Multifunctional Additive Performance of Acrylate-Styrene Copolymers

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Homo polymers (two homopolymers and six copolymers) of isodecyl acrylate and isooctyl acrylate and their respective copolymers with styrene were synthesized using benzoyl peroxide as initiator and characterized by spectral analysis, gel permeation chromatography and thermogravimetric measurements. Pour point (PP), viscosity index (VI) and anti wear (AW) performance of the additive doped base oils were evaluated to check the efficiency of the polymers as pour point depressant (PPD), viscosity index improver (VII) also known as viscosity modifier (VM) and anti wear (AW) additives for lube oil. A comparison of the above performances between the respective homopolymers and the copolymers is also analysed and reported. Analysis of different properties indicates that the isodecyl acrylate polymers have better lube oil additive property than that of isooctyl acrylate polymers. VI, PPD and AW values of the polymers doped in base oils depend on the nature of mineral base oils, polymer types and also on the concentration of the additives.

Keyword: Pour point, Viscosity index, Anti wear, Thermogravimetric analysis, Co-polymer.

Introduction

Lubricating oil which is also known as base oil or lube oil is the basic building block of a lubricant. The rheological properties such as fluidity of the oil at low temperature, viscosity and variation of viscosity with temperature govern the performance of lubricant base oils. To exhibit effective performance at low as well as at high temperatures, an engine lubricant should be fluid at low temperature and should have minimum variations of its viscosity with temperature. To improve the quality, lube oil always mixed with different types of additives. Additives impart a new and desirable property to the lube oil which was not originally present in the oil or enhance the performance already present in the lube oil. The quantity and quality of the additives depend on the nature of the base oil and also on the purpose of their use. Some of the important types of additives are antioxidants, detergents and dispersants, corrosion inhibitors, viscosity index improvers (VII), pour point depressants (PPD) etc. Of them VII, AW and PPD are the most widely used ingredients in modern lubricants. Pour point depressants (PPDs) are the chemical additives used to transport lube oils at low temperature. They are added to maintain oil flow ability below a certain temperature which is termed as pour point (PP) and defined as the temperature at which the flow ability of oil is totally ceased due to wax crystal lattice formation. These are basically polymeric compounds made of hydrocarbon chains. At the time when the temperature becomes low and the oil cools down, then during the development of wax crystal network, the hydrocarbon chains become inserted in the lattice and thus inhibit wax crystal formation or modify the wax crystal network. So they are also known as wax crystal modifiers. Among the different kinds of polymers, acrylic and methacrylic ester polymers are very efficient as crude oil wax crystal modifiers and wax deposition inhibitors. Viscosity is also a very important property of a lubricant. The viscosity of a liquid is a measure of its resistance to flow. High viscosity oil is less fluid than the one of low viscosity. At higher temperatures, the oil tend to thin out and flow more readily and vice-versa. The change in viscosity with the variation of temperature is expressed by a parameter known as viscosity index (VI). Higher VI of oil means the viscosity of the oil vary very less with the variation of temperature. Viscosity index improvers (VII) or viscosity modifiers (VM) are added to the lubricating oil to improve the VI of the oil. Acrylate-based organic polymers are increasingly used nowadays as additives to raise the pour point depressant (PPD) properties in lubricating oil because of their influence on the low-temperature flow

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ability. However, despite high performance of the polyacrylates, there are only few discrete works known on the acrylate chemistry functioning as the PPD. The present proposal aims to synthesize new co-polymers of long chain acrylates and evaluate their additive properties in comparison to the respective acrylate homo polymers in different lube base oil.

Furthermore, the newly made additives might play important role in controlling other performance of the lube oil such as, viscosity modifier (VM), anti-wear (AW) etc, which would also be examined. The results evaluated so far are encouraging and comprise the subject matter of the report.

**Experimental**

**Materials**

Toluene, Hydroquinone and H$_2$SO$_4$ were purchased from Merck Specialities Pvt. Ltd. Acrylic acid (stabilised with 0.02% Hydroquinone monomethyl ether) and isodecyl alcohol were obtained from Sisco Research Laboratories Pvt. Ltd. Hexane and isooctyl alcohol was purchased from S D Fine Chem. Ltd. Methanol was purchased from Thomas Baker (Chemicals) Pvt. Ltd. and styrene from Across Organics. Benzoyl peroxide (BZP) obtained from LOBA chemicals was recrystallised from CHCl$_3$-MeOH before use. Rest of the materials was used as they were obtained without further purification. Two different base oils (BO1 and BO2) were collected from IOCL, Dhakuria, Kolkata.

**Esterification – preparation of monomers**

Esterification was carried out by following the procedure as described in our earlier report. Isodecyl acrylate (IDA) was prepared by reacting 1.1 mole of acrylic acid with 1 mole of isodecyl alcohol. The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25 % (w/w) hydroquinone as polymerization inhibitor for acrylic acid and toluene as a solvent. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, decyl acrylate (DA).

Under the same procedure isooctyl acrylate (IOA) was also prepared from acrylic acid and isooctyl alcohol (isooctanol).

**Purification of prepared esters (monomers)**

The prepared esters were purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide, the ester was then left over night on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

**Preparation of copolymer and homopolymer**

Homopolymer of IDA and IOA (HIDA and HIOA, respectively) were prepared and in the preparation of IDA + styrene (St) and IOA + styrene copolymers, different mole fractions of styrene were used (table 1). The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask, desired mass of IDA and initiator (BZP) was placed followed by desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 80°C for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole fraction of styrene in the feed</th>
<th>Mole fraction of styrene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>By NMR method</td>
<td>By IR method</td>
</tr>
<tr>
<td>P-1</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>P-2</td>
<td>0.0155</td>
<td>0.0148</td>
</tr>
<tr>
<td>P-3</td>
<td>0.0425</td>
<td>0.0408</td>
</tr>
<tr>
<td>P-4</td>
<td>0.0711</td>
<td>0.0692</td>
</tr>
<tr>
<td>P-5</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>P-6</td>
<td>0.0135</td>
<td>0.0123</td>
</tr>
<tr>
<td>P-7</td>
<td>0.0391</td>
<td>0.0361</td>
</tr>
<tr>
<td>P-8</td>
<td>0.0637</td>
<td>0.0610</td>
</tr>
</tbody>
</table>

P-1 = homopolymer of isodecyl acrylate; P-2 to P-4 = copolymer of isodecyl acrylate + different mole fractions of styrene; P-5 = homopolymer of isooctyl acrylate; P-6 to P-8 = copolymer of isooctyl acrylate + different mole fractions of styrene.
followed by drying under vacuum at 40°C. Homopolymer of IDA, homopolymer of IOA and also copolymer of IOA with styrene were similarly prepared and purified under the same condition for use in reference experiments.

Measurements

Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range 400 to 4000 cm\(^{-1}\). NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl\(_3\) was used as solvent and TMS as reference material. The average molecular weights and the polydispersity of these polymers were measured in Water’s gel permeation chromatography equipment at room temperature using polystyrene standards for calibration in THF phase. Solution of the polymers in base oils were made by dilution method from their respective 10% stock solutions at about 60-70°C with continuous stirring until clear solutions were obtained. Kinematic viscosities of the prepared solutions were measured using Cannon-Fenske viscometer in a 100±0.1°C bath as per ASTM D-445 procedure.

Viscometric measurements

Viscometric properties were determined at 40°C in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time of flow of at least eight different concentrations of the sample solution. The time of flow of the solutions was manually determined by using a chronometer. In the single point measurement, the lowest value of solution concentration was chosen for calculation. The kinematic viscosity (\(\upsilon\)) of the sample solutions was determined at 40°C and 100°C from the following equation\(^{10}\).

\[
\upsilon = \frac{(Kt- L/t)}{\rho}
\]

Where \(K\) and \(L\) are the viscometric constants (where \(K = 0.03853\) and \(L = 2.4689\)) and \(t\) and \(\rho\) are time flow and density of experimental solution respectively.

Thermogravimetric analysis (TGA)

The thermograms in air were obtained on a mettler TA-3000 system, at a heating rate of 10 °C/min at room temperature under atmospheric pressure taking 0.2 g of each polymer sample in a platinum crucible.

Evaluation of PPD properties of the additives in lube oil

The prepared additives were evaluated as pour point depressants (PPD) using two different base oils through the pour point test according to the ASTM D 97-09 on a Cloud and Pour Point Tester model WIL-471(India).

Evaluation of the prepared additives as Viscosity Index Improver (VII) in lube oil

The Viscosity index values of the polymeric oil solutions have been determined according to the ASTM D2270 method and by using the following equations\(^{10}\).

\[
VI = 3.63(60-10^n)
\]

Where, \(n = (\ln \upsilon_1 - \ln k) / \ln \upsilon_2\) for which, \(\upsilon_1\) and \(\upsilon_2\) are the kinematic viscosities of the solution at lower and higher temperature respectively. The kinematic viscosity of the oil containing the different concentrations of the tested polymers was determined at 40°C and 100°C and \(k\) is a constant which is equal to 2.714 for the temperature range performed\(^{11}\). Different concentrations ranging between 1.0 and 6.0 % (w/w) were used to study the effect of copolymer concentration on the VI.

Evaluation of Anti wear properties of the prepared additives in lube oil

Anti wear properties of polymer-oil blends as well as of the mineral base stocks were studied in sliding contact by means of a Four-Ball Wear Test Machine as per ASTM D-4172\(^{12}\). The tests were carried out employing 20kg (196N) and 40kg (392N) load condition.

Determination of Average Molecular Weight

The average molecular weight of the prepared polymers was determined gel permeation chromatography (GPC). In GPC technique the number average (\(M_n\)) and weight average (\(M_w\)) molecular weights were determined using a Waters GPC system (polystyrene calibration) having molecular weight range \(10^2-5\times10^5\) g. mol\(^{-1}\) equipped with 2414 refractive index detector, Waters 515 HPLC pump, 717 plus auto sampler at 40°C. THF has been used as an eluent at a flow rate of 1.0 ml/min at 40°C. The instrument has been calibrated with polystyrene before the experiment. The polydispersity index, indicating the nature of the distribution of the molecular weights in the polymers\(^{13}\), was also calculated.

Results and discussion

Spectroscopic analysis

FT-IR spectrum of the homo polymer of iso decyl acrylate (HIDA) exhibited absorption at 1732 cm\(^{-1}\).
due to ester carbonyl stretching vibration. Peak at 1260 and at 1175 cm\(^{-1}\) can be explained owing to the C-O (ester bond) stretching vibration and the absorption bands at 975, 750 and 711 cm\(^{-1}\) were due to the bending of C-H bond. The broad peak ranging from 2900-3100 cm\(^{-1}\) was due to the presence of stretching vibration (C-H). In its \(^1\)H-NMR spectra, homo polymer of IDA showed a multiplet centered at 4.01 ppm due to the proton of -OCH\(_2\)- group; a broad singlet at 0.89 ppm was due to methyl groups of decyl chain. The proton decoupled \(^13\)C-NMR of the above sample was in complete agreement with the homopolymer which shows the presence of ester carbonyl group at 171 ppm and absence of any sp\(^2\) carbon in the range 130-150 ppm.FT-IR spectrum of the homo polymer of Isooctyl acrylate (HIOA) exhibited absorption at 1731 cm\(^{-1}\) due to ester carbonyl stretching vibration. Peak at 1260 and at 1164 cm\(^{-1}\) can be explained owing to the C-O (ester bond) stretching vibration and the absorption bands at 961, 775 and 720 cm\(^{-1}\) were due to the bending of C-H bond. The broad peak ranging from 2929-2950 cm\(^{-1}\) was due to the presence of stretching vibration (C-H). \(^1\)H and \(^13\)C-NMR was also in complete agreement with the homopolymer. In its \(^1\)H-NMR spectra, homo polymer of IOA showed a broad singlet centered at 4.01 ppm due to the proton of -OCH\(_2\)- group; a broad singlet at 0.89 ppm was due to methyl groups of isooctyl chain. The proton decoupled \(^13\)C NMR of the above sample shows no peak between 130-150 ppm which indicated the absence of any sp\(^2\) carbon. The presence of ester carbonyl group was indicated by the peak at 170 ppm. In the \(^1\)H NMR spectra of one of the respective copolymers, a broad multiplet centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet centered at 4.06 ppm was due to the proton of the –OCH\(_2\) group. The absence of singlets between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer. The proton decoupled \(^13\)C NMR spectrum of the above sample of copolymer was in complete agreement with the proposed structure of the copolymers (structure-I). The extent of incorporation of styrene in the polymer chain was determined (table 1) through a comparison of area of –OCH\(_2\) group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports\(^{14}\) as well as on the basis of our earlier paper\(^{15}\), which was further verified through an analysis of FT-IR spectral data following a method as also discussed in our earlier paper\(^{15}\).

**Thermogravimetric analysis**

A comparison between the TGA data for homo and copolymers shows that in case of IDA polymers, the copolymers are better in thermal stability than the respective homopolymers and with increasing concentration of styrene in the feed, the stability increases. Same trend is also observed for the homo and copolymers of IOA. In addition, comparison among the TGA values indicates that the IDA polymers (homo and co) are thermally more stable than the IOA polymers.

**GPC molecular weight**

As expected, the molecular weight (Mw and Mn) of the homo and copolymers of IDA (Mw and Mn of HIDA is 21×10\(^4\) and 10.5×10\(^4\) and those for IDA – St copolymer is 23 ×10\(^4\) and 12.4×10\(^4\) respectively) is always greater than those of the IOA polymers (Mw and Mn of HIOA is 13.5×10\(^4\) and 6.5×10\(^4\) and those for IOA – St copolymer is 8.5×10\(^4\) and 17.2 ×10\(^4\) respectively). Lower poly dispersity index (PDI) of the IDA polymers (PDI of HIDA is 1.2 and that for IDA –St copolymer is 1.8) in comparison to IOA polymers (PDI of HIOA is 3.37 and that for IOA – St copolymer is 2.11) indicated lesser extent of branching in the IDA polymers. Thus a better surface related additive performance is anticipated.

**Efficiency of the prepared polymers as pour point depressant (PPD)**

The PPD properties of the prepared polymers were tested by using 1- 6 % (w/w) polymer doped base oils and the experimental data are grouped in table 2. The data indicated that the prepared additives may be considered as efficient pour point depressants. The results for most of the polymers indicate that their efficiency as PPD go on increasing from 1 - 5 % (w/w). However, beyond the concentration of 5% the change is not significant. It is also observed that the styrene copolymers are more efficient than the respective acrylate homo polymers and the increase in styrene content enhances the performance. Also, homopolymer and copolymer of isodecyl...
The interaction between the polymer chain and the oil gets decreased, the polymer molecules change from a higher temperature, while the lube oil viscosity gets increased in all the cases. This may be because of the fact that, at a higher temperature, while the lube oil viscosity gets decreased, the polymer molecules change from tight coil to expanded ones as a result of increase in the interaction between the polymer chain and the base oil. This increase in volume results in an increase in the viscosity of the mixture and counter balances the normal reduction in viscosity of the oil with increasing temperature. The increase in concentration of the polymer also leads to an increase in total volume of polymer coils in the oil solutions as was already reported. As a consequence, a high concentration of polymer will impart a high viscosity index rather than its low concentration.

### Efficiency of the prepared compounds as viscosity index improvers

VI improver properties of the prepared homo and copolymers in terms of their viscosity index values are presented in table 3 in two different base oils BO1 and BO2. The data obtained clearly shows that the homopolymers (HIDA and HIOA) is of having lower VI values than their respective styrene copolymers and with the increase in styrene content in the feed, the VI is found to increase. Again, homopolymer of IDA and its copolymer with styrene are of having higher VI values than the respective IOA homo and copolymers, and with the increase in styrene content in the feed, the VI value is found to increase irrespective of the nature of the base oils. The data reveals that the VI values of the iso-octyl acrylate polymers are higher in comparison to the respective decyl acrylate polymers in both the base oils. Again, with increasing concentration of the polymer solutions, VI value is found to increase in all the cases. This may be because of the fact that, at a higher temperature, while the lube oil viscosity gets decreased, the polymer molecules change from tight coil to expanded ones as a result of increase in the interaction between the polymer chain and the base oil. This increase in volume results in an increase in the viscosity of the mixture and counter balances the normal reduction in viscosity of the oil with increasing temperature. The increase in concentration of the polymer also leads to an increase in total volume of polymer coils in the oil solutions as was already reported. As a consequence, a high concentration of polymer will impart a high viscosity index rather than its low concentration.

### Efficiency as anti wear additives

Employing a Four Ball Wear Test Machine as per ASTM test conditions, the anti wear contributions of the homo and copolymers due to the additive concentration / viscosity of the oil and due to the additive chemistry was determined. Experiments were conducted first with pure base oils followed by polymer-oil blends. The wear scar diameter (WSD) measured in all these cases are depicted in table 4.

### Effect of viscosity on AW performance

WSD (lower the WSD data, higher the AW benefit), is found to decrease with the viscosity of the pure base oil. The WSD data in the case of polymer - oil blends is also found to decrease with the additive concentration in the base oil i.e. the viscosity of the polymer doped base oil irrespective of the nature of...
the base oils. This observation is in agreement with the earlier reported data\textsuperscript{19}.

**Effect of Additive Concentration on AW performance**

Decrease in WSD (mm) with increasing concentration of the additives was found in both the base stocks irrespective of the types of additives (homopolymer or co-polymer). However, beyond 5% additive concentration no significant AW benefit was observed.

**Effect of additive chemistry on AW performance**

Acrylate-styrene copolymers always showed better AW performance in both the base oils followed by HIDA and HIOA polymers (table 4). This is due to the presence of aromatic ring of styrene in the copolymer structure, which increases the surface activity\textsuperscript{20,21} much more than the homopolymer samples in which the surface active phenomena is offered only by the ester functionality present in them. 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 ferrum atom using its lone pair of oxygen, thereby increasing tribological activity\textsuperscript{21,22}.

**Conclusions**

1. IDA polymers are thermally more stable than the IOA polymers. Increased styrene content enhances the thermal stability.
2. Acrylate – styrene copolymers showed excellent multifunctional (PPD, VM, AW) additive performance irrespective of the nature of base oils. In general the additive performance properties of the additives, doped in the base oils, increases gradually (up to a certain limit) with the increasing additive concentration in the polymer-oil blends.
3. Acrylate-styrene copolymers showed much better PPD, VII, AW properties than the respective homopolymers. Homopolymer of isodecyl acrylate exhibit better additive performance than isoocotyl acrylate. Again, with increasing styrene content in the copolymer, additive performance increases in all the cases.
4. The prepared copolymers can effectively be used as multifunctional lube oil additives.

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**References**