CHAPTER II

THEORY

Natural rubber (NR) has become an important industrial material, particularly in the tyre industry, and used in the manufacture of various products including household, engineering, medical, and commercial goods. *Heavea brasiliensis*, a tropical tree, is a major source of the world's rubber. Thailand has approximately 5 million acres of rubber plantations located mostly in the southern and eastern parts of the country and is the world's largest rubber producer followed by Indonesia and Malaysia with these three countries producing around 90% of the world's natural rubber (NR). However, Thailand is facing some problems with rubber production. During the collection of latex, dirt gets in the process, reducing the quality and thus reducing the price producers will receive. The economic crisis and the increasing use of synthetic rubber have added to the problems for the rubber industry in Thailand, and changes are needed in the NR industry if it is continue to remain success [4]. Research on the chemical modification of NR for special technical applications has been begun recently in Thailand. Among reactions acting on the polyisoprene backbone, epoxidation is a modern and efficient method of chemical modification having great perspectives for application [5].

2.1 Epoxidized liquid natural rubber (ENR)

2.1.1 Preparation of ENR

ENR is considered as one of the modified forms of natural rubber (NR) . It is derived from NR. In 1989, Boccaccio prepared ENR from NR using two steps of the reaction. The first one was the reduction of the molecular weight of NR and the second one is the epoxidation reaction of the polymeric chain. The molecular weight ($\overline{M}_v$) of ENR was consideredly lower than NR, i.e. $\overline{M}_v$ of NR is $\sim 10^6$ when $\overline{M}_v$ of ENR is $\sim 10^4$ [6].

In order to reduce molecular weight of NR, several methods can be done, mastication of NR in solid phase or chemical treatments of NR in solution or latex phase. In the case of introduction of epoxide ring onto unsaturated organic molecule, epoxidation can be carried out using preformed peracids or *in situ*

peracids [8]. Institut de Recherche Applique' sur les Polymers (IRAP) has published degradation reaction of NR by using phenylhydrazine/oxygen system in latex phase [7]. By varying the amount of phenylhydrazine using in the reaction, different molecular weight of degraded natural rubbers was obtained. When high amount of phenylhydrazine was used, the lower molecular weight of polymer was achieved. Therefore, by this method, low molecular weight NR or liquid natural rubber (LNR) can be prepared [7]. In the case of introduction of epoxide ring onto unsaturated organic molecule, epoxidation can be carried out using preformed peracids or *in situ* peracids. Gelling [9] reported the preparation and structure of epoxidsed natural rubber. Both peracetic acid or *in-situ* generation of performic acid can be employed. IRAP has also developed epoxidation reaction procedure by *in situ* perfomic acid of NR which has been degraded into liquid natural rubber (LNR) and still in latex form [6]. The *in situ* perfomic acid is obtained from the reaction of hydrogen peroxide and formic acid. The reaction of natural rubber using peracetic acid system in latex phase could be carried out without step of reduction molecular weight of natural rubber due to the epoxidation reaction of the polymer chain was obtained immediately [10]. The reaction can be schematized as following:

$$\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$$
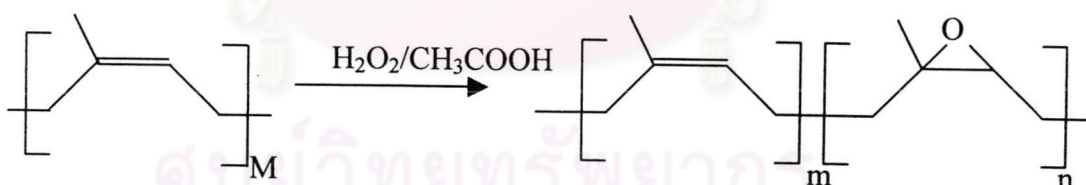
2.1.2 Epoxidation level determination

It is known that 100% chemical modification of polymeric chain is not practical and sometimes is not useful. Partial modification of non-polar polymer such as polypropylene or polyisoprene has been generally done in order that the main chain still posses its original properties. A few percent of epoxidation of NR are also required for further modification in the second step as a small amount of photosensitive group needed for photocrosslinking reaction. The method to determine the epoxidation level of ENR has therefore been defined.

Titration method [13] of epoxide ring with hydrogen bromide was also used but side reaction can be easily occurred by intramolecular cyclization. Elemental analysis, ^{1}H-NMR and ^{13}C-NMR spectroscopies are fairly simple methods published in several publications for determining epoxidation level of epoxidised polymer [11,12]. Glass transition (T_g) measurement by differential scanning calorimetry (DSC) method was also used to differentiate epoxidation level of epoxidised polymer. Burfield et al. [11] had compared DSC, NMR, elemental analysis and direct titration methods for determining epoxide ring of epoxidised natural rubber. They found that there were some limitation these methods. Direct HBr in glacial acetic acid titration could give fairly accurate information at low (<15 mol%) modification. Elemental analysis gave less satisfactory results. T_g data from DSC method could relate to epoxidation level through a calibration curve obtained from primary method such as NMR analysis. Both ^{1}H-NMR and ^{13}C-NMR provided the best results over the range of 20-75 mol% modification. The characteristic peaks of ENR used in ^{1}H-NMR and ^{13}C-NMR analysis and percentage of epoxidation modification equation appeared in several publications [13] and are shown below.

^{1}H-NMR
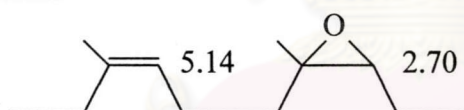
$$\text{mol\% epoxide} = 100 \left[\frac{A_{2.70}}{A_{5.14} + A_{2.70}} \right]$$
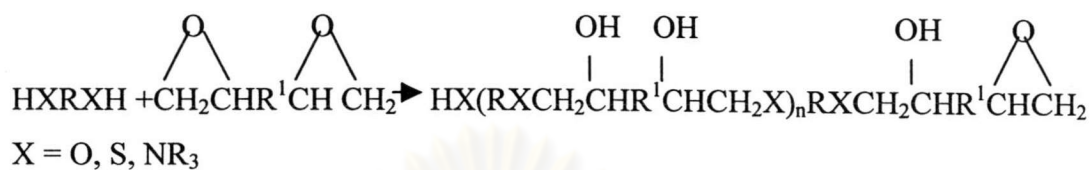
Note : $A_{2.70}$ = Intration of epoxide proton.

$A_{5.14}$ = Intration of olefinic proton.

2.2 Ring opening reaction of epoxide group

Organic epoxide molecule is a three-membrane ring ether compound which one of the three atoms is oxygen. It has been known that organic three-membered ring molecule is not a preferred form of sp^3 orbital of carbon atom. Therefore molecule containing epoxide ring is sensitive to ring opening reaction by several active hydrogen compounds. Epoxy resins are polymeric materials possessing epoxide ring. They are commercially available in low molecular weight molecules. In order to achieve a useful product, they were transferred to a crosslinked product

by a crosslinking agent [14]. The reaction mechanism is proceeded by the reaction between the crosslinking agent and epoxide moieties. In addition, reaction of compounds containing active hydrogen onto epoxides of epoxy resins has been published [15]. The general ring opening reaction of epoxide ring is shown below.

$$HXRXH + CH_2CHR^1CH\ CH_2 \longrightarrow HX(RXCH_2CHR^1\overset{OH}{CH}\overset{OH}{CH}CH_2X)_nRXCH_2CHR^1\overset{OH}{CH}CH_2$$

$X = O, S, NR_3$

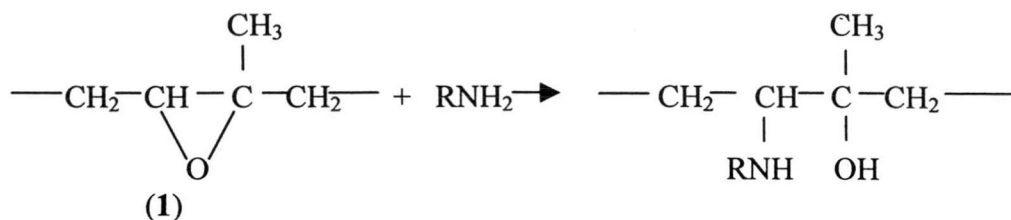R^1 are any of the possible organic moieties.

$n = 0, 1, 2, \ldots$

Active hydrogen compounds used in the above reaction:

- polyamines
- polyamides
- polyureas
- polyurethanes
- polyisocyanates
- polymercaptans
- polyhydric alcohols
- polyphenols
- polycarboxylic acids

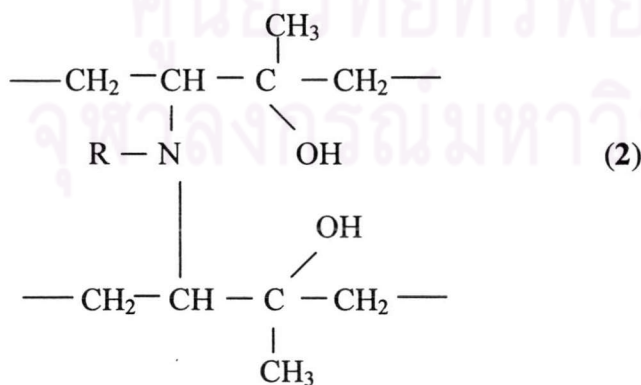## 2.2.1 Mechanism of ring opening reaction of epoxides

It has recently been conjectured [16,17] that non-oxidative crosslinking reaction occurring in natural rubber involved epoxide groups in the macromolecule. This proposal has been criticised because a key step in the mechanism involves ring clevage of trisubstituted rubber epoxides (1) by amine compounds, possibly amino acids, as shown in Scheme 1. This objection appeared serious in view of the fact Colclough et al. [18] have shown that the reaction of amines with the model epoxide (1-ethyl-2,2-dimethyloxiran) under anhydrous conditions was extremely slow, even at 140°C, let alone at the ambient temperatures under which natural rubber was known to undergo crosslinking.

$$-CH_2-CH-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2- \ + \ RNH_2 \longrightarrow \ -CH_2-CH-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2-$$

$$\overset{\diagdown O\diagup}{}$$

(1)

                              RNH   OH

Scheme 1

In 1976s, the reactions of this type have assumed some industrial importance, *inter alia* in the curing of epoxide-based resins [19]. The prototype reaction, between oxiran itself and ammonia was first documented by Wurtz [20] in 1860. A more thorough later investigation by Knorr [20] revealed that the completely dry reagents did not react, but in the presence of a small amount of water the reaction took place readily to yield a mixture of amino ethanols.

Since induced crosslinking reactions in epoxidised natural rubber occured under aqueous conditions [20], it was important to discover whether similar activating effects occurred in the case of trisubstituted epoxides, which would perhaps facilitate the reaction under ambient conditions, a possibility which have been largely overlooked in earlier work. It was of interest to find out if such reaction allowed the formation of amino-diols such as **(2)** or whether their formation would be precluded by steric considerations.

$$-CH_2-CH-\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-$$

                    R - N   OH   **(2)**

                              OH

$$-CH_2-CH-C-CH_2-$$

                              CH_3

Scheme 2

Burfield [20] chose methyloxirane and trimethyloxirane for model epoxides and selection some amines, e.g. cyclohexylamine and 2-aminoethanol. Reactions were investigated by mixing the amine and epoxide at room temperature in various stoichemistry under aqueous and dry conditions. It was found that anhydrous reactions were relatively very slow and reactions of trisubstituted amines were more difficult than monosubstituted due to effect of steric.

Perera [21] investigated reaction of aromatic amines with ENR in latex stage. It was found that the oxidizability of the raw rubber was adversely affected by the epoxidation reaction, and this difficulty was overcome [22] by the addition of a low molecular weight antioxidant just prior to isolation of the rubber from the latex. However, the oxidation resistance of ENR might be improved by binding an amine antioxidant to the polymer through the oxiran group. The results were shown that the amine antioxidant was added without neutralizing the latex, there was no addition of the amine to the rubber molecule; but ring expansion of the oxirane occurred. Once the medium was neutralized, and addition of secondary amines, took place crosslinking also occurred.

2.3 Membrane separation

Since membranes have widely in separation processes such as reverse osmosis, ultrafiltration, pervaporation, gas permeation and so, as shown in Table 2.1, it is of much interest to use membrane such as the silicalite membrane which has hydrophobic/organophilic characteristic to separate mixed xylenes. Basically, a feed consisting of a mixture of two or more components is partially separated by means of a semipermeable barrier (the membrane) through which one or more species move faster than another or other species. The most general membrane process is shown in Figure 2.1 where the feed mixture is separated into a retentate and a permeate. The feed, retentate, and permeate are usually liquid or gas, they may also be solid. The membrane is most often a thin, nonporous polymeric film, but may also be porous polymer, ceramic, or metal material, or even a liquid or gas. The optional sweep, shown in Figure 2.1, is a liquid or gas, used to help remove the permeate [23].

Table 2.1 Industrial applications of membrane separation processes [28].

1. Reverse osmosis:
     Desalinization of brackish water
     Treatment of wastewater to remove a wide variety of impurities
     Treatment of surface and ground water
     Concentration of foodstuffs
     Removal of alcohol from beer and wine
2. Dialysis:
     Separation of nickel sulfate from sulfuric acid
     Hemodialysis (removal of waste metabolites, excess body water, and restoration of electrolyte balance in blood)
3. Electrodialysis:
     Production of table salt from seawater
     Concentration of brines from reverse osmosis
     Treatment of wastewaters from electroplating
     Demineralization of cheese whey
     Production of ultrapure water for the semiconductor industry
4. Microfiltration:
     Sterilization of drugs
     Clarification and biological stabilization of beverages
     Purification of antibiotics
     Separation of mammalian cells from a liquid
5. Ultrafiltration:
     Preconcentration of milk before making cheese
     Clarification of fruit juice
     Recovery of vaccines and antibiotics from fermentation broth
     Color removal from Kraft black liquor in paper-making
6. Prevaporation:
     Dehydration of ethanol–water azeotrope
     Removal of water from organic solvents
     Removal of organics from water
7. Gas permeation:
     Separation of CO_2 or H_2 from methane and other hydrocarbons
     Adjustment of the H_2/CO ratio in synthesis gas
     Separation of air into nitrogen- and oxygen-enriched streams
     Recovery of helium
     Recovery of methane from biogas
8. Liquid membranes:
     Recovery of zinc from wastewater in the viscose fiber industry
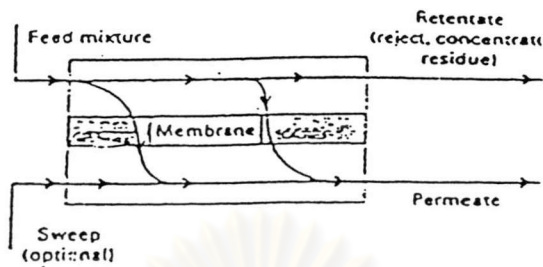   Recovery of nickel from electroplating solutions
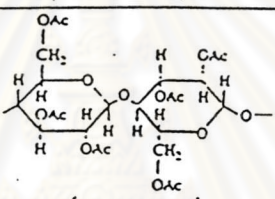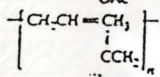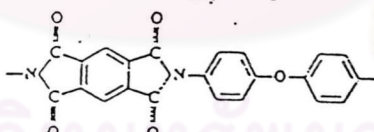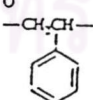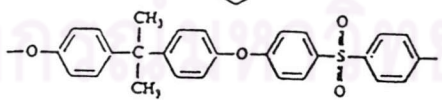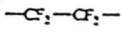
Figure 2.1 General membrane process [28]
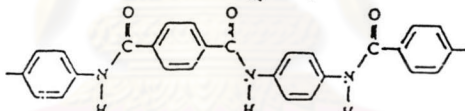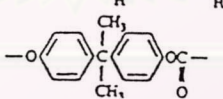
In membrane separations: (1) the two products are usually miscible, (2) the separating agent is a semipermeable barrier, and (3) a sharp separation is often difficult to achieve.

The replacement of the more common separation operations with membrane separation has the potential to save large amounts of energy. This replacement required the production of high mass-transfer flux, defect-free. Long-life membranes on a large scale and the fabrication of the membrane into compact, economical modules of high surface area per unit volume. The key to an efficient and economical membrane separation process is the membrane and the manner in which it is packaged and modularized. Desirable properties of membrane are (1) good permeability, (2) high selectivity, (3) chemical and mechanical compatibility with the processing environment, (4) stability, freedom from fouling, and reasonably useful life, (5) amenability to fabrication and packaging, and (6) ability to stand with the large pressure difference across the membrane thickness [28].

2.3.1 Membrane materials.

Almost all industrial membranes processes are made from natural or synthetic polymers. Natural polymers include wool, rubber, and cellulose. Synthetic polymers are produced by polymerization of a monomer by condensation or addition, or by the copolymerization of two different monomers. Table 2.2 shows the common polymers used in membranes.

Table 2.2 Common polymers used in membranes [28].

Polymer	Type	Representative Repeat Unit	Glass Transition Temp.. °C	Melting Temp.. °C
Cellulose triacetate	Crystalline			300
Polyisoprene (natural rubber)	Rubbery		−70	
Aromatic polyamide	Crystalline			275
Polycarbonate	Glassy		150	
Polyimide	Glassy		310–365	
Polystyrene	Glassy		74–110	
Polysulfone	Glassy		190	
Polytetrafluoroethylene (Teflon)	Crystalline			327

Polymer membrane can be dense or microporous. For dense amorphous membranes, no pores of microscopic dimensions are present, and diffusing species must dissolve into polymer and then diffuse through the polymer between the segments of macromolecular chains. Diffusion can be difficult, but highly selective for glassy polymers. If the polymer is partly crystalline, diffusion will occur almost exclusively through the amorphous regions, with decreasing the diffusion area and increasing the diffusion path.

A microporous membrane contains interconnected pores that are small (in the range of 0.005-20 μm), but large in comparison to the size of small molecules. The pores are formed by a variety of proprietary techniques. Such techniques are especially valuable for producing symmetric, microporous, crystalline membranes. Permeability for microporous membranes is high, but selectivity is low for small molecules. However, when molecules both smaller and larger than the pore size are in the feed to the membrane, the molecules may be separated almost perfectly by size.

The application of polymer membranes is generally limited to temperatures below about 200 °C and to the separation of mixtures that are chemically inert. When operation at high temperatures and/or with chemically active mixtures is necessary, membranes made of inorganic materials can be used. These include mainly microporous ceramics, metals, and carbon; and dense metals, such as palladium, that allow the selective diffusion of very small molecules such as hydrogen and helium [28].

Huang and Yeom investigated the permeation of aqueous ethanol through PVA membrane [24]. It was found that crosslinked PVA was reduced permeability but increase selectivity.

Harogoppad and Aminathan [25] studied the permeation of alkane solvent through polymer membranes (CR, SBR, EPDM, NR). The results were shown that NR was the best membrane for organic solvent due to high selectivity and efficiency.

Unnikrishnan [26] investigated the permeation of solvent mixture between hexane and acetone through crosslinked NR membrane. It was found that low permeability effect to increase efficiency and high selectivity.

John and Thomas [27] investigated the permeation of acetone and chlorinated hydrocarbon mixed solvent. It was found that specific membrane effect to increase selectivity.

2.3.2 Transport in membrane

The membranes can be macroporous, microporous, or dense (nonporous). Only microporous or dense membranes are permselective. However, macroporous membranes are widely used to support thin microporous and dense membranes when significant pressure differences across the membrane are necessary to achieve a reasonable throughout. If the membrane contains pores large enough to allow convective flow, separation will not occure. If the size of the pores is smaller than the mean free path of the gas molecules, then convective flow is replaced by Knudsen diffusion. If the pores are small enough, large molecules are unable to pass through them and are excluded by the membrane. This molecular sieve is potentially useful in separating molecules of different sizes. The membranes currently used in most commercial applications are solution-diffusion membranes These membranes are named because transport occurs when gas molecules dissolve into the membrane and then diffuse across it while solution-diffusion membranes can be made of a liquid layer supported on a porous support [29].