CHAPTER 1

INTRODUCTION

1.1   The Chemical Modification of Diene-Based Polymers

Diene-based polymers e.g., *cis*-1,4-polyisoprene (CPIP), polybutadiene (PBD), nitrile butadiene rubber (NBR), styrene-butadiene rubber (SBR), etc. are elastomers produced by polymerizing a diene monomer or a diene monomer with a functional olefin. Diene-based rubber molecules contain of carbon – carbon double bonds in the polymer backbone. The presence of unsaturated C=C bonds might undergo degradation or oxidation when exposed to oxygen and ozone, especially in harsh operating conditions. In contrast, double bonds are vital for postpolymerization processes such as vulcanization.

Chemical modification of polydiene is a useful process for synthesizing polymers, which are often inaccessible by conventional polymerization techniques (Bhowmick, 1988; McManus and Rempel, 1995; Singha et al., 1997a: 309-367). In other words, the chemical modification of polymer is a postpolymerization processing reaction which is used to improve and optimize the chemical and mechanical properties of existing polymers or synthetic novel polymers having a desirable functional group. It has been shown that the hydrogenation of 1,4-polybutadiene can lead to a thermoplastic material with a structure identical to a linear polyethylene. Perfect alternating copolymers of ethylene with propylene can be achieved by hydrogenating 1,4-polyisoprene.

In the broadest sense, vulcanization, grafting, degradation, oxidation, isomerization, hydrogenation, hydrocarboxylation, hydroesterification, etc. are all classified as chemical modification reactions. Of these, most catalytic polymer chemical modifications studies have been devoted to hydrogenation. The catalytic hydrogenation of acrylonitrile-butadiene copolymer or NBR is a significant commercial example, resulting in superior ozone, peroxide, oil, and solvent resistance at elevated temperatures compared with normal NBR (Oppelt et al., 1976; Rempel and Azizian, 1984).

The important aspects to be considered with respect to the possibility of catalytic chemical reaction on polymers are: (i) the reactivity of the parent polymer

(ii) the type and nature of catalyst i.e., its activity and selectivity (iii) the reaction conditions applied (iv) the functionalities such as nitrile, carbonyl, halogen, etc. contained in the parent polymer.

Hydrogenation, the addition of hydrogen (H_2) to an unsaturated moiety, e.g. olefin, is a simple process reducing the unsaturation level in the diene-based polymers. This modification process may lead to optimization of the physical properties of the polymers such as thermal stability, light stability, and solvent resistance. Diene elastomers can be hydrogenated by both non-catalytic and catalytic methods. For catalytic hydrogenation, there are examples of the use of both homogeneous and heterogeneous catalyst systems.

The main method of non-catalytic hydrogenation is carried out involves using diimide, generated *in situ*. At high temperature (110 – 160°C), *p*-toluenesulfonyl hydrazide (TSH) decomposes to form reactive diimide (N_2H_2), which subsequently reduces carbon-carbon unsaturation. The diimide hydrogenation is stoichiometric, and so far it is regarded as being unsuitable for large-scale processes. Since the reaction is carried out at high temperature, it causes degradation and cyclization of polymer leading to inferior physical and mechanical properties (Harwood et al., 1973; Nang et al., 1976).

Catalytic hydrogenations are of two types: heterogeneous and homogeneous catalytic hydrogenation depending on the state of the catalyst and the substrate. In heterogeneous hydrogenation, the catalytically active species and the substrate are in two different phases. The main advantage of this kind of catalyst is that the catalyst can be easily separated from the hydrogenated polymer by filtration of the catalyst, followed by evaporation of the solvent. The efficiency of the heterogeneous catalyst depends on its surface area and the nature of support. Being bulk solids, heterogeneous catalysts generally have higher thermal stability than homogeneous systems, thus reactions can be run under high condition giving rise to high reaction rates.

In homogeneous catalysis, the catalytically active species is molecularly dispersed within the polymer. Homogeneous complexes normally contain only one type of active site and as a result are more specific. Since all these active sites are available, homogeneous catalysts are potentially more efficient than heterogeneous catalysts. The selectivity of homogeneous catalyst is much more easily modified by selective ligand exchange. Therefore, many of the new developments used catalyst for

the reduction have involved the use of homogeneous catalysis (Olah and Molnar, 1995).

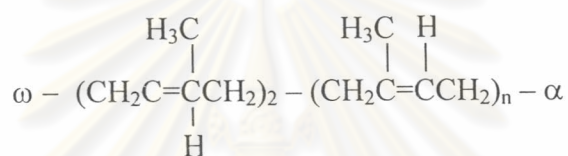## 1.2 Natural Rubber and Synthetic Polyisoprene

a) Natural Rubber

Hevea brasiliensis, a tropical tree, is a major source of the world's natural rubber. Natural rubber (NR) has become an important industrial material, especially in the tire industry. It is also used in the manufacture of various products including household, engineering, medical, and commercial goods. Natural rubber is one of the significant crops for the Thai economy. A number of advantages the Thai rubber industry has over other rivals included high potential to complete in the world market. Due to its lower production cost, Thailand's favorable climate for rubber planting, and production efficiency, all of which lead Thailand to become the largest natural rubber producer and exporter in the world throughout the last decade (Figure 1.1). Thailand has approximately 5 million acres of rubber plantations located mostly in the southern and eastern parts of the country. In 2001, Thai rubber yield was 2.41 million metric tons of which only 0.33 million metric tons were used by the local rubber industry and the remainder was exported.
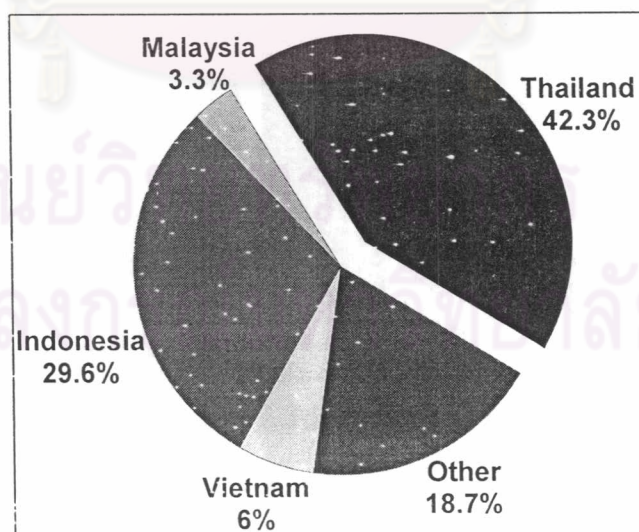
Source: IRSG - Rubber Statistical Bulletin and FAO

Figure 1.1: World natural rubber production (Amnuaikarn, 2001).

Natural rubber (NR) is a unique elastomeric polymer produced from natural rubber latex. Natural latex is defined as a milky fluid that consists of extremely small particles of rubber obtained from plants, principally from Brazilian rubber tree, *Hevea brasiliensis* dispersed in an aqueous medium. The rubber in natural latex is polyisoprene consisting of isoprene unit (C_5H_8) almost 100% in the *cis*-configuration (Brydson, 1978). Tanaka (2001) disclosed that the chemical structure of natural rubber is composed of an unidentified initiating terminal and two-*trans* isoprene unit and long sequence of *cis*-isoprene units terminated with an unidentified chain end group as shown in Figure 1.2.

$$\omega - (CH_2C\overset{\overset{\displaystyle H_3C}{|}}{=}CCH_2)_2 - (CH_2C\overset{\overset{\displaystyle H_3C}{|}}{=}\overset{\overset{\displaystyle H}{|}}{C}CH_2)_n - \alpha$$
$$\underset{\displaystyle H}{|}$$

ω and α: unidentified terminal group

Figure 1.2: The chemical structure of natural rubber (Tanaka, 2001).

Fresh latex has density of 0.975-0.980 g/ml with the pH of 6.5-7.0. Fresh natural latex contains about 35% rubber particles. The surface of the particles is covered with lipid and protein layers as shown in Figure 1.3. The outer layer proteins act to stabilize *Hevea* latex (Jacob et al., 1993). The average particle size is between 0.10 µm and 1.0 µm. The particle size distribution is very broad. The molecular weight of NR is in the region of one million with high polydispersity index. The dispersion in weight, M_w/M_n, is in the range of 2.5 to 10. The broad molecular weight distribution (MWD) of *Hevea* rubber may be derived from the branching and crosslinking reaction by certain special functional groups in rubber molecule. The distributions were either distinctly bimodal with two peaks, the one at lower molecular weight generally being less than that at higher weights, or skewed unimodal with a shoulder or plateau on the low molecular weight side of the peak (Roberts, 1988).
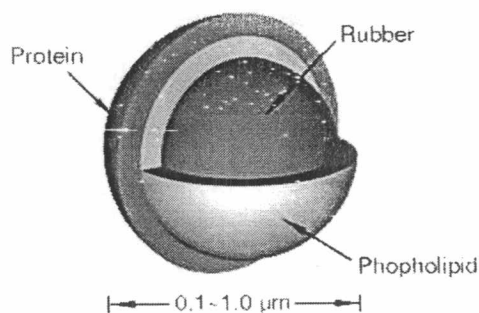
Figure 1.3: Presumed structure of solid rubber particle (Verhaar, 1959).

Natural latex contains small amount of non-rubber constituents such as proteins, carbohydrates, sterols, and other lipids (Tanaka et al., 1997; Tanaka, 2001). The overall compositions of NR are summarized in Table 1.1. It is well known that the rubber hydrocarbon in dry solid is comprised of two fractions called "sol" and "gel" (Tangpakdee and Tanaka, 1997a: 707-713). The sol phase is dissolved easily in good solvents such as cyclohexane, toluene, tetrahydrofuran, etc., while the gel phase is undissolved but highly swells in solvent. *Hevea* rubber contains 5-50% gel component. The gel content in rubber depends on the clonal origin of the rubber, processing condition and the period and temperature of storage. Insoluble phase consists of microgel and macrogel. The gel phase was presumed to consist of small crosslinked latex particles or "microgels". The microgels are combined into a matrix with the sol fraction and form an apparent gel phase as illustrated in Figure 1.4. Since the gel phase contains a nitrogeneous and mineral component, it is postulated that the gel phase is linked up with the network of protein via hydrogen bonding. The gel phase in NR is composed of two types of crosslinking points; one is formed by the intermolecular interaction of proteins and the other is concerned with phospholipids as shown in Figure 1.5 (Tanaka, 2001). The former crosslinking points are broken after deproteinization of latex or adding small amount of ethanol into toluene solution, while the latter points can be decomposed by transesterification. Moreover, proteins and phopholipids in NR can be decomposed by saponification. Therefore, the deproteinization of gel phase forms branched chains and transesterification of the branched chains brings about the linear rubber chain.

Table 1.1 Overall Composition in Percentage by Weight of Latices and Total Solids Films (TSC) (Roberts, 1988).

	Latex	TSC
Rubber[a]	59.67	97.61
Protein, etc[b]	1.06	1.73
Soap[c]	0.23	0.38
Salts	0.4	0.28[d]
Ammonia	0.68	-
Water	37.96	-

a   As measured by DRC test.
b   Includes carbohydrates, amino acids, sugars.
c   Calculated as ammonium stearate.
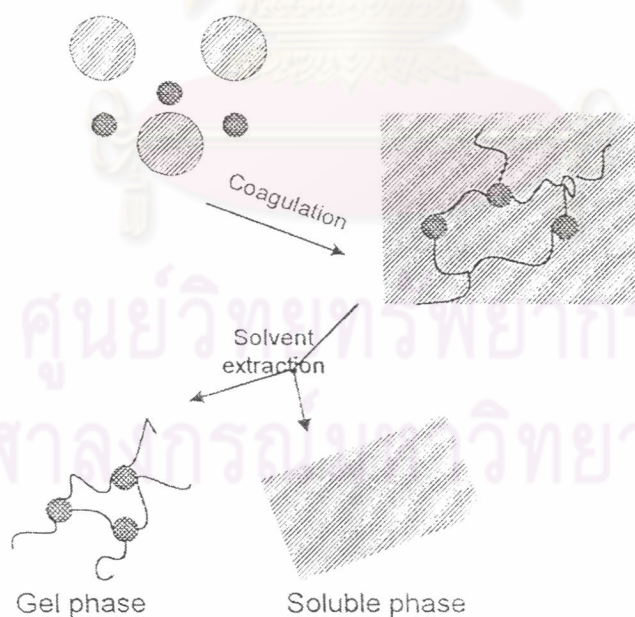d   Assuming carbonate, acetate, and formate are volatilized.

Figure 1.4: Schematic representation of gel phase on the latex and natural rubber (Allen, 1963).
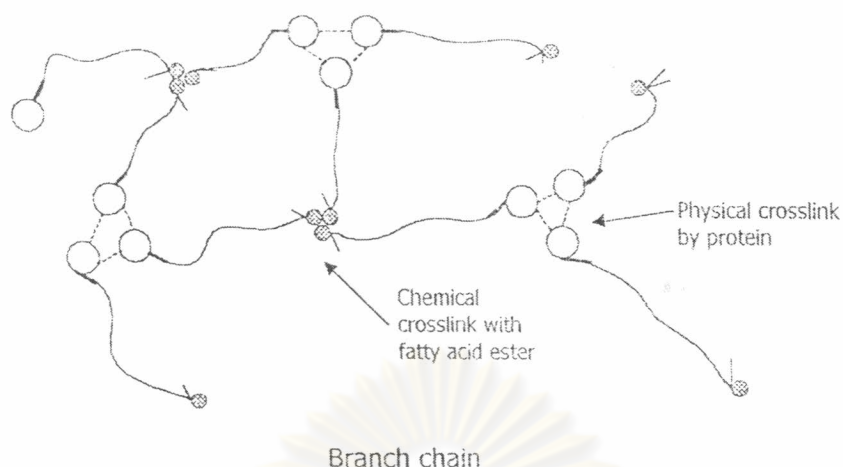
Figure 1.5: Presumed structure of branching and crosslinking in NR
(Tangpakdee and Tanaka, 1997b: 112-119).

Natural rubber includes all materials made from or containing natural latex. Products that contain NR are made using two commonly employed manufacturing processes, the natural rubber latex (NRL) process, and the dry natural rubber (DNR) process. The NRL manufacturing process involves the use of natural latex in a concentrated colloidal suspension. Products are formed from natural rubber latex by dipping, extruding, or coating, and are typically referred to as containing or made of natural rubber latex. Examples of products that may contain natural rubber latex include medical gloves, and condoms. The DNR manufacturing process involves the use of coagulated natural latex by 2% formic acid in the form of dried or milled sheets. It contains the dry rubber content (DRC) about 25-45 % w/v depending on the season of tapping, clonal and other factors. Products are formed from dry natural rubber by compression molding, extrusion, or by converting the sheets into a solution for dipping. These products are typically referred to as containing or made of dry natural rubber or crepe rubber. Examples of products that may contain dry natural rubber include syringe plungers, and vial stoppers.

b) Synthetic Polyisoprene

Polyisoprene can be made synthetically by polymerization of small molecules called isoprene by variety techniques including free radical and Ziegler-Natta catalyst. Four majors structure isomers of polyisoprene are shown schematically in Figure 1.6. The so-called 1,4 polymers are formed by isoprene monomers link together at carbon atom 4 of one unit to carbon atom 1 of the next, and so on in head-to-tail fashion. The arrangement of the substituent carbon atoms relative to double bond in 1,4 polymers can be in either *cis* or *trans* configuration. The 1,2 or 3,4 polymers are formed when incorporation into polymer chain occurs through either the first or second double bond, respectively (Painter and Coleman, 1997). Synthetic polyisoprene polymerized with Ziegler-Natta catalyst consists of the isoprene units in the *cis*-configuration more than 98%. *Cis*-1,4-polyisoprene (CPIP) is synthetic analog of NR which is chemically and structurally very similar. However, some of the non-rubber components in NR, such as proteins have been expected to bring about outstanding properties of NR.
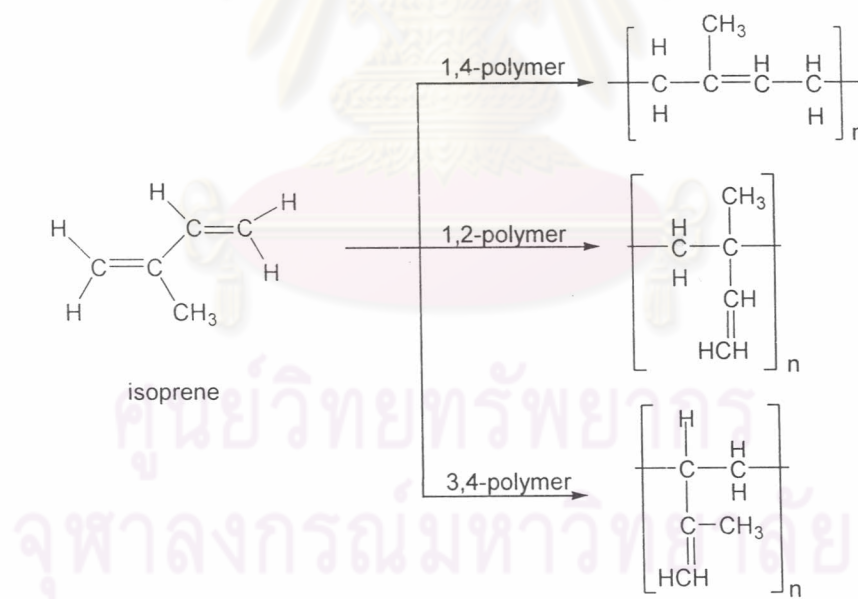

Figure 1.6: The structure isomers of polyisoprene.

Typical raw polymer and vulcanized properties of polyisoprene are similar to value obtained for natural rubber. Natural rubber and synthetic polyisoprene both exhibit good inherent tack, high compounded gum tensile, good hysteresis and good hot tensile properties. The specific difference of synthetic polyisoprene and natural rubber is the minimal variance in physical properties lot to lot. Polymerization conditions are narrowly controlled to assure that the polymer is highly specific chemically. In addition, there is a low level of non-polymer constituents as compared to natural rubber.

1.3 Hydrogenation of Natural Rubber (NR) and *Cis*-1,4-Polyisoprene (CPIP)

Many rubbers are elastomers because the double bonds prevent the polymer strands from forming extensive crystalline regions. Some rubbers such as NBR maintain their elastomeric properties when most or their entire unsaturated C=C bonds have been hydrogenated. To increase the ability of elastomers to withstand high temperatures, ozone and other chemical, hydrogenation has been subjected in numerous investigations. Since NR has a fixed *cis*-polyisoprene structure and cannot have its polymerization process tailored like that of the synthetic rubber industry, chemical modification is a useful process for an alteration of the polymer composition and improvements in certain physical and chemical properties of unsaturated elastomers (Bhowmick, 1988).

Hydrogenation of CPIP presents a rather difficult case for polydiene hydrogenation. The isopropenyl groups, which constitute the rubber macromolecules, are analogous to tri-substituted olefin derivatives and as a result of steric constraints the addition of hydrogen is expected to be slower than for di- or mono-substituted ethylenes. Lal and Mark (1987) reported the study of 1,4 polydienes hydrogenation which are *cis*-1,4-polybutadiene (*cis*-PBD), synthetic *cis*-1,4-polyisoprene (CPIP), *cis*-1,4-poly(2,3-dimethylbutadiene) (*cis*-PDMB), and *trans*-1,4-poly(2,4-hexadiene) (*trans*-2,4-PHXD) with diimide generated *in-situ*. It was found that the relative reactivity in the hydrogenation showed the following order: *cis*-PBD > CPIP > *trans*-2,4-PHXD > *cis*-PDMB > *trans*-PDMB (Lal and Mark, 1987). Clearly, the steric effect of the polymer substituents is very important in the hydrogenation rate. Moreover, due to impurities in the NR, the rate of NR hydrogenation is expected to be significantly lower than that of synthetic CPIP hydrogenation under identical

conditions. Quantitative hydrogenation of CPIP may be regarded as an alternating ethylene-propylene copolymer. The reaction scheme is shown in Figure 1.7.
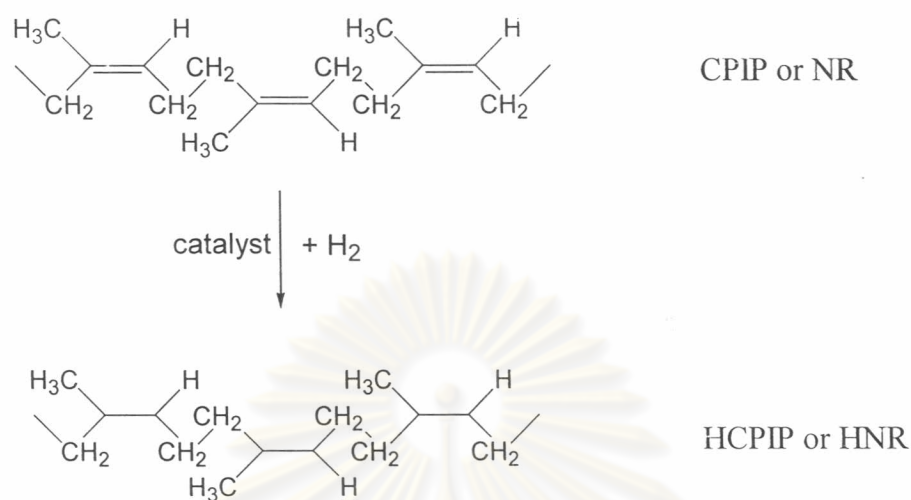

Figure 1.7: General structures of CPIP and HCPIP

The hydrogenation of unsaturated polymers can be accomplished with varying degrees of conversion by several methods, e.g., diimide reagents, heterogeneous catalysts, and homogeneous catalysts. Diimide has been generated *in-situ* from thermolysis of *p*-toluenesulfonyl hydrazide (TSH) as reducing agent in non-catalytic hydrogenation of polydienes. Many systematic observations of diimide reduction of diene-based polymers were reported (Harwood et al., 1973; Mango and Lenz, 1973; Nang et al., 1976; Lal and Mark, 1987; Hahn, 1992). This approach, however, leads to depolymerization, cyclization and incorporation of hydrazide fragments in the hydrogenated polyisoprene which is very undesirable. The diimide hydrogenation is stoichiometric and hence, unsuitable for large-scale processes.

Previously, heterogeneous catalytic hydrogenation of natural latex and synthetic isoprene rubber was investigated . Hydrogenation of NR and synthetic CPIP were carried out in the presence of a large amount of nickel-kieselguhr catalyst under 80-100 atm (Yakubchik et al., 1962). Shahab and Basheer (1978) hydrogenated NR and PBD in the presence of Pd on $CaCO_3$ at room temperature and atmospheric pressure for several days. The hydrogenation proceeds rapidly in the initial stage of the reaction but slows down considerably in the latter stage. The major advantages of

heterogeneous catalyst are that the solid can be easily separated from the polymer products and catalyst regeneration can be simply accomplished by burning-off deposited by-products on the catalyst surface. Nevertheless, the difficulty of orienting the long macromolecular chain on the catalytic active site may cause heterogeneous hydrogenation to require fairly severe reaction conditions. Such operating conditions may lead to certain undesirable side reactions such as chain scission and crosslinking.

In homogeneous catalysis, the catalytic active species is dispersed in the polymer substrates. There are certain advantages in homogeneous catalytic systems over their heterogeneous counterparts; namely: (i) activity at relative milder conditions, (ii) high selectivity, (iii) ease of modification, and (iv) ease of mechanistic study (Masters, 1980). The main principle of homogeneous catalytic hydrogenation involves the activation of molecular hydrogenation by transition metal complexes in solution and the subsequent transfer of hydrogen to the unsaturated substrate. High selectivity is an important characteristic of the homogeneous system. Heterogeneous catalyst is made up of a number of active species deposited on a carrier, there are different type of sites. Homogeneous transition metal catalysts consist generally of only one type of active site, which results in better selectivity and control of the reaction. The homogeneous catalyst also provides opportunity for enhancing the reactivity, selectivity and stability of the metal centered catalyst through the suitable complexation of the ligand system. For example, $RuHCl(CO)(PCy_3)_2$ is a better catalyst than $RuHCl(CO)_2(PCy_3)_2$ for NBR hydrogenation (Martin et al., 1992, 1997). The study of catalytic behavior of metal complexes is also facilitated by the use of important analytical tools such as infrared and nuclear magnetic resonance spectroscopy.

Ramp et al. (1962) studied the reduction of *cis*-PBD and CPIP by using triisobutyl borane catalyst. Since the reaction was carried out under high temperature (190 - 240°C) and high hydrogen pressure (135 – 170 psi), thermal degradation was found to occur. Shahab and Baseer (1978) used $RhCl(PPh_3)_3$ to hydrogenate NR in benzene. It was observed that only 25% hydrogenation was achieved at 65°C in 12 h. Recently, the quantitative hydrogenation of NR using $RhCl(PPh_3)_3$ as catalyst at high catalyst loading and long reaction time (> 20 h) has been reported (Singha et al., 1997b: 1647-1652). The reaction was carried out over the temperature range of 40 to 100°C with 10 – 40 bar of hydrogen pressure. The reaction kinetics of NR hydrogenation followed first order kinetics in residual double bonds. Thermal stability

of hydrogenated rubber was found to increase with an increase in the degree of hydrogenation. The glass transition temperature (T_g) is increased slightly on NR hydrogenation.

Gan et al. (1996) studied the use of a homogeneous catalyst prepared from nickel 2-ethylhexanoate catalyst and triisobutylaluminum for the hydrogenation of NR under mild reaction conditions. The observed kinetic studies showed first order with respect to the carbon - carbon double bond concentration as well as the hydrogen concentration. The maximum catalytic activity was achieved at Al/Ni ratio of 3.0. The reaction has a relatively low apparent activation energy of 26.0 kJ/mol. The impurities e.g. nitrogen content in commercial rubber reduced somewhat the catalyst activity.

More recently, Charmondusit et al. (2003) reported that $OsHCl(CO)(O_2)(PCy_3)_2$ has been found to be an excellent homogeneous catalyst for hydrogenation of CPIP, which more than 97% hydrogenation was observed at $130^{\circ}C$ in 15 minutes. The kinetic studies were carried out in the range of $115 - 140^{\circ}C$ with $35 - 69$ bar of hydrogen pressure. The results of investigation showed that the reaction exhibited a first order dependence on catalyst concentration and carbon - carbon double bond concentration and a second order with respect to hydrogen pressure. The apparent activation energy was found to be 109.3 kJ/mol. The relative viscosity of hydrogenated polymer indicated that no side reaction such as degradation or crosslinking occurred over the range of conditions studied. Natural rubber can be quantitatively hydrogenated using $OsHCl(CO)(O_2)(PCy_3)_2$ in combination with added acid (Charmondusit, 2001). The presence of a strong acid and the high coordinating power of the reaction solvent enhanced the rate of hydrogenation.

$[Ir(COD)py(PCy_3)]PF_6$ is also an efficient catalyst precursor for the hydrogenation of CPIP. It was observed that more than 98% hydrogenation was achieved at $130^{\circ}C$ in 35 minutes. The reaction was carried out in the temperature range of $120 - 140^{\circ}C$ with $14 - 55$ hydrogen bar. The rate of hydrogenation was first order with respect to hydrogen pressure and carbon-carbon double bond concentration. It also showed a first order dependence on catalyst concentration at low iridium concentration. At higher catalyst concentration, the hydrogenation rate becomes insensitive to further increases in the concentration of iridium. An apparent activation energy for CPIP hydrogenation, using iridium catalyst, of 79.8 kJ/mol was obtained. No degradation or crosslinking has been found under the range of conditions employed for the study.

1.4 Hydrogenation of Latex Elastomers

Hydrogenation of diene-based elastomers can be carried out using a variety of methods, for example: solution hydrogenation (Martin et al., 1997), latex hydrogenation (Guo and Rempel, 1997), and solid state hydrogenation (Gilliom, 1989) depending on the physical state of elastomers at the time of hydrogenation. In solution hydrogenation, the substrate polymer is dissolved in an appropriate solvent and followed by addition of catalyst at the desired reaction temperature and pressure. In the latex hydrogenation, the polymer particles are suspended in aqueous solution. The hydrogenation is performed with an oil soluble catalyst using organic solvent as co-solvent or with a water-soluble catalyst. In solid state hydrogenation, the catalyst is impregnated into polymer sheet and then hydrogenation is carried out under a particular pressure and temperature.

Many natural and synthetic rubbers are produced in the latex forms or emulsions such as NR, SBR, and NBR. A more economically feasible approach is to hydrogenate the elastomers in latex form. By applying such a process, the usual procedures for polymer hydrogenation, such as the precipitation of polymer from its emulsion, the drying process, and the redissolution of polymer into an organic solvent, can be avoided. Therefore, it would be interesting to investigate hydrogenation of elastomers in the emulsified form. Hydrogenation of polymer latex can be accomplished by using either water soluble catalysts or oil soluble catalysts.

Singha et al. (1994) reported hydrogenation of NBR latex in the presence of water soluble analog of Wilkinson catalyst, $RhCl(DPM)_3$ (DPM = diphenyl phosphino benzene *m*-sulfonate). The reaction was carried out at $75^{\circ}C$ and atmospheric hydrogen pressure yielding more than 60% mole hydrogenation. The degree of hydrogenation increased with increasing temperature, pressure, and catalyst concentration. However, the hydrogenation was accompanied by a partial loss in rubber solubility. Hydrogenation occurred with no significant change in the average particle size of latex as well as particle size distribution. Mudalige et al. (1997) investigated hydrogenation of diene-based polymer latex, i.e. PBD, SBR and NBR using water-soluble complexes, $[RhCl(HEXNa)_2]_2$ (HEXNa = $Ph_2P(CH_2)_5$-CO_2Na) at $100^{\circ}C$ and 5.5 MPa compared with $RhCl(TPPMS)_3$ (TPPMS = monosulphonated-triphenylphosphine). The selectivity of both catalysts enhanced the hydrogenation of

the 1,2 (vinyl) addition units over the 1,4 (internal) units in all the polymers was studied.

Guo and Rempel (1997) developed two processes for catalytic hydrogenation of NBR emulsions using an oil soluble catalyst, $RuCl_2(PPh_3)_3$. One of the processes involved a homogeneous system. An organic solvent which is miscible with the emulsion phase and which can also dissolve the polymer and catalyst is a key factor. Certain type of additives during the hydrogenation process such as ammonium sulfate, carboxylic acid were found to improve the catalyst activity. The additives had a beneficial effect in minimizing the gel content. The other process was carried out in a heterogeneous system. The solvent, which is capable of dissolving the catalyst and swelling the polymer but is not miscible with the aqueous emulsion phase, is used. A small amount of co-solvent, which is miscible with the emulsion phase, is applied to accelerate the hydrogenation rate. Quantitative hydrogenation of the carbon – carbon double bond of the NBR latex was achieved in both processes. More recently, Leube et al (2002) presented the invention to provide a process for selectively hydrogenation of unsaturated double bonds in an aqueous dispersion of the polymers using rhodium and/or ruthenium compounds or their salts as catalysts. This procedure was carried out with small amount of solvents.

1.5 Hydrogenation Catalyzed by Ruthenium (II) Based Catalysts

Throughout the past decade, ruthenium complexes have been reported as excellent catalysts for the production of highly saturated diene-based polymers. Although the activity of ruthenium complexes on internal double bonds are not as high as that of analogous rhodium complexes, the cost of ruthenium is ca. one-thirtieth that of the rhodium. Thus, it offers economical advantage and makes Ru complexes a possible alternative. Ruthenium(II) is a most useful choice of oxidation state for catalysis, since it is separated by two electrons from another stable oxidation state, Ru(IV). The stability of two oxidation state (x) and (x+2) for the metal, along with the presence of at least one vacant coordination site or labile ligand to allow coordination of the substrate molecule, are accepted as necessary for the efficient catalysis of hydrogenation by organometallic complexes (James, 1979).

A process for selective hydrogenation of carbon – carbon double bonds in polymer is affected homogeneous solution in the presence of certain divalent

ruthenium carbonyl complex catalysts containing phosphine ligands having bulky alkyl substituents. The ruthenium catalysts have the general formula:

$$RuXY(CO)ZL_2 \text{ or } RuX(NO)(CO)L_2$$

wherein X is a halogen atom, most preferable chlorine, or a carboxylate group, Y is a halogen atom, more preferably chlorine, a hydrogen atom, a phenyl group, a carboxylate group or phenylvinyl group, Z is carbonyl, pyridine, benzonitrile, trimethylphosphite or no ligand and L is a phosphine ligand having at least one bulky alkyl substituent, preferably tricyclohexyl or triisopropyl (Rempel et al., 1991).

Mohammadi (1987a) used $RuCl(CH_3COO)(CO)(P(C_6H_5)_3)_2$ as a catalyst in toluene solution to obtain 97% hydrogenation of polybutadiene at $150^{\circ}C$ under 4.1 MPa hydrogen pressure. The detailed kinetics of the PBD hydrogenation was also examined. The rate of hydrogenation increased with increasing initial C=C concentration and hydrogen pressure. A first order dependence on the reaction rate with respect to the total ruthenium concentration in the presence of excess triphenylphosphine was obtained. The reaction rate showed an inverse dependence on the added triphenylphosphine concentration.

Guo and Rempel (1992) and Rempel and Guo (1992) explored the hydrogenation of PBD and NBR in the presence of $RuCl(CO)(OCOPh)(PPh_3)_2$. About 97% hydrogenation of 1,2-PBD was achieved using $RuCl(CO)(OCOCH_3)(PPh_3)_2$ as catalyst in toluene under 4 MPa hydrogen pressure at $150^{\circ}C$. The increase in hydrogen pressure increased the hydrogenation rate and decreased the possibility of isomerization. The *cis*-PBD was hydrogenated in o-chlorobenzene at $85^{\circ}C$ under less than 101 kPa hydrogen pressure to give about 70% hydrogenation. The isomerization is one of the reasons for incomplete hydrogenation.

The investigated kinetic studies were shown to be first order dependence of the hydrogenation rate on carbon - carbon double bond concentration and hydrogen concentration. The reaction rate was first order with respect to ruthenium concentration at low concentration. At high concentration of Ru, the rate of hydrogenation became insensitive to further increase in catalyst concentration. This result may be explained by the formation of a dimeric Ru complex at high concentration of catalyst. The presence of triphenylphosphine on the hydrogenation rate retarded the formation of the active species and led to a decrease in the

hydrogenation rate. Only 40% completion of NBR hydrogenation was achieved at 105°C under 87 kPa hydrogen pressure. A first order dependence of hydrogenation rate on the olefin substrate and the total catalyst concentration was observed. The hydrogenation rate shows a first order towards zero order dependence with respect to hydrogen concentration. The rate of hydrogenation decreased with increasing nitrile content in the polymer.

The ruthenium-hydride complex $RuHCl(CO)(PCy_3)_2$ as shown in Figure 1.8 was found to be an effective catalyst for hydrogenation of terminal and cyclic alkenes (Yi and Lee 1999). Martin et al. (1992, 1997) discovered that complexes of the form $Ru(X)Cl(CO)(L)_2$ (where x = H or β-styryl, and L = a bulky phosphine such as tricyclohexyl and triisopropyl phosphine) exhibited the best catalytic activity for NBR hydrogenation. At 160°C under 40.3 bar hydrogen pressure quantitative hydrogenation of NBR was achieved in 20 min. The reaction kinetics exhibited an apparent pseudo first order dependence on the olefin substrate. The reaction rate followed a first order with respect to the catalyst concentration and hydrogen pressure. An increase in the amount of nitrile decreases the rate constant of reaction. The activation energy of NBR hydrogenation is 74.8 kJ/mol.
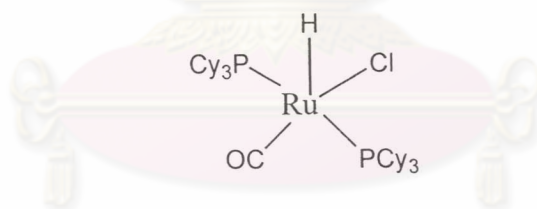

Figure 1.8: Structure of RuHCl(CO)(PCy₃)₂ (Yi and Lee, 1999)

Rao et al. (2001) disclosed that $RuCl_2(PPh_3)_3$ was found to be effective catalyst for hydrogenation of polybutadiene in toluene. Complete hydrogenation of PBD was obtained in 6 h under 50 bar of hydrogen pressure at 100°C. No gel formation was observed under any hydrogenation condition studied.

1.6 Objective and Scope

Although Thailand is the world's largest natural rubber producer, we are facing some problems with the rubber production due to insufficient workforce to do rubber cutting job. Furthermore, the marketing operation (e.g. the effect of price intervention by the government) causes Thai natural rubber to sell at low prices. The economic crisis and the increasing use of synthetic rubber have added to the problems for the rubber industry in Thailand. In order to improve the properties of Thai rubber and make natural rubber a higher value added material for specific applications, the chemical modification of the rubber has received increasing alternation.

The present study focuses of the feasibility of using catalytic hydrogenation to upgrade NR. Firstly, the details of synthetic polyisoprene hydrogenation has been investigated to elucidate the mechanism of the ruthenium based catalyst on this system by using kinetics, and spectroscopy. It was hoped that an understanding of the mechanism would help us to identify factors, which influence the activity and selectivity of the ruthenium bulky phosphine catalyst. Subsequently, hydrogenation of natural rubber in both solution and emulsion states were investigated. Upon hydrogenation, there are significant changes in chemical, physical and mechanical properties of the hydrogenated products. Therefore, the low temperature properties (glass transition temperature, T_g) and high temperature properties (the initial decomposition temperature; T_{id} and maximum decomposition temperature; T_{max}) of hydrogenated polymers comparing with parent polymer were also included. Subsequently, a dynamic model for the hydrogenation of synthetic polyisoprene in a CSTR and PFR was proposed to develop a potential new continuous process. Finally, important conclusions from this thesis are made and recommendations for future work are reported.