



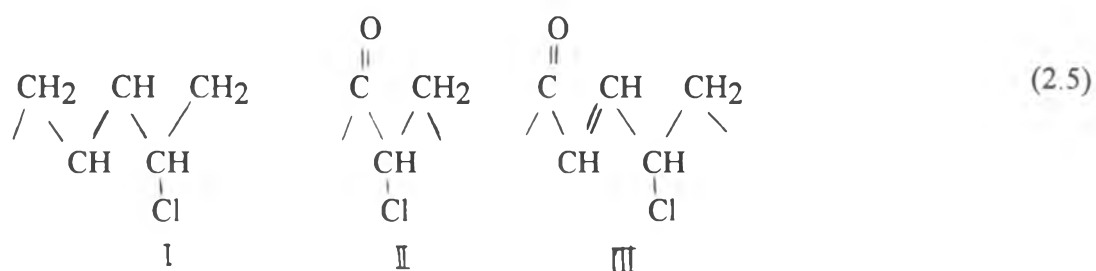
About 75% of the world PVC is produced by the suspension polymerization because it is easier to control particle size and shape. PVC molecules are largely amorphous and slightly branch molecules. PVC resin has poor mechanical properties and is well known for low thermal stability. These disadvantages can be improved by incorporating additives that lead to various better properties of the PVC compounds (2,3).

### PVC Degradation

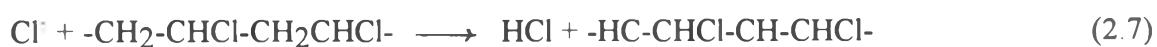
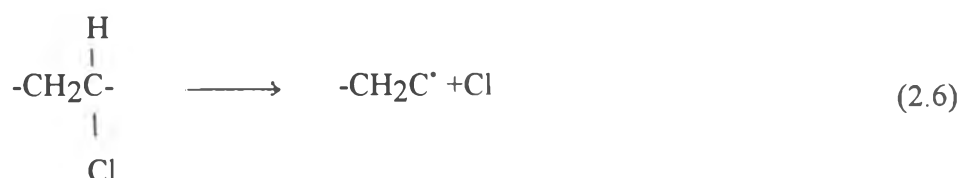
At temperature about 100°C and/or in the presence of light, PVC begins to decompose and then degrades. The reactions to damage PVC are dehydrochlorination, autooxidation and mechanochemical chain scission.

#### 1. Dehydrochlorination.

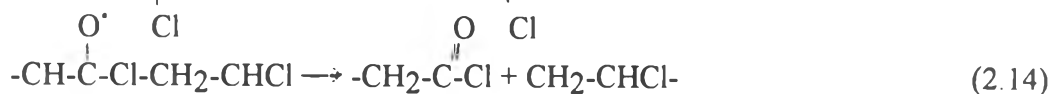
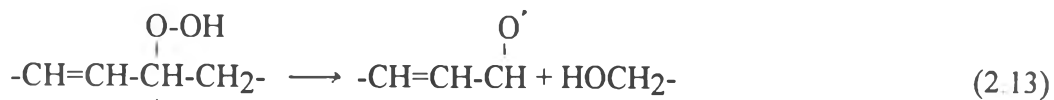
This reaction starts from the sites of the polymer chain with labile chlorine-carbon bonds (initiation sites) that are formed by autooxidation, chain termination, side reaction or copolymerization with traces of oxygen during the manufacturing process of PVC.



Shapiro (4) proposed that at high temperatures, chlorine atom is liberated from labile sites as initiation. Then chlorine atoms react with adjacent methylene hydrogen atoms leading to polyene sequences at propagation steps as shown in eqs.(2.6-2.8).







Among these reactions, dehydrochlorination often occurs and leads to increasing discolouration and change in physical and other properties (4-6).

### PVC Stabilization

In order to prevent PVC degradation, stabilizers are generally used. The main functions of stabilizers are to adsorb hydrogen chloride, eliminate initiation sites, prevent autooxidation, add stabilizer to polyene sequences and destruct carbenium salts (3-7).

#### 1. Type of Stabilizers.

The types of the stabilizers depend on the chemical structures are classified into 4 groups.

##### 1.1 Organotin Stabilizer.

General formula is  $R_2SnX_2$  where R is a methyl, butyl, octyl, benzyl group etc. and X is a carboxy, alkoxy, mercapto group, and some other substituents are highly effective stabilizers of PVC.

##### 1.2 Barium-cadmium Stabilizer.

General formulae are  $(RCOO)_2Ba$  and  $(RCOO)_2Cd$ . The two compounds are used because the synergism (interplayed by a combination of the individual actions) in the various mixture ratios, generally behaved as costabilizers. In application, barium-cadmium stabilizers that contain zinc compounds have to combine with liquid

phosphites and liquid epoxy plasticizers, and can provide improved early colour and transparency.

### 1.3 Lead Stabilizer.

Bivalent leads are used. Costabilizers like polyols and phosphites do not increase the efficiency of this group.

### 1.4 Metal-free Stabilizer.

General formula is  $\text{H}_3\text{C}-\text{HC}=\text{CH}-\text{COOR}$  when R is an alkyl group. Almost all metal-free stabilizers are nitrogen-containing compounds(7).

Costabilizers are compounds which do not pose a thermo stabilizing effect, but improve the efficiency of stabilizer systems. The costabilizers that are in available in commercial forms are the phosphite, the epoxy compounds or polyols. Epoxy compounds will be described detail later(4,5).

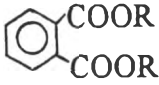
## PVC Plasticization

The plasticization effects of a plasticizer to PVC resin is well known. These effects are on the processing and the properties of the PVC that cause the different types and grades of the PVC.

### 1. Definition of a Plasticizer.

Plasticizers are substances or materials incorporated in another material to increase the latter flexibility, workability or distensibility as well as to modify the properties of the material. The most widely used of plasticizer in polymers is for PVC (8). There is no standard classification scheme for plasticizers used in PVC. The one which is based on chemical structure is more convenient and systematic than most other schemes. The plasticizers are divided into six general groups as in Table 2.1 (4).

Table 2.1 Plasticizer types

Type	Chemical structure	Synthesis
Phthalates		Esterification of phthalic anhydride and higher alcohols.
Epoxides	$R^{\Delta}(CH_2)_nCOOCH_2$ $R^{\Delta}(CH_2)_nCOOCH_2$ $R^{\Delta}(CH_2)_nCOOCH_2$	Epoxidation of unsaturated natural oils, and esters of fatty acids.
Esters of aliphatic dibasic acids	$RCOO(CH_2)_nCOOR$	Esterification of linear dicarboxylic acids such as adipic, azelaic and sebacic acid.
Phosphates	$PO(OR)_3$	Reaction of aliphatic alcohols and phenols with phosphorus oxychloride.
Polyesters	$R[(OOC(CH_2))_nCOO(CH_2)]OOCR$	Esterification of a polycarboxylic acid with a polyhydric alcohol, usually diacids and diols are used.
Miscellaneous	-	Typical examples are glycol and terephthalic acids.

The other scheme classifies the plasticizer as: primary plasticizer and secondary plasticizer. Primary plasticizers are able to gel the polymer rapidly in the normal processing temperature and suitable for use on their own and should not exude from the plasticized polymer. Secondary plasticizers have lower gelation capacity and limited compatibility with the polymer so that combination with a primary plasticizer is advised. In practice, the parameters that are the main criteria for a good plasticizer are compatibility of mixing the plasticizer and the polymer, effectively in imparting a desirable properties to the plasticized polymer and permanence of the plasticizer. However, most plasticizers are excellent in one of the above parameters that may also reduce performance in another. Combination of two or more plasticizers are often used for meeting simultaneously all the above three parameters(3-7,9).

## 2. Plasticization Theory.

There are many theories to explain the plasticization effect on the polymers. The accepted theories are the three that expressed in 2.1-2.3.

### 2.1 The Lubricity Theory.

The theory considers the result of intermolecular friction, which is the major force resisting the deformation of a thermoplastic polymer. The plasticizer would act as a lubricant to facilitate movement of polymer chains over each other, or segments of the chain although other parts of the chain are of gel network. The plasticizer gives internal lubricity.

### 2.2 The Gel Theory.

The gel theory is based on the proposition that rigidity of a thermoplastic polymer results from an internal three dimensional structure. This structure is formed by more or less loose of attachments that occur at intervals along the polymer chain caused by weak intermolecular forces such as dipole-dipole interaction or hydrogen bonding. According to this theory, when the plasticizer solvates the polymer, it destroys any points of attachment by replacing polymer-polymer interactions with polymer-plasticizer interactions. It has been suggested that the plasticizer might selectively solvates the polymer chain at these points.

### 2.3 The Free Volume Theory.

The free volume theory assumes that there is a free surface (volume) between molecules which was increased by increasing temperature or molecular motion and chain end groups of polymer. Therefore, decreasing the molecular weight of a polymer increases the free volume which is end group plasticization. Addition of flexible side chains produces the same result. These effects are achieved by internal plasticization and the free volume is fixed with regard to the polymer molecule. Enough free volume permits a freedom of movement as if there were a hole for a nearby atom, molecule, or chain segment to move into. The normal result of adding more free volume to a polymer is that it is plasticized(4,9).

### 3. PVC Plasticizer.

The PVC can be modified by adding plasticizers that leads to various different properties depending on the amount and type of the plasticizer used. For example, as the plasticizer amount is above 20 phr, PVC is softer and more flexible, reduces the modulus, tensile strength and gives greater elongation. In compounding of PVC, various sequential interactions take place between a plasticizer and PVC polymer. The exact form of interactions and the steps that may be distinguished in their progress, depend to some extent upon the nature of the polymer/plasticizer system concerned. However, a step-wise pattern of the PVC plasticization when a plasticizer and PVC are fused together can be described as follows:

#### 3.1 Adsorption.

The plasticizer is taken up by the PVC resin through adsorption on the particle surface and filling of intraparticle voids, adsorbed plasticizer may be removed from the PVC by centrifuging.

#### 3.2 Absorption.

The plasticizer diffuses into the primary PVC particle, enters the amorphous regions intermolecularly; this is accompanied by a slight decrease in resin/plasticizer volume at the outside and is followed by the resin surfaces beginning to expand and enters a gel stage; at this point, the resin/plasticizer interaction is physically irreversible.

#### 3.3 Fusion.

After the gelation stage, a step-wise diffusion process takes place as polymer molecules swell and undergo disentanglement and separation, polymer-plasticizer homogenization takes place. Ideally, resin grain boundaries begin to melt out and a continuous single phase plasticized PVC film is formed.

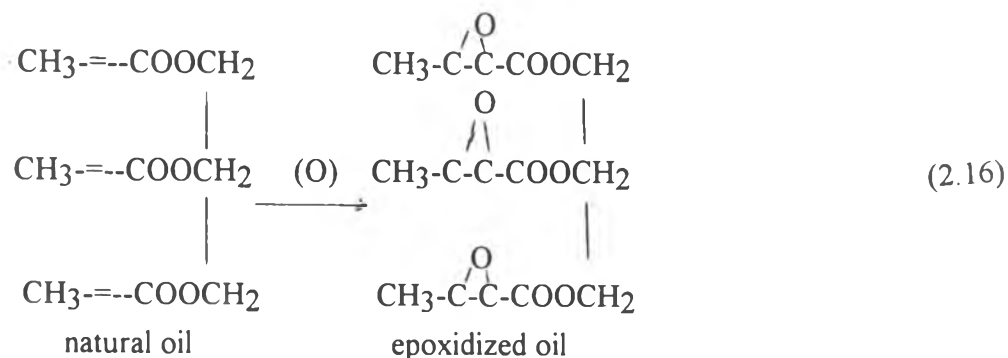
#### 3.4 Toughening.

After cooling, there is a brief period of apparent increase in Van der Waals force resulting in increased strength. Further, the plasticized PVC may be considered as solid solution in which there is continuous association and disassociation between the polymer - plasticizer, polymer-polymer, and plasticizer-plasticizer molecules(3,4,9).

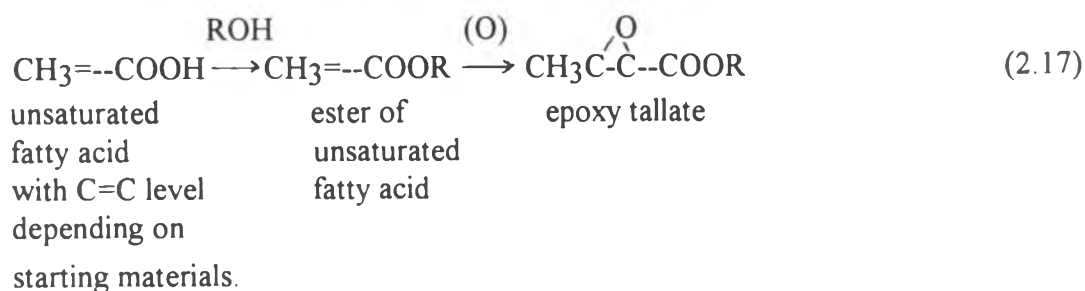


#### 4. Epoxy Plasticizer.

Epoxy plasticizers are commonly made by epoxidation of natural oils, which is shown in eq.(2.16) (4,5,9).




or unsaturated esters of C18 acid that predominates as in eq.(2.17)



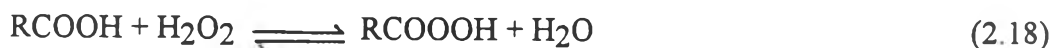
#### 4.1 Preparation of Epoxy Compounds (Epoxidation).

Epoxidation is an oxidation reaction in which an oxygen atom is introduced into a compound containing an unsaturated carbon to carbon bond to form a three membered-ring called epoxide, oxirane, ethylene oxide or 1,2-epoxy compound. The chemical structure is C-C. Epoxides are more reactive than the ordinary ethers because of the strained three membered-ring. They react with almost all nucleophilic substances causing ring opening accompanied by the formation of addition compounds as in Table 2.2 (10-12)

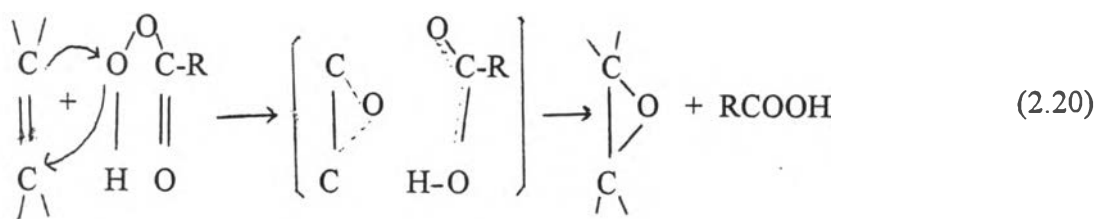
Table 2.2 Reaction of epoxides.

Reaction No.	Reagent	Product	Name
1	$H_2O/H^+$	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ HO \quad OH \end{array}$	vicinal diol
2	ROH	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ HO \quad OR \end{array}$	hydroxyether
3	RCOOH	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ HO \quad O-COR \end{array}$	hydroxyester
4	HX	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ HO \quad X \end{array}$	halohydrin
5	$H_2/cat$	$\begin{array}{c}   \quad   \\ -C-C- \\   \quad   \\ HO \quad H \end{array}$	alcohol
6	oxidizing agent	$\begin{array}{c}   \quad   \\ -C-COOH \\   \\ OH \end{array}$	hydroxycarboxylic acid
7	heat	$\text{>C=C-CH}_2\text{OH}$	allyl alcohol
8	$n(-C-C-)$ 	$-C-C-O-(C-C-O-)_n-C-C-O-$	polymer

Various epoxidation processes are discovered such as epoxidation with peracid, hydrogen peroxide, hydroperoxide, halohydrin, and with oxygen. Of all the available methods of converting unsaturated compounds to epoxides, epoxidation with hydrogen peroxide to generate peroxide of an organic acid is generally used for the preparation of epoxy plasticizer. The reaction occurs as in eqs.(2.18-2.19).



The mechanism proposed by P.D. Barlet (12) as eq.(2.20) is generally accepted.



Epoxidation is a second-order and an exothermic reaction. Organic acids used are carboxylic acid and acid anhydride but the carboxylic acid are preferred. Producing epoxy compounds in manufacturing are mainly from peracid epoxidation by in situ peracid and preformed peracid (11).

4.1.1 Preformed Peracid. In this method, peracid is generated from the reaction of organic acid and hydrogen peroxide in solution. The solution of epoxidation was neutralized before use.

4.1.2 In situ Peracid. This is the convenient and safe method. In this method the unsaturated compound used as a starting material is dissolved in acid such as carboxylic acid or acid anhydride, and hydrogen peroxide (in some case with a mineral acid catalyst) is added. As the reactants mix, the hydrogen peroxide and the organic acid react to form the peracid that reacts with the unsaturated compound to form an epoxide ring. The temperature should be as lowest as possible and the reaction time should be the shortest because epoxidation is reversible. The ratio of reactants must be in a good proportion to avoid side reactions causing ring opening and by product. Epoxidation with in situ performic and peracetic acid (with some catalyst) is established commercial processes for production of epoxy compounds.

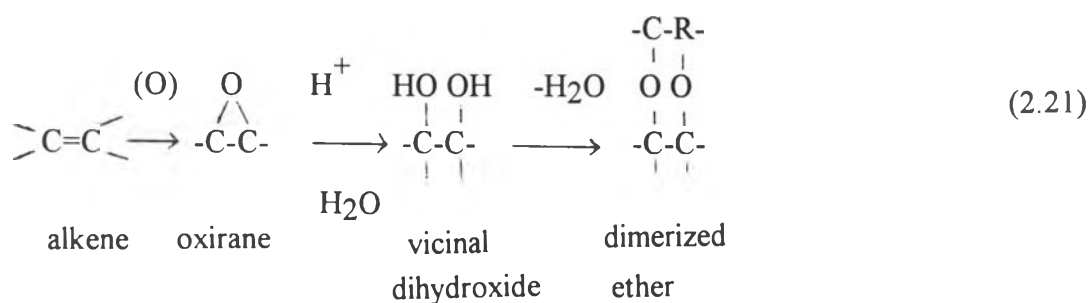
Commercial epoxy plasticizers are prepared by in situ method. Acetic acid and formic acid are usually used and sulfuric acid, phosphoric acid or cation exchange resin also are used as catalyst for each organic acid. The variables in epoxidation are molar ratio of reactants, reaction temperature, reaction time, type of catalyst and rate of agitation(12-14).

The unsaturated substances that are used as starting material are soybean oil, tall oil, castor oil, linseed oil, sunflower oil, fatty acids and ester of fatty acids. The most important representatives of epoxidized compounds have the following structure(4).

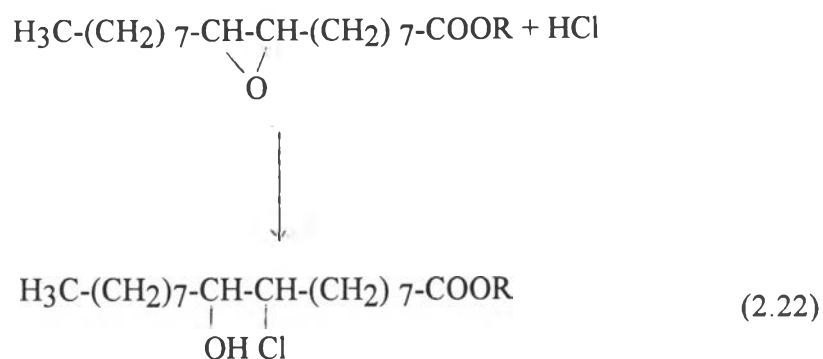


#### 4.2 The Function of the Epoxy Plasticizers.

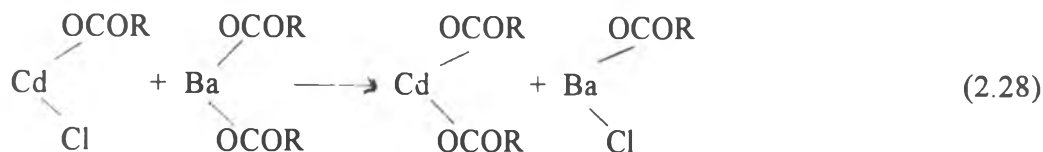
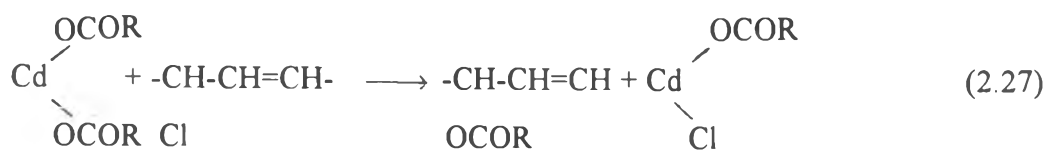
Epoxy plasticizers are considered as a type of secondary plasticizers, i.e. their sole use in larger amount may lead to exudation. The compatibility characteristics of epoxy plasticizer are not so good because of the incompleting epoxidation. The residual unsaturation and the scission of the epoxide ring form vicinal dihydroxide that taking place under aqueous acidic conditions. The vicinal dihydroxide is then capable of forming a dimerized ether while splitting off a mole of water as shown below:



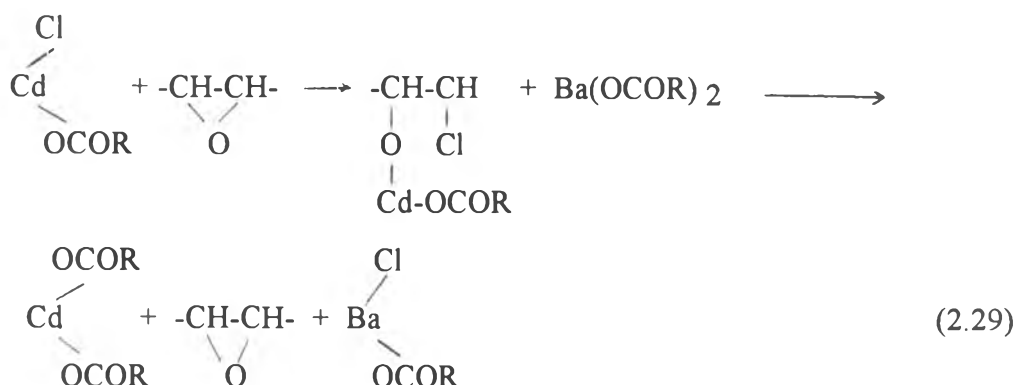
Vicinal dihydroxide and polyether contents effect on compatibility. The important function of epoxy plasticizers is costabilizing for heat and light stabilizers to scavenging hydrochloric acid formed in PVC during heating and/or light exposure(1,2,4-6). Epoxy plasticizers have oxirane oxygen content ranging from 4-7%. Epoxy plasticizers are able to bind hydrogen chloride as follows (4,5):







This is the synergistic effect that increases the plasticizing effect for the case of combination with epoxy plasticizer: (2,3)



### Literature Reviews

Prilezhaev, Russian chemist,(15) was the first who had prepared epoxy compound by the reaction of unsaturated substances with perbenzoic acid. The pinene oxide, glycol oxide, octylene oxide, etc. were synthesized. These products serve for the manufacture of pharmacy, perfume and colour.

Hilditch (16) oxidized oleic, elaidic and their esters using hydrogen peroxide in the presence of acetic acid, the products turned to be 9,10-dihydroxystearic acid on saponification.

In 1930, Nicolet and Poulter (17) prepared epoxides from oleic and elaidic acid by the reaction of chlorine with the solution of the potassium salts containing potassium carbonate, pure chlorohydrins were obtained. After heating with alcoholic alkali, epoxides occurred. The oleic acid chlorohydrin formed 45% of the epoxides while the elaidic acid chlorohydrin yielded

75% of the epoxide. Both of them melted at  $53.8^{\circ}\text{C}$ . By using perbenzoic acid or peracetic acid in chloroform, only dihydroxystearic acid was isolated as solid product.

King (18) used hydrogen peroxide in acetic acid to oxidize oleic acid, elaidic acid, methyl oleate and methyl elaidate at room temperature. The product of oleic acid was the mixture of monoacetyl derivatives of dihydroxy acid, no epoxide was detected. Elaidic acid and methyl ester of oleic and elaidic acid yielded 9,10-oxidostearic acid, elaidic acid epoxide, and monoacetyl derivatives of dihydroxy stearic acid. It was assumed that peracetic acid functions as perbenzoic acid to produce epoxy compound but epoxy ring is opened and hydroxy-acetoxy compounds were obtained together as in eq. (2.30). So oxidostearic acid was the primary product of an oxidation of oleic acid and elaidic acid by peracetic acid. Oleic acid epoxide transformed into the mixture of monoacetyl derivatives of dihydroxystearic acid easily in acetic acid, no epoxide separated. But elaidic acid epoxide that transformed slower produced a mixture of the products.

Findlay, Swern and Scanlan (19) epoxidized unsaturated fatty acids such as oleic acid, elaidic acid, methyl oleate and vegetable oils such as olive oil, rapeseed oil, cottonseed oil and soybean oil. Peracetic acid was prepared from acetic anhydride and hydrogen peroxide with or without sulfuric acid catalyst, and unsaturated substrate was added at mild temperature and short time. The products, epoxidized substrates, were separated for the first time.

Niederhauser and Koroly (13) prepared epoxidized esters of oleic and elaidic acid and soybean oil with hydrogen peroxide and formic acid at a temperature of  $20-75^{\circ}\text{C}$ . Hydrogen peroxide was presented in a ratio of 1-2 moles per mole of unsaturated ester and formic acid in 0.25-0.75 mole for each mole of double bond of ester. Inert solvent, saturated aliphatic and aromatic hydrocarbons or halogenated hydrocarbon were filled and it tended to prevent the ring opening. This is the important development of the in situ epoxidation and this is also the first report on the epoxy compounds used as PVC plasticizer and scavenger for acids such as hydrochloric acid, which formed in PVC degradation.

Food Machinery and Chemical Corporation (20) used the in situ of acetic acid, hydrogen peroxide and sulfuric acid to epoxidize ester of unsaturated acids, i.e. butyl cottonate and soybean oil, containing 12-22 carbon atoms at high temperatures (50-65 °C). The process was to add acetic acid and sulfuric acid into the esters and slowly added hydrogen peroxide. The ratio of acetic acids per mole of unsaturated ester was 0.25:1, hydrogen peroxide was slightly excess and sulfuric acid as catalyst was 0.5-5% by weight. Benzene and toluene were used as solvent for some reactions. The products had lower iodine values than the in situ epoxidation of perbenzoic acid and the coproduct, acetoxy derivative, was presented in a small amount.

French (12) improved the in situ peracetic acid epoxidation process of the compounds containing at least one unsaturated aliphatic hydrocarbon chain of 6-26 carbon atoms. The epoxidizable compound was mixed with acetic acid and inert solvent that were heated to a temperature of 50-65 °C and sulfuric acid (catalyst) and hydrogen peroxide were then added. The epoxidizable compounds were soybean oil, n-hexyl oleate and linseed oil. The products had high oxirane values, low iodine values and minimum side reactions. The ratio of hydrogen peroxide was 1.0 mole per mole of unsaturation, acetic acid was 0.25-0.6 mole per mole of unsaturation. Epoxidation process is improved by changing the type of catalysts. The famous one is the cation-exchange resin catalyst that is discovered by Du Pont.