INTRODUCTION

The Genesis of the polymers is in existence since the formation of the earth over for billions years ago, in its giant ‘laboratory’. Elements like carbon, hydrogen, oxygen and nitrogen, are capable of forming complex molecule. The original polymer was called protein’, got synthesized in nature from simple chemical compounds like methane, ammonia and carbon di-oxide. Mean while, polymers had also appeared in their other natural forms like wood, cotton, cellulose, starch etc., which man begin to use. Most of the synthetic polymer are of a relative ascent origin whether we are looking for fancy decoration articles, textiles, building materials or packing materials, the polymers have brought to the fore a scintillating range irresistible attractive choices. The polymers are synthesized following the chemical reaction, the polymerisation. The size of a polymer molecule depends on the number of repeat units it contains and that this number represents the degree of polymerisation. The molecular weight is related to the degree of polymerisation by an equation.

\[ M = Dp \times m \]
where M is the molecular weight of the polymer, Dp its degree of polymerisation m is the molecular weight of the monomer or the repeat units.

Depending on its ultimate form and use, a polymer may be classified as plastic, elastomer, fiber or liquid resin. Typical examples of plastic are polystyrene, poly(vinal chloride) and poly-methyl methacrylate. Plasticizers are an outgrowth of plastic industries. Poly(vinal chloride) (PVC), being inherently horny and brittle, would have had very limited use without plasticization. It is only with the help of plasticizers that PVC can be transformed into articles of varied softness ranging from blood backs to right profile. The continious requirement of new and varied applications keeps the plasticizers manufacturers and the product formulators in a constant search for more effective and efficient materials.

Castor oil, which is abundantly available in India at a very reasonable price, offer attractive possibilities for its conversion to various derivatives having good potential as vinyl plasticizers. The present studies is an attempt to explosure one such possibility with a view to produce commercially useful plasticizer for poly (viny1 chloride).
PLASTICIZERS AND PLASTICIZATION OF
POLY (VINYL CHLORIDE)

A brief review of plasticization:

The council of the International Union of Pure and Applied
Chemistry (IUPAC) in 1951 defined a plasticizer as a substance or
material incorporated in another material (usually a polymer—a plastic or
an elastomer) to increases its workability, flexibility or distensibility. Plasticizers are high boiling, chemically and thermally stable organic
liquid (or low melting solid or semi-solid in few cases). Their action is
essentially permanent as opposed to temporary function of solvents.
Plasticizer may lower melt viscosity, lower the temperature of a second
order transition ($T_g$) or lower the elastic modulus of the product without
altering the fundamental chemical character of the plasticized material.

Sears and Darby traced the history of plasticizer like materials to
very early civilisation. The uses of plasticizers in the modification of
polymer properties began during the 19th century. Hyatt brothers were
able to form the product, by adding camphor to nitrocellulose to make it
more easily moldable and less brittle in a finished form.

Polymers of vinyl chloride and process for making the same was
granted a patent product in 1929 by Ostromislensky. He speculated that
mechanism for plastification was probably a chemical reaction. During
1920 when **B.F. Goodrich Co.** was seeking uses for the horny, rigid and brittle polymers which they were able to make commercially from vinyl chloride. **Waldosemon**\(^5\) observed that boiling PVC particles in esters such as tricresyl phosphate and dibutyl phthalate gave a highly elastic and flexible adhesive like material which could also be molded into shapes. Thus, **Semon** is generally credited with being the first to synthesize the PVC resin. The survey of the literature reveals that (di-2-ethylhexyl) phthalate (DOP) became available commercially in 1940 and till today. DOP and other phthalate ester dominate the market of PVC plasticizers both in number and production volume.

Need for materials with specific characteristics improved quality and enhanced compatibility resulted in the development of speciality plasticizers. Initially only a few fatty acid esters, benzoates, tartarates and chlorinated hydrocarbons were available but were soon joined by adipates, azelates and sebacates. Epoxidised vegetable oils and fatty ester were specially attractive because of their synergistic thermo-stabilising effect\(^6\)\(^7\). Requirements from PVC cable industry for non-volatile plasticizers which could be thermally stressrd over a long period of time, were first satisfied with di (isotridecyl) phthalate and later on with trimellitates. Phosphate provided necessary flame retardant acation to the plasticized PVC formulation. Linear or predominantly linear C\(_6\)-C\(_{11}\)
alcohols available from new technology\(^{8-9}\) have given further impetus in recent years. Thus, from the survey of the literature the authors conclude that a large number of high performance plasticizers are now possible by systematic esterification with aliphatic or aromatic acid available in a large scale production.

**POLY (VINYL CHLORIDE) (PVC) AND ITS PLASTICIZATION**

The unplasticized poly (vinyl chloride) is a rigid polymer with the following chemical configuration.

\[
\left( \begin{array}{c}
\text{CH}_2 - \text{CH} - \\
| \\
\text{Cl} \\
\end{array} \right)_n
\]

In commercial PVC polymers, the value of \( n \) i.e. the degree of polymerisation ranges between 500 to 1500, this corresponds to a theoretical molecular weight range of about 31000-94000. The repeat units are linked exclusively head to-tail, i.e.,

\[
\text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2 - \text{Cl} - \text{CH} - \text{Cl}
\]

Structurally the PVC molecule is partially syndiotactic and does not have a completely regular structure. The reason is PVC has low crystallinity. The polymer molecules are either linear (or) only slightly branched, ‘PVC’ and ‘vinyls’ are often used broadly to refer to both the
homopolymer and the co-polymer as well as to the compounds containing either or both of them.

The major commercial production of the PVC in the world is through suspension polymerisation, (82%) of vinyl chloride gas while the rest is produces through Mass (10%) and emulsion (81%) polymerisation technique. The emulsion system has been advantage that the polymerisation could be done at lower temperature (20°C). Whereas high temperatures (52–80°C) are required for the suspension and bulk polymerisation.

Because of its unique molecular structure which accepts a wide range of plasticizers but limits their effect by an usual array of crystal system, PVC is especially suited for beneficial modifications, by plasticizers\(^\text{10}\) and accounts for over 80% of the total usage of plasticizers. Commercially manufactured PVC is partially crystalline\(^\text{11}\) consisting of crystallites surrounded by areas of relatively disorganisation (the amorphous region).

When the material is fully amorphous and the ‘use’ temperature is below its \(T_g\), the polymer will be in its glassy state and will behave like a brittle plast. When the ‘use’ temperature is above its \(T_g\), the same polymer will be in the rubbery state and will exhibits in elastomeric nature. A
crystallisable polymer whose $T_m$ is very much above the $T_{usc}$ temperature and attains a very high degree of crystallinity and becomes a fiber forming material. Even these amorphous regions are tightly bound by polar attraction between chlorine and hydrogen atoms in proximity. Given opportunity (compounding) and motivation (heat and shear) the plasticizer molecules penetrate the amorphous regions and disrupt intermolecular attractions. When enough plasticizer has entered the polymer matrix a general relaxation ensures and partial mobility is imparted to the PVC chains. The process is commonly referred to as plasticization$^{12}$.

From the time a plasticizer first comes in contact with PVC polymer until the production of final fused product and possibly even for some time after this a complex series of interactions occur.

**Sears, Darby and Touchette$^{13-14}$** summarised various stages of plasticization as follows.

(a) Irreversible uptake of plasticizer into the porous resin.

(b) Absorption of the plasticizer during which the total resin-plasticizer volume may decrease, although resin particle swell slowly on the outside.

(c) Diffusion of the plasticizer within the particles with little or no volume change, but involving high activation energies. At this stage
the plasticizer is probably present as clusters of molecules between bundles of polymer segments or molecules.

(d) The final stage of plasticization when the plasticizer molecules penetrate the bundles of polymer molecules so that they are no longer rigidly held together but behave as polymer in its rubbery rather than glassy state.

In some processes these step may not be sharply defined and may overlap. With the usual plasticizers for PVC, of moderate molecular weight, plasticization can only proceed through first two steps at room temperature. Step, (c) and (d) have high activation energies thus requiring a threshold temperature to get accomplished.

CLASSIFICATION OF PLASTICIZERS

Although the plasticizers can be classified in a number of different ways, but the following mode of classification are more generally practiced.

BASED ON MODE OF PLASTICIZATION

According to this mode, the plasticizers are classified as `external` (or) internal` plasticizers. The discrete materials which are added to the rigid polymers to effect plasticization but for the most part never chemically combined with it, are termed as `external plasticizers`. When
the originals polymers are modified or a related polymer is synthesized that will have the drived effects like more flexibility or better low temperature properties, the process is termed as 'internal plasticization'. The principle the internal plasticization involves monomers leading to homopolymers of high $T_g$, being selectively copolymerized with monomers whose homopolymers have substantially lower $T_g$.

It is observed that external plasticization permits greatest latitude in formulation properties and is generally less expensive. This makes it the most important method of plasticizing. The solvation $\leftrightarrow$ desolvation and the fact that the plasticizer is bound physically rather than chemically are characteristic of all externally plasticized system.

The advantage of internally plasticized system lies in strong chemical combination of hard and soft segments which cannot be separated from each other by extraction. However, the technique is limited, "every co-polymer is only suited to certain flexibility requirements". The survey of the mechanical properties of internally plasticized materials show a marked temperature dependence and the material have insufficient dimensional stability at elevated temperatures.
BASED ON CHEMICAL CONSTITUTION

According to chemical constitution and end usage, the plasticizers for vinyl resins can be divided in to following chemical classes.

1. Phthalates          General purpose
2. Epoxides            Stabilizers
3. Dibasic acid ester  Low temperature
4. Phosphates          Flame retardant
5. Polyester           Permanent
6. Extenders           Low cost.

MECHANISM OF PLASTICIZATION

Three favoured theories have been put forward to explain the mechanism and the effects of plasticization. The literature reveals that none of the theories is complete in itself but an understanding of the plasticization process can be gained by combining ideas from each theory.

1. Lubricity Theory:

In the lubricity theory initially proposed by KirkPatrick\textsuperscript{15} and others\textsuperscript{16-17} a plasticizer is considered to act as a lubricant for the sliding contact of the polymer chain thus facilitating deformation by reducing intermolecular friction.
2. Gel Theory:

Doolittle\textsuperscript{18} developed this theory and accordingly give the resistance to deformation of the amorphous polymers is due to the formation of a three dimensional honey comb structure with cross links originating from the active centers along the polymer chains. In a plasticized system while the polymer molecules are continually making and breaking their contact with each other that is equilibrium is established between aggregation and disaggregation, the plasticizers molecules are also attaching themselves to the active centers, a equilibrium between solvation and desolvation may attain. The combined effect is that at a given set of condition, a proportion of the active center will be solvated or masked by the plasticizers molecules and hence will be eliminated as potential cross-linking point resulting in the reduction in the intermolecular friction. But this theory is insufficient to some extent to explain a completely plasticized system. It has been suggested that in the case of PVC these active centers are the dipoles in the polymer chain.

Leuchs\textsuperscript{19} suggested two types of plasticizer action.

(i) **Hinge:** The Hinge type plasticizers are typified by the readily polymerisable aromatic compounds.
(ii) **Screen type:** The screen type plasticizers are typified by the polar aliphatic esters.

3. **Free Volume Theory:**

Free volume theory extends the above ideas and allows a quantitative measure of the plasticization effect. Free volume turn stands for the internal space available in a polymer for the movement of the polymer chains which imparts flexibility to the resin. Plasticizers increase free volume of the resin and also ensure that free volume is maintained as the plasticized system is cooled to room temperature. From the above observation it can be concluded that the plasticizer molecules that do not interact with the polymer chain must simply fill the free volume created by those molecules that do. This portion of the plasticizer can also be envisaged as providing screening action that prevents interaction between the neighbouring polymer chains and thus preventing the reformation of the rigid polymer network on cooling.

**PLASTICIZER MOLECULAR WEIGHT AND PLASTICIZER RETENTION IN PVC GEOMEMBRANES**

Timothy D. Stark et. al. studied the plasticizer molecular weight and retention in PVC geomembrane. Plasticizers are used to make PVC flexible so it can be used as a geomembrane for containment purpose.
Plasticizers can migrate from PVC geomembranes over time because of contact with air, librates and an absorbent solid material. Plasticizer migration can reduced the flexibility of PVC geomembranes resulting in brittle behavior. It has been observed that a minimum average plasticizers molecular weight of 400 be used to ensure long-term plasticizer retention in the field. The weighted average method for calculating the average molecular weight is recommended when two or more plasticizers are incorporated into the PVC geomembrane. PVC is the one of the oldest and most common plastic in used today because of the low cost, durability and versatility with respect to fabrication and property modification (Krauskopf 1993). A potential limitation in using plasticized PVC geomembrane is plasticizer retention when the plasticized PVC geomembrane is in contact with a surrounding medium. The brief description of the mechanism controlling plasticizer retention in contact with these three media, area, librates, a solid are given below—

1. Plasticizer retention in air:

Volatile loss (or) evaporation of external plasticizer from PVC into the surrounding air is a common mechanism of plasticizer migration volatile loss from PVC is composed of two major transfer process diffusion and evaporation from insite and the geomembrane surface. Paaonotantinou and Papaspysides (1994) experimentally show a linear
relationship between plasticizer loss due to diffusion and the square roots of time which is expressed as

\[
\frac{M_t}{M_w} = 2\sqrt{\frac{d_t}{\pi l^2}}
\]

where \(M_t\) is the amount of plasticizer loss at time \(t\), \(M_w\) is the amount of plasticizer loss at equilibrium, \(d\) is the diffusion coefficient, \(t\) is the time and \(l\) is the thickness of the PVC.

2. Plasticizer retention in liquid:

Plasticizer migration from plasticized PVC into liquids such as water, oils, waxes, alcohol and other agents can be represented by two mechanisms. If the molecular size of the extracting liquid is small enough to penetrate into the PVC polymer structure, extractent of the plasticizer can occurs. In the second case the factor controlling the migration process in the compatibility of the plasticizer and extracting the compatibility of the PVC resin and extractent (Nass and Heiberger 1986).

3. Plasticizer retention adjacent to soil:

Plasticizer migration from plasticized PVC into other polymeric materials has not been studied as plasticizer migration into air and liberates Wilcron (1995) summerises the effect of plasticizer migration
into receiving material that are used as coatings structural component and adhesive bond.

**VINYL RECYCLING**

Some PVC manufactures have placed vinyl recycling programs into action, recycling both manufacturing waste back into their products, as well as post consumer PVC construction material to reduce the load on landfills. A new process of PVC recycling is being developed in Europe and Japan called texiloop\(^2\). This process consists of recovering PVC plastic from composite material through dissolution and precipitate. It strives closed loop system, recycling its key solvent and hopefully making PVC a future technical nutrient.

**REQUIREMENT OF PVC PLASTICIZERS**

There are three basic functional requirements of a PVC plasticizers:-

1. **Compatibility:** The compatibility of a plasticizer with the given polymer is its most important property. The plasticizer should be compatible with the polymer system over both processing as well as service condition. It is also desirable that subsequent exposuer of the plasticized articles to commonly encountered substances and conditions
such as water, oil, air and sunlight etc. should not disturb the compatibility balance.

2. **Efficiency:** One of the basic functional requirements of a plasticizer is to impart flexibility and softness to the plastic materials. The less plasticizers needed to achieve a defined level of plasticization, more efficient is the plasticizer.

3. **Permanence:** It is highly desirable that plasticizer once incorporated into the PVC composition should be permanently retained. It’s loss would not only cause changes in the properties of the plasticized system but may also produce some external undesirable side effects that is blistering of the PVC floor tiles bonded due to migration of plasticizer from PVC tile. A permanent plasticizer resists its loss from the plasticized system occurring due to volatilization, extraction and migration.

**PLASTICIZERS DERIVED FROM VEGETABLE OILS AND FATS**

More than 90% of the plasticizer used in PVC industry is represented by high boiling organic esters of various organic acids and alcohols. The material commonly used for the manufacture of vinyl plasticizers are given in Table-1.
Table – 1

<table>
<thead>
<tr>
<th></th>
<th>Monobasic acid</th>
<th>Benzoic acid, Oleic acid, Tall oil fatty acid, coconut fatty acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Dibasic acid</td>
<td>Phthalic acid, Adipic acid, Sebacic acid</td>
</tr>
<tr>
<td>3</td>
<td>Tribasic acid</td>
<td>Trimellitic acid, Phosphoric acid, Phosphorous oxichloride</td>
</tr>
<tr>
<td>4</td>
<td>Alcohols</td>
<td>Normally butyl, Hexyl, Cyclohexyl</td>
</tr>
<tr>
<td>5</td>
<td>Glycols</td>
<td>Ethylene glycols, Propylene glycols, Dipropylene glycols, Butylene glycols</td>
</tr>
<tr>
<td>6</td>
<td>Miscellaneous</td>
<td>Phenol, Cresol, Soyabean oil, Linseed oil, Castor oil.</td>
</tr>
</tbody>
</table>

Table No. 2 Gives a breakdown of the consumption of various type of plasticizers for PVC in U.K. and U.S. market.
Table – 2

Types and relative proportion of plasticizers used in U.K. and U.S.

<table>
<thead>
<tr>
<th>Plasticizer Class</th>
<th>Consumption % by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U.K.</td>
</tr>
<tr>
<td>Phthalates</td>
<td>74.0</td>
</tr>
<tr>
<td>Phosphates</td>
<td>5.0</td>
</tr>
<tr>
<td>Aliphatic dibasic acid esters</td>
<td>2.0</td>
</tr>
<tr>
<td>Trimellititates</td>
<td>0.5</td>
</tr>
<tr>
<td>Polymerics</td>
<td>1.9</td>
</tr>
<tr>
<td>Epoxide</td>
<td>5.0</td>
</tr>
<tr>
<td>Chlorinated paraffins</td>
<td>9.5</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>1.9</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Consumption data shown above indicates that phthalates by far, are the most abundantly used plasticizers in the vinyl industry representing nearly 75% of the total plasticizer consumption. The diesters of phthalic
acid with C₈ alcohols offer the best balance of properties for general purpose use, mainly to impart the desired degree of flexibility and appropriate mechanical properties while other plasticizers are used only in minor amount to achieve special effects and/or cost reduction.

**STATUS OF VEGETABLE OIL BASED VINYL PLASTICIZERS**

Vegetable oils, an agricultural produce of the country are a rich source of various useful monobasic fatty acids like steric, oleic, ricinoleic, lenoleic, lenolenic, palmitic and lauric. A number of dibasic acids like sebacic acid, azelaic acid, dimeric lenoleic acid and other monobasic pelargonic acid can also be considered to have vegetable oil origin. Thus vegetable oils are the starting materials not only for the low temperature, stabilising plasticizers, but also for the highly permanent polymeric plasticizers.

Vegetable oil based plasticizers can be divided into following categories:

1. **Epoxidised vegetable oils:**

   These classes of epoxy plasticizers possess the best combination of economy and stabilising performance. Many oils of vegetable origin were studied as potential substances for making epoxy plasticizers are given in Table – 3.
Table – 3

Theoretical oxirane oxygen content of various vegetable oils.

<table>
<thead>
<tr>
<th>Vegetable Oil</th>
<th>Iodine Value</th>
<th>Double Bonds</th>
<th>Theoretical Oxirane Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed oil</td>
<td>170-204</td>
<td>0.670-0.800</td>
<td>9.67-11.9</td>
</tr>
<tr>
<td>Safflower oil</td>
<td>140-150</td>
<td>0.552-0.591</td>
<td>8.11-8.63</td>
</tr>
<tr>
<td>Soyabean oil</td>
<td>120-141</td>
<td>0474-0.556</td>
<td>7.03-8.16</td>
</tr>
<tr>
<td>Corn oil</td>
<td>102-121</td>
<td>0.406-0.504</td>
<td>6.09-7.44</td>
</tr>
<tr>
<td>Cottonseed oil</td>
<td>99-113</td>
<td>0.390-0.445</td>
<td>5.87-6.65</td>
</tr>
<tr>
<td>Rapeseed oil</td>
<td>97-108</td>
<td>0.382-0.426</td>
<td>5.76-6.37</td>
</tr>
<tr>
<td>Groundnut oil</td>
<td>84-100</td>
<td>0.331-0.394</td>
<td>5.03-5.93</td>
</tr>
</tbody>
</table>

Many did not possess enough unstauration to provide the oxirane oxygen content necessary for imparting adequate compatibility with PVC and to effectively function as heat and light stabilizers.

The epoxy polymers are basically polyethers one type of epoxy polymer or epoxy resin is prepared from apichlorophydrin and bisphenol–A. The reaction is carried out with excess of apichlorohydrin. The epoxy resin obtained through these reactions will be either highly viscous liquid or solid liquid with high melting point.
Epoxy resins are excellent structural adhesive. One of the principal constituent in many of the fibre-reinforced plastic is an epoxy polymer.

\[
\begin{align*}
2\text{CH}_2\text{CH}_2\text{Cl} + \text{HO} & \rightarrow \text{CH}_3\text{C}(-\text{O})\text{OH} \\
\text{Cl} & \text{CH}_2\text{CH}_2\text{O}(-\text{O})\text{C}(-\text{O})\text{OCH}_2\text{CH}_2\text{Cl} \\
& \text{NaOH} \\
\text{CH}_2\text{CH}_2\text{O}(-\text{O})\text{C}(-\text{O})\text{OCH}_2\text{CH}_2\text{O} \rightarrow \text{CH}_3(-\text{O})\text{C}(-\text{O})\text{OCH}_2\text{CH}_2\text{O} \\
\text{+ Bisphenol-A-[Excess]} \\
\end{align*}
\]

where \( x = \text{CH}_2\text{CH}_2\text{O} \)

\[
\begin{align*}
y = \text{CH}_3\text{C}(-\text{O})\text{OCH}_2\text{CH}_2\text{O} \end{align*}
\]
By availability and favourable economic soyabean oil forms the prominent base for epoxidised oils. Castor oil, due to the presence of large amount of ricinoleic acid, is difficult to epoxidised to high level due to the structural placement of the unsaturation or presence of interfering group\textsuperscript{22}.

2. Epoxidised alkyl ester:

The compatibility of the epoxidised oils with PVC is only fair due to the large percentage of incompatible component present in the triglyceride molecule and to the molecules being large and bulky. They also do not contribute to low temperature properties. Alkyl ester of oleic and tall oil fatty acid comprise the second important groups of epoxy plasticizers. The alkyl 9,10-epoxy estearates have the lowest oxirane oxygen content of the commercial epoxy plasticizers and consequently are much less efficient stabilizers than epoxidised vegetable oils. It is believe that they are quite efficient in imparting low temperature flexibility to PVC at room temperature.

Epoxide esters derived chiefly from oleates and tallates are more compatible than the corresponding estearates, unsaturated or hydroxy derivatives\textsuperscript{23-24}. During the survey of the literature the authors found that primary plasticizers such as D.O.P. can be incorporated into PVC in the concentration range 25-35\% of the total plasticizer\textsuperscript{24}.
The alcohols used for esterification include simple alcohols such as methyl, ethyl, butyl, hexyl, cyclohexyl, isoctyl and 'isodecyl' and ether alcohols such as methoxyethyl, butoxyethyl and tetrahydrofurfuryl alcohols. For reason of permanence, low temperature properties and cost, only butyl and 2-ethylhexyl ester have gained popularity.

Fatty acid ester of 2, 3-epoxytetrahydrodicyclopentadienol are effective plasticizers for PVC with physicomechanical property superior to D.O.P.²⁵.

Epoxidised bis alkyl esters which form an extention of this class, are prepared by the reaction of 1:2 molar ratio of ethylene or polyethylene glycol with tall oils fatty acids. One of the possible chemical structure of epoxidised ethylene glycol ditallate is shown below:

\[
\begin{array}{c}
\text{O} \\
R_1 - C - O - CH_2 CH_2 O\cdot C - R_2 \\
\end{array}
\]

where \(R_1 = \text{CH}_3 (\text{CH}_2)_7 \cdot \text{CH} \cdots \text{CH} \cdot (\text{CH}_2)_7\) and \(R_3 = \text{CH}_3 (\text{CH}_2)_4 \cdot \text{CH} \cdots \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdots \text{CH} \cdot (\text{CH}_2)_7\)

They have oxirane oxygen content 5.51 and 5.8%, higher than the 4.2 to 4.6% content typical of octyl epoxy tallates.
3. Ester of saturated fatty acid:

A low ratio of oxygen to aliphatic hydrocarbons limits the simple alkyl esters of saturated fatty acid to relatively low degree of solvancy and compatibility for PVC. Monocarboxylic acid ester with low molecular weight are too volatile, too sensitive to water and too poor as gellers to be used as plasticizers. The longer chain fatty esters is too incompatible that there is no question of using them as plasticizers. They are mostly used as lubricants for processing rigid and plasticized PVC.

It is observed that introduction of more oxygen into the molecule improves compatibility, fatty acid ester with polyhydric alcohols and their derivatives have found some use particularly where volatility and water susceptibility are not critical. Similarly, ester with ether alcohols such as methoxy ethyl and butoxy ethyl alcohol also show improved compatibility.

4. Ester of unsaturated fatty acids:

Technologically the important members of this group are alkyl oleates and tallates. They contribute low temperature properties to many polymers. Due to the presence of unsaturation they are relatively more compatible then their saturated acid counterparts. Aryl oleates due to the polarising nature of the aromatic nucleus are more compatible with vinlys.
The compatibility can be increased by esterifying with polyhydric alcohols or ether alcohols. Methoxy ethyloleate is a secondary plasticizer with TCP in PVC.

5. **Ester of dibasic acid:**

Ester of dibasic acids such as adipates, azelates and sebacates constitute and important class of plasticizers termed to as low temperature plasticizers. Compatibility of both sebacates and azelates with PVC decreases as the size of the alkyl groups becomes longer. The plasticization efficiency in the series drops moderately and their low temperature properties improve as the alkyl groups passes from butyl to octyl.

6. **Ester of chlorinated fatty acid:**

Chlorinated alkyl esters of fatty acid have been suggested as plasticizers for PVC. 3 to 6 chlorine atoms per molecule are apparently required to achieve good compatibility, but the introduction of highly polar chlorine atom increases the electric loss. Chlorination not only enhances the compatibility but also aids in non-burning characteristics. Stabilization is, however, necessary, usually with epoxy derivatives, to prevent splitting out of hydrogen chloride.
7. Polymeric plasticizers:

The polymeric plasticizers are viscous, liquid polyester formed by the condensation of glycols and dibasic acid fat derived acid such as sebacic and azelaic acids play an important role. However, it is a normal practice to include a third reactant, a monocarboxylic acid or monohydroxy alcohol in the polyester to modify or to end stop the product. Three general structures of polymeric plasticizers are given below.

\[
\text{HO--R--O--C--R'}--O--C--O--\cdots--H \quad \text{non terminated}
\]

\[
R^2 \quad C--O--\left\{\ldots--R--O--C--R'--C--O--\cdots--R--O--C--R^2\right\}_n \quad \text{Acid terminated}
\]

\[
R^2 \quad O--C--R'--C--O--\left\{\ldots--R--O--C--R'--C--O--\cdots--R^1\right\}_n \quad \text{Alcohol terminated}
\]

Polymeric plasticizers vary in average molecular weight from approximately 500-3000. Increasing molecular weight gives advantages
of increased viscosity, lower plasticizing efficiency, poor low temperature flexibility and difficult processing\textsuperscript{26}.

The longer chain fatty acid terminated polyesters are generally better on low temperature flexibility and efficiency than non-terminated or alcohol terminated polyester of about the same molecular weight. The polyesters terminated with unsaturated acid may cause problems of incompatibility and poor light stability.

8. Plasticizer derived from castor oil:

**Castor oil and its constitution:** Castor oils from the seeds of castor plant, ricinus communis, is the only commercially important vegetable oil containing a high percentage of one single hydroxy unsaturated fatty acid, the ricinoleic acid. Because of the presence of a hydroxyl group, castor oil is known for its uniqueness among vegetable oils.

It differs from other oils by its high hydroxyl value and from oils of comparable iodine value by its high specific gravity. It is soluble in alcohols but almost insoluble in petroleum solvents. Castor oil is strongly dextro-rotatory due to the presence of asymmetric carbon atom.

Ricinoleic acid constitutes a major portion of the fatty acid composition of the castor oil. According to various investigators the ricinoleic acid content of castor oil fatty acid range from 80 to 95%. The
literature reveals that the fatty acid composition of a typical castor oil sample of Indian origin is shown below:

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Amount (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmatic acid</td>
<td>0.9</td>
</tr>
<tr>
<td>Steric acid</td>
<td>1.2</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>0.2</td>
</tr>
<tr>
<td>Oleic</td>
<td>3.3</td>
</tr>
<tr>
<td>Linoleic</td>
<td>3.7</td>
</tr>
<tr>
<td>Ricinoleic</td>
<td>89.0</td>
</tr>
<tr>
<td>Dihydroxy esteric</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The chemical structure of the ricinoleic acid is shown below:

$$\text{CH}_3 (\text{CH}_2)_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C} = \text{C} \cdot \text{H} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$$

$$\text{OH}$$

Ricinoleic acid, 12-hydroxy-cis-9-octadecenoic acid.

Beside the presence of an end and carboxylic acid group and a double bond at C$_9$ and C$_{10}$ position, ricinoleic acid also carries a secondary hydroxyl group at C$_{12}$ position. Because of this
polyfunctionality, ricinoleic acid present at attractive possibility for derivatisation yielding many useful product.

CASTOR OIL AND ITS SIMPLE DERIVATIVES
AS VINYL PLASTICIZERS

The high hydroxyl value of castor oil tends to make it hydrophilic in nature. As a result castor oil itself has almost no compatibility with vinyls and finds wide spread use in the plasticization of cellulosics such as nitrocellulose and ethyl cellulose. According to Frith and Tuckett, it exhibits an improved to compatibility with nitrocellulose in the presence of solvent type plasticizers such as D.B.P. and T.C.P. In vinyls castor oil finds use only as a lubricant. It greatly aids the extrusion of PVC when used in small proportions.

Acetylation of free hydroxyl groups improve the compatibility of castor oil with vinyls. Acetylated castor oil is used world wide as a secondary plasticizer for PVC. It offers properties like low volatility, good dielectric properties and lubricity due to processing. It finds extensive use in PVC electrical cable industries where it is used with primary plasticizers DOP or TCP in concentration ranging from 10-20% the total plasticizer content. From the survey of the literature it is revealed that besides PVC, acetylated castor oil is also used as plasticizer for other
polymers like nitrocellulose\textsuperscript{27}, polyurethane\textsuperscript{32} and ethylenevinyl acetate co-polymer\textsuperscript{33}.

Compatibility of acetylated castor oil further increases considerably by the epoxidation of the unsaturated bond.

\begin{equation}
\begin{array}{c}
\text{CH} \quad \text{CH}_2 \quad \text{CH} = \text{CH} \\
\text{OH} \\
\text{Castor oil} \\
\downarrow \\
\text{CH} \quad \text{CH}_2 \quad \text{CH} = \text{CH} \\
\text{O}\text{C} \quad \text{CH}_3 \\
\text{O} \\
\downarrow \\
\text{Acetylated Castor Oil} \\
\downarrow \\
\text{CH} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH} \\
\text{O}\text{C} \quad \text{CH}_3 \\
\text{O}
\end{array}
\end{equation}

**Epoxidised acetylated castor oil:**

Epoxidised acetylated castor oil imparts flexibility and improves thermal stability to vinyl and may be used as a sole plasticizer in compositions where in the plasticizer content does not exceed 45 per hour\textsuperscript{30}. 
Recently it is revealed that besides, castor oil esterified rapeseed oil has been used as plasticizer in plastic processing\textsuperscript{34}. The plasticizers used in PVC coating in general but chlorinated paraffins in particular are criticised because of their environmentally harmful action, waste water and air pollution.

**ESTER OF RICINOLEIC ACID AS VINYL PLASTICIZERS**

Due to the presence of double bond at C\textsubscript{9}–C\textsubscript{10} and a hydroxyl group at C\textsubscript{12} ricinoleates show all around excellent compatibility with various resins and rubbers but limited to nitrocellulose, ethyl cellulose, oil resistant nitrile rubbers, allyl starch and polyvinylbutyral. Additional compatibility accompanied by increased water susceptibility characterize the monoricinoleates of polyhydric alcohols such as ethylene glycol, propylene glycol and glycerole. Glycerole has been used as plasticizer for waxes.

The acetyl ricinoleates are definitely superior and cover a greater usage. Methyl and butyl acetylricinoleates are secondary plasticizers for PVC. These products possess low viscosity, excellent plasticization and processing characterization\textsuperscript{34}. Acetylated ricinoleates of lower alcohols are also useful for wetting and dispersing fillers and pigments. Methyl ester is generally compatible and is an all purpose plasticizer. It is
considered superior to all other castor oil derivatives because it gives very low brittle point temperature and flexural modulus. Other important properties favoured by methyl acetyl ricinoleate are stabilization of organosoles and plastisols and case of processing by virtue of its antistick character.

**MISCELLANEOUS VINYL PLASTICIZER BASED ON RICINOLEIC ACID**

To extend the scope and commercial uses of castor oil based plasticizers for vinyl there is a mention in the literature of various other derivatives of ricinoleic acid, their evaluation as plasticizers for vinyl polymers.

**ESTER OF HYDROXY STERIC ACID**\(^{35}\):

Till then 31acyloxy or aryloxy ester prepared from hydroxy steric acid were evaluated as plasticizer for PVC copolymer. Many of them were found to be primary plasticizer having outstanding low temperature performance when employed or used at a 35% level. Formulation of these compound compare quite favourable in tensile properties and volatility behaviour with those product containing di-2-ethylhexylester of phthalic, sebacic, azelaic and adipic acids.
(1) MORPHOLEIN DERIVATIVES OF RICINOLEIC ACID:\textsuperscript{36}:

Morpholein derivatives like

(i) \textit{4-Ricinoleoyl morpholein}:

\[
\text{CH}_3 \quad \text{(CH}_2)_5 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} = \text{CH} \quad \text{(CH}_2)_7 \quad \text{CON} \quad \text{O} \\
\text{OH}
\]

(ii) \textit{4-[12-Acetoxy ricinoleoyl morpholein]}:

\[
\text{CH}_3 \quad \text{(CH}_2)_5 \quad \text{CH} \quad \text{CH}_2 \cdot \text{CH} = \text{CH} \cdot \text{(CH}_2)_7 \cdot \text{CON} \quad \text{O} \\
\text{O} \quad \text{C} \cdot \text{CH}_3 \\
\text{O}
\]

(iii) \textit{4-[12-\text{\-b-cyano ethoxyoleoyl}] Morpholein}:

\[
\text{CH}_3 \quad \text{(CH}_2)_7 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} = \text{CH} \quad \text{(CH}_2)_7 \quad \text{CON} \quad \text{O} \\
\text{O} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CN}
\]

The above derivatives exhibited satisfactory milling and molding characteristics but it is found that all were not equally compatible acetylated and cyano ethylated morpholides to the poorly compatible unmodified morpholide of 12-hydroxy-stearic acid. The unmodified morpholide of ricinoleic acid was found to be borderline case after 60 days.

(2) ACETYL ESTER OF RICINYL ESTER OF PENTAERYTHRITOL:\textsuperscript{37}:

The structure of these ester are shown below:
\[ R_2 \quad R_2 \quad R_1 \quad R_3 \]

\[ R_1 \quad C \quad R_1 \quad C \quad R_2 \quad \text{HOH} \quad C \quad \text{CHOO} \quad C \quad \text{CH}_3 \]

where

\[ R_1 = \text{CH}_2\text{OH}, \quad R_2 = \text{CH}_3(\text{CH}_2)_5\text{CH} \cdot \text{CH}_2\text{CH} = \text{CH} (\text{CH}_2)_7\text{COOCH}_2 \]

\[ \text{OH} \]

\[ R_3 = \text{acetylated } R_1 \text{ and } R_4 \text{ acetylated } R_2 \text{ where prepared by acetyling either the direct esterification products of pentaerythritol and ricinoleic acid or the interesterification product of castor oil with pentaerythritol. The plasticizer thus produce where reported to be usable as primary or secondary plasticizer for PVC and could be incorporated as sole plasticizer up to 100 per hour level without showing any sign of incompatibility.} \]

(3) EPOXIDISED ACETYLATED DI RICINOLEATE OF DIHYDRIC ORGANIC COMPOUND\(^{38}\):

The compound coded as ACETOFLEX-GE was produced by epoxidation of acetylated ethylene glycol diricinoleate and evaluated for compatibility and thermal stability on compounding with PVC. The results were compared with those obtained with its unepoxidised counter part and acetylated castor oil.
(5) **PHTHALY ESTER OF ALKYL RICINOLEATES**\(^{39}\):

Ester of alkyl ricinoleates with monoester of phthalic acid having the general formula.

\[
\text{CH}_3 \quad \text{(CH}_2\text{)}_5 \quad \text{CH} = \text{CH} \quad \text{(CH}_2\text{)}_7 \quad \text{COOR}_1
\]

\[
\begin{array}{c}
\text{COO} \\
\text{COOR}^2
\end{array}
\]

where \( R^1 \) and \( R^2 \) vary from \( \text{CH}_3 \) to \( \text{C}_{10}\text{H}_{21} \). Exhibit lower volatility and better processing characteristics.

**2. OBJECTIVE OF THE PRESENT STUDIES**

From the survey of the existing literature the authors have concluded that simple esters of ricinoleic acid, though find extensive use as plasticizers for cellulosics, oil resistant nitrile rubber and polyvinyl butryl, have no compatibility with PVC.

Acetylation of the hydroxyl group improve their compatibility and as a result alkyl acetyl ricinoleates enjoy a greater usage. They are more compatible and permanent low temperature plasticizer for vinyl and rubber. Methyl acetyl ricinoleate (MAR) is an important member of this family which is consider superior to another castor oil derivatives as it provide very low brittleness temperature \( T_b \) and flexural modules\(^{31}\). In addition to being low temperature plasticizer, alkyl acetyl ricinoleates are
characterised by low viscosity, excellent plasticization and processibility. Because of their non-toxic nature, they can also be used for application requiring contact with food materials. Acetylated ricinoleates of lower alcohols are useful as dispersing agent for fillers and pigments\textsuperscript{31}.

In spite of so many advantages, acetylated ricinoleate suffer from serious defects which have their limited their use inflexible PVC. These defects may be summerised as limited compatibility, susceptibility to oxidation, compatibility in stability. The present research work is an attempt to enhance the compatibility of the alkyl acetyl ricinoleate so that they can be used in PVC formulations in high proportions with primary plasticizer and thus find a better place in the vinyl industry. The compatibility is one of the essential requirements of a plasticizer which enable it to be incorporated into the polymer composition in significant amount without the fear of exudation. It is a function of the solvent power of the plasticizer which in turn depends on the size molecular weight, shape and polarity of plasticizer molecule. Thermodynamically\textsuperscript{40} the polar region of plasticizer molecule Induce an interaction which result in lowering of overall energy of the system relative to its constituent groups. This stability confers compatibility between the plasticizer and the PVC.

Extensive literature search from chemical abstract, encyclopedia, books and journals revels that a considerable amount of the research work
has been carried out for improving the performance of the ricinoleate plasticizer but no-work on improvement of compatibility of the alkyl ricinoleate by introducing polar halogen groups through esterification with halogenated organic acid has been reported from any part of the world. Therefore, it was thought worthwhile to prepare a plan to synthesized alkyl halo acetyl ricinoleates by esterifying alkyl ricinoleates with halo acetic acid and evaluate them as plasticizer for PVC. Employing morden analytical technique to, determining various physico-chemical constant like iodine value, saponification value, viscosity, refractive index, melting point, boiling point, oxirane value and acid number of epoxy compound. Besides all major interesterification product as plasticizer and their derivatives will be evaluated as plasticizers for PVC using lower of glass transition temperature ($T_g$), migration test and compatibility studies.

In order to accomplish the present piece research the authors have a systematic plane in their mind methyl and ethyl ricinoleate produced through interesterification of castor oil were taken as the starting materials. The halo acid used for esterification included both monochloro and monobromo acetic acid. Simply to studied the effect of halogen interchange on the plasticizer performance. Specifically low molecular weight alcohols, methyl alcohol and ethyl alcohol were used for
alcoholysing the castor oil with a view to produced low viscosity product
with higher plasticization efficiency. The esterification was carried out by
refluxing alkyl ricinoleates with requisite quantities of the halo-acid in
presence of para toluene sulphuric acid (PTS) as catalyst and benzene as
an entnainer to facilitate azeotropic removal of waster of esterification.
The important chemical reaction involves are given below:

1. Interestertification of castor oil:

Assuming castor oil to be a triglyceride of ricinoleic acid, this
reaction can be represented as

\[
\begin{align*}
\text{CH}_2\text{OCOR} & \quad \text{CH}_2\text{OH} \\
\text{CH-OCOR} + 3\text{R}^1\cdot \text{OH} \quad \overset{\text{Sodium hydroxide}}{\text{(Catalyst)}} \quad 3\text{RCOOR}^2 + \text{CHOH} \\
\text{CH}_2\text{OCOR} & \quad \text{alkyl ricinoleate} \\
\text{Castor oil} & \quad \text{CH}_2\text{OH} \quad \text{Glycerol}
\end{align*}
\]

(Glyceryl triricinoleate)

Here \( R = (\text{CH}_2)_7 \cdot \text{CH} = \text{CH} --- \text{CH}_2 \cdot \text{CH(CH}_2)_9 \cdot \text{CH}_3 \)

\( R^1 = \text{CH}_3 \text{ OR C}_2\text{H}_5 \)
2. Esterification:

\[
\begin{align*}
\text{Alkyl ricinoleate} & \quad \text{Catalyst (PTS)} \quad \text{Entnainer (benzene)} \\
\text{CH}_3(CH_2)_5\text{CHCH}_2\text{CH} = \text{CH(CH}_2)_7\text{COOR}^1 + X \quad \text{CH}_2\text{COOH} \\
\text{OH} & \quad \text{haloacetic acid} \\
\text{CH}_3(CH_2)_5\text{CHCH}_2\text{CH} = \text{CH(CH}_2)_7\text{COOR}^1 + \text{H}_2\text{O} \\
\text{O.C.CH}_2 - X & \quad \text{water} \\
\end{align*}
\]

alkyl haloacetyl ricinoleate.

The following four compounds resulted from the above reactions

(i) Methyl chloroacetyl ricinoleate: Chemical structure –

\[
\begin{align*}
\text{CH}_3(CH_2)_5\text{CHCH}_2\text{CH} = \text{CH(CH}_2)_7\text{COOCCH}_3 \\
\text{O.C.CH}_2\cdot\text{Cl} & \quad \text{O}
\end{align*}
\]

(ii) Ethyl chloroacetyl ricinoleate: Chemical structure –

\[
\begin{align*}
\text{CH}_3(CH_2)_5\text{CHCH}_2\text{CH} = \text{CH(CH}_2)_7\text{COOC}_2\text{H}_5 \\
\text{O.C.CH}_2\cdot\text{Cl} & \quad \text{O}
\end{align*}
\]
(iii) **Methyl bromoacetyl ricinoleate:** Chemical structure –

\[ \text{CH}_3 (\text{CH}_2)_5 \text{CH} \cdot \text{CH}_2 \cdot \text{CH} = \text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOCH}_3 \]

\[ \text{O} \longrightarrow \text{C} \cdot \text{CH}_2 
\longrightarrow \text{Br} 
\text{O} \]

(iv) **Ethyl bromoacetyl ricinoleate:** Chemical structure –

\[ \text{CH}_3'(\text{CH}_2)_5 \text{CH} \cdot \text{CH}_2 \cdot \text{CH} = \text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOC}_2\text{H}_5 \]

\[ \text{O} \longrightarrow \text{C} \text{CH}_2 
\longrightarrow \text{Br} 
\text{O} \]

All evaluation exercise of the plasticizers synthesized under the present studies was carried out in relation to their unhalogenated precursor “methyl acetyl ricinoleate” as in way, these halogenated compounds can be thought of as structural modifications or derivatives of methyl acetyl ricinoleate [structure (i)] where in one hydrogen atom of the acetoxy group has been substituted by halogen atom (structure ii).

\[ \begin{align*}
\text{CH}_3 & \end{align*} \]

\[ \text{O} \longrightarrow \text{C} 
\longrightarrow \text{CH}_3 
\text{O} \]

\[ \begin{align*}
\text{C} & \end{align*} \]

\[ \text{C} \end{align*} \]

\[ \text{C} \end{align*} \]

\[ \text{X} = \text{Cl} \text{ (or) Br} \]

Methyl acetyl ricinoleate

Methyl haloacetyl ricinoleate

I

II
The unsaturation which still existed in alkyl haloacetyl ricinoleate was eliminated by epoxidation. This is one of the most advantageous means of eliminating unsaturation in the plasticizers. The epoxidation was carried out by treating the unsaturated compound with peracetic acid generated by the action of hydrogen peroxide on glaceal acetic acid. Sodium hydrogen phosphate was used as catalyst. The chain of chemical reaction involved are given below:

\[
\begin{align*}
\text{CH}_3\text{COOH} + \text{H}_2\text{O}_2 & \rightarrow \text{CH}_3\text{CO}_2\text{OH} + \text{H}_2\text{O} \\
\text{acetic acid} & \quad \text{hydrogen peroxide} & \quad \text{peracetic acid}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 \left(\text{CH}_2\right)_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} = \text{CH} \left(\text{CH}_2\right)_7 \cdot \text{COOR} + \text{CH}_3 \cdot \text{CO}_2\text{OH} \\
\text{alkyl haloacetyl ricinoleate} & \quad \text{Peracetic acid}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 \left(\text{CH}_2\right)_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} = \text{CH} \left(\text{CH}_2\right)_7 \cdot \text{COOR} + \text{CH}_3 \cdot \text{COOH} \\
\text{alkyl haloacetyl epoxy ricinoleate} & \quad \text{acetic acid}
\end{align*}
\]

Here \( R = \text{alkyl group, CH}_3 \) (or) \( \text{C}_2\text{H}_5 \)

\( X = \text{halide group, Cl} \) (or) \( \text{Br} \)
Epoxidation of the various alkyl haloacetyl ricinoleates resulted in
the development of four new compounds, namely

(i) **Methyl chloroacetyl epoxy ricinoleate:** Chemical structure –

\[
\begin{align*}
\text{O} \\
\text{CH}_3\cdot(CH_2)_5\cdot\text{CH} \rightarrow \text{CH}_2\cdot\text{CH} \rightarrow \text{CH} \cdot (CH_2)_7 \text{ COOCH}_3 \\
\text{O} \text{C} \cdot \text{CH}_2\text{Cl} \\
\text{O}
\end{align*}
\]

(ii) **Ethyl chloroacetyl epoxy ricinoleate:** Chemical structure –

\[
\begin{align*}
\text{O} \\
\text{CH}_3\cdot(CH_2)_5\cdot\text{CH} \rightarrow \text{CH}_2\cdot\text{CH} \rightarrow \text{CH} \cdot (CH_2)_7 \text{ COOC}_2\text{H}_5 \\
\text{O} \text{C} \cdot \text{CH}_2\text{Cl} \\
\text{O}
\end{align*}
\]

(iii) **Methyl bromoacetyl epoxy ricinoleate:** Chemical structure –

\[
\begin{align*}
\text{O} \\
\text{CH}_3\cdot(CH_2)_5\cdot\text{CH} \rightarrow \text{CH}_2\cdot\text{CH} \rightarrow \text{CH} \cdot (CH_2)_7 \text{ COOCH}_3 \\
\text{O} \text{C} \cdot \text{CH}_2\text{Br} \\
\text{O}
\end{align*}
\]
(iv) **Ethyl bromoacetyl epoxy ricinoleate:** Chemical structure –

\[ \text{CH}_3\left(\text{CH}_2\right)_5\text{CH} - \text{CH}_2\text{CH} - \text{CH}\left(\text{CH}_2\right)_7\text{COOC}_2\text{H}_5 \]

\[ \text{O} - \text{C} - \text{CH}_2\text{Br} \]

From the above reactions the logical conclusion may be drawn that epoxidation of the unsaturated bond not only resulted in plasticizers with improved compatibility with the vinyls but also induced thermal stability and almost eliminated the problem of compatibility in stability. The evaluation of the plasticizers for properties such as plasticizing efficiency, permanence and low temperature performance has also been undertaking as a part of the present studies.

Summing up the present piece of investigation covers:

1. Inter esterification of castor oil be carried out using different alkyl alcohols to obtain glycerol and a mixture of alkyl ester of various fatty acids present in the castor oil as glycerides.

2. The mixture of inter esterification products of castor oil will be rich in alkyl ricinoleates, so these ricinoleates will be recovered in pure form using the various separation techniques like vaccum distillation and fractional crystallization.
3. Alkyl ricinoleates obtained as above will be esterifying at C-12 position under suitable experimental conditions using chloro acetic acid and bromo acetic acid to get the desired products.

4. (i) The derivatives obtained as above will be characterize employing modern analytical techniques viz. I. R., thin layer chromatography (TLC), gas liquid chromatography (GLC), high pressure liquid chromatography (HPLC).

(ii) To determine the various physico-chemical constants like iodine value, saponification value, viscosity, refractive index, melting point, boiling point, oxirane value and acid number of epoxy compounds.

All major interesterification products of castor oil and their derivatives will be evaluated as plasticizers for PVC using lowering of glass transition temperature ($T_g$), migration test and compatibility studies.

4. MECHANICAL PROPERTIES

J. L. Vats et. al\textsuperscript{42-44} studied the mechanical analysis, impact strength and morphological behaviour of ethylene propylene diene terpolymer poly (vinyl chloride) and impact modification of PVC. The products due to high impact strength find numerous applications practically in every possible field.
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