CHAPTER I

INTRODUCTION

1.1 Natural rubber

Nearly 2000 species of trees, shrubs or vines of the tropical and temperate regions produce latex from which natural rubber or a closely related substance can be obtained. However, the latex from the tree of Hevea brasiliensis is the only important commercial source of natural rubber. The tree is indigenous to the Amazon valley.

Natural rubber has been known to the inhabitants of South America for centuries. Christopher Columbus is considered to be the first European to discover it during his second voyage in 1493-6 [1,2].

Rubber was introduced to the western world by Charles de la Condamine, who sent samples to France from Peru in 1736 and published the results of his observations in 1745. By the end of the eighteenth century, Europe and America were using a few tons of rubber per year. However, users found it difficult to work with solid rubber. Moreover, articles made from natural rubber turned sticky

in hot weather and stiffened in the cold.

Two important developments in the nineteenth century enabled these problems to be solved and laid the foundation for the multibillion-dollar modern rubber industry. In 1820, Thomas Hancock invented a machine called the "masticator" that allowed solid rubber to be softened, mixed and shaped. In 1839, Charles Goodyear discovered the process of vulcanization. He found that heating a mixture of rubber and sulfur yielded products that had much better properties than the raw rubber.

Soon a variety of articles from rubber started to come into the market and the demand of rubber grew rapidly. Exports of raw rubber increased from a few hundred tons in 1846 to almost 10,000 tons by 1880. It was soon apparent that Brazil would not be able to meet future demand. The British considered the possibility of cultivating rubber in Asia and by 1880 Hevea seedlings were widely distributed in Asia.

The land used for rubber cultivation and the production of natural rubber has grown steadily as expected since World War II. In 1983, more than 7.5 million hectares of land in the world were under rubber cultivation and about 4 million metric tons of rubber were

produced. The Southeast Asia region accounted for about 80% of the total production. Malaysia was the biggest producer, followed by Indonesia and Thailand. The world production of natural rubber is shown in Table 1.1.

Table 1.1 World production of natural rubber (1983).

Country	Tons ('000)
Malaysia	1,569
Indonesia	997
Thailand	587
India	168
China	159
Sri Lanka	140
Philippines	75
Liberia	65
Others	257
Total	4,010

Source: IRSG, Rubber Statistical Bulletin 38 (12), 2, 1984.

1.1.1 Properties of raw natural rubber

Natural rubber latex consists of particles of rubber hydrocarbon and non-rubber constituents suspended in an aqueous serum phase. The average dry rubber content of latex may range between 30 % and 45 %. A typical composition of fresh latex is shown in Table 1.2 [1].
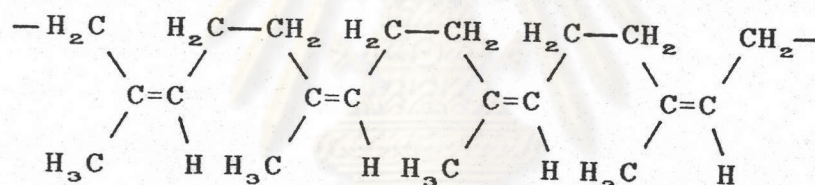
Table 1.2 Typical composition of fresh latex and dry rubber.

Composition	Latex , %	Dry rubber , %
Rubber hydrocarbon	36.0	93.7
Protein	1.4	2.2
Carbohydrates	1.6	0.4
Neutral lipids	1.0	2.4
Glycolipids & phospholipids	0.6	1.0
Inorganic constituents	0.5	0.2
Others	0.4	0.1
Water	58.5	–

1.1.2 Physical and chemical properties

The chemical constitution of natural rubber has, since the nineteenth century, been the subject of research done by many famous chemists including Faraday who found a component corresponding to C_5H_8. The rubber hydrocarbon in freshly tapped latex is almost completely soluble (more than 95%) in common solvents such as toluene and tetrahydrofuran. It has a chemical structure of almost 100 % cis-1,4-polyisoprene units.

$$
\begin{array}{ccccccccc}
-H_2C & & H_2C-CH_2 & & H_2C-CH_2 & & H_2C-CH_2 & & CH_2- \\
\diagdown & & \diagup \quad \diagdown & & \diagup \quad \diagdown & & \diagup \quad \diagdown & & \diagup \\
& C=C & & C=C & & C=C & & C=C & \\
\diagup & \diagdown & \diagup & \diagdown & \diagup & \diagdown & \diagup & \diagdown & \\
H_3C & \quad H & H_3C & \quad H & H_3C & \quad H & H_3C & \quad H &
\end{array}
$$

X-ray analysis has since confirmed these views and most of the properties of rubber can be explained on the long chain molecule pattern.

Determination of molecular weight of the rubber molecule, based on classical theories and studies on macromolecules, has shown a figure of 200,000 - 400,000; i.e., one molecule would consist of 3,000-6,000 isoprene units.

1.1.3 Non-rubber substances

During the preparation of dry rubber, large quantities of the water-soluble non-rubber substances are lost, but most of the lipids are retained together with more than half the proteins and small quantities of inorganic salts and others substances. Each of these classes of non-rubber substances consists of many individual substances. The lipids, for example, consist of mono, di, and triglycerides, sterol and sterol esters, tocotrienols and their esters, free fatty acids, glycolipids and phospholipids. Natural rubber usually contains more than 100 individual chemical compounds. Some of these non-rubber substances greatly influence the properties of natural rubber, in both the raw and vulcanized states.

The properties affected by the non-rubber substances are summarized in Table 1.3 [1].

Table 1.3 Properties of natural rubber influenced by non-rubber substances

Property	Influence of non-rubbers
Latex stability	Carbohydrate acts as substrates for bacterial growth, leads to increase volatile acid formation and lowers stability.
Color	Yellow caused by β-carotenes. Dark caused by enzymic reaction of polyphenol oxidase.
Cure	Phospholipids and some proteins are natural accelerators; fatty acids are activators.
Oxidation	Tocotrienols are natural antioxidants. Copper, manganese and iron ions are pro-oxidants.
Storage hardening	Proteins and free amino acids react with abnormal groups in rubber.
Crystallization	Unstrained crystallization rate increased by stearic acid, some water-soluble substances retard rate.

Table 1.3 (continued)

Property	Influence of non-rubbers
Creep and stress	High contents of proteins and ash lead to moisture absorption, which results in high creep and stress relaxation in vulcanizates.
Modulus	Increased by proteins.
Filler effect	Proteins act as fillers. One part of protein is equivalent to 3 parts of HAF black.
Heat build-up	Heat build-up in the Goodrich flexo-meter test is decreased by fatty acid and increased by proteins.
Tear strength	Increased by proteins.
Dynamic crack growth	Resistance increased by proteins.

1.1.4 Product applications

With its wide range of useful properties,
natural rubber can be used in a large variety of
applications. The approximate usage of natural rubber
by products is shown in Table 1.4 [1].

Table 1.4 Use of natural rubber in products.

Products	Percent
Tire and tire products	70-72
Mechanical goods	9-10
Latex products	7-8
Footwear	4-5
Engineering products	3-4
Adhesives	1-2
Others	2-3

1.1.5 Natural rubber in Thailand

The data from the Industrial Economics &
Planning Division, Ministry of Industry [3] showed that
in 1982, Thailand produced 562,210 tons of natural rubber
and exported 546,689 tons or 97 % of total production.
The remaining 3% was used in the country. Since it is
uneconomical to transport preserved field latex over long
distances to consumer countries, the normal precedure is
to change the latex form before shipment. Therefore,
after the natural rubber latex has been collected from
the field, it is changed into many forms of rubber, i.e.
raw sheet, smoked sheet, block rubber, crepe rubber and
concentrated latex. There are various products made from
different types of rubber which are produced in Thailand
as shown in Table 1.5.

Table 1.5 Rubber products produced from different types
of rubber.

No	Products	Types of rubber
1	Mould foams for mattresses	Concentrated latex 60%
2	Elastic thread for undergarments	Smoked sheet
3	Toyballons	Concentrated latex 60%
4	Inner tubes for motor-vehicles	Smoked sheet
5	Belts	Smoked sheet
6	Rubber shoes, slippers	Scraps of smoked sheet, smoked sheet, block rubber, crepe rubber
7	Battery jackets (boxes)	Smoked sheet
8	Spare parts for automobiles	Smoked sheet
9	Rubber soles	Rubber sheet, scraps of rubber sheet
10	Hoses, water pipes	Crepe rubber, scraps of crepe rubber
11	Wheels	Scraps of smoked sheet
12	Medical devices, electric goods, furniture upholstery	Crepe rubber

Table 1.5 (continued)

No	Products	Types of rubber
13	Adhesives, adhesives for footwear	Smoked sheet
14	Condoms (Contraceptives), rubber dolls	Smoked sheet
15	Spare parts for thermos	Scraps of smoked sheet, block rubber
16	Household gloves, nipples	Concentrated latex 60%
17	Golf balls	Rubber sheet
18	Spread foams for carpets	Concentrated latex 60%
19	Rubber sponge	Concentrated latex 60%
20	Rubber rings	Smoked sheet

Source : Southern Industrial Economics Centre, Industrial
Economics & Planning Division, Ministry of Industry

1.2 Liquid natural rubber (LNR)

As mentioned above, natural rubber can be used in many applications, but there are some applications which are not possible with solid high-molecular-weight rubbers such as adhesives, binders, cold vulcanizing mixtures, manufacture of flexible casts and surface casting materials.

Liquid natural rubber can be prepared by mechanical or chemical treatments.

1.2.1 Mechanical treatment [4,5]

Mechanical degradation has been utilized for processing natural rubber since the middle of the nineteenth century. The mechanical treatment of rubbers is called "mastication," a term derived from the Latin word masticare ="to chew." Mastication is usually carried out on roll mills or in the plasticators (internal mixers). In the presence of air, it leads to a marked decrease in the average molecular weight of the rubber, thus increasing its plasticity. Typical results demonstrating the decrease in the molecular weight as a function of the mastication time are shown in Figure 1.1.
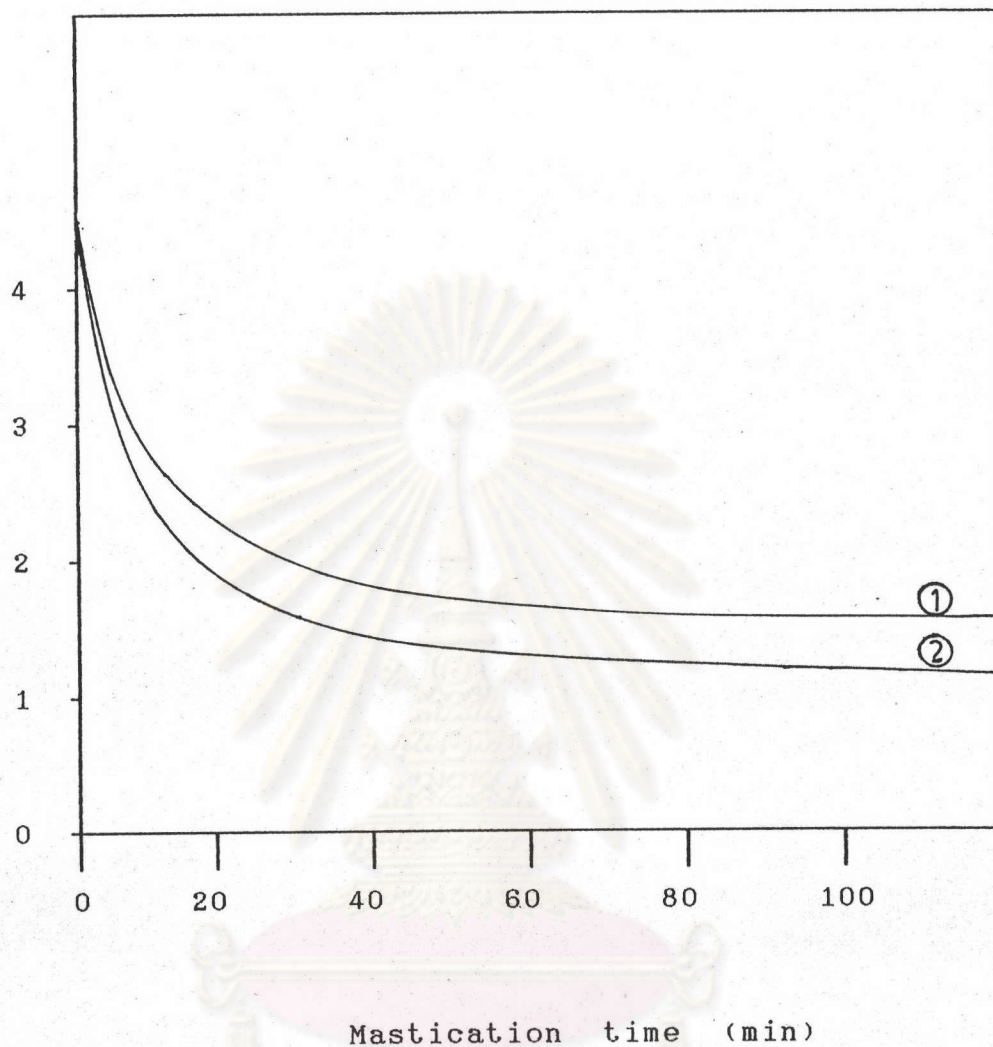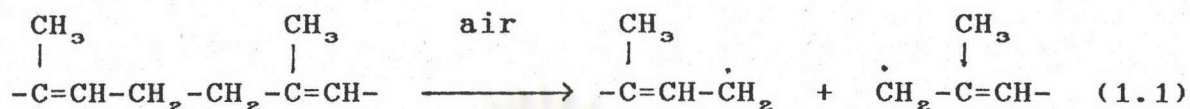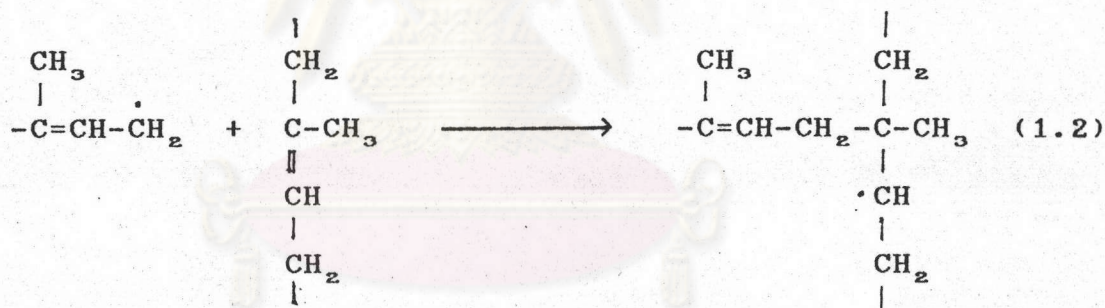
$\overline{M}w \times 10^{-5}$

Mastication time (min)

Fig 1.1 Mastication of natural rubber in an internal
mixer in the presence of air at 52°C and the
rotor speeds of 46 rpm (1) and 245 rpm (2).

Under mastication, bond scission is assumed to occur in the main chains leading to allyl type radicals.

$$
\begin{array}{c}
CH_3 \qquad\qquad CH_3 \qquad\quad air \qquad\; CH_3 \qquad\qquad\qquad\quad CH_3 \\[2pt]
| \qquad\qquad\quad | \qquad\qquad\qquad\qquad | \qquad\qquad\qquad\qquad\quad\; | \\[2pt]
-C{=}CH{-}CH_2{-}CH_2{-}C{=}CH{-} \;\longrightarrow\; -C{=}CH{-}\overset{\bullet}{C}H_2 \;+\; \overset{\bullet}{C}H_2{-}C{=}CH{-} \qquad (1.1)
\end{array}
$$

In an inert atmosphere, mechanical treatment readily leads to intermolecular crosslinking. Branching and crosslinking become feasible through the reaction of macroradicals, formed according to the reaction shown above, with double bonds of other macromolecules.

$$
\begin{array}{c}
\qquad\qquad\qquad\qquad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\[2pt]
CH_3 \qquad\quad CH_2 \qquad\qquad\qquad\qquad CH_3 \qquad\quad CH_2 \\[2pt]
| \qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\; | \qquad\qquad\quad | \\[2pt]
-C{=}CH{-}\overset{\bullet}{C}H_2 \;+\; C{-}CH_3 \;\longrightarrow\; -C{=}CH{-}CH_2{-}C{-}CH_3 \qquad (1.2) \\[2pt]
\qquad\qquad\qquad\quad \| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\[2pt]
\qquad\qquad\qquad\quad CH \qquad\qquad\qquad\qquad\qquad\qquad\; \overset{\bullet}{\,}CH \\[2pt]
\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\; | \\[2pt]
\qquad\qquad\qquad\quad CH_2 \qquad\qquad\qquad\qquad\qquad\qquad CH_2 \\[2pt]
\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\; |
\end{array}
$$

Mastication is always carried out under conditions which prevent crosslinking, i.e. in the presence of radical scavengers. Usually, molecular oxygen contained in the air is sufficient to completely suppress gel formation.

1.2.2 Chemical treatment

The first liquid natural rubber was produced by K.V. Hardman [5] in 1923 . The studies of the development of a method to obtain low molecular weight polyisoprene from natural rubber have been continued by the researchers from I.F.C., I.R.A.P. and I.R.C.A. in France. The chemical production of LNR is based on chemical oxidative degradation of natural rubber (in the latex phase) using a redox system. The redox system used is composed of an oxidizer such as organic peroxide, perhydrol and atmospheric oxygen associated with a reducer such as sulphanilic acid or aromatic hydrazine. The depolymerization reaction can take place in an organic solvent or directly in the latex phase. For economic and operating reasons, the phenylhydrazine/oxygen system has been chosen to produce liquid natural rubber in latex phase. This reaction is schematically represented in Figure 1.2.

Natural rubber

```
+------------------------------------+
|                                    |
|            cis-1,4                 |
|                                    |
+------------------------------------+
```

$C_6H_5NHNH_2$

O_2 (air)

Δ

```
            +------------------------------------+
            |                                    |
X ----------|            cis-1,4                 |---------- X
            |                                    |
            +------------------------------------+
```

Depolymerized natural rubber

= Liquid natural rubber

$3,000 < \overline{M}n < 20,000$
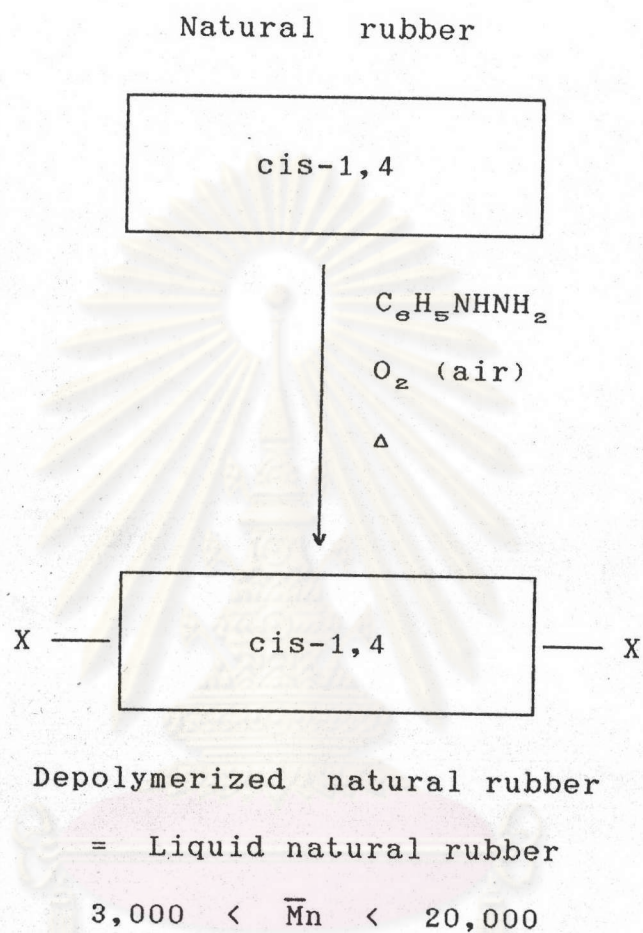
Fig 1.2 Natural rubber depolymerization by
phenylhydrazine in an oxidizing medium.

1.3 Copolymers [6-10]

The simultaneous polymerization of two or more bifunctional or bi-bi functional monomer systems, each of which is capable of polymerizing by itself (homopolymerization), is a process called "copolymerization," and the product is called "copolymer." For example, styrene and butadiene can individually undergo homopolymerization; combined, they readily copolymerize in such a way that their units are randomly distributed along the chain structure. By varying both the kinds and relative amounts of the two monomers used in the copolymerization, a series of products may be manufactured with a considerable spread in chemical, physical and mechanical properties. The range of useful products may be further extended by the copolymerization of three, four or even more monomeric species, often with radically different structures and chemical composition.

For copolymerization of two bifunctional or two bi-bifunctional monomer systems, we can define four types of copolymers. These represent ideal models that are not always obtained in practice. They are defined and illustrated schematically below, using symbols A and B for the repeating structures:

(a) Random copolymers. The units A and B recur in random length sequences along the polymer chain.

-A-B-B-B-B-A-A-A-A-B-A-A-B-B-B-A-A-B-B-B-B-A-A-A-B-A-B-A-

(b) Alternating copolymers. The units appear in the chain of alternating positions.

-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-

(c) Block copolymers. The units appear in long alternating segments of random length.

-A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-A-A-A-A-B-B-B-B-

(d) Graft copolymers. One of the units makes up the main chain, whereas the other units appear in short branches grafted to this chain.

```
-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-
   |              |              |              |
   B              B              B              B
   |              |              |              |
   B              B              B              B
   |              |              |              |
   B              B              B              B
   |              |                             |
   B                                            B
   |                                            |
```
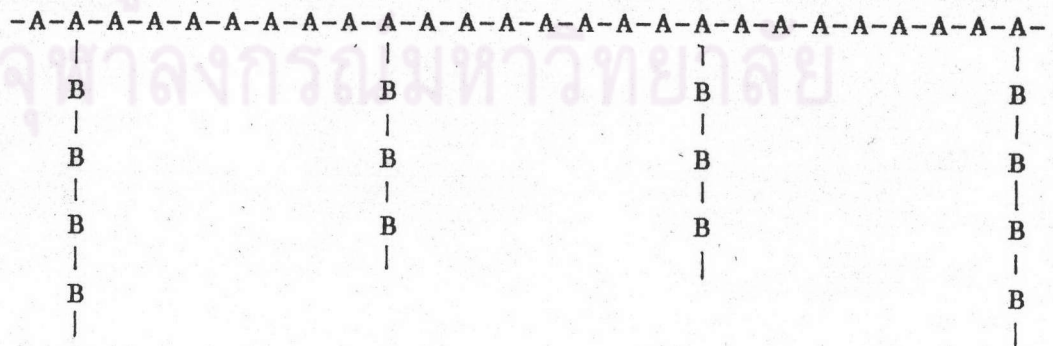
The process by which a polymer is synthesized or modified is the most important step in producing a useful polymer. Since different polymeric materials can result from polymerizing the same monomer by different methods, the different types of copolymer can be obtained from different polymerization processes. In this thesis, only the graft copolymerization process is presented in more detail.

The synthesis of a graft copolymer requires the formation of a reactive center on a polymer molecule in the presence of a polymerizable monomer. Most methods of synthesizing graft copolymers involve the use of radical polymerization, although ionic graft copoly-merization is receiving increasing attention. Graft copolymerization is carried out in either a homogeneous or heterogeneous system depending on whether the polymer being grafted to is soluble or insoluble in the monomer.

Methods of synthesizing graft copolymers

1.3.1 Radical graft copolymerization

1.3.2 Ionic graft copolymerization

1.3.1 <u>Radical graft copolymerization</u> can be divided into 4 types.

(a) Chain transfer and copolymerization

The radical polymerization of a monomer using an initiator such as benzoyl peroxide can result in grafting due to radical formation on the polymer backbone. After the polymer radicals are formed by chain transfer between the propagating radical and the polymer, the grafting of monomers onto the polymer backbone then occurs, for example the grafting of styrene monomer onto 1,4-polybutadiene.

$$-CH_2CH=CHCH_2- \; + \; -CH_2\overset{\centerdot}{C}H\phi \longrightarrow -\overset{\centerdot}{C}HCH=CHCH_2- \; + \; -CH_2CH_2\phi \quad (1.3)$$

$$-\overset{\centerdot}{C}HCH=CH-CH_2- \; + \; nCH_2=CH\phi \longrightarrow \underset{\underset{\displaystyle (CH_2CH\phi)_n}{|}}{-CH-CH=CHCH_2-} \quad (1.4)$$
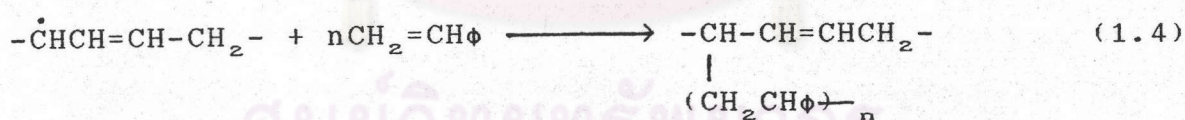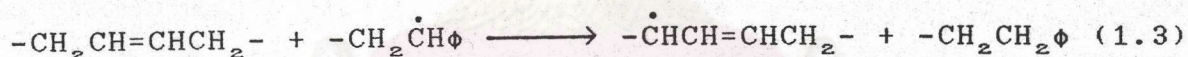
(b) Ionizing radiation

Polymeric radicals can alternately be produced by the irradiation of polymer-monomer system with ionizing radiation, for example, the grafting of polyethylene with styrene monomer.

$$-CH_2CH_2- \xrightarrow{\text{radiation}} -CH_2\overset{\cdot}{C}H- + \overset{\cdot}{H} \qquad (1.5)$$

$$-CH_2\overset{\cdot}{C}H- + nCH_2=CH\phi \longrightarrow \begin{array}{c} -CH_2CH- \\ | \\ (CH_2CH\phi)_n \end{array} \qquad (1.6)$$
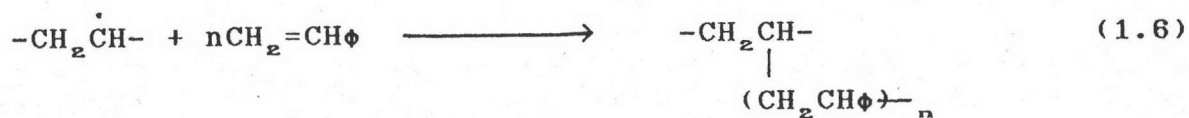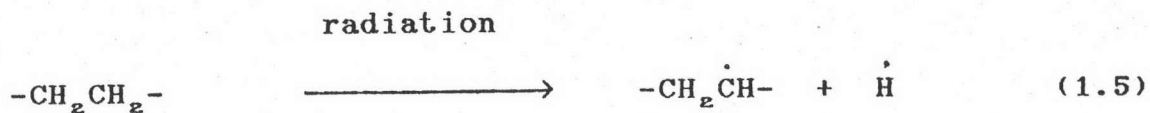
(c) Ultraviolet radiation

Graft copolymerization can also be achieved by irradiation of a polymer-monomer system with ultraviolet radiation, often in the presence of a photosensitisizer such as benzoquinone or benzoin. UV-initiated grafting is generally limited to surface modification of a polymer.

(d) Redox initiation

Redox initiation is often an efficient method of initiating graft copolymerization. Hydroxyl-containing polymer such as poly(vinyl alcohol), cellulose and starch undergo redox reaction with ceric ion or other oxidizing agents to form polymer radicals capable of initiating polymerization.

$$-CH_2CH- + Ce^{4+} \longrightarrow -CH_2-\overset{\bullet}{C}- + H^+ + Ce^{3+} \qquad (1.7)$$
$$\quad\;\; | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\quad\;\; OH \qquad\qquad\qquad\qquad\qquad\;\; OH$$
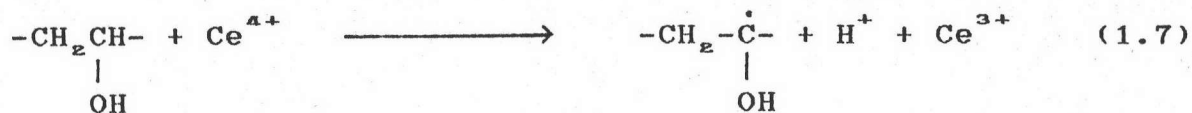
Redox initiation usually results in grafting with a minimum homopolymerization since only the polymeric radical is formed (eq 1.7). It is, however, limited to polymer containing the necessary functional group. Besides hydroxyl-containing polymer, polymers with amide, halogen and nitrile groups have been found to undergo redox initiation with appropriate oxidizing or reducing agents.

1.3.2 Ionic graft copolymerization

Ionic graft copolymerization is an interesting process. A variety of graft copolymers can be potentially synthesized by using this process in greater quantities than that by radical initiation processes. A wider range of monomers can also be used--including alkene, carbonyl and cyclic monomers. However, it is considerably more difficult to form the polymeric anion or cation necessary to initiate graft copolymerization compared to forming a polymeric radical.

Ionic graft copolymerization can be divided into two types : (a) anionic initiation and (b) cationic initiation

(a) Anionic initiation

Metallation of a polymer by treatment with strong base, for example, is the reaction of 1,4-polybutadiene with t-butyllithium:

$$-CH_2CH=CHCH_2- \xrightarrow{\text{BuLi}} -\bar{C}HCH=CHCH_2- \qquad (1.8)$$
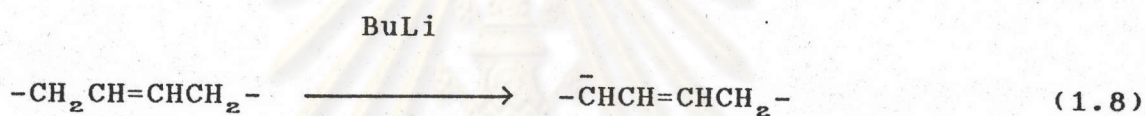
or polyamide with sodium:

$$-NH-CO- \xrightarrow{\text{Na}} -\overset{..}{\bar{N}}-CO- \qquad (1.9)$$
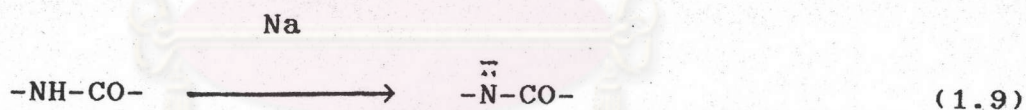
Either yields polymeric anions which can initiate the graft copolymerization of a monomer such as styrene, formaldehyde, acrylonitrile and ethylene oxide.

Copolymers of acrylic acid or ester or other polymer-containing carboxylate groups have been used to initiate graft copolymerization. Coupling of polymers to form graft copolymers can also be accomplished

by nucleophilic substitution. The reaction between living polystyryl carbanion and poly(vinyl chloride) is an example.

$$-CH_2CH- \ + \ -CH_2\overset{..}{\overset{-}{C}}H\phi \ \longrightarrow \ \begin{matrix} CH_2CH- \\ | \\ CH\phi CH_2- \end{matrix} \qquad (1.10)$$
$$\overset{|}{Cl}$$
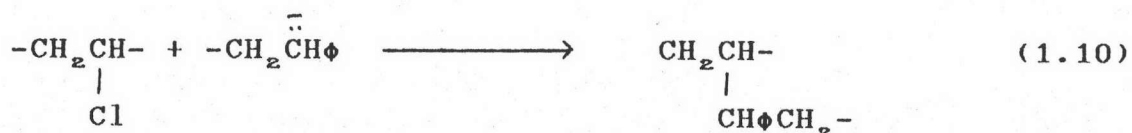
(b) Cationic initiation

Polymeric carbonium ion has been formed by reaction of a chlorine-containing polymer such as poly (vinyl chloride), chloromethylated polystyrene and chlorinated polybutadiene with $AlCl_3$, BCl_3 , R_2AlCl or $AgSbF_6$, for example:

$$-CH_2-CH- \ + \ AgSbF_6 \ \longrightarrow \ AgCl\downarrow \ + \ -CH_2\overset{+}{C}H- \qquad (1.11)$$
$$\overset{|}{Cl}$$

$$-CH_2\overset{+}{C}H- \ + \ CH_2=CH\phi \ \longrightarrow \ \begin{matrix} -CH_2CH- \\ | \\ CH_2-\overset{+}{C}H\phi- \end{matrix} \qquad (1.12)$$
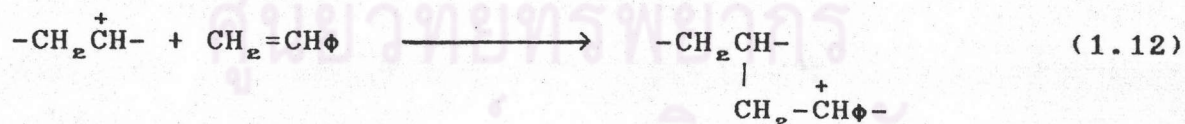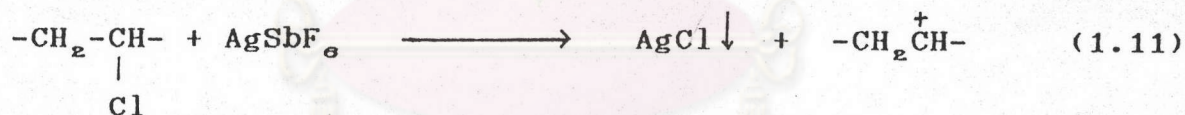
The polymeric carbonium ion can initiate the polymerization of isobutylene, tetrahydrofuran and other monomers.

1.4 Graft copolymerization of natural rubber with vinyl monomers.

Graft copolymerization of natural rubber with vinyl monomer onto natural rubber has been investigated by many researchers [9-10]. The earliest recorded attempt to modify natural rubber by polymerization with vinyl monomer was performed by Bacon and his coworkers in 1938. But the patents describing materials which were obtained from polymerization of vinyl monomer (especially styrene) onto dissolved natural rubber began to appear in the 1930's. The polymerization of methyl methacrylate (MMA) in rubber latex using benzoyl peroxide (BPO) as a catalyst was also studied at about the same time. More successful polymerization was later effected by using water soluble catalysts such as persulphates or organic hydroperoxide. The polymerization reaction can be carried out with rubber in solid form, in solution (either in the monomer or in a matual solvent), or as latex.

The polymerization of a monomer proceeded in the presence of rubber under a given set of conditions does not necessarily signify that combination has occurred only between the two components, since the monomer can be obviously polymerized quite independently. However, the intermediates involved in vinyl polymerization are highly

reactive both towards the double bonds and towards the relatively labile α-methylenic C-H bond presented in natural rubber.

The successful grafting of vinyl monomers onto natural rubber involves the creation of free radical on the backbone of rubber molecules. This can be achieved by several methods [10-16], such as chemical and irradiation. Of all these methods, the chemical method has attracted most attention in recent years. Generally, graft copolymerization of typical vinyl monomers onto natural rubber has been studied by using benzoyl peroxide as the initiator.

Mishra and Kual [11] carried out graft copolymerization of natural rubber using benzoyl peroxide as an initiator with several vinyl monomers, namely methyl acrylate, ethyl acrylate and butyl acrylate, and they also compared the reactivity of these monomers. The results showed that the reactivity of these vinyl monomers were different and followed the order:

ethyl acrylate > butyl acrylate > methyl acrylate

The method of irradiation grafting of methyl methacrylate monomer onto natural rubber latex has also

been studied [12]. Irradiation was carried out using a Panoramic Co-60 Irradiator, 55 kCi activity. The physical properties of the product (tensile strength, modulus, elongation at break, etc.) were measured and compared with the product obtained from the conventional method using hydroperoxide-polyamine initiator. (The major use of this product is in the field of adhesives.) The experimental results are in agreement with the results of several studies dealing with grafting of natural rubber using conventional method.

Recently, a series of graft copolymerization of natural rubber with vinyl monomers using redox systems has been reported. Lenka and his colleagues have investigated the graft copolymerization of natural rubber with methyl methacrylate using several couples of redox initiator-quinquevalent vanadium ion [13], acetylacetonate complex of manganese (III) [14], potassium peroxydisulphate/silver ion [15], potassium bromate/thiourea [16], and dimethyl aniline/cupric ion [17]. The features of study included the effects of monomer concentration, initiator concentration, reaction temperature, reaction time, etc. on the extent of grafting. The results manifested that the grafting efficiency was strongly dependent on the reaction conditions.

Although a number of processes for graft copolymerization of many vinyl monomers onto natural rubber using the metal ion redox system have been investigated previously, 2-ethoxyethyl methacrylate has never been used for grafting onto natural rubber. This study involves the graft copolymerization of 2-ethoxyethyl methacrylate onto natural rubber using N,N-dimethyl aniline/cupric ion as a redox couple.

1.5 Background and justification

The preliminary survey of natural rubber and its applications as previously described reveals that Thailand, which ranks third among the world producers and exporters of natural rubber, has low production of rubber products (about 3%) for domestic use. Among the products (shown in Table 1.5), adhesive is the one being produced for both domestic use and export. Table 1.6 shows the exported value of adhesive. However, the amount of adhesive imported is larger than the amount exported, as the data shows in Table 1.7. The reason for this as revealed by the Southern Industrial Economics Centre, Industrial Economics & Planning Division, Ministry of Industry, is that Thailand's import of adhesive is due to poor quality of locally produced rubber adhesive, i.e. long drying time and poor adhesion property. So Thai adhesive cannot be used with materials

requiring strong adhesion power. At present, the development of adhesive production is being conducted by the Natural Rubber Research Institute, Department of Agriculture.

It is expected that the investigation of graft copolymerization of 2-ethoxyethyl methacrylate onto natural rubber may be a method of choice to modify the chemical structure of natural rubber for improving its adhesive property. It may also be a means to develop the processing of adhesive production as well as the wider usage of natural resources in the future.

Table 1.6 Quantities and value of imported adhesive distributed by countries from 1982-1986

Year / Country	1982 Quantity	1982 Value	1983 Quantity	1983 Value	1984 Quantity	1984 Value	1985 Quantity	1985 Value	1986 Quantity	1986 Value
Japan	41,203	3,419,998	59,033	5,063,117	53,797	4,630,735	42,473	4,626,689	26,797	4,467,115
Republic of Korea	6,119	250,778	85,025	3,096,782	144,312	5,187,240	305,614	11,760,937	359,082	12,579,212
Malaysia	41,563	1,168,435	52,065	1,380,373	15,396	424,371	9,904	279,892	10,856	272,632
Singapore	1,608	39,504	1,084	62,898	39	3,222	126	21,746	6,740	338,213
Taiwan	149,215	6,204,257	166,905	6,430,541	193,210	7,926,826	158,260	7,645,827	324,461	11,544,423
France	214	31,039	30	8,562	22	1,020	17,412	593,365	2,143	130,603
Federal Republic of Germany	11,424	184,625	1,408	224,222	5,511	647,633	1,298	205,660	3,080	453,039
Sweden	41	8,959	257	37,913	215	36,323	1,703	155,933	40	29,484
Switzerland	50	10,024	-	-	400	20,835	405	47,452	-	-
United Kingdom	5,598	336,130	14,839	610,462	15,583	603,727	11,267	514,902	49,739	1,532,072
United States of America	19,193	1,355,813	29,731	2,010,799	17,135	1,441,552	66,845	8,425,714	31,699	2,724,709

1.6 Aims of the investigation

1. To study the effects of reagents and reaction conditions on the extent of grafting of 2-ethoxyethyl methacrylate onto natural rubber using N,N-dimethyl aniline/cupric ion redox system.

2. To test the adhesion property of grafted product with different extents of grafting.