIP type of viscosity modifier was better AW additive than the others (PMA, OCP). SSI and PSL increased gradually with increasing additive concentration, irrespective of base oil used. At a given concentration, SSI or PSL of the viscosity modifiers followed the order SIP>> OCP > PMA in both the base stocks. SIP doped base oils showed higher viscosity index compare to OCP and PMA. Viscosity index of the polymer doped base oils increased with increasing additive concentration. Additive performance of the viscosity modifiers found dependent mainly on concentration. SIP type of viscosity modifier was better VM and AW additive and better thickening agent than PMA and OCP.

2.2.6. References

References are given in BIBLIOGRAPHY under Chapter III of Part II (PP 218-219).

2.2.7. Tables and figures

Table 2.5: Properties of base oils

Properties	Base oils	
	BO1	BO2
Density ($kg \cdot m^{-3}$) at 313 K	839.98	918.68
Viscosity ($m^2 \cdot s^{-1}$) at 313 K	5.97×10^{-6}	20.31×10^{-6}
Viscosity ($m^2 \cdot s^{-1}$) at 373 K	1.48×10^{-6}	3.25×10^{-6}
Cloud point/ °C	-10	-8
Pour point/ °C	-3	-6

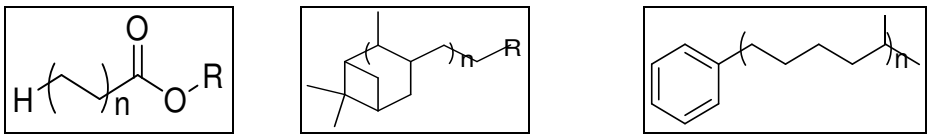
BO1: base oil type 1, BO2: base oil type 2

Table 2.6: Molecular Weight (GPC) Characteristics of the samples

Samples	Mn	Mw	PDI
PMA	87,000	165,000	1.89
OCP	83,000	154,000	1.85
SIP	185,000	240,000	1.29

PMA: poly methacrylate, OCP: olefin copolymer, SIP: styrene-isoprene polymer

Figure 2.10: Structures of the samples



PMA OCP SIP

Figure 2.11: TGA data of the samples

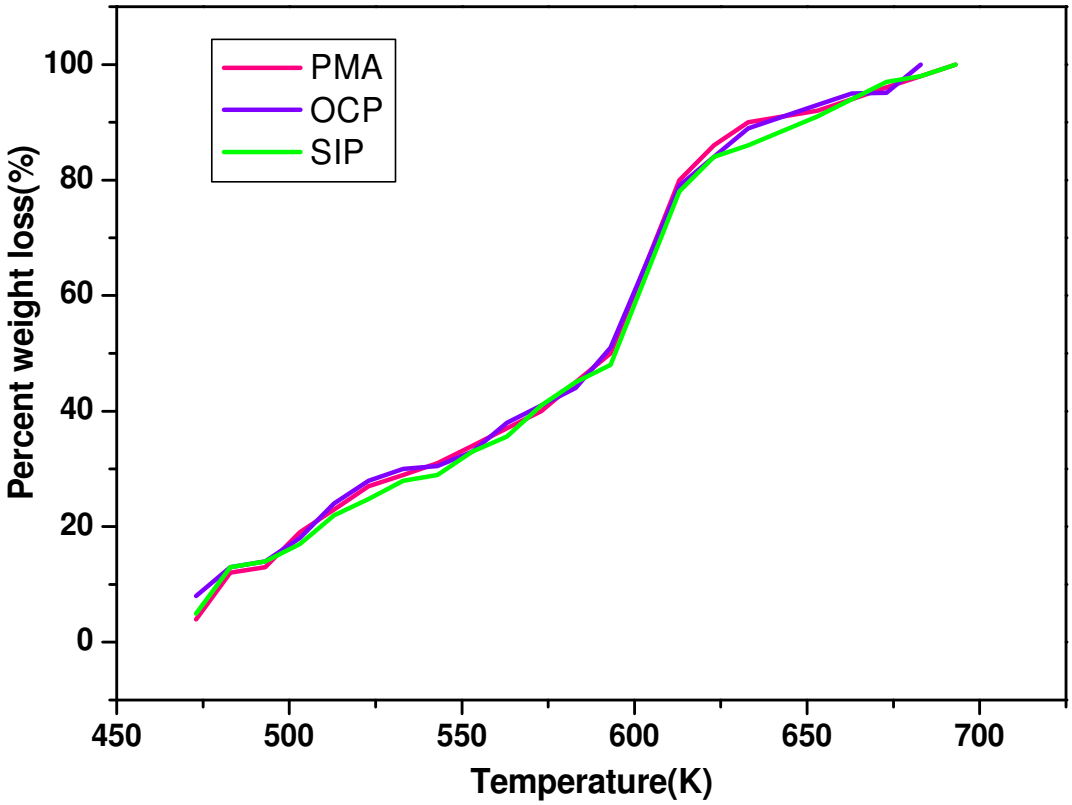


Figure 2.12(a): Plot of viscosity index vs. additive concentration in BO1

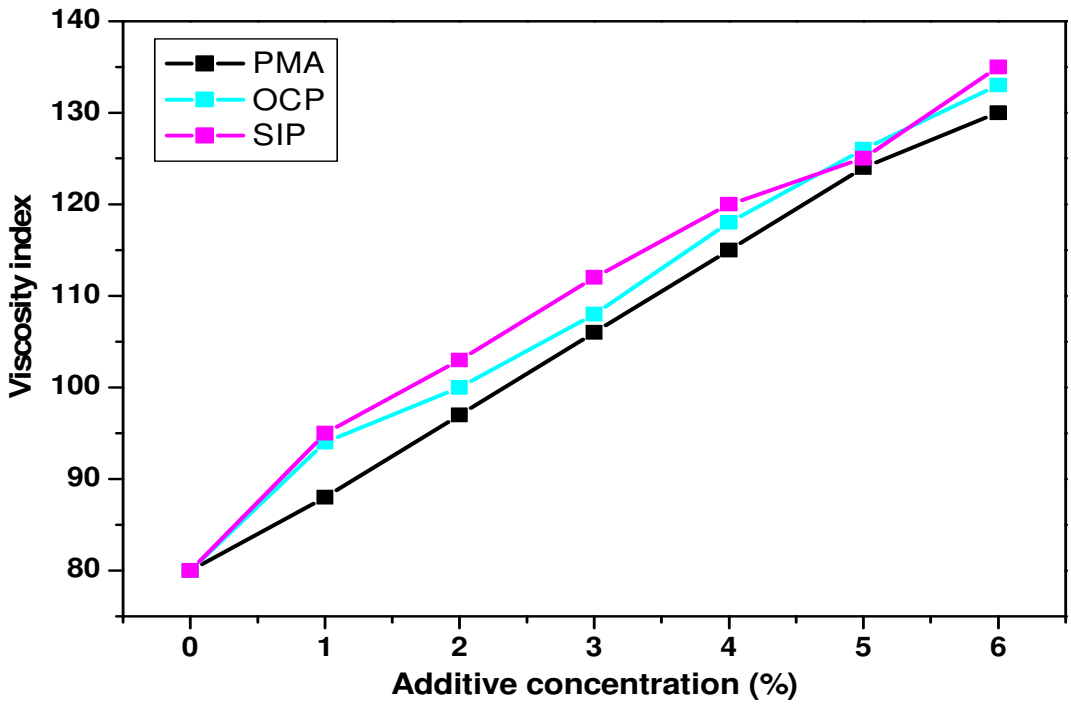


Figure 2.12(b): Plot of viscosity index vs. additive concentration in BO2

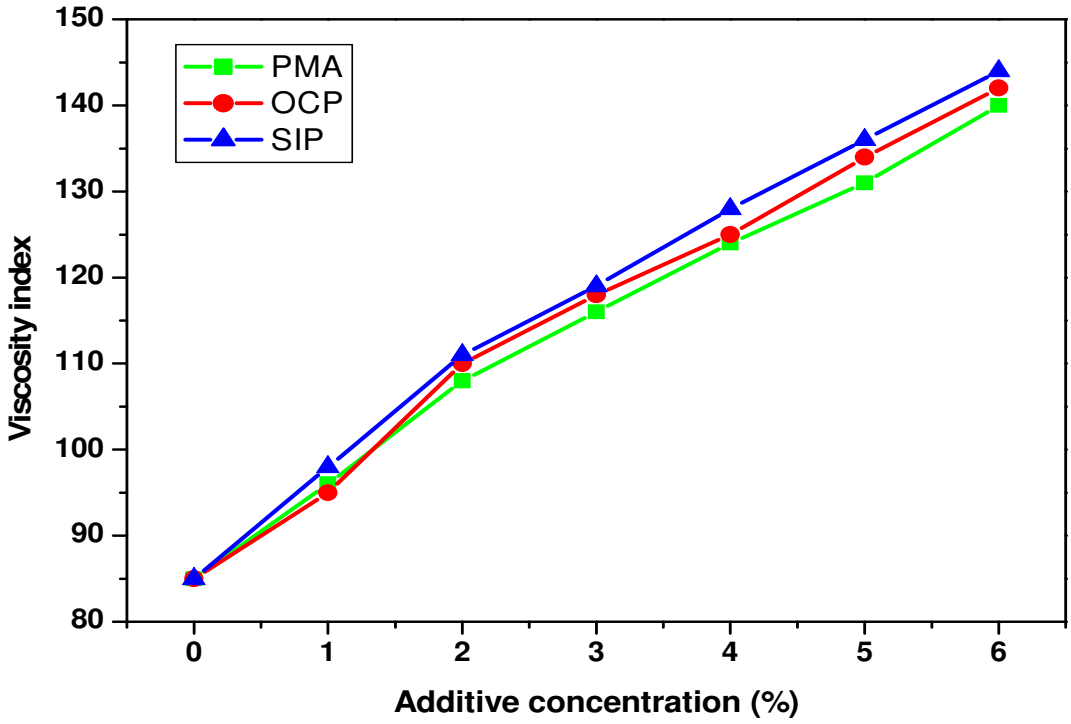


Figure 2.13(a): Plot of wear scar diameter vs. additive concentration in BO1 at 20kg load

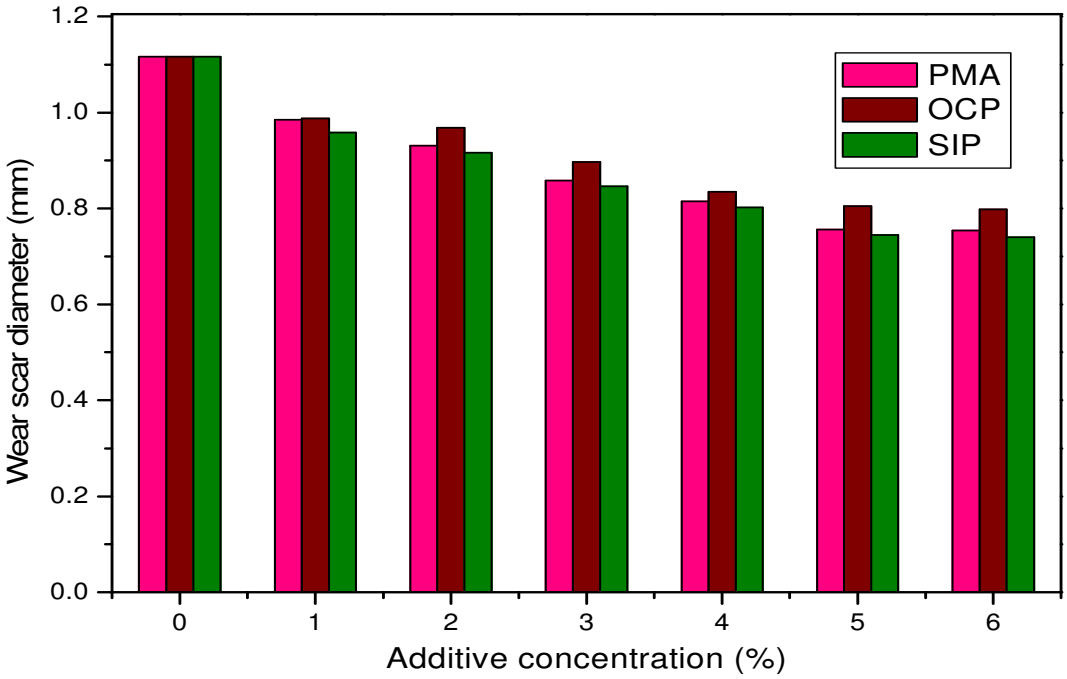


Figure 2.13(b): Plot of wear scar diameter vs. additive concentration in BO1 at 40kg load

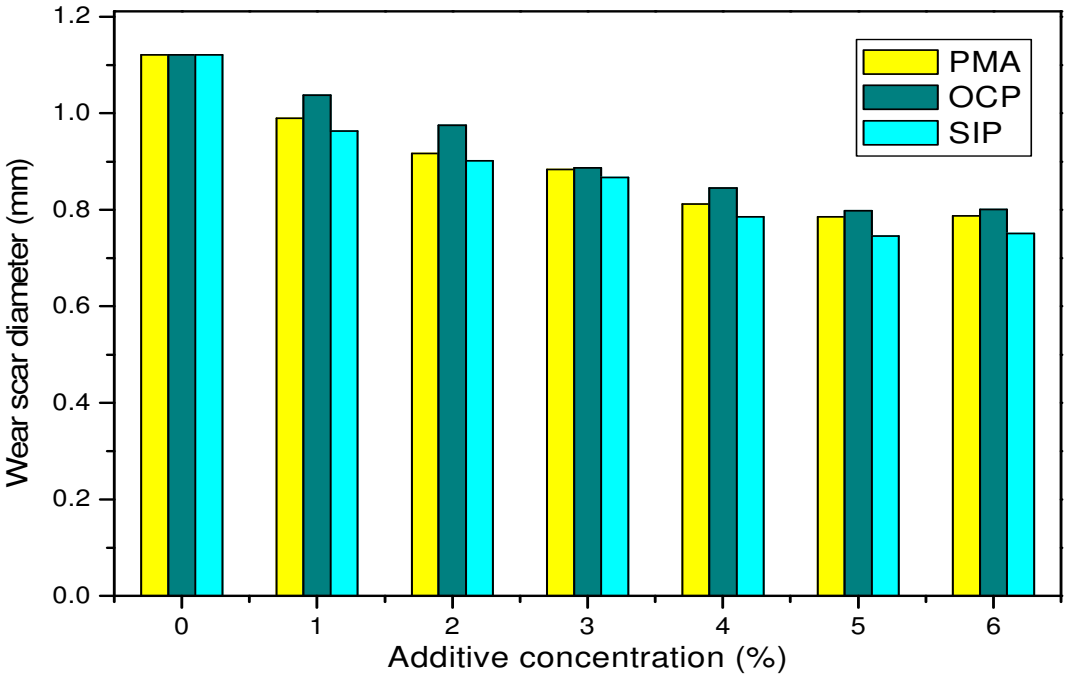


Figure 2.13(c): Plot of wear scar diameter vs. additive concentration in BO2 at 20kg load

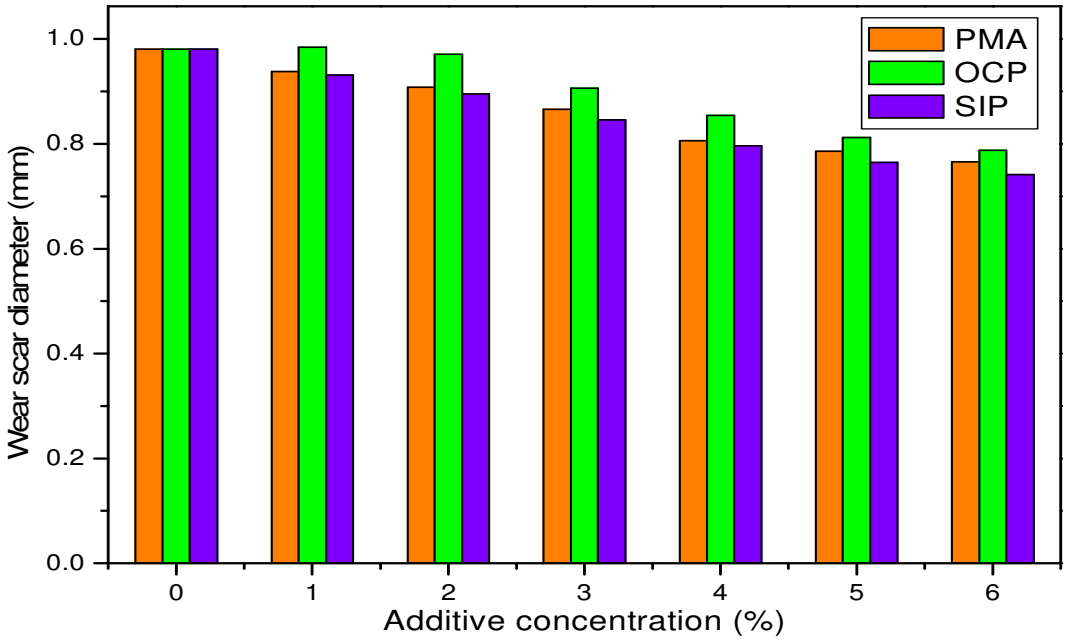


Figure 2.13(d): Plot of wear scar diameter vs. additive concentration in BO2 at 40kg load

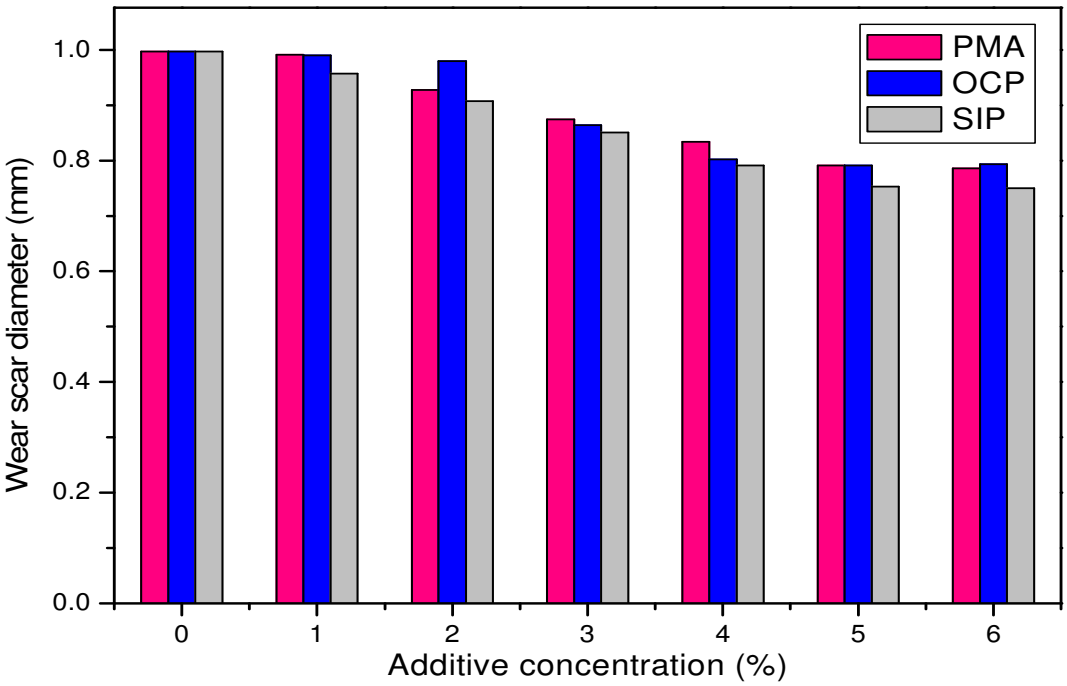


Figure 2.14: Interaction between iron surface and oxygen of ester functionality of PMA

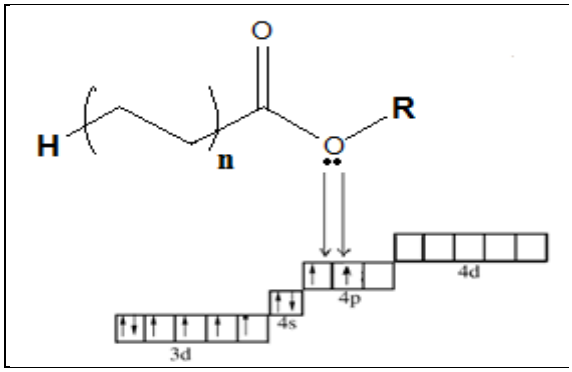


Figure 2.15(a): Plot of shear stability index vs. additive concentration in BO1

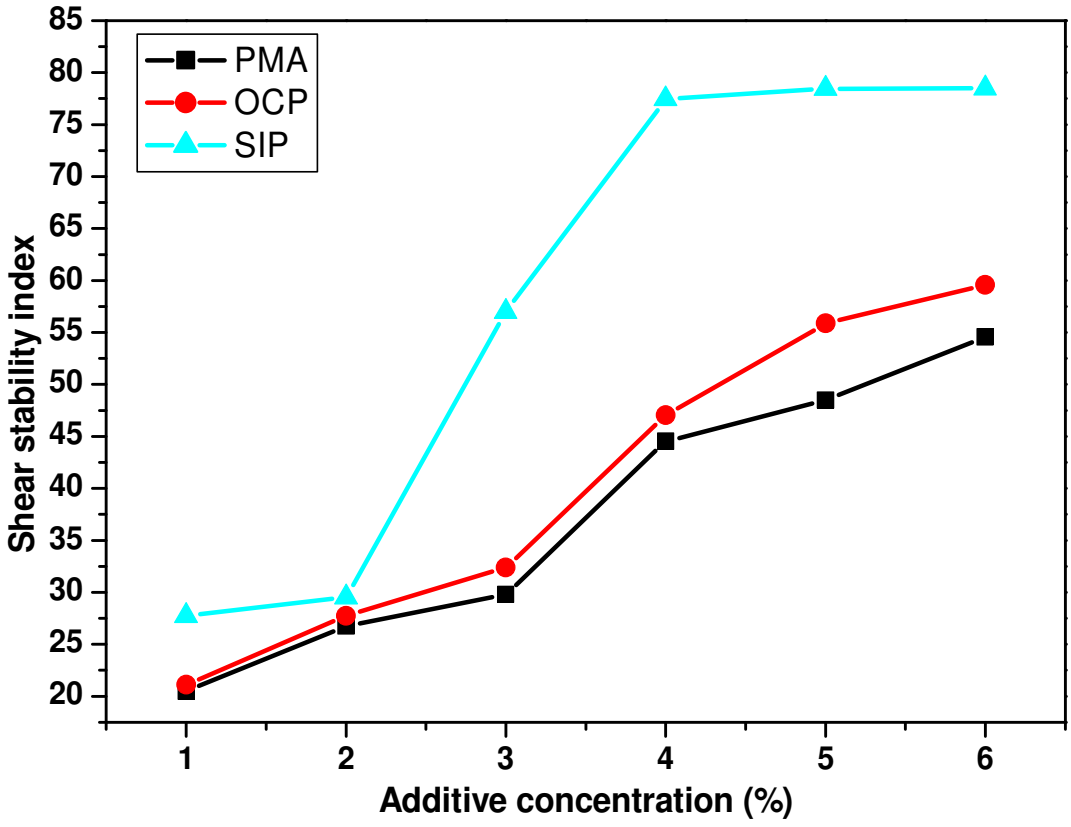


Figure 2.15(b): Plot of shear stability index vs. additive concentration in BO2

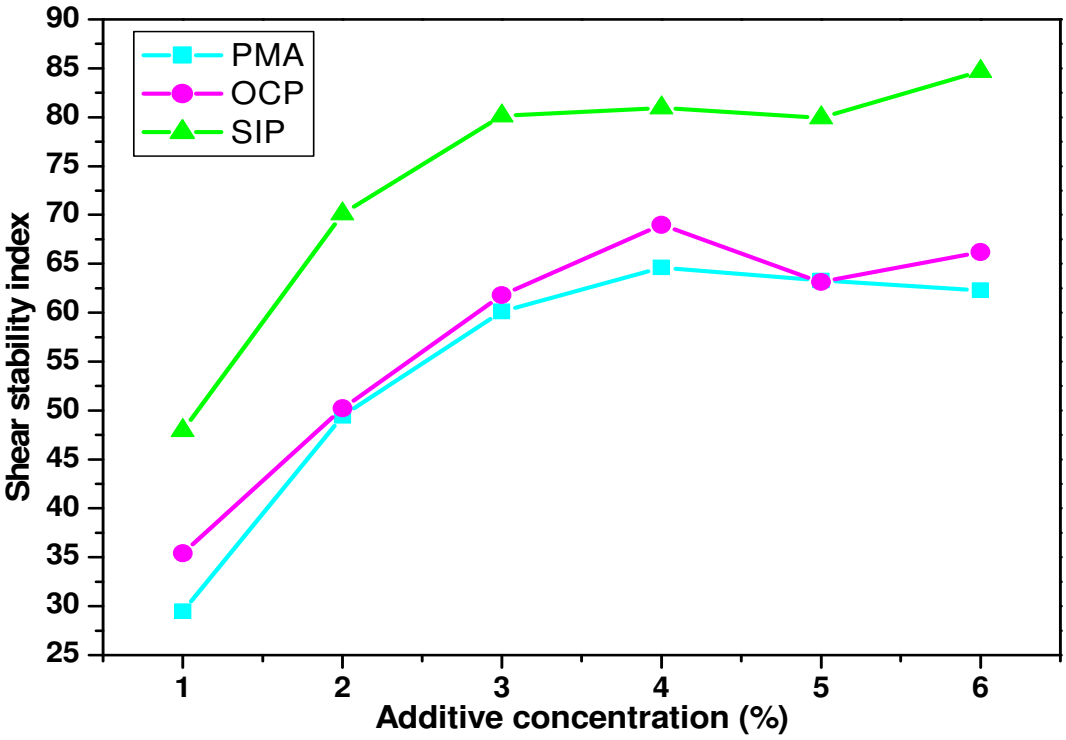


Figure 2.16(a): Plot of percent shear loss vs. additive concentration in BO1

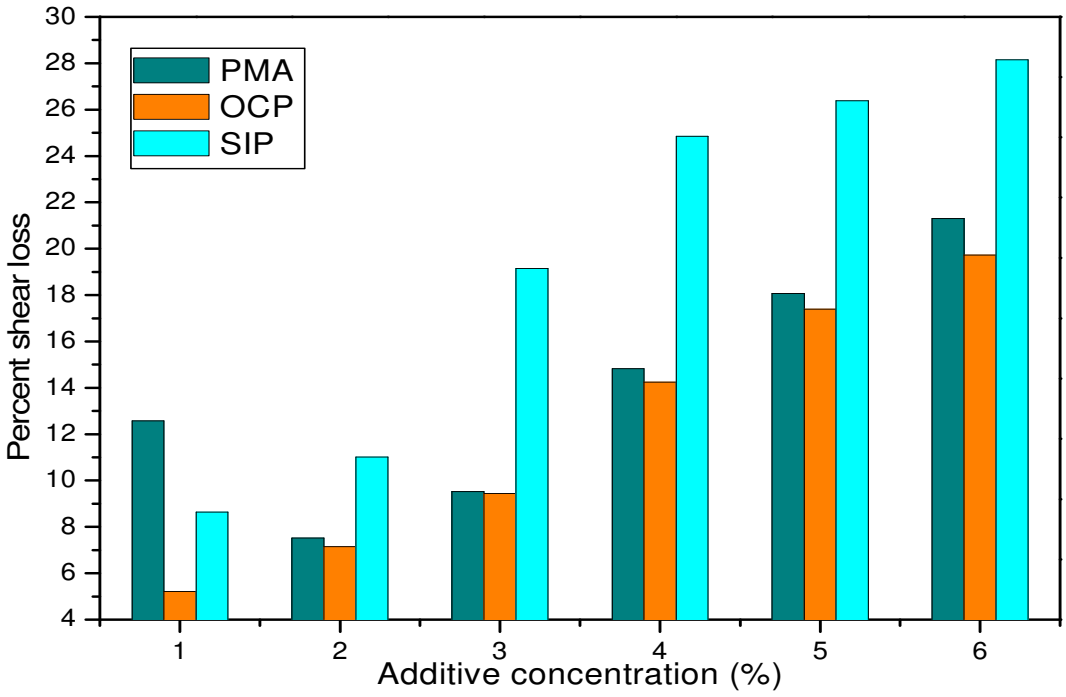


Figure 2.16(b): Plot of percent shear loss vs. additive concentration in BO2

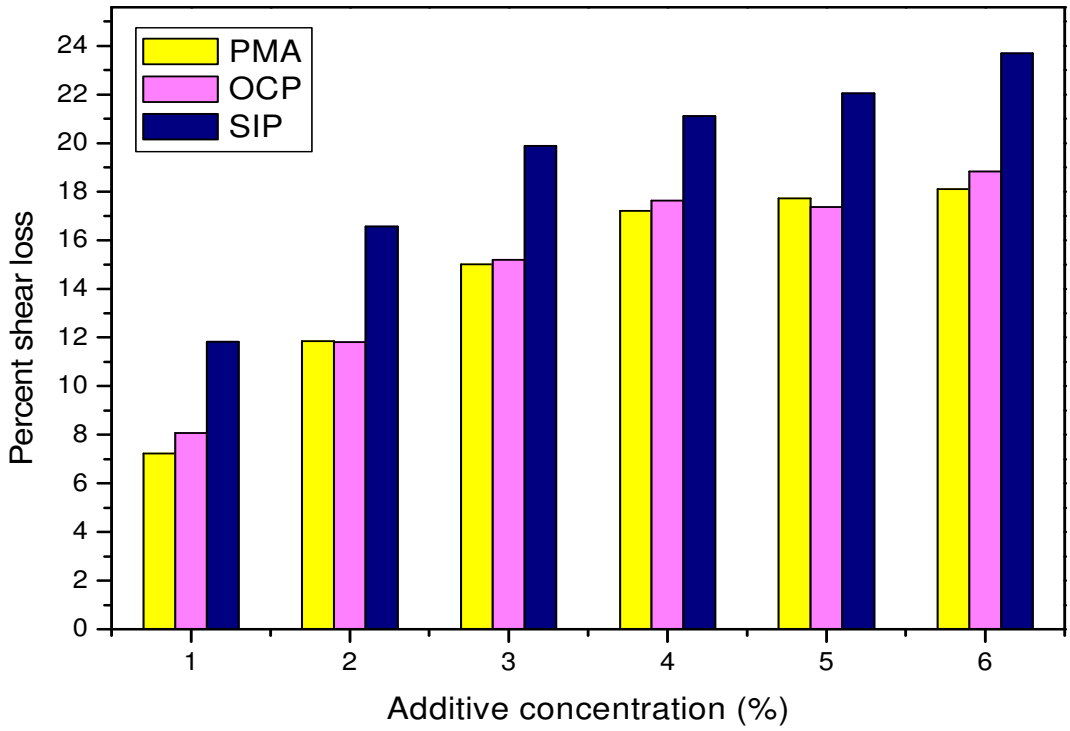


Figure 2.17(a): Plot of thickening vs. additive concentration in BO1

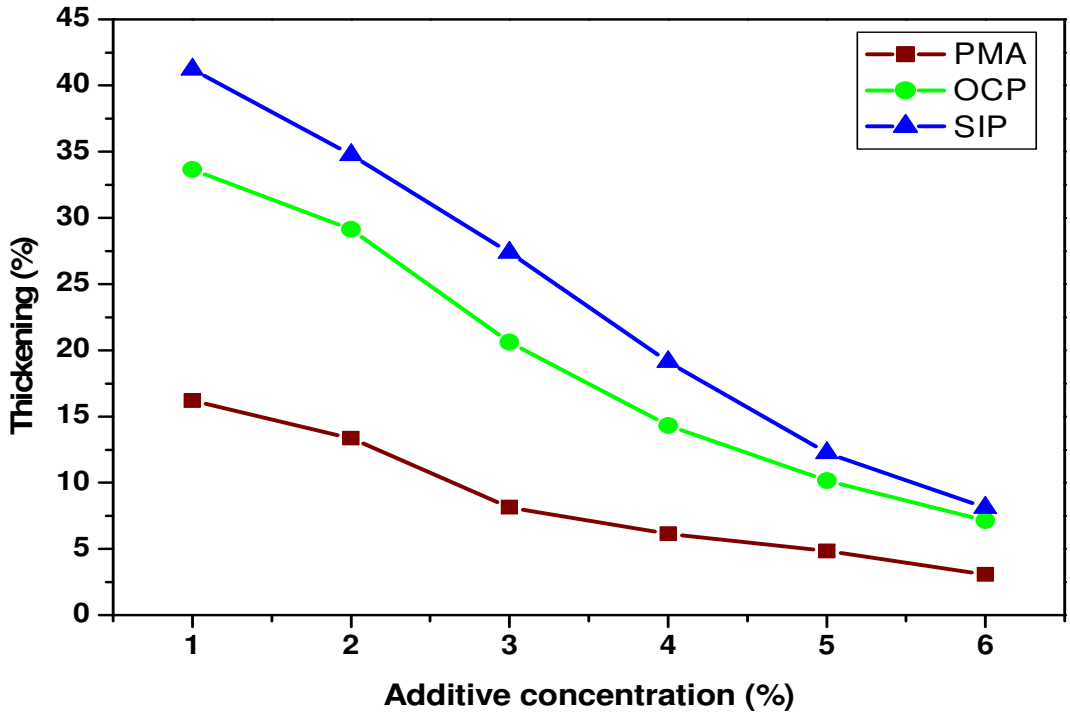
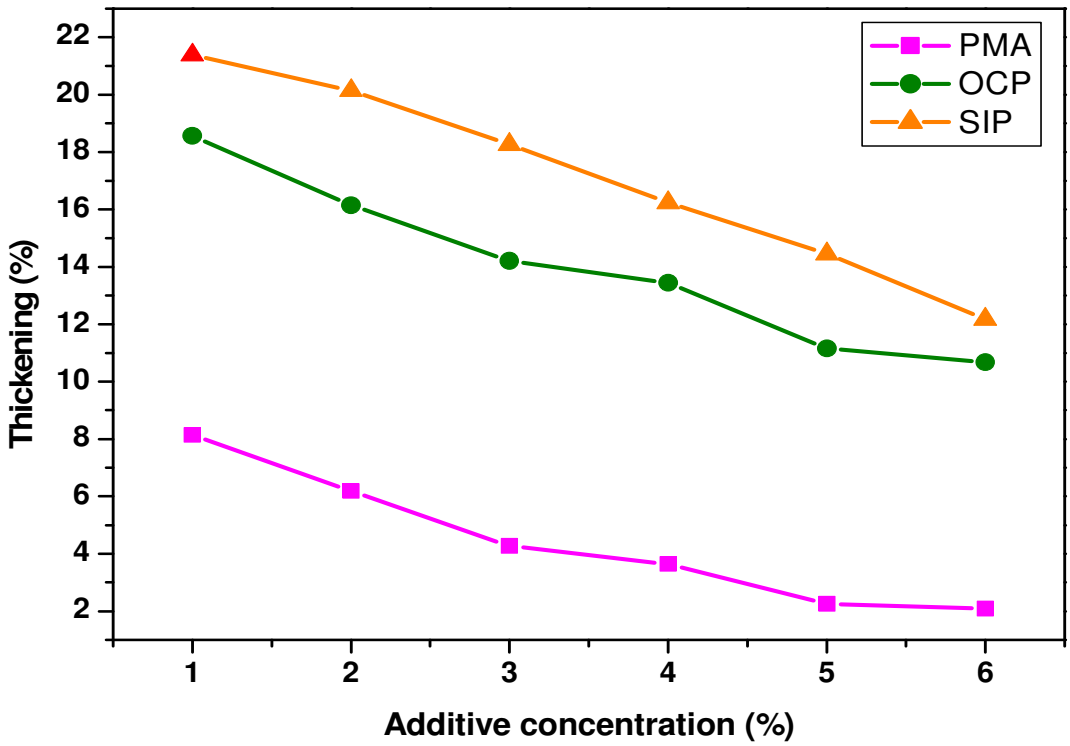



Figure 2.17(b): Plot of thickening vs. additive concentration in BO2