CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Natural Rubber

2.1.1 Composition of Natural Rubber

Natural rubber is commonly obtained from the latex of *Hevea brasiliensis*, a large tree that is indigenous to South America and which has been cultivated for many years in the Far East (principally in Malaya and Indonesia) and in Africa.

The non-aqueous components of the exudation of *Hevea brasiliensis* are a complex mixture of which about 94 percent are rubber hydrogenation. The other components include proteins, carbohydrates, sterols, and other lipids. The bulk rubber obtained from the latex contains these substances and transformation products derived from them by hydrolysis and bacterial action. These non-rubber substances, although only present in low concentrations, may influence the reactions of the rubber hydrocarbon as, for example, during vulcanization and grafting and their presence should always be borne in mind when considering the chemistry of natural rubber. The composition of acid coagulated natural rubber is shown in Table 2.1.

Table 2.1 The composition of acid coagulated natural rubber [2]

| Composition	Percent
Rubber hydrocarbon	93.7
Neutral lipids	2.4
Glycolipids, Phospholipids	1.0
Proteins	2.2
Carbohydrates	0.4
Inorganic constituents	0.2
Others	0.1

2.1.2 Structure of Natural Rubber [3]

The structural formulas of natural rubber molecules are $(C_5H_8)_n$, where the isoprene monomer is represented by formula, C_5H_8 where n is about 20,000. The empirical formula for the natural rubber molecule appears to have been first determined by Faraday who reported his finding in 1826. He concluded that carbon and hydrogen were the only elements present and his results corresponded to the formula C_5H_8. While this result was obtained, using a product, which contained associated non-rubbery materials, subsequent studies with highly purified materials have confirmed Faraday's conclusion.

The isoprene was found to have the formula C_5H_8, for which Tilden proposed the structure.

$$CH_2\!=\!\underset{\underset{\displaystyle CH_3}{|}}{C}\!-\!CH\!=\!CH_2$$
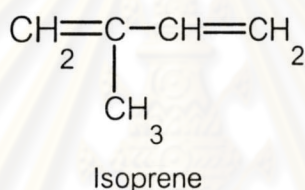
Isoprene

The linear structure proposed by Pickles provided for the possibility of structure isomerism with both *cis-* and *trans-* repeating units.
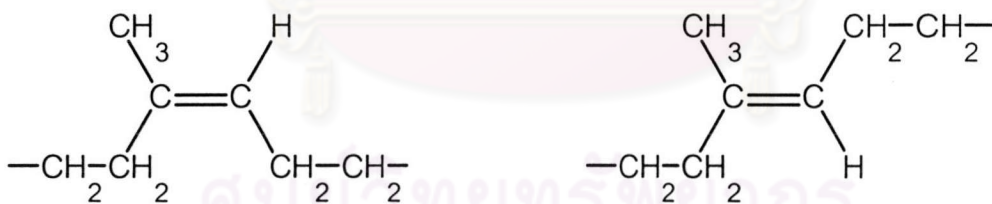
cis-1,4-polyisoprene   *trans*-1,4-polyisoprene

It was known that this is the major hydrocarbon component of both gutta percha and balata (at the time important in belting, submarine cable, golf ball and container applications) was a polyisoprene which when reacted with bromine and ozone gave similar results to those obtained with natural rubber. It was tempting to suggest that one isomer was that of gutta percha and balata and the other that of natural rubber. The earlier work of Staudinger suggested that the *trans*-isomer was natural rubber and gutta percha, the *cis-*. However later studies of X-ray fiber diagrams of stretched rubber

led Meyer and Mark to the view that natural rubber was the *cis*-polymer, a view reinforced by Bunn (1942) which elucidated the structure and unit cell of crystalline stretched rubber molecules.
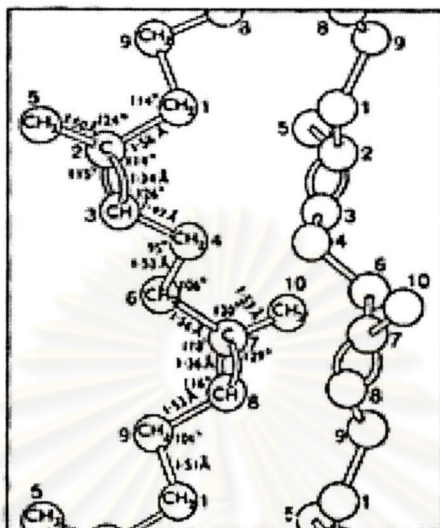

Figure 2.1 Unit cell structure, of the natural rubber molecule.

(From Bunn, 1942)

The possibility that the natural rubber molecule might contain a mixture of *cis*- and *trans*- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that natural rubber was the *cis*-polymer.

The natural rubber was at least 97% *cis*-1,4-polyisoprene. The absence of measurable amounts of 1,2-structure and an infrared band at 890 cm^{-1} was at one time thought to be due possible to the products of a 3,4-structure.

1,4-polyisoprene   1,2-polyisoprene   3,4-polyisoprene
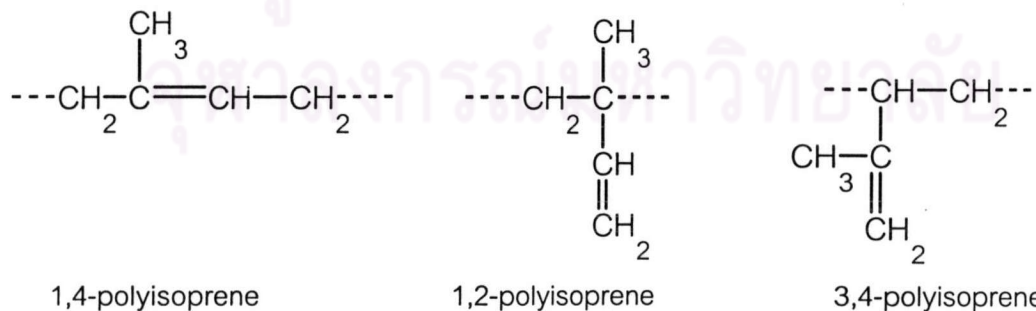
Time-averaging techniques using high resolution NMR which are capable of detecting 3,4-groups at concentrations of less than 0.3% have, however, failed to establish the existence of any such moiety and have also failed to show up any trace of

trans-materials. The conclusion must, therefore, be that the molecule is more than 99% *cis*-1,4-polyisoprene. Since all the evidence points to the conclusion that the natural rubber molecule is not obtained in nature by the polymerization of isoprene the absence of detectable pendant groups as would be produced by 1,2- and 3,4- addition is hardly surprising.

2.1.3 Molecular Weight and Molecular Weight Distribution of Natural Rubber

In 1971, gel permeation chromatography (GPC) was used to determine the molecular weight and molecular weight distribution (MWD) of rubbers.

Rubber from *Hevea brasiliensis* is a high molecular weight polymer with broad molecular weight distribution. *Hevea* rubber in freshly tapped latex has been confirmed to have a bimodal distribution by GPC analysis. The distributions of various clonal *Hevea* rubbers are classified into three types [4]:

Type 1. Distinctly bimodal distribution where the peaks are of nearly the same height;

- Type 2. Distinctly bimodal distribution where the peak in the low molecular weight region is small; and

- Type 3. A skewed unimodal distribution with a 'shoulder' or 'plateau' in the low molecular weight region.

Differences in molecular weight distribution can be observed on commercial Hevea rubbers as shown in Figure 2.2 (A). The average molecular weight is M_w=1.6-2.3 x 10^6 and M_n=2.0-5.2 x 10^5; the molecular weight of polydispersity expressed by M_w/M_n is extremely wide ranging from 2.8 to 10.0. On the other hand, rubber from guayule and synthetic *cis*-polyisoprenes made with a Ziegler initiator system show a unimodal distribution; typical GPC curves are shown in Figure 2.2 (B).

The broad molecular weight distribution of Hevea rubber is estimated to be associated with branching and crosslinking reactions through some special functional groups.
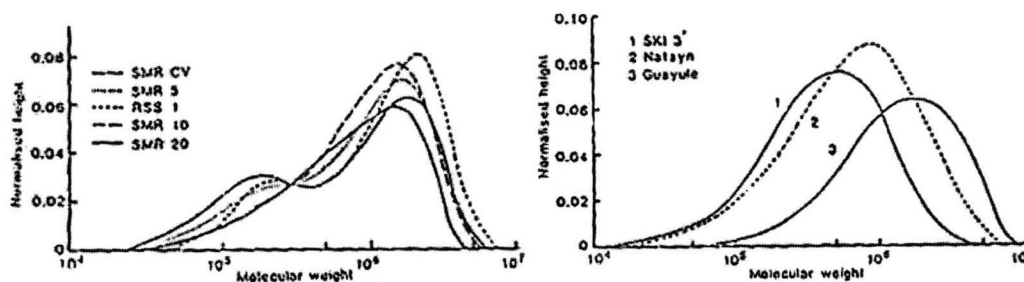
Figure 2.2 Typical molecular weight distribution of (A) commercial Hevea rubbers and
(B) guayule rubber and synthetic *cis*-polyisoprene.

2.2 Hydrogenation of Rubber

Hydrogenation is a reaction that is used to reduce the degree of unsaturation in the olefinic compound or polymers by adding hydrogen atoms to the unsaturated unit as shown in equation [5].
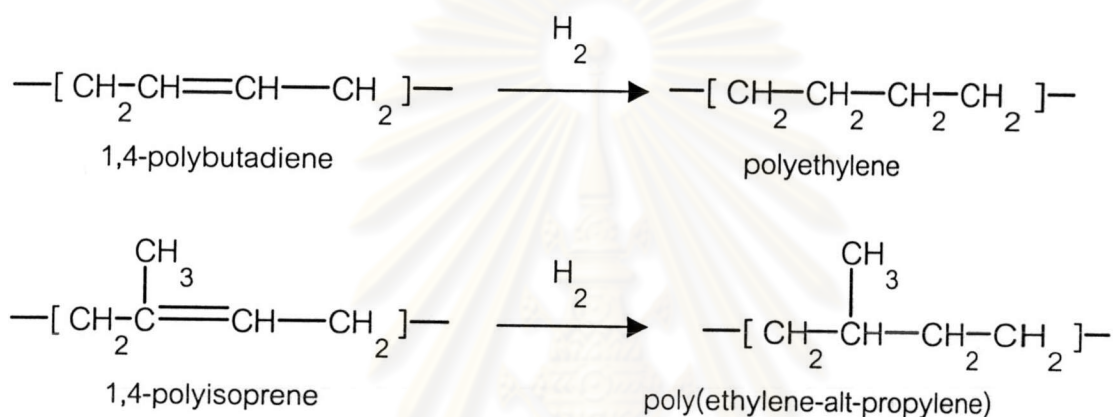
$$--CH=CH-- \xrightarrow{H_2} --CH_2—CH_2--$$
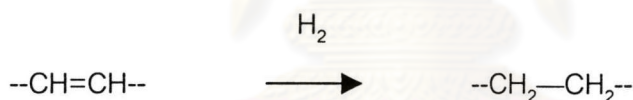
It is an important method for generating new products. Nevertheless, it leads to significant changes in the chemical and physical properties of the polymers. Quantitative hydrogenation of unsaturated polymers prepared by controlled polymerization, provides a means of synthesizing saturated polymers with controlled molecular weights, microstructures, and stereochemistries that might not be available through monomer polymerizations alone. For example, polymerization of vinylcyclohexane produces primarily isotactic, head-to-tail poly(vinylcyclohexane), but atactic, head-to-head poly(vinylcyclohexane) can be produced by the hydrogenation of poly(2,3-diphynylbutadiene).

Polymers with controlled degrees of functional groups at desired polymer chain length are useful building blocks for custom designing specially polymer systems. Catalytic reactions on template polymers which produce polymer products with the

desired density of one or more functional groups are one method of synthesizing these unique polymer building blocks. For example, key connector groups catalytically placed on a template polymer can aid in attaching other polymer chains or monomer groups in order to achieve the desired assembly.

In principle the hydrogenation of a diene rubber is one of the simplest reactions. Complete hydrogenation of polybutadiene would give a polyethylene structure whilst hydrogenation of polyisoprene that of an alternating ethylene-propylene copolymer [3].
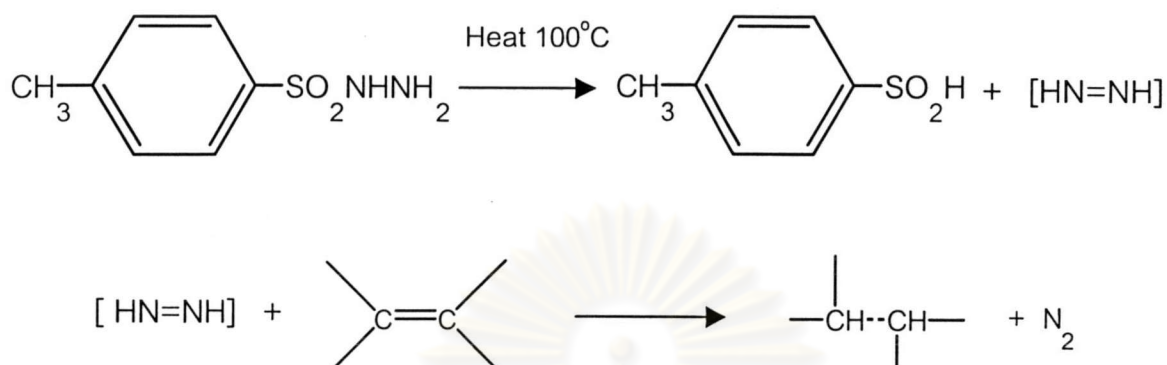
$$-[\ CH_2-CH=CH-CH_2\ ]- \xrightarrow{H_2} -[\ CH_2-CH_2-CH_2-CH_2\ ]-$$

1,4-polybutadiene　　　　　　　　　　　polyethylene

$$-[\ CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2\ ]- \xrightarrow{H_2} -[\ CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2\ ]-$$

1,4-polyisoprene　　　　　　　　poly(ethylene-alt-propylene)

2.2.1 Hydrogenation Method

Hydrogenation of polymers can be achieved by two methods: non–catalytic hydrogenation and catalytic hydrogenation. Such methods differ in yield, selectivity, side reactions and catalyst poisoning and removal.

2.2.1.1 Non-Catalyst Hydrogenation [6]

A method for hydrogenation without having to use catalysts has been found. This method makes use of diimide (N_2H_2) as a hydrogen donating agent. Diimide (HN=NH) can be produced by various ways: 1) the carboxylation of the potassium azodicarboxylate, 2) the oxidation of hydrazine, 3) the thermal decomposition of arenesulphonyl hydrazides, 4) the decomposition of hydroxylamine-o-sulfonic acid or chloramine, 5) the thermal decomposition of anthracene-9,10-bisimine, and 6) the photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione.

Compounds such as *p*-toluenesulphonyl hydrazide (TSH) decompose at moderate temperature ($150^{\circ}C$) to give diimide (N_2H_2) with proposed mechanism shown in equation.

$$CH_3\text{—}\bigcirc\text{—}SO_2NHNH_2 \xrightarrow{\text{Heat } 100^{\circ}C} CH_3\text{—}\bigcirc\text{—}SO_2H + [HN=NH]$$

$$[HN=NH] + {}_{\diagdown}^{\diagup}C=C{}_{\diagup}^{\diagdown} \longrightarrow \text{—}CH\text{··}CH\text{—} + N_2$$

In a typical reaction a concentrated solution of polymer in a solvent such as diglyme is heated with an excess of *p*-toluene sulphonyl hydrazide (THS). The diimide is generated *in situ* to react with the alkene. Diene polymers have been hydrogenated using non-catalytic reagent. Under favorable conditions, polybutadiene and polyisoprene were almost completely hydrogenated. The disadvantage of these reagents is that the reaction is known to lead to chain scission and incorporation of hydrazide fragments in the polymer, leading to deterioration of the elastomeric properties [7].

2.2.1.2 Catalytic hydrogenation

Hydrogenation is carried out by activated molecular hydrogen in the presence of transition metal catalyst. High quality equipment is required to perform hydrogenation at moderate to high hydrogen pressure. Catalytic hydrogenation can be divided by catalyst used in two groups:

   A) Heterogeneous catalytic hydrogenation

   B) Homogeneous catalytic hydrogenation

A. Heterogeneous catalytic hydrogenation

This type of catalysts is divided into two groups, supported and unsupported catalyst, with the former group being further divided into those for use in slurry processes and those for use in fixed-bed operations. Catalysts for slurry processes are usually fine powders, whereas fixed-bed catalysts are usually in the form of cylinders, spheres, or granules [8]. Hydrogenation relies on an insoluble transition metal catalyst to promote hydrogen addition to the unsaturated double bond.

The most common hydrogenation catalysts are nickel and the platinum metals: platinum, palladium, rhodium, and ruthenium. Cobalt and copper chromium oxide ("copper chromite") are also used and some work indicates that ruthenium has catalytic properties which make it useful for the hydrogenation of some functional groups. Other metals such as thallium, osmium, iridium, and copper have been reported to behave as catalysts for hydrogenation.

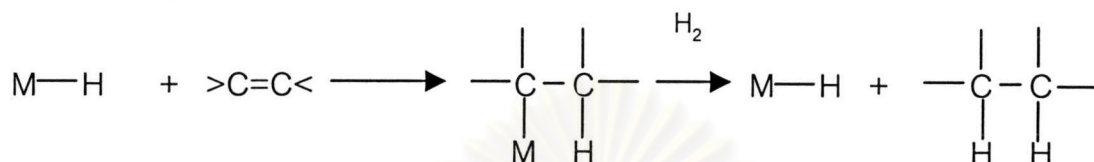Feature of heterogeneous catalytic hydrogenation are summarized as follows [9]:

- Higher yield conversion than homogeneous catalyst;
- Minimal chain scission;
- No metal contamination;
- Ease of catalyst extraction;
- Reaction rates are slower than homogeneous hydrogenation so more vigorous reaction conditions are required.

Examples of heterogeneous catalyst are:

- Black nickel oxide
- Palladium on calcium carbonate (Pd-$CaCO_3$)
- Palladium on barium sulphate (Pd-$BaSO_4$)

B. Homogeneous catalytic hydrogenation [10]

The homogeneous hydrogenation of olefins is one of the best understood and one of the simplest of transition metal-catalyzed reactions. Two basic steps are involved: (1) metal hydride addition to the olefin and (2) hydrogenolysis of the metal alkyl bond reformation of the metal hydride catalyst.

$$
M-H \ + \ >C=C< \longrightarrow -\underset{\underset{M}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}- \ \overset{H_2}{\longrightarrow} \ M-H \ + \ -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-
$$

In detail, however, the reaction involves several additional steps. The hydride catalyst will probably exist, at least, mainly as a coordinately saturated complex. If this is the case, then dissociation generally will be required initially in order to have a position available for coordination of the reaction olefin. The olefin π complex formed could then undergo a shift of hydrogen from the metal to one carbon of the coordinated double bond with concurrent formation of a metal-carbon σ-bond to the other carbon of the double bond. This step would produce a coordinately unsaturated metal alkyl. This complex will then probably react reversibly with another potential ligand in the solution before reacting with hydrogen by oxidative addition. The elimination of the product hydrocarbon by a second hydrogen shift form metal to carbon (a reductive elimination) now leaves the coordinately unsaturated hydride available for coordination with either another olefin molecule to continue the catalytic cycle or some other coordinating species in the solution. The true situation may be even more complicated than these equations indicated since both the olefin-metal hydride π complex and the dihydridoalkyl metal complex intermediates generally may exist in more than one isomeric form. Only isomers which have the reacting hydrogen and the carbon groups cis to each other can directly undergo the necessary reactions. It must be emphasized, however, that complete identification of all the possible intermediates in any of these reactions (and most other transition metal reactions) has not been made. This is an extremely difficult task because at least some of the intermediates are very reactive and unstable, and exist only in low concentrations. Although this detailed mechanism is believed to be basically correct for at least of the known homogeneous hydrogenation

catalysts (and presumably for heterogeneous ones as well), there are variations possible and some of these may be observed as more cases are investigated. It is not certain, for example, that π complexing of the olefin to the hydride is always necessary before addition can occur, nor is it clear whether oxidative addition of hydrogen is always necessary before hydrogen cleavage of the metal alkyl bond can occur. Four-centered transition states could be imagined as alternatives.

Both homogeneous and heterogeneous catalytic hydrogenations require special equipment. It is sophisticated that the reactions concern pressure range, pressure control, temperature control and agitation. Additionally, various factors influencing the catalytic hydrogenation process are listed below [11]:

- Types of catalyst which affected selectivity to give the desired product;
- Activity of the catalyst (reaction time) and productivity;
- Types of support which concerned with catalyst performance; and
- Solvents which influenced not only solubility of reactants and products but also activity and selectivity of catalysts.

2.2.2 Hydrogenation of natural rubber

The conversion of natural rubber to hydrogenated natural rubber can be brought about by homogeneous and heterogeneous catalysts, as well as by non-catalytic hydrogenation. Recently noble metal catalysts, such as Rh, Ni, and Pd have been explored for hydrogenation of natural rubber. The advantage of these metal catalysts is that they can quantitatively and selectively hydrogenated the carbon-carbon unsaturation in the diene elastomer. There are many reports of hydrogenation of polyisoprene, polybutadiene (PBD), chloroprene rubber (CR), acrylonitrile-butadiene (NBR) copolymer, and styrene-butadiene (SBR) copolymer using transition metal compound [7,12-29]. Natural rubber has been hydrogenated by using transition metal compound [7,18,19]. Generally, hydrogenation of natural rubber involves catalytic reduction for long duration such as rhodium complexes [7], or noble metal supported catalysts. For example, RhCl(PPh$_3$)$_3$ complex was found to be suitable catalyst system for the hydrogenation of natural rubber. Studies have shown that Rh complexes are

amongst the best catalyst for the process. The high cost of Rh led to interest into the examination of catalysts based on less expensive metals. There are no reports of hydrogenation of natural rubber using Ru based catalysts, which are preferable because of its significantly lower cost than Rh based catalysts. $RuCl_2(PPh_3)_3$ have been most successful for synthetic rubber hydrogenation, such as poly(styrene-co-butadiene) [12], poly(nitrile-co-butadiene) [13] and polybutadiene [14]. In the present study, the hydrogenation of natural rubber is carried out using a soluble $RuCl_2(PPh_3)_3$ catalyst.

2.3 Literature survey

Mango and Len [15] studied hydrogenated polyisoprene by using non catalytic reagents, such as using *p*-toluenesulfonyl hydrazide (THS). The reaction is known to lead to chain scission and incorporation of hydrazide fragments in the polymer, leading to deterioration of elastomeric properties.

Hahn [16] studied and improved method for the diimide hydrogenation of butadiene an isoprene containing polymer. The hydrogenation of unsaturated polymers with diimide generated *in-situ* by thermolysis of *p*-toluenesulfonyl hydrazide saturated diene based polymers. The by products from TSH, particularly *p*-toluenesulfinic acid, can attack at olefinic sites, adding *p*-tolylsulfone functionality found to eliminate these side reactions in butadiene containing polymers and copolymers, enabling the preparation of polymers devoid of backbone unsaturation. However, it had no effect on isoprene containing polymers.

Schulz and Worsfold [17] studied the heterogeneous hydrogenation of polyisoprene. It was found that it is possible to hydrogenate polyisoprene, prepared anionically, at room temperature and a hydrogen pressure of 1 atmosphere using 5%Pd/$CaCO_3$ catalyst. It is necessary to carry out the hydrogenation directly on the polymerization mixture. Partial hydrogenated polymer shows that long sequences of polyisoprene are hydrogenated. Pd/$CaCO_3$ sensitivity to oxidation leads to a build up of centers that rapidly poison the comparatively low concentration of sites accessible to the polymer. Because of the low rate of polymer desorption, the catalyst is rapidly deactivated.

Burfield and Lim [18] concluded the catalytic hydrogenation of natural rubber. This work reports the synthesis of hydrogenated polyisoprene by a two component homogeneous catalyst system based on Ni(II) salts in combination with trialkylaluminum compounds. Hydrogenation proceeds smoothly at ambient temperatures and at relatively low hydrogen pressures, for rubbers in cyclohexane solution. The hydrogenation rate is enhanced by increased catalyst concentrations and hydrogen pressure, and is also dependent on the catalyst/co-catalyst ratio. The temperature of maximum decomposition rate is increased from about $360^{\circ}C$ for natural rubber to $440\,^{\circ}C$ for fully hydrogenation analogue. Partial hydrogenation (42 mole percent) also has a substantial effect ($T_{max}=432\,^{\circ}C$) and suggests that considerable changes in decomposition behavior may be anticipated even at only modest modification levels.

Gan, *et al.* [19] studied the hydrogenation of natural rubber using nickel-2-ethylhexanoate catalyst in combination with triisobuthylaluminium. Kinetic studies for the homogeneous hydrogenation of natural rubber, in the presence of nickel 2-ethylhexanoate and triisobutylaluminum, have been carried out by monitoring the change in hydrogen pressure in a Parr reactor of fixed volume. ^{1}H-NMR spectroscopy provides the measurements of the extent of hydrogenation. The reaction kinetics, in the presence of a fixed amount of catalyst, showed an overall second-order kinetic with respect to $[H_2]$ and $[C=C]$. The reaction has a relatively low apparent activation energy of 26 kJ/mol and is therefore suitable for the hydrogenation of natural rubber at ambient condition to minimize side reactions. The impurities in commercial rubbers have a slight effect on the catalyst activity.

Singha, *et al.* [7] studies homogeneous catalytic hydrogenation of natural rubber using $RhCl(PPh_3)_3$. Natural rubber could be quantitatively hydrogenated to a strictly alternating ethylene-propylene copolymer using a homogeneous $RhCl(PPh_3)_3$ catalyst. The effect of concentration of rubber, catalyst and triphenylphosphine, temperature, pressure, and solvent on the course of hydrogenation was evaluated. The thermal properties of the hydrogenated natural rubber are compared with natural rubber. Hydrogenation of natural rubber in toluene was carried out using $RhCl(PPh_3)_3$ as a catalyst in temperature range 40 to$100^{\circ}C$ and 10 to 40 kg/cm^2 of hydrogen pressure. Quantitative hydrogenation could be achieved after 22 hr using 1.3 mol% catalyst

at 100 ^{o}C and 40 kg/cm^2 hydrogen pressure. This was confirmed by quantitative hydrogen absorption, IR, NMR and iodine value.