Chapter 3
Epoxidation of oleic acid and vegetable oils: Synthesis, characterization and utilization as biolubricants and additives for plastics

3.1 Objectives and background of investigation

Epoxidised vegetable oils have been receiving growing commercial interest in recent years (Chapter 1, section 1.3.5). Epoxidation of fatty acids e.g. oleic acid derived from vegetable oils is an important, yet less studied, approach for producing value added oleochemicals. The utilization of epoxidised fatty acids will open a wide range of feasible reactions that can be carried out under moderate reaction conditions due to the high reactivity of the oxirane ring. Few such reactions which lead to the transformations of epoxidised oleochemicals to the multi-functionalized building blocks for exploration under biolubricant chemistry and additive technology have been studied under present investigations.

3.1.1 Synthesis and characterization of epoxidised oleic acid, oleates and vegetables oils

For clean and efficient epoxidation of vegetable oils/ fatty acids, the easily available low cost technology is mainly the epoxidation with peroxyacetic acid and per oxyformic acid, which is generally catalyzed by soluble mineral acids like sulfuric, tungstic or molybdic acids. Literature review (Chapter 1, section 1.3.1) indicates that H₂SO₄ is the most efficient and effective catalyst. When organic peracid is preformed, there are some handling problems, as the concentrated peracid is unstable and explosive. Hence the epoxidation using in situ generated peracetic acid has the greatest technological importance for safety reasons. This procedure, however, has several drawbacks that require improvement: (i) the selectivity to epoxidized products is relatively low due to acid-catalyzed oxirane ring opening side reactions, (ii) the separation of acidic by-products, whose presence may be detrimental for further applications, is not easy, (iii) the side reactions such as hydrolysis of the ester groups may occur, (iv) the handling of highly-concentrated hydrogen peroxide and organic acids is dangerous and (v) being strong acid, H₂SO₄ leads to many side reactions such as oxirane-ring opening to diols, hydroxy esters, estolides and other dimer formations. Furthermore it causes the equipment corrosion and must be neutralized and removed from the end product. For all these reasons, present work reports optimisation studies on the two phase non-catalytic
peracid epoxidation of different oils and oleic acid that combine desirable features of *in situ* and *ex situ* methods. In present investigations, this work analyzes the impact of the main process variables (agitation, effect of solvent, temperature, reactant concentration and molar ratio, catalytic vs noncatalytic) on the double bond conversion, epoxidation yield, oxirane selectivity and ring stability against degradation by hydrolysis. Different peracids (performic, peracetic, and m-CPBA) were investigated in reference to the reaction conditions, degree of epoxidation and retention of ring. Moreover different modes of addition (*in situ* vs *ex situ*), different contacting patterns (batch vs semi batch) and removal of water by azeotropic vacuum distillation were explored along with the conventional epoxidation methods. Efforts were undertaken to establish the feasibility of noncatalytic epoxidation through evaluation of various modes of contacting with epoxidising reagents.

Although there are many studies on the epoxidation of soybean, palm, castor, corn, mahua, jatropha oil etc., there have been only a few reports on the epoxidation of oleic acid\(^1,2\). It is the most widespread, easily available, and renewable raw material that constitutes no less than 40% of all aliphatic acids synthesized in nature\(^3\). Epoxidised oleic acid produced by reacting organic carboxylic acids with hydrogen peroxide either performed in two stages or *in situ* has not reported much in the literature. Oleic acids are more thermally stable than polyunsaturated fatty acids and therefore are highly desired component in vegetable oils for lubricant and plasticizers applications. Hence the epoxidation of oleic acid was chosen as the model reaction. In addition, epoxidations were performed on different oils such as soyabean, sunflower, castor and mustard, methyl oleate and metallic soaps of oleic acid to understand the difference in reactivity of oleic acid, salts, monoester and triglycerides towards peracids. Epoxidation of different oils, conducted under similar conditions, will present an idea about the influence of fatty acid composition on rate of epoxidation.

The goal of present investigation was thus to develop and optimize the peroxyacid epoxidation of oleic acid and vegetable oils and the best epoxidation system was suggested on the basis of technical, environmental and economical considerations. The results of the work reported in present Chapter were used to undertake the kinetic and thermodynamic modeling of the *in situ* and *ex situ* batch mode peracetic and performic acid epoxidation of oleic acid and reported under **Chapter 4**.
3.1.2 Synthesis and evaluation of 2-ethyl hexanol (2-EH) esters of epoxidised mustard oil as biolubricant

The global lubricant market is about 45 million metric ton (MMT) valued at 48 billion USD. Currently, the Indian lubricant industry is the seventh largest lubricant market in the world and according to an estimate\(^4\), Indian lubricant consumption will cross 2 MMT by 2014-15. Biolubricants, the biodegradable, environmentally friendly products derived from vegetable oils such as high oleic canola, castor, palm, sunflower and rapeseed, are a very small part of the overall lubricant market, predominantly used in the US and Europe, as their high costs (over double the price of standard lubricants) limits their appeal elsewhere. On the other hand, although expensive, the vegetable oils and oleochemicals are known to possess several desirable characteristics for use in industrial lubricant applications such as rolling, cutting, drawing, quenching operations, and greases either alone or in combination with mineral oils: low volatility, high flash point, high viscosity index, excellent lubricity, superior anticorrosion properties, good solubilizing capacity for contaminants and additives, better affinity to metal surfaces, eco-compatibility, renewable and non-toxic. The long fatty acid chain and presence of polar groups in the vegetable oil structure makes it amphiphilic in nature, therefore allowing them to be used as both boundary and hydrodynamic lubricants. In the future, increasing environmental concerns and emphasis on shift from non-biodegradable lubricants to the environmentally safe and green biolubricants will drive high-powered growth.

Besides cost, the widespread use of vegetable oils as lubricant base stocks especially as automotive and industrial fluids is precluded mainly by their poor cold flow properties due to the presence of saturated fatty acids and inferior thermal and oxidation stability characteristics on account of presence of polyunsaturated fatty acids. This confines their use as lubricants to a modest range of temperature. Oxirane ring opening of epoxidised oil, by acidic or alkaline catalysed reaction with suitable organic acid or aliphatic alcohol, provides interesting polyfunctional compounds useful as biolubricant\(^5\).

Mustard oil, which is abundantly available low cost vegetable oil in the tropical area and 2-ethylhexanol (2-EH), which is used as an intermediate\(^6,7\) in the manufacture of various esters such as plasticizers, monomers, lubricant additives and solvents, were employed as feedstock in the preparation of lubricant base oil that will fulfil the increasing demands for stability during various tribochemical processes and withstand extremes of temperature variations. Present experimental work thus envisages the improvement in cold flow properties as well as thermal and oxidative stability of mustard oil by epoxidation of
double bonds followed by adding 2-EH side chains through ring opening using different acid catalysts including sulphamic acid. Use of this green catalyst has not been reported so far in ring opening reactions. Besides verification of epoxidation and ring opening synthesis, the experimental investigations included the analysis of performance of mustard oil based biolubricant in reference to pour point, oxidative stability and viscosity index to allow for their rapid commercialization.

3.1.3 Synthesis and utilization of epoxidised zinc oleate as additives for plastics

Plasticizer is an additive to enhance plastic workability and flexibility, while stabilizers are added for enhancement of thermal and UV durability. Plasticizers used in plastic industries such as dioctyl phthalate (DOP) are petroleum derivatives which are hazardous to human health. In 2005, the global plasticizer demand\(^8\) was 6.0 MMT and phthalates contributed to 90% (5.4 MT) of global plasticizer demand due to excellent balance of cost and performance. DOP plasticizers, however, migrate at constant rate in solid and also in liquid medium which contact directly with polyvinyl chloride (PVC) plastic and have been detected in water, food and soil. Moreover these non biodegradable petrochemical plasticizers provide only flexibility, but do not contribute to heat and light stability. This is most important since, like other chlorinated polymers, PVC tend to degrade under heat and light action. As a result, additional stabilizing additives based on metals like cadmium, lead and barium are added to plastics to achieve stability to heat and light. These stabilizers are toxic and therefore unsuitable for many applications, particularly for food packaging and medicinal uses. Epoxidized soybean oil, the most common epoxidised oil used as plasticizer, was utilized only at 2.3% (0.14 MMT)\(^8\) primarily due to their high cost. But offer of additional performance benefits can make their overall economics favourable.

The suitable additive for PVC plastics has to be renewable cost-effective, stable, compatible with PVC and low in color, volatility, odour and toxicity. It should have good permanence, and impart thermal and UV stability to the PVC formulation besides favorable role in plasticization. Oleic acid is more thermally stable than polyunsaturated fats, and therefore are highly desired components in vegetables oils for lubricant and plasticizer applications. In present work, the combination of epoxidised oleic acid and metallic soaps in one molecule i.e. synthesis of epoxidised zinc oleates (EZnOA) was investigated for synergistic action of stabilizer and plasticizer for PVC polymer composite. Thus an attempt has been made to combine plasticization and stabilisation activity in one molecule (EZnOA) which is safer, nontoxic, biodegradable and based on renewable
resources. Owing to the presence of oxirane ring in the molecule, EZnOA would impart thermal and photo-stability to the polymer composite. Presence of Zn will promote stabilization activity based on esterification reaction. Epoxy structure would alter the mechanical properties of polymer. The role of EZnOA as additive for PVC plastic was distinguished on the basis of analysis by several sophisticated instruments such as FESEM with EDX, UTM, colour matching spectrometer and TGA.

3.2 Raw materials and chemicals

i. Vegetable oils and oleic acid

The renewable feedstock for epoxidation in present investigation includes oleic acid, refined oils such as sunflower, castor, soyabean and mustard oils. Oleic acid was obtained from s d fine Chem. Ltd. Mumbai. Refined oils were purchased from local market. GC analysis for determination of fatty acid composition of different oils and oleic acid were performed as described under section 2.4.2 and have been reported in Table 3.1.

Table 3.1 % fatty acid (FA) composition and other characteristics of different oils and fatty acids

<table>
<thead>
<tr>
<th>Oil/fatty acid</th>
<th>% FA composition by GC</th>
<th>Other Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₁₄ C₁₆ C₁₈ C₁₈:1 C₁₈:2 C₁₈:3 Special FA</td>
<td>SV IV AV ρ (20°C)</td>
</tr>
<tr>
<td>Castor oil</td>
<td>21.2 10 2.2 6 - - [C₁₈:₁ 12 OH] 85</td>
<td>182 88 4.9 0.96</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>0.05 0.09 6.8 39.4 50.8 - -</td>
<td>197 111.9 0.52 0.9205</td>
</tr>
<tr>
<td>Soyabean oil</td>
<td>- 10.87 3.54 21.39 53.67 6.70 -</td>
<td>- 119.0 0.33 0.9221</td>
</tr>
<tr>
<td>Mustard oil</td>
<td>- 1.5 0.4 22 14.2 6.8 [C₂₂:₁ 47]</td>
<td>172 110.6 1.2 0.9243</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>- 3.4 1.1 80.6 14.9 -</td>
<td>98 195.2 0.89</td>
</tr>
</tbody>
</table>


ii. AEROXIDE® Alu C (nano-alumina)

AEROXIDE® Alu C (Al₂O₃ content > 99.8%, by wt based on ignited material) is a registered trademark of Evonik Industries. It is a very fine fumed metal oxide (average particle size of 13 nm) with a high specific surface area (BET- 100 m²/g). The XRD spectrograph of nano alumina has been presented in Fig. 3.1. The material has 57.6%
crystallinity in cubic lattice form (a=7.90000, a/b=1.00000, b/c=1.00000). In present investigation, it was used as catalyst for the epoxidation of mustard oil.

![Graph showing XRD spectrograph of AEROXIDE® Alu C (nano alumina)](image)

**Fig. 3.1 XRD spectrograph of AEROXIDE® Alu C (nano alumina)**

In addition, the sources and characteristics other chemicals, utilized in present research work, have been reported in **Table 3.2**.

**Table 3.2 Sources and characteristics of raw materials/ reagents/ additives for epoxidation of oleic, linoleic acid, mustard oil, metallic soap**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of the chemical</th>
<th>Mol. Wt. g/mol</th>
<th>Density (g/ml, 25°C)</th>
<th>B.P., (°C) at 760 mm of Hg</th>
<th>M.P./ F.P. (°C)</th>
<th>Minimum Assay (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrogen Peroxide 50%</td>
<td>34.01</td>
<td>1.1904</td>
<td>150.2</td>
<td>-0.43</td>
<td>48.52</td>
<td>Merck</td>
</tr>
<tr>
<td>2</td>
<td>Glacial acetic acid</td>
<td>60.05</td>
<td>1.049</td>
<td>118-119</td>
<td>16</td>
<td>99.5</td>
<td>S. D. Fine</td>
</tr>
<tr>
<td>3</td>
<td>Formic acid 85% (LR)</td>
<td>46.03</td>
<td>1.193</td>
<td>100.8</td>
<td>8.4</td>
<td>85</td>
<td>Merck</td>
</tr>
<tr>
<td>4</td>
<td>m-Chloro perbenzoic acid (m-CPBA)</td>
<td>172.57</td>
<td>--</td>
<td>--</td>
<td>92.94</td>
<td>--</td>
<td>Avra</td>
</tr>
<tr>
<td>5</td>
<td>Zinc chloride</td>
<td>136.28</td>
<td>2.907</td>
<td>--</td>
<td>292</td>
<td>97.0</td>
<td>S. D. Fine</td>
</tr>
<tr>
<td>6</td>
<td>Dioctyl phthalate</td>
<td>390.54</td>
<td>0.98</td>
<td>385</td>
<td>-50</td>
<td>98</td>
<td>Merck</td>
</tr>
<tr>
<td>7</td>
<td>Zn stearate</td>
<td>632.35</td>
<td>1.095</td>
<td>--</td>
<td>120-130</td>
<td>--</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>8</td>
<td>Ca stearate</td>
<td>607.02</td>
<td>1.08</td>
<td>--</td>
<td>155</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>Stearic acid</td>
<td>284.48</td>
<td>0.847</td>
<td>383</td>
<td>69.6</td>
<td>--</td>
<td>S. D. Fine</td>
</tr>
<tr>
<td>10</td>
<td>2-Ethyl hexanol (2EH)</td>
<td>130.23</td>
<td>0.830</td>
<td>181-185</td>
<td>--</td>
<td>99</td>
<td>S. D. Fine</td>
</tr>
<tr>
<td>11</td>
<td>Sulphamic Acid</td>
<td>97.07</td>
<td>--</td>
<td>--</td>
<td>205</td>
<td>99</td>
<td>--</td>
</tr>
<tr>
<td>17</td>
<td>PVC 57-01 (PVC polymer)</td>
<td>-</td>
<td>0.49</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Reliance</td>
</tr>
</tbody>
</table>
3.3 Experimental methodology

3.3.1 Epoxidation of oleic acid, methyl oleate, vegetable oils and metallic oleates

The peracid in situ or ex situ process for epoxidation of oleic acid and various vegetable oils- sunflower, soyabean, castor and mustard was investigated through variations of following parameters: reactant molar ratio, temperature, nature of solvent, presence or absence of catalyst, stirring speed, type of per acid (peracetic, performic, m-chloroperbenzoic acid), mode and rate of addition of H₂O₂/ acetic (AA) or formic (FoA) acid, reaction period and contacting patterns (batch/ semi batch mode/ azeotropic distillation).

3.3.1.1 Peracid epoxidation of oleic acid and methyl oleate

Epoxidation was conducted in batch or semi batch mode. Since commercial grade oleic acid carries 14.9% linoleic acid (Table 3.1), the diepoxides are also obtained along with monoepoxides (Fig. 3.2).

A. In situ peracid batch epoxidation process

A 250 ml flat bottom three neck glass reactor/ six station reaction system (Carousel 6+ model, Radleys Tech., US) equipped with magnetic stirrer with speed controller and energy regulator capable of maintaining temperature within ±0.5°C, was charged with oleic acid/ methyl oleate, toluene as solvent, hydrogen peroxide and AA/ FoA at preselected molar ratio. The stirring speed was chosen to enable a constant reaction temperature to be maintained and homogenisation of the reactor composition (condition essential to provide kinetically controlled regime). In some of the experiments, the reaction flask was cooled with water to control exothermicity. The reaction was thus conducted under vigorous stirring at 50-80°C until the TLC (hexane:ethyl acetate::9:1 as developing solvent) analysis indicated the completion of the reaction (reaction period-2 hrs). It was allowed to cool and then transferred to a separating funnel. The organic layer was washed with brine (3 X 10 ml), dried over Na₂SO₄ and concentrated under reduced pressure in rotary evaporator to yield epoxidised oleic acid (EOA) as white powdery solid. In order to understand the role of catalyst, two additional batches employing conc. H₂SO₄ as catalyst were conducted. Peracid epoxidation of methyl oleate was also accomplished in a similar manner.

B. Ex situ batch peracid epoxidation

Initially, the mixture of organic acid (AA/ FoA) and conc. H₂O₂ was stirred for 30 min and preformed peracid was added to the solution of oleic acid in toluene. The reactor setup and
subsequent process was same as that reported for *in situ* batch peracid epoxidation under 3.3.1.1 A.

\[
\begin{align*}
\text{H}_3\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{C} \rightarrow \text{OH} & \quad + \quad \text{CH}_3-\text{CO}_3\text{H} \\
\text{Oleic Acid} & \quad \text{Toluene} \quad 50 - 80^\circ \text{C} \\
\text{H}_3\text{C}-(\text{CH}_2)_7-\text{HC}-(\text{CH}_2)_7-\text{C} \rightarrow \text{OH} & \\
(9,10 \text{ Epoxystearic acid})
\end{align*}
\]

Fig. 3.2 Peracid epoxidation of oleic and linoleic acid

C. Semi batch peracid epoxidation process

a. Peracid epoxidation with semi batch mode of addition of H\textsubscript{2}O\textsubscript{2} and/ or organic acid

In a typical non catalytic epoxidation setup, oleic acid and suitable solvent (toluene/ carbon tetrachloride) were charged in the beginning to the 250 ml three neck glass reactor equipped with the magnetic stirrer, dropping cylinder and energy regulator. Either hydrogen peroxide alone or the mixture of hydrogen peroxide and AA/ FoA was placed in addition cylinder and added drop wise to the oleic acid solution, maintained at 38-70\(^\circ\)C, at a rate such that the addition was completed within 1-3 hrs. The reaction was continued under vigorous stirring at 38-70\(^\circ\)C until the TLC (hexane:ethyl acetate::9:1 as developing solvent) analysis indicated the completion of the reaction (reaction period= 1-5 hrs). It was allowed to cool and then transferred to a separating funnel. The organic layer was washed with brine (3 X 10 ml), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure in rotary evaporator to yield epoxidised oleic acid (EOA) as a white powdery solid.
b. Semi batch epoxidation reactor using dean and stark setup for azeotropic distillation.

Semi batch epoxidation reactor using dean and stark setup was devised to remove water through azeotropic distillation. The mixture of oleic acid, toluene as a solvent, hydrogen peroxide and AA/ FoA at preselected molar ratio was placed in a 250 ml three neck flask, equipped with the magnetic stirrer and energy regulator and connected to the dean and stark setup for azeotropic removal of water under vacuum/ at atmospheric pressure and recycle of solvent back to the reactor. The reaction period was varied from 1-3 hrs for different reaction temperatures (45-110°C). The reaction mixture was then cooled to room temperature and subjected to the brine washing (3 X 10 ml). The removal of solvent under reduced pressure in rotary evaporator yielded EOA in white solid powder form.

EOA, obtained through batch (A/B) or semi batch (C-a/b) setup, was characterized for following analytical values determined using procedure described under section 3.4.1- acid value (AV), iodine value (IV), hydroxyl value (HV) and epoxy equivalent weight (EEW). These analytical numbers formed the basis of calculations of epoxidation conversion, yield and selectivity. FTIR and 1H NMR analysis, as described under section 3.4.4, were also conducted to provide confirmatory clues about the structure of the products. The results of the analytical characterizations have been presented in Table 3.4-3.6 and discussed under section 3.5.1. These results were also used for the kinetic and thermodynamic modeling of epoxidation as reported under Chapter 4.

3.3.1.2 Peracetic/ performic acid epoxidation of sunflower, soyabean and castor oils

Epoxidation of sunflower, castor, soyabean oil was accomplished using the same batch setup and process used for the epoxidation of oleic acid (section 3.3.1.1 A). The results of the analytical characterizations have been reported in Table 3.7 and discussed under section 3.5.2.

3.3.1.3 Performic acid epoxidation of mustard oil (EMO)

A suitable amount of mustard oil was placed in a 4 neck glass resin kettle equipped with mechanical stirrer with speed regulator, dropping cylinder, thermometer pocket and energy regulator. Calculated amount of formic acid, nano alumina (5% by wt on mustard oil) activated by conc. H₂SO₄ as a catalyst and hexane as solvent, based on preselected molar ratio, were added to the resin kettle and the mixture was stirred for about half an hour at 70°C. Then predefined amount of 50% aqueous H₂O₂ was placed in dropping cylinder and added over the period of 1 hr. The reaction was continued at 70°C under vigorous stirring for 4 hrs (Fig. 3.3). Then the reaction mixture was cooled to room
temperature and the organic layer was collected after brine washing with H₂O (3 X 10 ml). The solvent- hexane was removed under reduced pressure using rotary vacuum evaporator (Supervac model with vertical column, RPM= 400, Superfit India). The product EMO was analyzed for AV, HV, IV, EEW, viscosity and pour point (refer section 3.4.1 and 3.4.2 for procedural details) and the corresponding results are recorded in Table 3.7. FTIR analysis (section 3.4.4) was also performed for functional group analysis.

The process adopted for ring opening of EMO has been presented under section 3.3.2.

![Fig. 3.3 Performic acid epoxidation of mustard oil (EMO) using acid activated nano alumina catalyst](image)

**3.3.1.4 Epoxidation of metallic oleates**

**A. Preparation of metallic salts of oleic acid**

**a. Preparation of sodium oleate**

Dissolve given amount of oleic acid in ethanol at 1:2 w/v ratios. Then add predetermined (based on AV titration) amount of 1 N NaOH to this solution and reflux the solution for 10 min. Evaporate the solvent through rotary vacuum evaporator to obtain sodium oleate.

**b. Preparation of potassium oleate**

Ethanolic solution of oleic acid (1:2 w/v) was refluxed with predetermined amount of 1 N KOH for 10 min evaporate the solvent through rotary vacuum evaporator to obtain potassium oleate.

**c. Metathetic preparation of zinc oleate**

It was prepared by metathesis/ coprecipitation reaction between sodium oleate and zinc chloride in alcohol solution (Fig. 3.4). Dissolve 0.022 gm zinc chloride and 0.044 gm
sodium oleate at 1:2 molar ratio slowly, with continuous stirring, in a mixture of solvent composed of 3 parts of ethanol, 2.5 parts of distilled water and 5 parts of cyclohexane. Reflux the mixture at 70\(^0\)C for 4 hrs. Upper organic layer was washed 3 times with 30 ml warm distilled water. Solvent was evaporated through rotary evaporator. The white zinc oleate product was dried in oven at 60\(^0\)C to constant weight (Fig. 3.4).

\[
2 \text{R-COO}Na + \text{ZnCl}_2 \rightarrow (\text{RCOO})_2\text{Zn} + 2\text{NaCl}
\]

**Fig. 3.4 Metathetic preparation of zinc oleate.**

The metallic oleates were epoxidised as per following setup and process.

**B. m-Chloro-perbenzoic acid (m-CPBA) epoxidation of metallic oleates**

The m-CPBA epoxidation (Fig. 3.5) of metallic oleates, as described below, were carried out in six station reaction assembly (Carousel 6+ model, Radleys Tech., US) equipped with magnetic stirring system (RPM=500) and electrical heating system with energy regulator capable of maintaining reaction temperature within ±0.5\(^0\)C.

**Fig. 3.5 m-CPBA epoxidation of zinc oleate.**

**a. Synthesis of epoxidised zinc oleate**

To the continuously stirred solution of zinc oleate in ethyl acetate (1:2 w/v), add solution of m-CPBA in ethyl acetate (1:3 w/v) drop wise at such a rate that the addition was completed within 1hr. The zinc oleate: m-CPBA reactant molar ratio was chosen as 1:2.3. Continue stirring until TLC (hexane:ethyl acetate::9:1) indicated completion of the reaction (1 hr). Then wash with 10% Na\(_2\)CO\(_3\) (1 X 100 ml) to obtain neutral pH followed by extraction with hexane for transfer of epoxidised oleic acid to hexane layer and that of epoxidised zinc oleate to aqueous layer. Concentrate the aqueous layer and then add acetone. Blow the nitrogen gas continuously through the product solution to remove water. Dissolve the product in isopropyl alcohol and filter the solution to eliminate impurities.
Evaporate the solvent through rotary evaporator to get white solid product of epoxidised zinc oleate.

**b. Synthesis of epoxidised sodium oleate**

To the stirred solution of sodium oleate in ethyl acetate (1:2 w/v), add solution of m-CPBA in ethyl acetate (1:3 w/v) drop wise at such a rate that the addition was completed within 1 hr. The sodium oleate: m-CPBA reactant molar ratio was chosen as 1:1.5. Continue stirring until TLC (hexane:ethyl acetate::9:1) analysis indicated completion of the reaction (1 hr). Then wash with 10% Na₂CO₃ (1 x 100 ml) to obtain neutral pH. Extract this solution with diethyl ether. Ethereal layer carries epoxidised oleic acid while aqueous layer holds epoxidised sodium oleate. Brine precipitation (2 X 100 ml) and subsequent drying of the product on anhydrous sodium sulphate affords the white solid product of epoxidised sodium oleate.

**c. Synthesis of epoxidised potassium oleate**

To the stirred solution of potassium oleate in ethyl acetate (1:2 w/v), add solution of m-CPBA in ethyl acetate (1:3 w/v) drop wise at such a rate that the addition was completed within 1 hr. The potassium oleate: m-CPBA reactant molar ratio was chosen as 1:1.5. Continue stirring until TLC (hexane:ethyl acetate::9:1) analysis indicated completion of the reaction (1 hr). Then wash with 10% K₂CO₃ (1 x 100 ml) to obtain neutral pH. Extract this solution with diethyl ether. Ethereal layer contains epoxidised oleic acid and aqueous layer carries epoxidised potassium oleate. To aqueous layer, add KCl solution to precipitate epoxidised potassium oleate.

The metallic salts of epoxidised oleate were analyzed for IV, EEW and TGA characteristics (refer section 3.4.1 and 3.4.3 for procedural details) and the corresponding results are recorded in Table 3.8. FTIR analysis (section 3.4.4) was used as a qualitative tool for the confirmation of the formation of epoxy group at 1158, 845 and 822 cm⁻¹.

**3.3.2 Preparation of biolubricants based on oxirane ring-opening reaction of epoxidised mustard oil (EMO) with 2-ethyl hexanol (2-EH)**

The ring opening and simultaneous partial esterification of EMO with 2-ethyl hexanol (2-EH) is a one-pot, one-step process (Fig. 3.6). The effectiveness of following materials, as catalysts for oxirane ring-opening reaction of EMO with 2-EH, was examined: conc. H₂SO₄, sulphamic acid, methane sulphonic acid. The catalyst loading was varied between 3-6%. The reaction mixture, containing EMO, 2-EH and catalyst, was placed in a six station reaction assembly equipped with magnetic stirring system (RPM=500) and electrical heating system with energy regulator capable of maintaining reaction...
temperature within ±0.5°C. The mixture was heated to 120°C and the reaction was continued under vigorous stirring until TLC (hexane:ethyl acetate::9:1 as developing solvent) indicated the completion of the reaction (reaction period= 3-6 hrs). The reaction mixture was then cooled to room temperature followed by addition of ethyl acetate. The organic layer was washed first with NaHCO₃ solution and thereafter with brine (3 X 50 ml) and dried over Na₂SO₄. The removal of solvent was accomplished in rotary vacuum evaporator to yield the desired biolubricant product. It was analyzed for obtaining following characteristics: HV, EEW, viscosity, viscosity index, oxidative stability and pour point (refer section 3.4.1 and 3.4.2 for procedural details) and the corresponding results are recorded in Table 3.9. FTIR analysis (section 3.4.4) was used to monitor the reaction by noting the disappearance of epoxy group at 1158, 845 and 822 cm⁻¹ in FTIR spectrum. The disappearance of peak at 2.8-3.2 ppm in the ¹H NMR spectrum (section 3.4.4) corresponding to the hydrogen in the epoxy proton provided the confirmation of product structure. The discussion on overall results is presented under section 3.5.4.

![Fig. 3.6 The oxirane ring opening of epoxidised mustard oil with 2-ethyl hexanol](image)

### 3.3.3 Preparation of PVC composite using epoxidised zinc oleate (EZnOA) as additive

PVC polymer composites were prepared using 30 phr (parts per hundred part of resin) of dioctyl phthalate (DOP), 0.5 phr of stearic acid as internal lubricant/processing aid, and 1 phr of stabilizer (EZnOA, EZnOA + Zn stearate, Zn stearate + Ca stearate) as shown in Table 3.3. These composite formulations were melt intercalated using a Brabender Plastograph EC equipped with an electrically heated mixing head (W 50 EHT mixer) having 55 cc processing volume capacity and two non interchangeable rotors. The processing temperature, rotor speed, and blending time were set at 155°C, 30 rpm, and 10 min, respectively. The sample volume of each blending was kept 90% of the actual
volume capacity of the mixer. The sample mass was kept 62 g. The composites, obtained in the form of lumps, were crushed to get the coarser particles/ granules (approximately 3-4 mm size) suitable as feed for compression moulding to obtain tensile specimens.

### Table 3.3 Formulation of PVC composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>Concentration (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>PVC</td>
<td>100</td>
</tr>
<tr>
<td>DOP</td>
<td>30</td>
</tr>
<tr>
<td>EZnOA</td>
<td>1</td>
</tr>
<tr>
<td>Zn stearate</td>
<td>_</td>
</tr>
<tr>
<td>Ca stearate</td>
<td>_</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The PVC composites were characterized by using thermo gravimetric analysis (TGA), UTM, Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX), colour matching spectrophotometer, congo red test, static oven test, FTIR (refer section 3.4.3 and 3.4.4 for procedural details) and the results of analysis have been interpreted under section 3.5.5.

### 3.4 Techniques for analysis and characterizations

The physical and chemical characterisations of raw materials (oil/ oleic acid), intermediates and epoxidised products as well as the reaction monitoring were conducted by using various analytical methods. The functional group tracking, structural confirmations and thermal/ mechanical/ flow characteristics of % conversion, the intermediates and the final target molecules were carried out by using sophisticated instrumental techniques.

#### 3.4.1 Analytical techniques for monitoring of epoxidation and ring opening reactions

**3.4.1.1 Acid value (AV)**

The AV determination was performed using procedure given under section 2.4.1.1 of Chapter 2. This determination provides molecular weight of pure fatty acids and % free fatty acids (% FFA) for oils.
3.4.1.2 Hydroxyl value (HV)
The HV determination was performed using procedure given under section 2.4.1.2 of Chapter 2. It provides information on stability of oxirane oxygen or extent of ring opening reaction.

3.4.1.3 Epoxy equivalent weight (EEW)
EEW determination provides extent of formation of oxirane oxygen and is defined as grams of epoxidised oil or fatty acids containing one gram equivalent of epoxy group. 0.5 to 1 gm of epoxidised compound was mixed with 25 cc, of hydrochlorination reagent (2.6 ml conc. HCl + 100 ml methyl ethyl ketone). Shake the flask vigorously and keep aside for 15 min, to ensure complete reaction between HCl and epoxidised compound followed by addition of 25 cc, neutral alcohol. It was then back titrated against standardized 0.2 N alc. NaOH solution using cresol red as indicator. The end point of titration was from red to yellow to violet. Blank titration was also carried out. EEW was calculated using Eq.3.1.

\[
EEW = \frac{\text{Weight of sample in gm} \times 1000}{(\text{blank-sample}) \times N_{\text{NaOH}}} \quad \text{Eq.3.1}
\]

Where \(N_{\text{NaOH}}\) is the exact normality of NaOH (in MeOH).

For determination of EEW of oleic acid, sample titration in absence of hydrochlorination reagent was conducted against 0.2 N alc. NaOH and the corresponding burette reading was added in blank reading.

3.4.1.4 Iodine value (IV)
The IV determination was performed using procedure given under section 2.4.1.3 of Chapter 2. This method is used to monitor reaction of double bond with oxygen provided by peracids. While IV provides epoxidation conversion, EEW supplies yield of epoxidised product.

3.4.2 Techniques for evaluation of 2-ethyl hexanol (2EH) esters of epoxidised mustard oil (EMO) as lubricant

3.4.2.1 Pour point analysis
Pour points of mustard oil, EMO and 2-EH esters of EMO were determined by following ASTM method D 97 at an accuracy of ±3°C. Test jars, thermometers, corks, and rubber rings fully met ASTM D 97 specifications. All runs were carried out at least in duplicate. Sample temperature was measured in 5°C increments at the top of the sample until it stopped pouring.
3.4.2.2 Viscometric analysis and determination of viscosity index
The viscosities of mustard oil, EMO and 2-EH esters were estimated using Ostwald viscometer at two different temperatures - 40 and 100°C. The viscosity index was then determined according to ASTM D 2270 method.

3.4.2.3 Oxidative stability analysis
It was determined by following IEC method 60296-C. Place the 25 g of sample and Cu wire of 90 cm length and 1-2 mm thickness in a test tube carrying rubber cork with two glass tubings. Through one glass tubing, air was allowed to bubble continuously through the sample. The outlet of second tubing was immersed in beaker carrying water. The test was conducted for 160 hrs (> 6 days). The average of AV of degraded product in test tube at the end of 6 days and AV of water determined on daily basis was reported as (total acid number) TAN. % sludge content was determined through extensive dilution of degraded product with demineralised water (5 lit) and subsequent filtration of the diluted product.

3.4.3 Techniques for evaluation of plasticization and stabilization activity of epoxidised zinc oleate (EZnOA) in PVC polymer composites

3.4.3.1 Congo Red Test
The dehydrochlorination method based on congo red test (VDE 0472, part 614, ISO 182) was conducted to evaluate the residual heat stability of PVC composites which is very common in cable industries. The PVC sheet sample was cut into small pieces and place 1 gm sample from each batch was placed in a test tube. The tube was then immersed in a glycerine bath maintained at 200°C. HCl released from the sample as a result of thermal dehydrochlorination causes a color change of moist congo red or universal indicator paper on top of the test tube. Time interval between the insertion of the sample in the heating medium and the detection of colour change was determined as measure of residual heat stability.

3.4.3.2 Static Oven Test and Colour Matching Spectrophotometer
The prepared PVC composites were heated in a static air oven at 140°C for 90 min and analysed for colour change using colour matching spectrophotometer (Gretag Macbeth, Color Eye XTH, Novoscan). It was used to determine CIE (internationally agreed system of colour specification) values for PVC film through comparison with original sheet as corresponding reference standard using D65 illuminant. The assessment of colour of PVC film was conducted to understand the change in hue (H), chroma (C), lightness (L), (a) (a⁺ - redness, a⁻ - greenness), and (b) (b⁺ - yellowness, b⁻ - blueness) as a result of thermal
degradation. The colour differences between the original and heated PVC films were expressed on the basis of $\Delta E$ value (Eq. 3.2)

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2}$$  \hspace{1cm} \text{Eq. 3.2}

3.4.3.3 Thermo Gravimetric Analysis (TGA)

Thermogravimetric analyzer (TGA, Shimadzu Japan, model: TGA-50=50H) was used to determine thermal stability characteristics of the epoxidised zinc oleates and PVC composites using temperature programming from 0 to 600°C at the heating rate of 10°C/min. Testing was carried out under inert atmosphere (N$_2$) with a flow rate of 50 ml/min to remove all corrosive gases and avoid thermoxidative degradation. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed.

3.4.3.4 Universal Testing Machine (UTM) measurements

The tensile behavior of the PVC composites, plasticized and stabilised with epoxidised zinc oleate and other additives, was evaluated according to the ASTM D 638, using Universal Tensile Tester LR50K [Lloyd Instrument Ltd., U. K.] at the crosshead speed of 25 mm/min.

3.4.3.5 Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX)

Micro-structural characterization of the filmed samples of PVC composites was conducted by using Field Emission Scanning Electron Microscope (FESEM) and Energy dispersive X-Ray (EDX). The instrument details are given under section 2.4.2.6 of Chapter 2. The changes in surface morphology of PVC composites as a function heating at 140°C for 90 min were examined through FESEM analysis. At least two different microphotographs were taken at different magnifications. The PVC composites were characterized by an Energy Dispersive X-ray (EDX) instrument to investigate the effect of heating at 140°C for 90 min on the elemental composition of the samples. Either two or three points from the cross section areas of PVC films were chosen and investigated. Average values were obtained.

3.4.4 Instrumental Analysis

3.4.4.1 Fourier Transform Infra Red (FTIR) spectroscopy

FTIR analysis was performed using procedure described under section 2.4.2.1 of Chapter 2 to monitor the progress of epoxidation/ ring opening reaction.
3.4.4.2 $^1$HNMR spectroscopy

The $^1$HNMR spectra were recorded on Bruker Avance 400 spectrometer (Bruker, Rheinstetten, Germany) operated at 400 MHz using CDCl$_3$ as solvent.

3.4.4.3 Gas Chromatography (GC)

The determination of fatty acid composition of sunflower/ mustard/ castor/ soyabean oils and oleic acid by GC was performed using procedure given under section 2.4.2.2 of Chapter 2.

3.4.4.4 X-Ray diffraction (XRD) spectrometer

XRD analysis of nanoalumina was performed. The instrument details are given under section 2.4.2.5 of Chapter 2.

3.5 Results and discussion

3.5.1 Synthesis and characterization of epoxidised oleic acid

The procedure adopted for the non-catalytic/ catalytic in situ/ ex situ peracid epoxidation of oleic acid (OA), so called Prilezhaev epoxidation process and the corresponding specific setup- batch/ semibatch has been described under section 3.3.1.1 A-C. The peracids were generated by reacting the relevant acid with hydrogen peroxide under pre-selected conditions and molar ratio. The course of the reaction was represented by changes in the iodine value (IV), epoxy equivalent weight (EEW) and hydroxyl value (HV) with the parameters under study to estimate the degree of double bond conversion in oleic acid and the selectivity of transformation to epoxidized oleic acid in relation to the total amount of oleic acid undergoing the transformation. The methodologies used for determination of analytical parameters are given under section 3.4.1. The results of investigations have been presented in Table 3.4-3.6. FTIR and NMR analysis was also performed to understand the progress of epoxidation. Epoxidised oleic acid with higher oxirane oxygen value and lower iodine value is considered to be of better quality. Almost complete double bond conversion of oleic acid was obtained within 3 hrs. However the control of reaction parameters is essential to ensure oxirane stability. Since there is abundant possibility for side reactions, it is important that the epoxidation process be carried out at low temperature (50$^\circ$C) and short reaction period (1-2 hrs).

FTIR Spectroscopic analysis

Fig. 3.7-3.9 presents spectra of epoxidised oleic acid. A characteristic peak of oxirane was observed at 910-945 cm$^{-1}$ indicating the conversion of the polyene to polyepoxide. The intensity of this signal is more in batch E10 and E8 (in situ peracid epoxidation of oleic acid), E18, E16 (in semi batch reactor), The identification of this
signal and the diminishing band of double bonds at 3020 cm\(^{-1}\), are the complementary evidences of the occurrence of epoxidation reaction. Ring breathing frequency of epoxy ring (C-O-C stretching from oxirane vibration) at 1200-1250 cm\(^{-1}\) was also observed. Absence of signal at 3425 cm\(^{-1}\) indicates ring opening side reaction was not observed.

Fig. 3.7 FTIR spectra of \textit{in situ} peracid batch epoxidation of oleic acid
Fig. 3.8 FTIR spectra of epoxidation of oleic acid in semi batch reactor
Fig. 3.9 FTIR spectra of epoxidation of oleic acid in semi batch reactor using Dean and Stark setup
NMR analysis:

Fig. 3.10 presents \(^1\)HNMR spectrum of epoxidised oleic acid. The signals associated to the epoxy group were: -CH- hydrogens of epoxy group \((-\text{CH-O-CH}^-\) are sited at \(\delta\) 2.4 ppm with integral 0.2086, -CH- hydrogens adjacent to epoxy group appeared at \(\delta\) 1.40 ppm with 6.837 integral, -CH\(_2\)- hydrogens between two epoxy group were sited at \(\delta\) 1.5 ppm with integral value 0.6492. The signal at \(\delta\) 1 ppm was due to hydrogens of ending methyl group \(-\text{CH}_3\)\(-\text{CH}_2\)\(_n\), the integral value for this peak was 0.792. The signal at \(\delta\) 1.20-1.52 ppm was due to methylene hydrogens at integral value -CH\(_2\)- at integral value 15.36. The signal at \(\delta\) 1.57 ppm is due to hydrogens \(\beta\) to carbonyl group. The acidic protons were sited at \(\delta\) 9.2 ppm at integral 1.28.

Fig. 3.10 \(^1\)HNMR of epoxidised oleic acid

3.5.1.2 Methods of calculations of conversion, yield and selectivity of epoxidation

Since the characterisations used to follow the epoxidation reaction- IV (g of Iodine/100g EOA), HV (mg KOH/g of EOA) and EEW (g EOA/ oxirane group) were defined on different basis, they were converted into IN (Iodine Number- gmol of double bond/100g OA), HN (Hydroxy Number-gmoles OH/100g of OA) and EN (Epoxy Number-gmol of epoxy/100g OA), respectively to ensure the common basis of comparison and permit calculations of conversion, yield, and selectivity with due ease. The adaptations of IV, HV and EEW into IN, HN, EN respectively were carried as given below:
i. To convert $IV_t$ into $IN_t$, multiply $IV_t$ (IV at time t) by 0.00394 i.e. $IN_t=0.00394X IV_t$

ii. To convert $EEW_t$ into $EN_t$, divide 100 by $EEW_t$ (EEW at time t) i.e. $EN_t=100/EEW_t$

iii. To convert $HV_t$ into $HN_t$, by $HV_t$ (HV at time t) by 561 i.e. $HN_t=HV_t/561$

The progress of the epoxidation reaction was monitored in terms of calculations of oleic double bond conversion (% $X_{IN}$), epoxidation conversion (% $X_{EN}$), epoxidation yield ($% Y_{EN/IN}$) and selectivity ($S_{EN/ROPN}$). The logic for calculations of double bond conversion, epoxy formation, epoxy yield and selectivity of epoxidation was as presented below.

% double bond conversion based on iodine number (IN) = $% X_{IN} = \frac{IN_t-IN_0}{IN_0} \times 100$ Eq.3.3

Eq.3.3 represents the fraction of total double bonds in oleic acid undergoing the epoxidation, where $IN_0$= initial iodine number of oleic acid before epoxidation= 0.3861 mol/100g OA and $IN_t$= iodine number (mol/100g OA) of oleic acid after epoxidation for reaction time t.

% Epoxidation conversion calculated from epoxy number $% X_{EN} = \frac{EN_t}{EN_{max}} \times 100$ Eq.3.4

Here $EN_t$ represents epoxy number (mol/100g OA) of oleic acid after epoxidation for reaction time (t) and $EN_{max}$ is the epoxy number of oleic acid calculated from the initial molar concentration of double bonds (i.e. max. epoxy formation at 100% selectivity).

Since $EN_{max} = IN_0 = 0.3861$ mol/100g OA , dividing Eq. 3.4 by Eq. 3.3, we obtain Eq. 3.5 for the yield of EOA calculated from the epoxy number and iodine number.

Yield= $% Y_{EN/IN} = [\text{moles of desired product (epoxy groups) formed}] / [\text{moles of double bond in oleic acid reacted}]$

$% Y_{EN/IN} = \frac{EN_t}{IN_0-IN_t} \times 100$ Eq.3.5

It represents fraction of total double bonds in oleic acid reacted that is converted into desired product i.e. oxirane oxygen.

Selectivity= (moles of desired product formed) / (moles of undesired material formed)

$S_{EN/ROPN} = \frac{EN_t}{ROPN_t} = \frac{C_{EO}}{C_{ROP}}$ Eq. 3.6

Where $ROPN_t$ represents hydroxy acetate number (mol/100g OA) of oleic acid after epoxidation for reaction time (t) (calculated on the basis of material balance calculations
presented under Chapter 4, Section 4.5 B) and the term C represents corresponding concentrations.

3.5.1.3 The influence of reaction parameters on the batch epoxidation of oleic acid (OA) with peracetic acid/ performic acid (PAA/ PFA)

The influence of reaction parameters such as temperature (50-80°C), type of organic acid (glacial acetic acid (AA)/ formic acid (FoA)), molar ratio of H₂O₂/ OA (5-10:1), molar ratio of AA/ FoA to OA (5-6/1, 6-7/1), stirring speed (500–1000 rpm), presence or absence of H₂SO₄ catalyst and reaction time (30 min-180 min) on the epoxidation of double bonds in oleic acid as well as on the oxirane ring stability were investigated in this study and the optimum conditions were established. Although H₂SO₄ is known to be the most efficient and effective epoxidation catalyst, but for reasons presented under section 3.1.1, non catalytic epoxidation process was emphasized in present investigation. The selection of processing parameters (e.g. temperature, stirring speed, reactant molar ratios/ concentrations) has to be such that the epoxidation will proceed faster than the generation of peracid. Otherwise, generated peracid may decompose under the reaction conditions and the process would proceed slowly. In addition, the reaction environment contains water and organic acids, which may cause the decomposition of the epoxy groups e.g. due to hydrolysis or acylation, which needs to be minimised. Besides process optimization, the effects of specific peracid generation mode—*in situ* vs *ex situ* process were studied. The results are presented in Table 3.4.

**Effect of stirring speed**

It is essential to operate the process at highest feasible speed to eliminate the effect of resistance to mass transfer of peracetic acid (PAA)/ performic acid (PFA) from aqueous phase to organic phase and ensure that the reaction was kinetically controlled. Upper stirring speed limit was set by two considerations. Firstly it was decided by the requirement of homogeneity which necessitates higher mixing speed. On the other hand sometimes the epoxidation proceeds slowly at higher rpm and a concurrent decrease of epoxy number take place. This was a result of deleterious reaction such as hydroxy acetylation and hydroxylation (section 4, Chapter 4), esterification, and rearrangement of the oxirane groups of the epoxidized oleic acid. Hence the epoxidation was conducted at the optimum stirring speed of 500 rpm.

**Influence of reaction time (t, min)**

In order to investigate the influence of reaction time (t) on the course of epoxidation, syntheses were carried out for 30, 60 and 120 min (batches E1, E2, E3
respectively in Table 3.4). In all the three batches, the molar ratio of oleic acid (OA):H$_2$O$_2$:acetic acid (AA):1:4.9:4.9 was maintained. No catalyst was employed and the reaction temperature (T) was 50°C. In the initial period of 30 min, marginal drop (11 units) in iodine value (IV) with consequent formation of oxirane ring (0.0435 gmoles of epoxy/100g) was observed. Although epoxide formation was negligible, there was no ring opening as evidenced by zero hydroxyl value (HV). Thus although % double bond conversion was just 11.4, the epoxy yield was 98.6%. When the process was carried out under these conditions for longer period, the highest epoxy formation (EN= 0.1622 gmoles/100g) was achieved after 2 hrs. However the rise in epoxy formation was not proportional to the drop in IV because of ring opening reactions (HV= 87.6). Corresponding to the 74% conversion of double bonds, the conversion to epoxies and epoxy yield were just 42% and 56.5%, respectively. Epoxy conversion refers to the epoxy formation in relation to the theoretically maximum epoxies obtainable under 100% selective transformation of double bonds to epoxies. Epoxy yield, on the other hand, refers to epoxy formation in relation to the overall double bond conversion (i.e. 56.5% of 74%). Thus epoxy yield calculations takes into account the occurrence of side reactions and was found to decrease from 98.6% to 56.5%. After 1 hr reaction period, the process becomes non selective. Hence, the reaction time of 1 hr was the most advantageous for minimization of ring opening reactions.

**Effect of initial hydrogen peroxide to oleic acid molar ratio (H$_2$O$_2$:OA)**

In above referred studies on influence of retention time (t), it was observed that in batch E3 the degradation reactions caused the epoxidation process to be nonselective. Hence in batch E4 (Table 3.4), the availability of H$_2$O$_2$ was doubled to speed up the *in situ* generation of PAA and thereby increase epoxy yield. Amount of toluene was also doubled to counter balance the rise in water content of the batch with increased supply of H$_2$O$_2$. All other parameters (t, T, OA:AA) were similar to those of previous batches. With an increase in hydrogen peroxide-to-ethylenic unsaturation molar ratio, the double bond conversion was slightly lower to that reported for batch E3 but epoxy conversion, yield and selectivity were marginally increased. Hydrogen peroxide was consumed in the process of generation of PAA with byproduct water formation, hydrogen peroxide gets continuously diluted. Hence an excess of hydrogen peroxide (or higher conc. of H$_2$O$_2$) relative to ethylenic unsaturation was considered reasonable for maintaining higher epoxy yield i.e. reduced possibility of oxirane degradation. The probable reason for slight reduction in double bond conversion could be due to the reduced rate of transfer of PAA
from aqueous phase to organic region (partial development of diffusion controlled regime). Higher availability of initial moles of H₂O (due to increased supply of H₂O₂ at 50% conc.) in relation to AA (3.83) in comparison to 1.95 in batch E3 could be the reason for slow transfer of peracid. This also implied the reduced availability of PAA for hydrolysis of epoxy ring in organic phase. In addition, interpretation of results of same batch E4 in terms of AA availability in following section provides further inputs on epoxidation of OA.

**Effect of initial acetic acid/oleic acid molar ratio and concentration of acetic acid**

Acetic acid (AA) takes part in the overall reaction as a catalyst in the formation of oxirane ring and as a reactant in the hydrolysis of the oxirane ring. To attain the maximum oxirane oxygen content, the optimum level of the AA should be maintained which also provides sufficient acid for the formation of peracetic acid. In order to accelerate the PAA generation rate, higher initial AA/OA molar ratio was maintained and role of AA as reactant for ring degradation reactions was contained by reducing its concentration (e.g. through increased availability of H₂O₂ and/ or solvent). The batch E4 (Table 3.4) retains same initial AA/OA molar ratio of 4.9:1 of batch E3 but the concentration of AA was lowest- 2.2 gmoles/lit (Table 4.4 in Chapter 4). Under these conditions, the selectivity of transformation of the unsaturated bonds in OA to the epoxy groups was found to be the highest.

**Influence of solvent**

The presence of an inert solvent like toluene in the reaction mixture stabilized the epoxide product and minimized the side reactions, such as the opening of the epoxy ring. The yield and selectivity results for batch E4 explained the positive influence of doubling of solvent availability along with doubling of H₂O₂.

Batch E5 was conducted using butanol as solvent. All other reaction parameters were same as that of batch E4. The increase in double bond conversion efficiency over those in batches E3 and E4 highlighted the role of slightly polar solvent-butanol in promoting the ease of transfer of PAA from aqueous phase to organic region. Acetic acid (AA) regenerated after epoxidation must transfer itself from organic to aqueous phase. Now due to the affinity between butanol and AA, the regenerated AA may be slow in leaving the organic phase. The longer presence of AA may promote ring degradation reaction which explained the drop in yield and selectivity from 59 to 55 and from 1.9 to 1.67, respectively. Hence in spite of more drop in IV, epoxy formation remains more or
less same. Thus selectivity of epoxy formation was governed by several inter related parameters, which cannot be considered in isolation.

In all subsequent batches, toluene was retained as solvent for ensuring oxirane stability.

**Influence of temperature (T) on epoxidation of oleic acid**

The lower double bond conversion in E4 formed the basis of planning of batch E6 and E7 at higher temperature of 80\(^{\circ}\)C. Batch E6 retained the reaction parameters of batch E3 except temperature (T). The 30\(^{\circ}\)C rise in temperature in Batch E6 permitted increase in double bond conversion efficiency to 94\%, a 27\% rise over that for batch E3, all other conditions remaining same. However there was fall in epoxy yield and selectivity which implied that around 57\% of total double bond conversion proceeded for ring opening as against 43.5\% for batch E3. Thus higher reaction temperature caused simultaneous rise in rate of epoxidation and oxirane ring opening reactions.

Batch E4 achieved marginally better selective and stable formation of epoxy groups but the double bond conversion was reduced. Batch E6 achieved higher double bond conversion at the expense of fall in selectivity. To achieve higher double bond conversion while ensuring oxirane ring stability, batch E7 employing same molar ratio as that of batch E4, was conducted at 80\(^{\circ}\)C. In order to increase PAA availability for same molar ratio, solvent to water molar ratio of E3 was selected. In batch E4, the solvent content was doubled. In present batch E7, although \(\text{H}_2\text{O}_2\) was doubled over E6, the same solvent ratio was retained. Now there was appreciable rise in, epoxy conversion, yield and selectivity over those for batch E6. However the results obtained for batch E4 at 50\(^{\circ}\)C could not be reproduced for batch E7 conducted at 80\(^{\circ}\)C. Increasing temperature showed a favorable effect on the formation of PAA. This resulted not only in more rapid epoxidation, but also in higher rate of hydrolysis (oxirane cleavage) of the product. Reaction at lower temperature showed lower rate but gave more stable oxirane ring. The change in maximum oxirane content for the 30\(^{\circ}\)C increase in temperature appeared insignificant and this implied that moderate temperatures of 50\(^{\circ}\)C were more appropriate for epoxidation of oleic acid with PAA generated *in situ* for optimum oxirane levels at which hydrolysis rate was not high. But this fixed the maximum double bond conversion efficiency.

**Effect of \(\text{H}_2\text{SO}_4\) catalyst**

So far all batches were conducted under non catalytic mode. Since the selectivity of Batch E2 (i.e. conduction of reaction for 60 min at 1:4.9:4.9 molar ratio) was found to
be highest, batch E8 was planned with following conditions: 1% H$_2$SO$_4$ catalyst, rise in H$_2$O$_2$ as well as acetic acid molar ratio to 1:6.3:6.3 from 1:4.9:4.9 of E3 and 1 hr reaction period. With use of H$_2$SO$_4$ as catalyst, the reduction of IV to 5.4 was achieved within 1 hr at 50°C in comparison to batch E6 at 80°C for 2 hrs. However there was extensive drop in epoxy yield and selectivity indicating the failure H$_2$SO$_4$ as catalyst in promoting selectivity. The epoxide EOA was the desired product. The products of epoxidation are capable of further reaction if there was even a trace of H$^+$ ions. In all previous investigations, PAA was formed from acetic acid and H$_2$O$_2$ in absence of sulfuric acid as catalyst. Hence stability of oxirane oxygen was ensured. Thus the use of H$_2$SO$_4$ was avoided in all batches meant for facilitation of selective epoxidation process.

**Ex situ process**

All previous batches were based on *in situ* generation of PAA. The presence of an acid during *in situ* epoxidation caused the opening of the oxirane ring with formation of undesirable secondary products. Hence in all previous *in situ* batches, the highest attainable epoxy yield, corresponding to the double bond conversion of 75% within 2 hrs at 50°C, was 60%.

The batch E9 was conducted in *ex situ* mode. The PAA was generated separately by mixing H$_2$O$_2$ and acetic acid for 30 min. The epoxidation parameters (molar ratio, temperature and time) were same as those of batch E8 except no employment of catalyst. Thus *ex situ* process was operated with higher concentration of H$_2$O$_2$ and acetic acid. The adoption of *ex situ* process caused 80% double bond conversion with 100% transformation to epoxy group only (*Table 3.4*). The epoxy yield was 100%. This was because the *ex situ* process ensured high availability of PAA (almost 23 moles of PAA/ mole of oleic acid). Restriction of reaction period to 1 hr and monitoring of reaction exotherm was very much essential (so as to contain reaction temperature to 50°C) which made possible the feasible the 100% epoxy yield. Thus *ex situ* mode of epoxidation achieved more double bond formation efficiency and stability of oxirane oxygen formation. Similar results, presented under PFA epoxidation, were obtained using *ex situ* PFA epoxidation (Batch E11).

Since preformed PAA was freed from H$^+$ ions and water, the extent of ring opening reactions was minimized. On the contrary, *in situ* formation of PAA in the reaction mixture will not be selective owing to the presence of H$^+$ ions and water of reaction. In homogeneous acid-catalyzed *in situ* PAA generation, free acid (H$^+$) is liberated, and also AA is available for ring opening reactions to proceed.
Performic acid batch epoxidation

So far in all batches (E1-E9), AA was used as the source of peracid which is cheap and easily available. The rate of generation of PFA is known to be much greater than that of PAA.

Batch E10 was based on PFA epoxidation using higher H$_2$O$_2$ and formic acid (FoA) at a molar ratio of OA:H$_2$O$_2$:FoA::1:9.9:7 and 50°C temperature. The process results in lowest IV drop (IV= 15) amongst all non catalytic processes employed at 50°C. In comparison to the batches E3, E4 and E5, higher epoxy formation (54%), yield (64%) and selectivity (2.3) was obtained. With these batches, E10 shared certain common parameters (reaction temperature, time, no catalyst, similar molar ratio, solvent). This indicated that PFA was more selective in epoxidation over that by PAA.

This success was attained in *in situ* mode of operation. When PFA generation was carried out in *ex situ* mode (Batch E11), the double bond conversion of 93% was attained within 1 hr at 50°C. This was similar to those obtained with batches E6, E7 and E8, But batches E6 and E7 attained these conversions at 80°C while H$_2$SO$_4$ was employed as catalyst in batch E8. The epoxidation in these 3 batches however were completely nonselective and associated with extensive ring opening results. In comparison, the combination of *ex situ* process and use of PFA permitted 100% retention of oxirane ring.

Epoxidation of methyl oleate

The primary feedstock for oleochemicals as presented in Chapter 1 could be fatty acid, FAME, metallic soap and the oil itself. The investigations on *in situ* and *ex situ* PAA and PFA batch epoxidation of oleic acid have been already reported. The batches E12 and E13 were conducted on methyl oleate. H$_2$SO$_4$ was employed as catalyst at 1%. All parameters were similar to those employed for batch E8 (peracid epoxidation of oleic acid).

The comparison of results of batch E12 with those of batch E8 have indicated that under similar conditions, the double bond conversion efficiency of methyl oleate drops down from 94.5% to 69.5%. Thus methyl esters were found to be less reactive feedstock in comparison to oleic acid. Although double bond reactivity was less, the process permitted higher selectivity and epoxy ring stability. In this respect, the results were similar to that of batch E4 (this batch attained highest ring stability results amongst all batches of PAA *in situ* epoxidations). PFA *in situ* epoxidation of methyl oleate (batch E13) presented results similar to those of PAA epoxidation of methyl oleate (batch E12).
Table 3.4 *In situ* and *ex situ* peracid batch epoxidation of oleic acid (OA) and methyl oleate (mOA)\(^1\)

Solvent used: toluene, Org. acid- acetic/ formic acid

\[ IV_{\text{OA}} = 98.0, \ IN_{\text{OA}} = 0.3861 \text{mol/100g OA} \]

<table>
<thead>
<tr>
<th>Batch Code</th>
<th>T, °C</th>
<th>Molar ratio OA: H(_2)O(_2): Org. acid</th>
<th>Initial molar ratio of H(_2)O/ org. Acid</th>
<th>Molar ratio solvent: H(_2)O</th>
<th>( t, \text{ min} )</th>
<th>Characteristics of product(^2)</th>
<th>% Double bond conv.</th>
<th>% Epoxi. Conv.</th>
<th>%Y_{EN/IN}</th>
<th>YIELD</th>
<th>Selectivity S_{EN/HAN}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>50</td>
<td>1:4.9:4.9</td>
<td>1.95</td>
<td>0.28</td>
<td>30</td>
<td>IV = 86.8, IN(_t) = 0.342, EEW = 2298.8, EN(_t) = 0.0435, HV = 0, HN(_t) = 11.4</td>
<td>11.3</td>
<td>98.6</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
<td>55.5, IN(_t) = 0.219, EEW = 884.9, EN(_t) = 0.113, HV = 45.5, HN(_t) = 0.08115</td>
<td>43.36</td>
<td>29.3</td>
<td>67.6</td>
<td>4.18</td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
<td>25.1, IN(_t) = 0.0989, EEW = 616.5, EN(_t) = 0.1622, HV = 87.6, HN(_t) = 0.1561</td>
<td>74.4</td>
<td>42.0</td>
<td>56.5</td>
<td>1.71</td>
<td></td>
</tr>
<tr>
<td>E4</td>
<td>50</td>
<td>1:9.9:4.9</td>
<td>3.83</td>
<td>0.56</td>
<td>120</td>
<td>26.2, IN(_t) = 0.1032, EEW = 590.3, EN(_t) = 0.1694, HV = 78.0, HN(_t) = 0.139</td>
<td>73.26</td>
<td>43.9</td>
<td>59.9</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>E5</td>
<td>50</td>
<td>1:9.9:4.9 (butanol)</td>
<td>3.83</td>
<td>0.66</td>
<td>120</td>
<td>18.7, IN(_t) = 0.0736, EEW = 580.7, EN(_t) = 0.1722, HV = 99.4, HN(_t) = 0.1772</td>
<td>80.94</td>
<td>44.6</td>
<td>55.1</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>E6</td>
<td>80</td>
<td>1:4.9:4.9</td>
<td>1.95</td>
<td>0.28</td>
<td>120</td>
<td>5.6, IN(_t) = 0.02, EEW = 640.8, EN(_t) = 0.16, HV = 155.7, HN(_t) = 0.2776</td>
<td>94.3</td>
<td>40.4</td>
<td>42.9</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>E7</td>
<td>80</td>
<td>1:9.9:4.9</td>
<td>3.83</td>
<td>0.28</td>
<td>120</td>
<td>6.6, IN(_t) = 0.03, EEW = 586.5, EN(_t) = 0.1705, HV = 134.7, HN(_t) = 0.2401</td>
<td>93.26</td>
<td>44.2</td>
<td>47.9</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

*Peracetic acid in situ epoxidation, no catalyst*

<table>
<thead>
<tr>
<th>Batch Code</th>
<th>T, °C</th>
<th>Molar ratio OA: H(_2)O(_2): Org. acid</th>
<th>Initial molar ratio of H(_2)O/ org. Acid</th>
<th>Molar ratio solvent: H(_2)O</th>
<th>( t, \text{ min} )</th>
<th>Characteristics of product(^2)</th>
<th>% Double bond conv.</th>
<th>% Epoxi. Conv.</th>
<th>%Y_{EN/IN}</th>
<th>YIELD</th>
<th>Selectivity S_{EN/HAN}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E8</td>
<td>50</td>
<td>1:6.3:6.3</td>
<td>1.98</td>
<td>0.25</td>
<td>60</td>
<td>IV = 5.4, IN(_t) = 0.02, EEW = 1119.6, EN(_t) = 0.08932, HV = 201.3, HN(_t) = 0.3589</td>
<td>94.49</td>
<td>23.1</td>
<td>24.4</td>
<td>0.46</td>
<td></td>
</tr>
</tbody>
</table>
### Peracetic acid ex situ epoxidation, no catalyst

| E9  | 50 | 1:6.3:6.3 | 1.98 | 0.25 | 60 | 19.5 | 0.077 | 323.7 | 0.3093 | 0 | 0 | 80.0 | 80.0 | 100 | - |

### Performic acid in situ epoxidation, no catalyst

| E10 | 50 | 1:9.9:7.0 | 3.08 | 0.24 | 120 | 15.1 | 0.06 | 476.2 | 0.21 | 79.2 | 0.1411 | 84.6 | 54.4 | 64.4 | 2.3 |

### Performic acid ex situ epoxidation, no catalyst

| E11 | 50 | 1:6.3:6.3 | 2.37 | 0.21 | 60 | 7.4 | 0.0292 | 280.1 | 0.357 | 0 | 0 | 92.5 | 92.5 | 100 | - |

### Peracetic acid in situ epoxidation of methyl oleate, 1% H$_2$SO$_4$ catalyst on wt of mOA

| E12 | 50 | 1:6.6:6.6 | 1.96 | 0.25 | 60 | 29.2 | 0.115 | 605.8 | 0.1651 | 71.0 | 0.1266 | 69.46 | 42.75 | 60.9 | 1.93 |

### Performic acid in situ epoxidation of methyl oleate, 1% H$_2$SO$_4$ catalyst on wt of mOA

| E13 | 50 | 1:6.6:6.6 | 2.34 | 0.21 | 60 | 28.2 | 0.11 | 672.3 | 0.159 | 81.6 | 0.1455 | 70.50 | 41.3 | 57.7 | 1.82 |

**Note:** 1. Refer section 3.3.1.1-A and B for process details. 2. Refer sections 3.4.1 (3.4.1.1-3.4.1.2) and 3.5.1.2 for characterization methodology and procedure for calculations, respectively.
PFA epoxidation batches were expected to deliver more selectivity and higher yield (e.g. batch E10). Slower response of methyl oleate to a fast reactive epoxidising agent like PFA might have transferred control from kinetic regime to thermodynamic regime. Rate of epoxidation should be faster than the rate of generation and decomposition of performic acid. With slow reacting feedstock such as methyl oleate, more decomposition of PFA must have occurred that reduced the availability of peracid for epoxidation. This also results in more availability of FoA in organic phase causing reduction in selectivity from 1.93 (batch E12) to 1.82 (batch E13).

Results in Table 3.4 proved that the double bonds on the methyl oleate were less reactive than the double bonds of the oleic acid. Thus, steric factors inherent in the methyl oleate structure may have reduced the reactivity of the unsaturated sites.

Epoxidation would be carried out to reach maximum conversion (epoxy yield) especially if the product was to be used for further chemical transformations through ring opening (e.g. run E9, E11). On the other hand, epoxidation may be employed to obtain a product in the most economical way- simpler reaction conditions yielding adequate epoxidation with due ring stability (e.g. E3, E4, E5). This would be desired when its use was aimed for plasticizer applications.

3.5.1.4 Semibatch mode of generation and addition of PAA/ PFA for epoxidation of oleic acid

The results and discussion on batch peracid epoxidation of oleic acid have proved that PFA was better over PAA as epoxidising reagent and ex situ mode of operation assured 100% yield of epoxy products. Under similar conditions, the maximum obtainable epoxy yield in in situ PAA epoxidation of oleic acid was 60%. On the other hand, ex situ mode of operation required careful control of exotherm and use of higher concentrations of organic acid- AA/ FoA. The double bond and epoxidation conversions with ex situ PAA epoxidations were still lower ~80%.

Semibatch mode of operation was designed to combine desirable features of in situ and ex situ mode of operation. In order to provide conditions conducive to oxirane stability, the rate of generation of PAA was regulated through discontinuous addition of acetic acid and H₂O₂. The rate of epoxidation was chosen to be higher than the rate of generation of PAA to minimize PAA decomposition and reduce PAA availability for degradation reactions. In all runs, oleic acid was taken in the beginning. Thus it was supplied at highest initial concentration. Epoxidising reagents were added over specific period. Thus at any time, their concentrations were lower. The marginally generated
peracid would be immediately utilized by oleic acid, which was available at higher concentration.

The process details have been described under section 3.3.1.1.C.a. The results are presented in Table 3.5. The run E14 attained poor double bond conversions. The reaction period was inadequate due to the slower reactivity of PAA. When the same process was repeated with PFA epoxidation (run E17), improvement in results were accomplished. The double bond conversion efficiency was better than that obtained for PAA ex situ epoxidation of oleic acid (batch E9). Thus semibatch process can be designed for providing performance better than that of ex situ processes. However there was some ring opening as indicated by attainment of HV of 34.

Table 3.5 Semibatch peracid epoxidation of oleic acid
Solvent: Toluene, Org. acid-acetic (AA)/ formic (FoA) acid

<table>
<thead>
<tr>
<th>Batch Code</th>
<th>T, °C</th>
<th>Molar ratio OA: H$_2$O$_2$: Org. acid</th>
<th>Initial molar ratio of H$_2$O/Org. acid</th>
<th>Molar ratio solvent: H$_2$O</th>
<th>Mode of addition and t, min</th>
<th>Characteristics of product$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV</td>
</tr>
<tr>
<td><strong>Peracetic acid epoxidation, no catalyst</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E14</td>
<td>50</td>
<td>1:4.9:4.9</td>
<td>1.95</td>
<td>1.1</td>
<td>H$_2$O$_2$ added over 60 min at an interval of 15 min (0, 15, 30 45 min), AA taken in the beginning, total t = 60 min</td>
<td>68.2</td>
</tr>
<tr>
<td>E15</td>
<td>40</td>
<td>1:12.3:12.3</td>
<td>1.96</td>
<td>1.2</td>
<td>AA+ H$_2$O$_2$, addition=60 min, Additional reaction t= 120 min, total t=180 min</td>
<td>0</td>
</tr>
<tr>
<td>E16</td>
<td>40</td>
<td>1:12.3:12.3</td>
<td>1.96</td>
<td>1.2</td>
<td>AA+ H$_2$O$_2$, addition=120 min, Additional reaction t= 180 min, total t=300 min</td>
<td>0</td>
</tr>
<tr>
<td><strong>Performic acid epoxidation, no catalyst</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E17</td>
<td>40-70 (exotherm)</td>
<td>1:4.9:3.5</td>
<td>3.1</td>
<td>0.98</td>
<td>same as E14, total t = 60 min</td>
<td>8.8</td>
</tr>
<tr>
<td>E18</td>
<td>40-62 (exotherm)</td>
<td>1:12.3:8.7</td>
<td>3.1</td>
<td>1.0</td>
<td>same as E16, total t = 300 min</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: 1. Refer section 3.3.1.1-C.a for process details. 2. Refer section 3.4.1 (3.4.1.1-3.4.1.4) for characterization methodology.

In order to take care of slow reactivity of PAA as observed in run E14, the mixture of acetic acid and H$_2$O$_2$ was added over 1 hr period in run E15. The rate of addition was
further slowed down in batch E16. In addition, both runs employed three times rise in reactant molar ratio. The selectivity maximization results were evident. In run E15, the complete double bond conversion was accomplished within 3 hrs. But there was extensive ring opening. In run E16, the retarded addition rate of PAA generating mixture (50% drop in addition rate) enhanced the formation of epoxy group with corresponding drop in ring opening. Thus increase in double bond conversion (100%) was accompanied with due stability of oxirane ring. 100% double bond conversion was not possible even in ex situ PFA batch epoxidation (E11). When PFA epoxidation process was repeated (run E18) on the lines of run E16, better control in ring opening was observed. It is essential to note that all semibatch epoxidation runs were conducted at 40\(^{\circ}\)C. But no separate efforts were exercised to regulate reaction temperature through dissipation of heat generated through exotherm by cooling. In PAA semibatch epoxidation process, slower rate of additions controlled the exotherm. However in PFA semibatch epoxidation, due to faster reactivity of PFA, even with slower addition, exotherm was built up causing rise in reaction temperature. This, in turn, caused reduction in the selectivity of PFA epoxidation reaction in comparison to PFA ex situ epoxidation (run E11).

The semibatch mode of addition of peracid generating mixture, thus, were observed to combine the desirable features of in situ and ex situ processes, faster reaction rate and selectivity of ex situ epoxidation and safety, cleanliness and ease of separation of products associated with in situ process. The semibatch mode of addition however requires relatively larger excess of H\(_2\)O\(_2\), acetic acid and longer reaction period. The reduction in reaction period through faster addition of reagents (e.g. in run E15, 1hr) always resulted in more ring opening. Cost consideration will favour PAA semibatch epoxidation (run E16) while the objective of achieving maximum ring stability would be achieved with the PFA semibatch epoxidation (run E18). Thus the results presented the choice to the processor for selection of particular setup in terms of cost and desirable product specifications.

### 3.5.1.5 Semibatch epoxidation with azeotropic distillation process (use of Dean and Stark setup)

In batch epoxidation process, one observes continuous dilution of H\(_2\)O\(_2\) by water generated through the decomposition of former during the generation of peracids. Semibatch epoxidation process, under azeotropic conditions, was conducted in presence of specific solvent (e.g. toluene) which formed the minimum boiling azeotrope with water. Part of the water was, thus, removed continuously from the reaction mass as heteroazeotropic solvent- water mixture through distillation. After condensation and phase...
separation, the solvent was returned into the reaction mass. Thus it was possible to maintain the concentration of hydrogen peroxide at higher level by continuously removing the water, which shifted the equilibrium of peracid generation reaction to the right. Peracid, which limits the chemistry of the epoxidation, was formed simultaneously with water removal. The process and the corresponding setup have been described under section 3.3.1.1.C.b. The results of epoxidation with azeotropic distillation are presented in Table 3.6. The double bond conversion was found to be almost 100% in all four runs (E19- E22). However due to the requirement of higher reaction temperature such as 110°C in run E19 and 90°C in run E21 for azeotropic distillation, extensive ring opening occurred as indicated by HV and EEW results. In order to reduce distillation temperature (e.g. 44°C in run E22, PFA epoxidation), vacuum was applied. But even then the process was accompanied with ring opening. Higher rate of degradation reactions and inferior oxirane stability were observed in PFA epoxidation under both conditions- atmospheric and vacuum distillation. The double bond conversions were lower than that attained with PAA epoxidation. This may be because of more loss of PFA in comparison to PAA through decomposition at higher temperature. Careful analysis of material balance of semibatch epoxidation with azeotropic process revealed that:

i. rate of generation of PAA/ PFA has increased due to increased availability of H₂O₂ as a function of reaction period. This led to more double bond conversions.

ii. Due to elimination of water, there was corresponding increase in organic acid (AA/ FoA) concentration alongwith rise in H₂O₂ concentration. While H₂O₂ gets consumed during peracid generation, organic acid was generated during epoxidation. Thus the availability of organic acid at higher concentration caused the extensive ring opening reactions. Since formic acid was more reactive, rate of ring degradation reactions were found to be higher during PFA semibatch epoxidation with azeotropic distillation.

Hence it was concluded that the concept of azeotropic distillation was not feasible from the point of view of oxirane ring stability. Moreover the process necessitated the use of excess of flammable solvents which reduced the safety of the process. However if the aim was to obtain multifunctional oleochemicals through concurrent epoxidation and ring opening, then semibatch epoxidation with azeotropic distillation offered the best option. The process, which was associated with higher double bond conversion efficiency and simultaneous ring opening reactions, could then be monitored with specific aim of synthesis of multifunctional derivatives.
Table 3.6 Semibatch peracid epoxidation of oleic acid using Dean and Stark setup
Solvent used: toluene, Org. acid-acetic/ formic acid, semi-batch reactor mode

<table>
<thead>
<tr>
<th>Batch Code</th>
<th>T, °C</th>
<th>Molar ratio OA:H₂O₂:org. acid</th>
<th>Initial molar ratio of H₂O/organic acid</th>
<th>Molar ratio solvent: H₂O</th>
<th>t, min</th>
<th>Characteristics of product*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IV            HV  EEW</td>
</tr>
<tr>
<td>Peracetic acid epoxidation, no catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E19</td>
<td>110</td>
<td>1:4.9:4.9</td>
<td>1.95</td>
<td>0.55</td>
<td>180</td>
<td>0.8           87.0   1205.0</td>
</tr>
<tr>
<td>E20</td>
<td>80</td>
<td>under vacuum</td>
<td>1:4.9:4.9</td>
<td>1.95</td>
<td>1.38</td>
<td>60            3.2     68.6   664.4</td>
</tr>
<tr>
<td>Performic acid epoxidation, no catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E21</td>
<td>90</td>
<td>1:4.9:3.5</td>
<td>3.10</td>
<td>0.49</td>
<td>140</td>
<td>2.4           234.8  3425.0</td>
</tr>
<tr>
<td>E22</td>
<td>44</td>
<td>under vacuum</td>
<td>1:4.9:3.4</td>
<td>3.10</td>
<td>1.23</td>
<td>105           6.0     157.4  1438.3</td>
</tr>
</tbody>
</table>

Note: 1. Refer section 3.3.1.1-C.b for process details. 2. Refer section 3.4.1 (3.4.1.1-3.4.1.2) for characterization methodology.

3.5.2 Epoxidation of vegetable oils

3.5.2.1 Synthesis and characterization of epoxidised sunflower/soyabean/caster oil
The procedure adopted for the non-catalytic in situ/ ex situ peracid epoxidation of sunflower, castor, and soyabean oils and the corresponding batch setup has been described under section 3.3.1.2. The results of investigations have been presented in Table 3.7.

The epoxidation of oils was performed at room temperature and the exotherm generated due to the use of PFA as epoxidising reagent was controlled through cooling. In general, use of PFA as epoxidising agent was found to provide lowest EEW (maximum epoxy formation), highest double bond conversion and minimum ring opening reactions, in all batches conducted for soyabean, sunflower, and mustard oil. PAA epoxidation, under similar conditions, were found to be less effective in spite of use of 2.5 times excess of H₂O₂ and PAA over PFA epoxidation process. The magnitude of double bond conversion was less and there was marginal ring opening.

Under similar conditions, rate of epoxidation of sunflower oil was lower than that of soyabean oil. The sunflower and soyabean oils used in this experiment vary only in the number of double bonds. The role of steric and electronic factors explaining the higher reactivity of linolenic acid over other acids has been already interpreted by ref. 144 under Chapter 1 (section 1.3.3). In general, double bonds further from the glycerol center (i.e. position 15 in linolenic acid) were more reactive than double bonds near the glycerol center (9 position in oleic or 9 or 12 positions in linoleic acid) due to less steric hindrance. Secondly higher the degree of unsaturations, greater will be the rate of epoxidation. As the
number of double bonds increases, the electron density increases and this correspondingly caused rise in rate of epoxidation. This explains the higher double bond reactivity of linolenic acid present in soyabean oil and correspondingly higher rate of epoxidation in soyabean oil in comparison to sunflower oil.

Table 3.7 Peracid epoxidation of sunflower, soyabean, castor and mustard oil

Reaction period (t): for mustard oil: 300 min and for all remaining oils: 180 min

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E23</td>
<td>36</td>
<td>1:37.6:37.5 (PAA)</td>
<td>1.94</td>
<td>1.2 (CCl₄)</td>
<td>In situ batch reactor</td>
<td>17.2 12.3 1097.5</td>
</tr>
<tr>
<td>E24</td>
<td>38</td>
<td>1:15.0:12.6 (PFA)</td>
<td>2.64</td>
<td>1.2 (Toluene)</td>
<td></td>
<td>5.7 0 245.0</td>
</tr>
</tbody>
</table>

Peracid epoxidation of soyabean oil

| E25        | 38   | 1:37.6:37.5 (PAA)               | 1.94                                 | 1.2 (CCl₄)              | In situ batch reactor | 43.07 26.7 1512.8             |
| E26        | 40   | 1:15.0:12.6 (PFA)               | 2.64                                 | 1.2 (Toluene)           |                     | 6.0 0 285.0                   |

Peracid epoxidation of sunflower oil

| E27        | 38   | 1:16.4:13.7 (PFA)               | 2.64                                 | 1.2 (Toluene)           | In situ batch reactor | 52.1 176.4 5200               |

Peracid epoxidation of castor oil

| E28        | 70   | 1:2.6:2.3 (PFA)                 | 2.6                                  | 0.34 (Hexane)           | Semibatch with drop wise addition of H₂O₂ over 1 hr | 0.3 3.4 232.4 |

Note: 1. Refer section 3.3.1.2 for process details for soyabean/sunflower/caster oils and 3.3.2.1 for mustard oil. 2. Refer section 3.4.1 (3.4.1.1- 3.4.1.4) for characterization methodology. Org. A.= organic acid, PAA= peracetic acid, PFA= performic acid

PFA epoxidation of castor oil was much lower than those of sunflower and soyabean oils. Castor oil differs from other oils in respect of availability of the hydroxy functionality close to the double bonds in ricinoleic acid (principal fatty acid in castor oil). Thus the double bond (C₉ position), which is also close to glycerol linkage, finds itself in different environment than the same double bond in oleic acid. Thus steric and electronic
factors are primarily responsible for the less reactivity of castor oil in comparison to other oils. Thus the results in Table 3.7 explained the influence of fatty acid composition on epoxidation activity of vegetable oils.

3.5.2.2 Semibatch performic acid epoxidation of mustard oil with intermittent addition of H₂O₂

The semibatch procedure adopted for the catalytic in situ PFA epoxidation of mustard oil has been described under section 3.3.3 and presented under Fig. 3.3. The results of investigations have been reported in Table 3.7. Due to the use of nano alumina activated by conc. H₂SO₄ as catalyst, % epoxy yield was increased with almost complete drop in IV from 110.6 to 0.3. The stability of oxirane ring can be easily judged from the values of EEW of 232.4 and HV of 3.4. The role of semibatch mode of operation in ensuring higher double bond conversion efficiency while effecting best oxirane stability has already been emphasized under section 3.5.1.4.

The characteristic signals in the FTIR spectrum of epoxidized mustard oil at 815-950 cm⁻¹ were related to the quaternary carbons of the oxirane ring; C-O-C stretching from oxirane vibration appeared at 1250 cm⁻¹. Disappearance of the band at 3000 - 3050 cm⁻¹ showed that C=C has been used up. The reaction completion was further confirmed by the appearance of peak at 2.8-3.2 ppm in the ¹HNMR spectrum corresponding to the hydrogen in the epoxy proton.

Fig. 3.11 ¹HNMR of epoxidised mustard oil
Thus the optimised combinations of semibatch addition of H$_2$O$_2$, use of formic acid as source of organic acid and use of acid activated alumina formed the basis of complete and stable epoxidation of mustard oil. Moreover the intermittent addition process permitted the convenient and safe preparation and handling of PFA. Under these conditions, the highest epoxy number and one of the lowest iodine number were achieved. The results and discussion on ring opening reaction of epoxidised mustard oil (EMO) with 2-ethyl hexanol (2-EH) and the evaluation of 2-EH ester of EMO as biolubricant have been presented under section 3.5.4.

### 3.5.3 m-CPBA epoxidation of alkali metal and zinc oleate

Initially sodium, potassium, and zinc oleates were prepared and their epoxidation were carried out using m-CPBA (m-chloroperbenzoic acid) as epoxidising agent and \textit{ex situ} epoxidising process as described under section 3.3.3.2 and Fig. 3.5. m-CPBA, which is preformed peracid, is most selective epoxidising peracid. The effect of different reaction temperatures and feedstock on the extent of epoxidation, as presented by IV and EEW analysis, is presented in Table 3.8. All m-CPBA epoxidation reactions presented highest
selectivity (zero HV). In terms of m-CPBA double bond conversion efficiency, sodium oleate was found to be the best feedstock (batch E29), while m-CPBA epoxidation of zinc oleate was found to be feasible even at 50°C (batch E32).

![Fig. 3.13 FTIR spectrum of epoxidised zinc oleate](image1)

The formation of synthesized epoxidised zinc oleate was confirmed further by FTIR (Fig. 3.13) and $^1$HNMR analysis (Fig. 3.14). Disappearance of the band at 3010 cm$^{-1}$ showed that $\text{C}=$C has been used up. Bands 839-1035 cm$^{-1}$ corresponded to quaternary carbons of the oxirane ring and C-O-C stretching from oxirane vibration appeared at 1105 cm$^{-1}$. $^1$HNMR spectrum (Fig. 3.14) of epoxidised zinc oleate displayed the decrease of the peak area at 2.01 ppm from the $\text{--CH}_2\text{--CH=CH--CH}_2$ protons, whereas new signals were formed at 1.50 ppm ($\text{--CH}_2\text{--CHOCH--CH}_2$) and 2.89 ppm ($\text{--CHOCH}$).
Table 3.8 Epoxidation of metallic oleates

<table>
<thead>
<tr>
<th>Batch code</th>
<th>Oleates</th>
<th>Epoxidation Temp., °C</th>
<th>IV</th>
<th>EEW</th>
</tr>
</thead>
<tbody>
<tr>
<td>E29</td>
<td>Sodium oleate</td>
<td>20</td>
<td>9.5</td>
<td>744.4</td>
</tr>
<tr>
<td>E30</td>
<td>Potassium oleate</td>
<td>20</td>
<td>10.3</td>
<td>796.9</td>
</tr>
<tr>
<td>E31</td>
<td>Zinc oleate</td>
<td>20</td>
<td>12.7</td>
<td>817.1</td>
</tr>
<tr>
<td>E32</td>
<td></td>
<td>5</td>
<td>15.3</td>
<td>949.6</td>
</tr>
</tbody>
</table>

Epoxidised zinc oleate being more hydrophobic amongst the three epoxidised metallic oleates, it was more suitable as additives for plastics. Use of epoxidised zinc oleate as additive for PVC polymer has been explored under section 3.5.5.

3.5.4 Synthesis 2-ethyl hexanol esters (2-EH) of epoxidised mustard oil (EMO) for utilization as biolubricant

The low temperature flow property and high temperature stability of vegetable oils is extremely poor and this restricts their use especially as automotive and industrial fluids. Present investigation dealt with the study of ring opening reactions of epoxidised mustard oil (EMO) by 2-EH in presence of various acidic catalysts and analysed the effect of epoxidation and ring opening on tribochemistry of mustard oil for use in industrial applications as evidenced by pour point, viscosity index (VI) and oxidation stability measurements.

3.5.4.1 Acid catalysed oxirane ring opening of epoxidised mustard oil (EMO) with 2-ethyl hexanol (2-EH)

The procedure adopted for the catalytic ring opening of epoxidised mustard oil (EMO) in accordance to the Fig. 3.6 has been described under section 3.3.2. The effectiveness of following materials, as catalysts for oxirane ring-opening reaction of EMO with 2-ethyl hexanol (2-EH), was examined: conc. H2SO4, sulphamic acid, methane sulphonic acid. The process was monitored using technique described under sections 3.4.1, 3.4.2 and 3.4.4 and the results of these investigations have been reported in Table 3.9. The experimental programme included the process conditions known to lead to extensive opening of the oxirane ring accompanied with hydroxy ester formation namely: high temperature (120°C), 60% excess use of 2-EH and low pH (high acid catalyst concentration). As the hydrolysis reaction proceeds at the liquid-liquid interphase, the intensity of mixing of the organic phase was highly relevant. Oxirane ring possesses a high potential energy due to its angular strain hence the ring-opening reaction was associated.
with the evolution of thermal energy (heat). The dominant effect was the enthalpy change although structural changes results in significant entropy change\(^9\). Initially the reaction kinetics was controlled by the chemical reactivity of the functional groups, but later on becomes diffusion controlled and the degree of the conversion levels off and tends to a limiting value\(^{10}\). Hence the agitation speed of 500 rpm was chosen to eliminate interphase mass transfer resistance due to likely onset of diffusion controlled regime with increase in extent of ring opening. In general, the ring opening resulted in generation of hydroxy ester with hydroxy value (HV) and specific gravity in the range from 97.5-102.9 and from 0.87998-0.90199, respectively. The impact of main process variables (type of catalyst, catalyst concentration, reaction period) on the extent of opening of the epoxide ring of EMO by attack of 2-EH in two-phase (polar-organic) systems and corresponding changes in lubricant characteristics of 2-EH esters of EMO was studied.

The pH due to acidic catalyst concentration has a double influence on the hydrolysis rate: onset of the break-up point (due to a decrease on the surface tension once enough hydroxy esters are formed) and attack on the oxirane ring proper. In general, conducting reaction for longer period (3-6 hrs) and/ or utilising more catalyst concentration (1-2\%) cause rise in extent of ring opening/ hydrolysis reaction as measured by EEW. With more ring opening, i.e. disappearance of oxirane ring, weight of EMO corresponding to 1 epoxy group (EEW) increases. With increase in EEW (thus corresponding rise in molecular weight) at \(40^\circ\)C also increases. Thus the parameters EEW and viscosity at \(40^\circ\)C form the direct measure of extent of ring opening reactions. Since conc. H\(_2\)SO\(_4\) is strongest acidic catalyst in terms of pH, it was expected to exhibit highest catalytic effectiveness. As shown in Table 3.9, the 2-EH ester with highest EEW of 8200 (i.e. maximum ring opening reaction), viscosity (23.1 cst) and density (0.9019 g/cc) was obtained with usage of conc. H\(_2\)SO\(_4\) catalyst at 2\% and conducting the ring opening reaction for 6 hrs. Methane sulphonic acid, on the other hand, was found to be the least effective catalyst amongst all the three catalysts. It was incapable of accelerating ring opening reaction even at 2\% concentration and after conducting reaction for 6 hrs (lowest EEW 3117.9). Sulphamic acid, although not as effective as H\(_2\)SO\(_4\), catalysed sufficient ring opening at 1\% for 6 hrs reaction period. It was more effective at higher loading of 2\% and followed closely to conc. H\(_2\)SO\(_4\), in its role as catalyst, as evidenced by EEW and viscosity index measurements. Use of sulphamic acid as ring opening catalyst has not been reported in literature. It is a green non corrosive catalyst. On the other hand H\(_2\)SO\(_4\) is
Table 3.9 Acid catalysed ring opening of epoxidised mustard oil (EMO) with 2-ethyl hexanol (2EH)
Stirring speed: 500 RPM, Temperature: 120°C, EMO: 2EH (epoxy:OH) molar ratio: 1:1.63

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conc. (H_2SO_4)</th>
<th>(CH_3SO_3H)</th>
<th>(NH_2SO_3H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. % by wt</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>time, hrs</td>
<td>3</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Batch Code</td>
<td>(B_1)</td>
<td>(B_2)</td>
<td>(B_3)</td>
</tr>
<tr>
<td>EEW</td>
<td>2510.6</td>
<td>5074.8</td>
<td>3737.1</td>
</tr>
<tr>
<td>Sp. gravity, (25^\circ C)</td>
<td>0.8842</td>
<td>0.89773</td>
<td>0.89512</td>
</tr>
<tr>
<td>Viscosity @ (40^\circ C), cSt</td>
<td>10.17</td>
<td>11.87</td>
<td>15.89</td>
</tr>
<tr>
<td>Viscosity @ (100^\circ C)</td>
<td>2.82</td>
<td>3.27</td>
<td>3.93</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>127.0</td>
<td>153.0</td>
<td>149.0</td>
</tr>
<tr>
<td>Pour point, (0^\circ C)</td>
<td>-35</td>
<td>-16</td>
<td>-28</td>
</tr>
<tr>
<td>Results of oxidation stability</td>
<td>Total acid number (TAN) = 1.18 % sludge content = 0.16</td>
<td>TAN = 1.21 % sludge content = 0.76</td>
<td>TAN = 1.34 % sludge content = 0.28</td>
</tr>
</tbody>
</table>

Note: 1. Refer section 3.3.2 for process details for ring opening of EMO. 2. Refer section 3.4.1 and 3.4.2 for characterization methodology.
corrosive and caused side reaction. Thus present study establishes use of sulphamic acid as ring opening catalyst.

**FTIR and NMR analysis**

The FTIR (Fig. 3.15 and Fig. 3.16) and $^1$HNMR (Fig. 3.17-3.20) spectroscopic analysis were conducted to investigate the effect of ring opening on structural variation in EMO. Appearance of OH stretching vibration around 3400-3550 cm$^{-1}$ corresponding to -OH group, indicates ring opening reaction. The completion of ring-opening reaction was monitored by disappearance of epoxy signals at 1158, 845 and 822 cm$^{-1}$ in the FTIR spectra.

![FTIR spectra of 2-EH esters of EMO for 3hr batches](image)

**Fig. 3.15 FTIR spectra of 2-EH esters of EMO for 3hr batches**
Fig. 3.16 FTIR spectra of 2-EH esters of EMO for 6hr batches

The $^1$HNMR spectrum of 2-EH esters of EMO showed that the peak at 2.8-3.2 ppm corresponding to the hydrogen in the epoxy protons had disappeared indicating opening of epoxy ring. The methine proton of -CH$_2$(O)-CH(O)-CH$_2$(O)- glycerol structure at 5.1-5.3 ppm and methylene proton of -CH$_3$(O)-CH(O)-CH$_2$(O)- glycerol structure at 4.0-4.4 ppm were observed showing that the glycerin structure was intact in the product. A very small multiple peak at 2.7 ppm assigned to the methylene protons between two carbon-carbon double bonds observed possibly due to small amounts of the double bond left during epoxidation of mustard oil. A signal at 2.3 ppm assigned to the methylene protons adjacent to the carbonyl groups was observed and supports the supposition of triglyceride ester structure.
**Fig. 3.17** $^1$HNMR of 2-EH esters of EMO (batch B₁)

**Fig. 3.18** $^1$HNMR of 2-EH esters of EMO (batch B₂)
Fig. 3.19 $^1$HNMR of 2-EH esters of EMO (batch $B_3$)

Fig. 3.20 $^1$HNMR of 2-EH esters of EMO (batch $B_4$)
3.5.4.2 Evaluation of 2-EH esters of EMO as biolubricant

Table 3.9 presents changes in physical properties of EMO (through formation of 2-EH esters) as function of extent of ring opening. These characteristics were determined by following procedures given under 3.4.2.

A. Analysis of viscosity index (VI) of 2-EH esters of EMO

A high viscosity index (VI) indicated that the product retains viscosity at high temperature and thus possesses favourable high temperature characteristics. Mustard oil possesses high VI of 200.1 (viscosity at 40°C=45.13, 100°C=9.46). when one undertakes epoxidation of mustard oil to enhance low temperature flow and oxidative stability characteristics, major decline in VI was observed. The ring opening of EMO facilitated restoration VI characteristics. The VI results are presented in Fig. 3.21. The VI of 2-EH esters of EMO was found to increase with increase in extent of ring opening. In this respect, batch B4 (2% H₂SO₄, 6 hrs), which also reports maximum ring opening (EEW 8194), offers highest VI of 177. In fact, all batches catalysed by H₂SO₄ (except B1 batch) present favourable high temperature viscosity characteristics. Sulphamic acid catalysed batches (B9-B12) exhibit moderate VI characteristics in the range of 133-159 (except B9) and in this reference displays catalytic effectiveness next to H₂SO₄. Since methane sulphonic acid catalysed batches do not give 2-EH esters with high EEW, the corresponding VI characteristics were also found to be inferior (105-130).

![Viscosity Index](image)

**Fig. 3.21 Viscosity index of various 2EH esters of EMO**
B. Analysis of pour point (PP) of 2-EH esters of EMO

The important parameter in determining how well 2-EH ester will behave as a potential lubricant is to evaluate the pour point (PP). The prepared 2-EH esters (B₁-B₁₂) described above were screened for low-temperature flow behaviour through determination of PP as described under section 3.4.2.1. The PP results are presented in Fig. 3.22.

The pour point of mustard oil and EMO were 24°C and -15°C, respectively. Thus epoxidation of mustard oil improved the low temperature behaviour of oil rich in high molecular weight fatty acid- erucic acid (Table 3.1- FA composition). H₂SO₄ was found to be the most effective catalyst in reference to the all low temperature flow property through ring opening of EMO. Formation of 2-EH ester with favourable lowest pour point was observed for H₂SO₄ catalysed B1 batch: -35°C followed by batch B3: -28°C (Table 3.9). Thus use of branched alcohol- 2-EH for partial ring opening imparts positive effect on the low-temperature performance of the resultant products. As the branching increased through hydroxy ester formation, the corresponding improvement in PP is due to the greater ability of the branched esters to more effectively disrupt macrocrystalline formation at reduced temperatures. In addition, use of stronger acid such as H₂SO₄ is known to result in side reactions such as isomerisation and additional branching (e.g. iso structure formation from linear hydrocarbon chain) in original structure of EMO. The combined impact of the two factors (use of 2-EH and H₂SO₄) resulted in major depression in PP. However with increase in extent of ring opening, the average molecular weight of 2-EH ester of EMO also increased. This may be the reason for drop in PP values of H₂SO₄ catalysed batches- B2 and B4. In addition to H₂SO₄ catalysed B3 batch, methane sulphonic acid catalysed batch B5, which exhibits lowest EEW and VI, displays second highest depression in PP (13°C) of EMO through ring opening. This implies that while B5 2-EH ester was acceptable for low temperature flow characteristics, the advantage was negated by inferior high temperature characteristics. On the other hand, H₂SO₄ catalysed Batch B3 represents optimum balance between PP (-28°C) and VI (149) characteristics. All other batches from B6-B₁₂ do not present depression in PP values. In fact, the PP characteristics of batches B8 and B₁₂ were inferior even to that of EMO. The rise in molecular weight (as indicated by increase in EEW) with more ring opening of 2-EH esters of EMO counterbalances the microcrystalline disruption effect due to the introduction of branched esters. Sulfamic acid catalysed products were not acceptable in term of PP characterisation. For enhancement of low temperature characteristic it was
essential to restrict extent of ring opening. In this respect batch B1, B3 and B4 were acceptable.

![Graph showing pour points of various 2EH esters of EMO](image)

**Fig. 3.22 Pour points of various 2EH esters of EMO**

C. Analysis of oxidation stability of 2-EH esters of EMO

The oxidative stability analysis was performed according to the IEC procedure described under section 3.4.2.3. As per industrial specifications, the lubricant must possess vatable acidity in terms of total acid number (TAN) below 1.2 and % sludge content below 0.8. The analysis of results reported in Table 3.9 indicated that all the H$_2$SO$_4$ catalysed batches fulfilled these specifications. The results were on the expected lines because the double bonds in mustard oil were completely epoxidised. More or less complete elimination of ethylenic unsaturation gave the 2-EH esters of EMO a complete freedom from oxidative degradation. Moreover higher EEW (or higher molecular weight) increases the stability of product. Sulphamic acid catalysed batches fulfilled the obligation of % sludge content. However these batches carried slightly higher TAN values. Methane sulphonic acid catalysed batches just passed the % sludge and TAN specifications. It should be remembered that these results are obtained on base oil. In industrial formulations, the required specifications are fine tuned through use of additives. Thus all 2-EH ester of EMO fulfilled the industrial requirements of oxidation stability.
In short, the biolubricants based on 2-EH esters obtained through H$_2$SO$_4$ catalysed ring opening of EMO satisfied the low temperature flow properties, high temperature lubrication characteristics and oxidative stability specifications of commercial lubricant market. This justified the choice of H$_2$SO$_4$ as the most effective ring opening catalyst. Sulphamic acid catalysed batches fulfil VI and oxidation stability specifications. Thus these products are acceptable as biolubricants in applications involving use or exposure to high temperatures. Through proper controlling of ring opening, methane sulphonnic acid catalysed batches can be made to oblige flow characteristics. The results established the feasibility of utilisation of 2-EH esters of EMO as biolubricant and sulphamic acid as green catalyst for ring opening.

3.5.5 Evaluation of epoxidised zinc oleate (EZnOA) as additive for PVC polymer composites

The three different PVC composites were prepared based on formulations reported under Table 3.3 [section 3.3.3.3] and analysed by using procedures described under section 3.4.3.

The FTIR spectrum of original polyvinyl chloride PVC 57 is shown in the Fig. 3.23. The bands in the region of 615-681 cm$^{-1}$ were corresponding to C-Cl stretching vibrations. These bands were of complex origin and depend on the conformational structure of the polymer and the spatial position of the atoms surrounding the C-Cl bonds. The bands at 2911 cm$^{-1}$ and 2967 cm$^{-1}$ were corresponding to -CH$_2$- and -CH- stretching groups. The two bands at 1251 cm$^{-1}$ and 1326 cm$^{-1}$ were corresponding to -CH in -CHCl stretching groups. These characteristic peaks were consistent with the literature\textsuperscript{11}. The minor band at 1733 cm$^{-1}$ could be due to the presence of soaps and plasticizers present in emulsion type PVC. This peak gets enhanced in Fig. 3.24. The analysis of FTIR spectrum Fig. 3.24 of batch I (PVC + EZnOA) implied the compatibility between epoxidised zinc oleate (EZnOA) as additive with PVC. The PVC-EZnOA interactions solubilise the PVC as indicated by entirely changed form of Fig. 3.24 in comparison to Fig. 3.23. It was also shown that these molecules break polymer polymer interactions and mask the interactive site (600-700 cm$^{-1}$) of PVC polymer. The bands at 1622 cm$^{-1}$ and 1469 cm$^{-1}$ were corresponding to -CH- asymmetric stretching and symmetric stretching vibrations\textsuperscript{12}. In addition to the intended effect on plasticization and stabilization, the solubility in organic solvents, miscibility and compatibility with the PVC polymer and intended use of the polymer (eg. nontoxicity in food packaging materials) were essential in choosing correct
an additive in polymer formulation. Besides being nontoxic, biodegradable and renewable additive, the FTIR analysis proved the miscibility and compatibility of EZnOA with PVC.

![FTIR spectrum of PVC 57](image1)

**Fig. 3.23 FTIR spectrum of PVC 57**

![FTIR spectrum of PVC 57 stabilised with EZnOA](image2)

**Fig. 3.24 FTIR spectrum of PVC 57 stabilised with EZnOA**
Following subsections presents result and discussion on modification of thermal, morphological and mechanical characteristics of PVC in relation to the use of EZnOA as additives.

3.5.5.1 Influence of EZnOA on thermal stability of PVC polymer

The thermal degradation of PVC occurs by an autocatalytic dehydrochlorination reaction with the subsequent formation of conjugated double bonds. Dehydrochlorination is initiated at the labile site in the polymer chains. This leads to an extensive discoloration of the polymer and deterioration of its physical and mechanical properties. Zinc soaps are used as important stabilisers to prevent this deterioration. According to the Frye-Horst mechanism\textsuperscript{11}, stabilization arises from the reaction of the fatty acid salt of Zn with PVC through esterifying displacement of labile chlorine atoms with more heat stable carboxylate groups. The progressive dehydrochlorination reaction is prevented in this way, but the zinc chloride (ZnCl\textsubscript{2}), produced as a result of the esterification reaction, will cause further rapid degradation. This problem is solved by the synergistic effect of combining alkaline earth (Ca) carboxylates with covalent metal carboxylates. Alkaline earth carboxylates undergo ester exchange reactions with covalent metal chlorides, thus regenerating the covalent metal carboxylates. Unlike the covalent metal chloride, alkaline earth chlorides do not promote dehydrochlorination. Thus the alkaline earth carboxylates do not act as primary stabilizers of PVC resin but serve to regenerate the active stabilizer and remove the potentially destructive effect of the covalent metal chloride\textsuperscript{13}. Thus the batch III, which carried the equivalent combinations of Zn and Ca stearate was formulated. It has been also shown that the mechanism for stabilization of PVC by epoxidised oleochemicals involved the HCl trapping by epoxy moiety through addition reactions and in turn decreasing the rate of degradation. \textbf{Thus, for epoxidised zinc oleate, the mechanism of stabilization of PVC would be dual- HCl trapping reactions and substitution of labile chlorine atoms by carboxylate groups.} Consequently, under equivalent concentrations, the epoxidised zinc oleates are expected to be more effective stabilizers of PVC than the epoxidised olate. The stabilizing effect of EZnOA on thermal degradation of PVC in the absence and presence of Zn stearates was investigated through formulation of batch I and II, respectively (\textbf{Table 3.3}). Although Ca/Zn stabilizers are more expensive and less effective than many other stabilizer systems, they are non-toxic and find use in food packaging materials, children’s toys and bottle seals.
A. Thermogravimetric studies of EZnOA

Since the epoxidised zinc oleates (EZnOA), were proposed to be used as additive for PVC polymer, the thermal characterisation of zinc oleates and EZnOA, based on TGA analysis (section 3.4.3.3), were initially conducted and reported in Fig. 3.25 and Fig. 3.26, respectively. The details of the TGA instrument have been given under section 3.4.3.3.

The comparison of Fig. 3.25 and Fig. 3.26 revealed the impact of epoxidation in enhancement of thermal stability of EZnOA in comparison to that of zinc oleate in initial phase (upto 140°C). However, the epoxidation of zinc oleate increased its organic content. Hence the TGA weight loss of EZnOA was higher than that of zinc oleate. The diagram also showed that EZnOA was thermally stable upto 368°C which was sufficient to withstand the processing temperature of PVC. In the second stage (368°C onwards), major loss of the order of 36.7% occurred in the temperature range of 368-394°C. At 486°C, the overall loss was 78%. Thus the additive, EZnOA was thermally stable in the processing range of PVC polymer.

![Fig. 3.25 TGA diagram of Zn oleate](image-url)
B. TGA analysis of PVC in presence of EZnOA and/or zinc stearate

The EZnOA based compositions Batch I and II were evaluated against standard combinations of Zn and Ca stearates by studying the mass losses of PVC due to HCl release and evaporation of DOP during TGA heating to 600°C. Fig. 3.27 shows TGA curves for PVC sheet carrying DOP plasticizer and stabilised with EZnOA alone (curve 1), mixture of EZnOA and zinc stearate (curve 2), mixture of zinc stearate and calcium stearate (curve 3), it was observed that the thermal degradation of PVC sheet, for all the three additive compositions was a two-step process as reported in the previous study. The thermal decomposition in the first stage was mainly the dehydrochlorination of polymer resulting in the evolution of HCl and the formation of conjugated double bonds. The thermal decomposition in the second stage was mainly the cyclisation of conjugated polyene sequences to form aromatic compounds with simultaneous cracking and pyrolysis of dehydrochlorinated product to low hydrocarbons of linear or cyclic structure.
Fig. 3.27 TGA curves of (1) PVC stabilized with epoxidised Zn oleate, (2) PVC stabilized with 50% Zn stearate and 50% epoxidised Zn oleate, (3) PVC stabilized with Zn and Ca stearates

TGA curve 3 shows loss in batch III (Ca + Zn stearate) due to the volatilization of the low boiling components (volatiles and moisture) between 100 and 225°C. This loss was very negligible in PVC sheets I (EZnOA) and II (EZnOA + Zn stearate) due to the hydrophobic effect imparted by epoxidised zinc oleate. The first stage degradation onset was obtained after 225°C where sample shows a significant drop in weight, mainly due to the dehydrochlorination of PVC resulting in the formation of conjugated double bonds. Within the range of 200-400°C, the loss of DOP was also expected to occur. In between 300°C to 450°C, a pleatue region was observed. In the second stage (450°C onwards), the degradation of polymer, which had already become the dehydrochlorinated product, continued with loss through cracking and pyrolysis of dehydrochlorinated polymer. In both stages of degradation, the thermal stability achieved due to incorporation of EZnOA in PVC sheet I and II was found to be greater over that achieved due to the combination of metal carboxylates- zinc stearate and calcium stearate in PVC sheet III compositions, as indicated by comparatively less weight loss or superior effect on char formation of PVC. In particular, the stage 2 degradation resistance built up due to incorporation of EZnOA alone was more superior. Incorporation of EZnOA thus reduces the thermal
decomposition in both stages. The residual mass for PVC sheet I was found to be 20% even at 600°C. In comparison, almost complete weight loss was observed for PVC sheet III. Stage 1 degradation for III additive composition (Zn and Ca stearate) was extended over higher temperature range and the pleatue region between stage 1 and stage 2 was correspondingly shorter.

PVC composite II, stabilised with combination of EZnOA and zinc stearates, was also found to be superior over PVC composite III. It again establishes the stabilising influence of EZnOA and also indicates the synergism between EZnOA and zinc stearate. Thus the epoxidation of metallic carboxylates enhanced their role as thermal stabiliser.

C. Analysis of thermal stability of PVC sheet based on congo red test

Congo red test was used to evaluate the residual heat stability of PVC sheets imparted by the methodology has been reported under section 3.4.3.1. While TGA analysis revealed the resistance to all kinds of thermal degradations, Congo red test provided the analysis of resistance against dehydrochlorination only. It was observed that PVC plastisized with DOP, in absence of any additive, undergoes dehydrochlorination within seconds. Addition of EZnOA enhanced the residual heat stability of PVC sheet against dehydrochlorination to 3.5 min. The synergistic combination of EZnOA with zinc stearate in PVC sheet II, as indicated previously by TGA analysis, increased residual heat stability to 4.5 min. The combination of calcium stearate with zinc stearate provided the best residual heat stability of 7.21 min. The TGA and congo red test analysis taken together signified that EZnOA, as additive for PVC, promoted the overall thermal stability of PVC polymer. On the other hand, the calcium and zinc stearate combination was found to be effective against dehydrochlorination only.

<table>
<thead>
<tr>
<th>Table 3.10 Results of congo red test</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC sheet I</td>
</tr>
<tr>
<td>Dehydrochlorination Time (min)</td>
</tr>
</tbody>
</table>

D. Static oven test, FTIR and ΔE colour analysis of PVC sheets

The prepared PVC films were heated in static air oven at 140°C for 90 min. Fig. 3.28 presents FTIR spectrum of PVC sheet I after conducting static oven test. The comparison with Fig. 3.24 (spectrum before conducting the test) indicates disappearance of bands corresponding to C-Cl stretching vibrations (636 cm⁻¹). The change in the colour of the PVC film, as a result of thermal degradation, was an indication of the presence of
conjugated dienes in it. The color changes from yellow-orange-brown as number of conjugated double bond sequences increases. Formation of four conjugated double bonds cause light yellow colour whereas six conjugated double bonds impart yellow colour. Degraded PVC with eight and eleven conjugated double bonds in its chain possess orange and red colour respectively \(^{16}\).

**Fig. 3.28** FTIR spectrum of PVC 57 stabilised with E ZnOA heated at 140° C for 90 min.

**Table 3.11** \( L, a, b \) and \( \Delta E \) values of the PVC composite samples as a function of heating

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>PVC composite</th>
<th>Condition</th>
<th>( L )</th>
<th>( dL )</th>
<th>( A )</th>
<th>( da )</th>
<th>( B )</th>
<th>( db )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>Control</td>
<td>36.222</td>
<td>-0.937</td>
<td>1.502</td>
<td>1.294</td>
<td>7.780</td>
<td>1.660</td>
<td>2.304</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>140°C</td>
<td>35.285</td>
<td></td>
<td>2.796</td>
<td></td>
<td>9.440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>II</td>
<td>Control</td>
<td>37.487</td>
<td>-0.259</td>
<td>0.220</td>
<td>0.549</td>
<td>5.160</td>
<td>1.720</td>
<td>1.824</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>140°C</td>
<td>37.228</td>
<td></td>
<td>0.768</td>
<td></td>
<td>6.880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>III</td>
<td>Control</td>
<td>35.351</td>
<td>0.196</td>
<td>0.599</td>
<td>0.566</td>
<td>5.980</td>
<td>2.140</td>
<td>2.222</td>
</tr>
<tr>
<td>6</td>
<td>III</td>
<td>140°C</td>
<td>35.546</td>
<td></td>
<td>1.165</td>
<td></td>
<td>8.120</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The L, a, b and ΔE colour measurements, for PVC sheets on exposure to 140°C for 90 min in static oven are reported in Table 3.11. The measurements were carried by using a colour matching spectrophotometer as described under section 3.4.3.2. A colour measurement movement in the +a direction depicts a shift towards red. Along the b axis, +b movement represented a shift towards yellow. L= 0 stands for black or total absorption, while L= 100 represented perfect white. Thus drop in L value indicates increasing greyness and ultimately development of black colour. As seen from Table 3.11, highest yellowness (+db) was recorded for PVC sheet III stabilized with Zn and Ca stearate. The formation of yellow films was the result of dehydrochlorination with conjugated double bond formation. The colour of the PVC sheets I and II turned slightly black on L scale in long heating periods as indicated by drop in dL. It indicates discoloration of oleochemical additives alongwith degradation of polymer by ZnCl₂. The PVC sheet sample III stabilized with Zn and Ca stearate were still white on L scale at the end of 90 min. This is because CaCl₂ produced from dehydrochlorination does not accelerate the decomposition process as other product ZnCl₂ did in PVC sheets I and II. On overall colour scale (ΔE) as well as on red scale (da, higher of conjugation), the synergistic combination of EZnOA and Zn stearate presented the lowest colour development which means a success in retarded degradation of PVC by dehydrochlorination. This synergism results were in agreement with similar results obtained under TGA and congo red tests. The combined analysis of congo red test and static oven tests implies that the combination of Zn and Ca stearate was good in preventing dehydrochlorination in initial stage only i.e. it delays the onset of dehydrochlorination (longer congo red test duration). On the other hand, the combination of EZnOA and Zn stearate presents better defence against building up of higher extent of conjugated polymer sequences (say > 6). This has constructive effect on built up of resistance to second stage thermal degradation. The better second stage degradation resistance built up by EZnOA, as indicated in TGA analysis (Fig. 3.27), justified the conclusion drawn on the basis of combined analysis of congo red test and static oven test.

3.5.5.2 FESEM Morphology and EDAX analysis of PVC sheets

Field emission scanning electron microscope (FESEM) micrographs (Fig. 3.29 a-c) of PVC sheet with different additive compositions (Batch I-III) were taken to investigate the heat effects (140°C for 90 min) on the morphology of PVC at nano scale (500 nm). The plasticizer DOP and EZnOA have solvated the PVC thoroughly and homogeneously (Fig. 3.29 a). The combined solvating effect of DOP and EZnOA provided through mixing of batch I formulation which resulted in the formation of defect
free film surface. Although there were pores in the micrographs, it was obvious that when the temperature was increased up to 140°C, the number of air bubbles and regions of heterogeneity appearing decrease and a more homogeneous PVC film was achieved (Fig. 3.29 a’). In PVC sheet II, there was part replacement of EZnOA by Zn stearate. Thus the corresponding drop in solvating effect have caused rise in regions of heterogeneity which were apparent in Fig. 3.29 b. After heating, there was attainment of some degree of homogeneity (Fig. 3.29 b’) but it was still lower in comparison to that of PVC sheet I (Fig. 3.29 a’). Surface of PVC sheet III exhibited more number of cracks and non homogeneous regions in comparison to PVC sheets I and II. Thus the solvating effect of Zn and Ca stearate combination was observed to be lower in comparison to EZnOA. In short, FESEM analysis proved unambiguously the solvating efficiency of EZnOA in comparison to other additive combinations.
Fig. 3.29 FESEM surface imaging of (a) PVC sheet I before heating, (a’) PVC sheet I after heating at 140°C, (b) PVC sheet II before heating, (b’) PVC sheet II after heating at 140°C, (c) PVC sheet III before heating and (c’) PVC sheet III after heating at 140°C.

Elemental Analyses of PVC sheets

PVC films were analyzed by EDX coupled with a FESEM to have an idea on the change in surface elemental compositions of the films after heating to 140°C for 90 min. A sample EDX spectrograph is also given in Fig. 3.30 as an example. Two or three different points on the film surface were chosen and evaluated. The elemental analysis, along with the theoretical composition\(^\text{17}\) of PVC sheet, are reported in Table 3.12.

Table 3.12 Elemental analysis of PVC sheets at 140°C for 90 minutes

<table>
<thead>
<tr>
<th>Element wt.%</th>
<th>The theoretical compositions(^\text{16})</th>
<th>EDX Elemental analyses of particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVC+ DOP(100:30)</td>
<td>PVC sheet I</td>
</tr>
<tr>
<td>C</td>
<td>46.6</td>
<td>74.71</td>
</tr>
<tr>
<td>O</td>
<td>3.78</td>
<td>8.62</td>
</tr>
<tr>
<td>Cl</td>
<td>43.65</td>
<td>16.56</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Carbon (C) content for all samples were reported between 68 and 79% which is higher than the sheet but close to the theoretical weight % of carbon in DOP (73.81%)\(^\text{17}\). The chlorine (Cl) content of the films at 140°C was reported between 14 and 23.5% which is lower than the value in PVC sheet (43.65%) indicating that the partial
dehydrochlorination has occurred. The oxygen content (O) in the films was reported to be higher primarily due to presence of air voids\(^7\).

![XRD spectrograph of PVC sheet I](image)

**Fig. 3.30 XRD spectrograph of PVC sheet I**

### 3.5.5.3 Influence of EZnOA and other additives on mechanical properties of PVC sheets

Table 3.13 presents the mechanical properties of PVC sheet as a function of type and % loading of stabilising additives determined using UTM. The ratio of tensile stress to longitudinal strain gives Young’s modulus. Elongation-at-break is a measure of how much strain is withstood by PVC sheet before breaking and the tensile strength, or tensile-at-break, is a measure of the stress when the sample breaks. The Young’s modulus and tensile strength results were found to be highest for PVC sheet I stabilized with EZnOA. The multifunctionality of EZnOA (carboxyl, epoxy and metal salts) molecules may act as bridges between the PVC matrix, avoiding the depletion force-induced phase separation and providing more uniform distribution or better homogenization. Accordingly, more force is required to break this physical network. The modulus and strength results thus underlined the contribution of EZnOA in enhancement of stiffness of PVC sheets over other additives compositions.
Table 3.13 Mechanical properties of PVC sheets

<table>
<thead>
<tr>
<th>PVC sheet</th>
<th>Tensile Strength (Mpa)</th>
<th>% Elongation</th>
<th>Youngs Modulus (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch I</td>
<td>15.215</td>
<td>175.08</td>
<td>345.45</td>
</tr>
<tr>
<td>Batch II</td>
<td>14.5</td>
<td>307.43</td>
<td>260.54</td>
</tr>
<tr>
<td>Batch III</td>
<td>14.6</td>
<td>201.21</td>
<td>251.13</td>
</tr>
</tbody>
</table>

The elongation is usually inversely proportional to tensile strength and is related to the plasticization characteristics. In this respect, EZnOA (Batch I) is slightly inferior in comparison to the combination of Zn and Ca stearate (Batch III). Although EZnOA alone as additive displayed lower elongation-at-break, it exhibited synergism with Zn stearate (PVC sheet II) in securing slippage of polymer chains for highest elongation without break. The combination exhibited 52% and 75% rise in elongation over composition III and I, respectively. The integrated product of the tensile strength and elongation at break represents work to break and was also found to be highest for PVC sheet II indicating the moderately better efficiency of synergistic combination of EZnOA and Zn stearate as additive over that of combination of Zn and Ca stearate in enhancing work to break along with plasticization. The work-to-break values also represent the relative wear lives of polymers. Thus PVC sheets stabilised with EZnOA and Zn stearate exhibited better wear resistance and toughness along with the plasticization.

In short, epoxidised zinc oleate (EZnOA), provided good compatibility with PVC and other additives as evidenced by FESEM morphological analysis and played the important role in strengthening the thermal and mechanical properties of polymer sheets. The synergistic combinations EZnOA with zinc stearate were established on the basis of evidences generated through TGA analysis, congo red test, colour analysis, EDX elemental characteristics and UTM measurements.

References

11 Göktepe, S.E. *M.S. Thesis*, Graduate School of Natural and Applied Sciences, Ege University, 1996.

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