

โครงสร้างและสมบัติของน้ำยาจรรยาชาติไฮโดรจินेटโดยใช้  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$   
เป็นตัวเร่งปฏิกิริยาและไดอิมิดรีดักชัน



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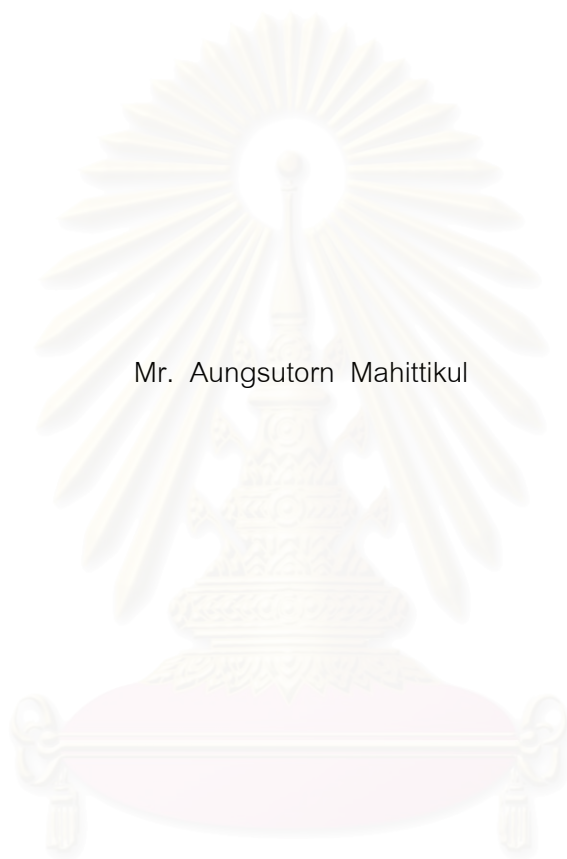
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

STRUCTURE AND PROPERTIES OF HYDROGENATED NATURAL RUBBER LATEX  
USING  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  AS A CATALYST AND DIIMIDE REDUCTION



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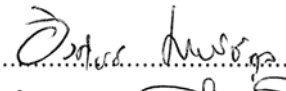
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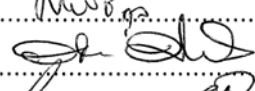
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อังศุธร มหิทธิกุล : โครงสร้างและสมบัติของน้ำยางธรรมชาติไฮโดรจีเนตโดยใช้  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  เป็นตัวเร่งปฏิกิริยาและไดอิมิดรีดักชัน (STRUCTURE AND PROPERTIES OF HYDROGENATED NATURAL RUBBER LATEX USING  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  AS A CATALYST AND DIIMIDE REDUCTION อ. ที่ปรึกษา : ศ.ดร.ภัทรพรรณ ประศาสน์สารกิจ, อ. ที่ปรึกษาร่วม : Prof. Garry L. Rempel, 222 หน้า. ISBN 974-53-2451-5.

น้ำยางธรรมชาติประกอบด้วยซิส-1,4-พอลิไอโซพรีนเป็นองค์ประกอบหลัก ซึ่งมีความต้านทานต่อการออกซิเดชันและการสลายตัวด้วยโอโซนและความร้อนเนื่องจากพันธะคู่ของคาร์บอน - คาร์บอนในโครงสร้างหลักของพอลิเมอร์ ไฮโดรจีเนชันถูกนำมาใช้เพื่อเพิ่มความต้านทานของพอลิเมอร์ต่อการสลายตัวด้วยความร้อนและออกซิเดชันโดยการลดปริมาณความไม่อิ่มตัวในไดอีนพอลิเมอร์หลายชนิด จุดประสงค์ของงานวิจัยนี้เพื่อศึกษาไฮโดรจีเนชันของน้ำยางธรรมชาติผ่านสามระบบ ไฮโดรจีเนชันด้วยตัวเร่งปฏิกิริยาเอกพันธ์ ไฮโดรจีเนชันไม่ใช้ตัวเร่งปฏิกิริยาและไดอิมิดรีดักชัน ระดับไฮโดรจีเนชันได้จากการวัดด้วยเทคนิคทางโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโคปี สำหรับกระบวนการที่ใช้ตัวเร่งปฏิกิริยาเอกพันธ์ ข้อมูลทางจลนพลศาสตร์ในเทอมของปริมาณแก๊สไฮโดรเจนที่ถูกใช้ไปเป็นฟังก์ชันกับเวลาได้จากเครื่องแก๊สอัพเทค ผลการทดลองทางจลนพลศาสตร์แสดงให้เห็นว่าไฮโดรจีเนชันของน้ำยางธรรมชาติใช้ตัวเร่งปฏิกิริยา  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  และ  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  เป็นปฏิกิริยาอันดับหนึ่งขึ้นกับความเข้มข้นของตัวเร่งปฏิกิริยาและเป็นปฏิกิริยาผกผันกับความเข้มข้นของยางธรรมชาติเนื่องจากสิ่งปนเปื้อนในยาง ไฮโดรจีเนชันแบบไม่ใช้ตัวเร่งปฏิกิริยาที่ใช้ p-TSH เป็นตัวรีดิวซ์เป็นวิธีที่มีประสิทธิภาพ และพบว่าระดับไฮโดรจีเนชันเพิ่มขึ้นเมื่อเพิ่มอัตราส่วนของ p-TSH/C=C สำหรับไดอิมิดรีดักชัน ยางไฮโดรจีเนตอยู่ในรูปแบบของเหลวและระดับไฮโดรจีเนชันเพิ่มขึ้นเมื่อเพิ่มปริมาณไดอิมิดที่มีประสิทธิภาพ จากไมโครกราฟ TEM อนุภาคยางไฮโดรจีเนตแสดงโมเดลแบบชั้นสำหรับไฮโดรจีเนชัน เสถียรภาพเชิงความร้อนของยางธรรมชาติถูกปรับปรุงได้ด้วยไฮโดรจีเนชัน น้ำหนักโมเลกุลและการแจกแจงน้ำหนักโมเลกุลของยางธรรมชาติไฮโดรจีเนตไม่เปลี่ยนแปลงระหว่างไฮโดรจีเนชัน นอกจากนี้ยังได้ศึกษาสมบัติเชิงกลและความต้านทานต่อโอโซนของของผสมยางธรรมชาติไฮโดรจีเนตวัลคาไนซ์อีกด้วย

ภาควิชา.....เคมีเทคนิค..... ลายมือชื่อนิสิต..... 

สาขาวิชา.....เคมีเทคนิค..... ลายมือชื่ออาจารย์ที่ปรึกษา..... 

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KEY WORD: HYDROGENATION / NATURAL RUBBER LATEX /  
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AUNGSUTORN MAHITTIKUL : STRUCTURE AND PROPERTIES OF  
HYDROGENATED NATURAL RUBBER LATEX USING  
 $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  AS A CATALYST AND DIIMIDE REDUCTION.  
THESIS ADVISOR : PROF. PATTARAPAN PRASASSARAKICH, THESIS  
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Natural rubber latex (NRL) is comprised of *cis*-1,4-polyisoprene as the major component which has poor resistance to oxidation and degradation by ozone and long term heating due to the presence of carbon-carbon double bonds in the polymer backbone. Hydrogenation is a useful method, which has been used to improve oxidative, and thermal degradation resistance of diene based polymers. The purpose of the present work is to study the hydrogenation of NRL via three systems: homogenous catalytic hydrogenation, noncatalytic hydrogenation and diimide hydrogenation. The level of hydrogenation was determined via a  $^1\text{H-NMR}$  spectroscopic technique. For homogeneous catalytic hydrogenation, kinetic data were collected using a computer controlled gas-uptake apparatus in terms of hydrogen consumption as a function of time. The kinetic results indicated that the hydrogenation of NRL catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  exhibited a first-order behavior with respect to catalyst concentration and an inverse behavior dependence on rubber concentration due to impurities present in the rubber. Noncatalytic hydrogenation using p-TSH as reducing agent was also very effective method and it was also found that the degree of hydrogenation increased with increasing ratio of p-TSH /C=C. For diimide hydrogenation, the HNR product was in liquid form and the degree of hydrogenation was increased with increasing effective diimide amount. From TEM micrograph, diimide hydrogenated rubber particle exhibited a layer model for hydrogenation. The thermal stability of NR was improved by hydrogenation. The molecular weight and molecular weight distribution of hydrogenated NR were not changed during hydrogenation. In addition, the mechanical properties and ozone resistance of vulcanized HNR blends were also investigated.

Department.....Chemical Technology.....Student's signature.....

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*A. Mahittikul*  
*Garry L. Rempel*

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## NOMENCLATURES

A	:	Pre-Exponential Factor
CCD Camera	:	Charge Coupled Devices Camera
cod	:	1,5-cyclooctadiene
3-CPA	:	3-Chloropropionic acid
DMA	:	Dynamic Mechanical Analysis
DSC	:	Differential Scanning Calorimetry
DPNRL	:	Deprotienized Natural Rubber Latex
EPDM	:	Ethylene – Propylene Copolymer
FTIR	:	Fourier Transform Infrared Spectroscopy
GPC	:	Gel Permeation Chromatography
HNR	:	Hydrogenated Natural Rubber
HNRL	:	Hydrogenated Natural Rubber Latex
HNRBo	:	Hydrogenated Natural Rubber Latex by Diimide reduction in presence of boric acid
HNRDii	:	Hydrogenated Natural Rubber Latex by Diimide reduction in presence of cupric ion
HNRIr	:	Hydrogenated Natural Rubber Latex by Iridium Catalyst
HNROs	:	Hydrogenated Natural Rubber Latex by Osmium Catalyst
HNRTSH	:	Hydrogenated Natural Rubber Latex by Noncatalytic Hydrogenation
HPIP	:	Hydrogenated <i>Cis</i> -1,4-Polyisoprene
HSBR	:	Hydrogenated Styrene – Butadiene Rubber
Ir	:	Iridium
k'	:	Pseudo-First-Order Rate Constant
MBT	:	2 – Mercaptobenzothiazole
MBTS	:	Dibenzothiazole disulfide
MCB	:	Monochlorobenzene
MWD	:	Molecular Weight Distribution
NBR	:	Acrylonitrile – Butadiene Rubber
NBRL	:	Acrylonitrile – Butadiene Rubber Latex
NMR	:	Nuclear Magnetic Resonance Spectroscopy

NR	:	Natural Rubber
NRL	:	Natural Rubber Latex
ODR	:	Oscillating Disk Rheometer
Os	:	Osmium
PCy <sub>3</sub>	:	Tricyclohexylphosphine
Pd	:	Palladium
PIP	:	Synthetic <i>Cis</i> -1,4-Polyisoprene
PiPr <sub>3</sub>	:	Triisopropylphosphine
pphm	:	Part Per Hundred Million
p-TSA	:	<i>p</i> -Toluenesulfonic acid
p-TSH	:	<i>p</i> -Toluenesulfonyl hydrazide
Rh	:	Rhodium
Ru	:	Ruthenium
SBR	:	Styrene – Butadiene Rubber
SBRL	:	Styrene – Butadiene Rubber Latex
T <sub>g</sub>	:	Glass Transition Temperature
T <sub>id</sub>	:	Initial Decomposition Temperature
T <sub>max</sub>	:	Maximum Decomposition Temperature
TEM	:	Transmission Electron Microscope
THF	:	Tetrahydrofuran
TGA	:	Thermogravimetric Analysis
TMTD	:	Tetramethyl thiuram disulphide
x	:	Extent of Hydrogenation
X	:	Impurities in Natural Rubber
ZnO	:	Zinc Oxide
η <sub>rel</sub>	:	Relative Viscosity

# CHAPTER I

## INTRODUCTION

### 1.1 Natural Rubber Latex

Natural rubber latex, collected by tapping *Hevea Brasilliensis* trees, is a colloidal suspension of rubber particles in an aqueous serum phase. The latex excreted by tapping is termed fresh natural rubber latex. The rubber in natural latex is primarily polyisoprene consisting of isoprene units ( $C_5H_8$ ) which are in the *cis*-configuration (Brydson, 1978). Tanaka (2001) reported that the rubber chain is composed of unidentified initiating terminal groups, two *trans* isoprene units and a long chain of *cis*-isoprene units terminated with unidentified chain end groups. The unidentified initiating and chain end groups are possibly oligopeptides ( $\omega'$ ) and a fatty acid ester ( $\alpha'$ ), respectively. The chemical structure of natural rubber is depicted in Figure 1.1. The major polymer structure component of natural rubber determined by using infrared (FTIR), nuclear magnetic resonance (NMR) and X-ray is polyisoprene with the isoprene unit having a *cis*-1,4- configuration of about 94%.

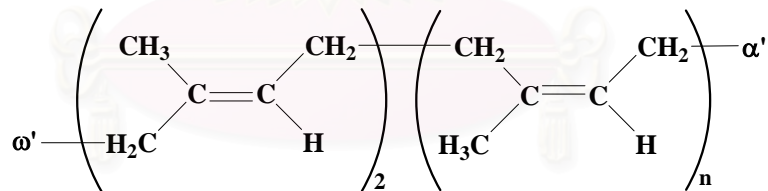


Figure 1.1 Chemical structure of natural rubber.

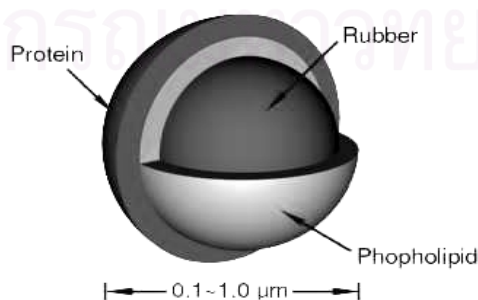
Fresh latex consists of approximately 25-40% dry rubber content (DRC) and 5-10% non-rubber substances. The non-rubber components include proteins, carbohydrates, liquid, and inorganic salts. Its composition varies according to clones of the rubber tree, age of the rubber tree, and the tapping method. The composition of a typical fresh latex is presented in Table 1.1



**Table 1.1** Typical Composition of Fresh Natural Rubber Latex (Morton, 1999)

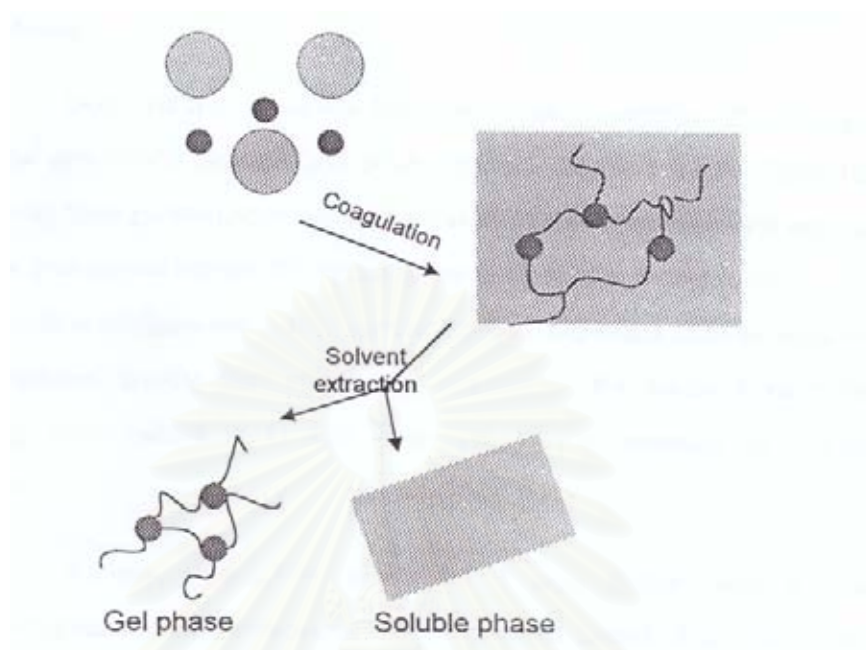
	% Composition
Rubber hydrocarbon	36.0
Proteins	1.4
Carbohydrates	1.6
Neutral lipids	1.0
Glycolipids + phospholipids	0.6
Inorganic constituents	0.5
Others	0.4
Water	58.5

The surface of the rubber particles is covered with lipid and protein layers as shown in Figure 1.2. The outer layer proteins act to stabilize *Hevea* latex (Jacob et al., 1993). The particle size distribution is very broad. The average particle size is between 0.1  $\mu\text{m}$  and 1.0  $\mu\text{m}$ . The weight average molecular weight of NR is in the region of one million with a high polydispersity index. The polydispersity 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 the rubber polymer. The molecular weight distributions are distinctly bimodal with two peaks, the one at lower molecular weight generally being less than that at higher molecular weights, or skewed unimodal with a shoulder or plateau on the low molecular weight side of the peak (Roberts, 1988).

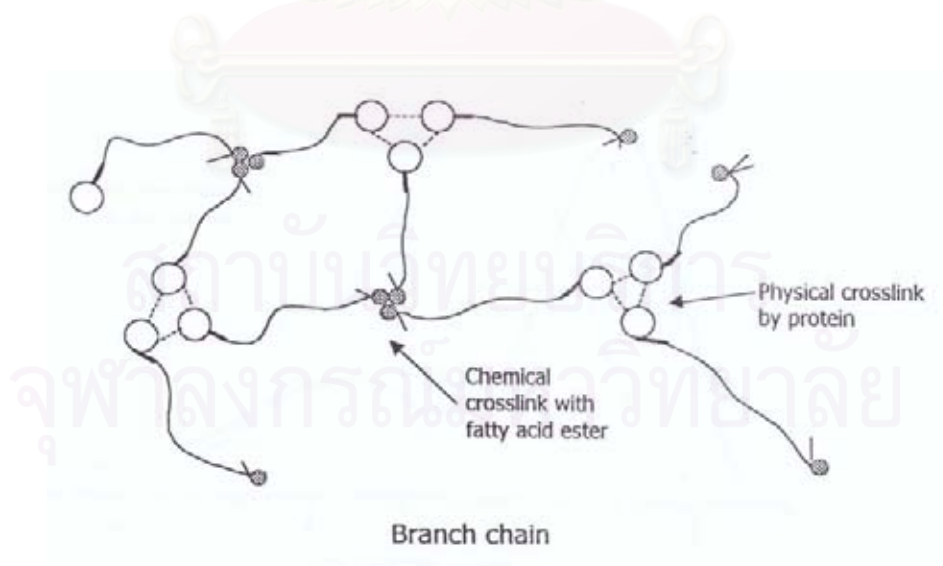
**Figure 1.2** Presumed structure of a rubber particle (Verhaar, 1959).

It is well known that the rubber hydrocarbons in dry solid form are comprised of two fractions called “sol” and “gel” (Tangpakdee and Tanaka, 1997a). The sol phase is dissolved easily in solvents such as cyclohexane, toluene, tetrahydrofuran, etc., while the gel phase is insoluble but swells considerably in the same solvent. *Hevea* rubber contains 5-50% gel component. The gel content in rubber depends on the clonal origin of the rubber tree, processing conditions and the period and temperature of storage. The insoluble phase consists of microgel and macrogel. The gel component presumably consists 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 1.3. Since the gel phase contains nitrogenous and mineral components, it is postulated that the gel phase is linked up with the network of the 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 1.4 (Tangpakdee and Tanaka, 1997b). The former crosslinking points are broken after deproteinization of latex or by adding a small amount of ethanol into toluene solution, while the latter points can be decomposed by transesterification. Moreover, proteins and phospholipids in NR can be decomposed by saponification. Therefore, the deproteinization of the gel phase forms branched chains and transesterification of the branched chains which brings about the linear rubber chain.

In general, fresh latex has a density of  $0.975 - 0.980 \text{ g/cm}^3$  with a pH of 6.5-7.0 and a refractive index of 1.5910 and a surface energy from  $40 - 45 \text{ erg}\cdot\text{ml}^{-1}$ . Rubber does not dissolve in water, alcohol, or acetone, but it swells and disperses or partly solubilizes in benzene, toluene, gasoline, carbon disulfide, turpentine, chloroform, carbon tetrachloride, and other halogen containing solvents. To prevent the production of bacteria in the rubber, adding ammonia preserves the natural rubber. Not only does the increased concentration of fresh rubber latex reduce the volume of latex for transportation, but it also reduces the ratio of non-aqueous substances required to dry rubber content. In addition, several of the industrial processes use a latex, having a concentration higher than 33% wt. There are several concentration methods, which have been used for natural rubber such as evaporation, creaming, centrifugation and electrodecantation.



**Figure 1.3** Schematic representation of gel phase of the latex and natural rubber (Allen et al., 1963).



**Figure 1.4** Presumed structure of branching and crosslinking in NR (Tangpakdee and Tanaka, 1997b).

Among the methods currently used for the concentration of natural rubber latex, centrifugation is most the important; about 90 % of concentrated latex used in industry is produced by centrifugation. Centrifugation involves the use of centrifugal disc concentrators to separate the blended field latex into latex concentrate and a low rubber content serum called “ latex skim”. The designation “High Ammonia” (HA) indicates that the centrifuged latex is preserved with ammonia alone.

Concentrated latex consists of approximately 60 % DRC. Most of the rubber particles in this cream phase are large particles, which show a size distribution ranging from 0.1 – 0.3 mm. The molecular weight of the rubber from the cream phase has a typical bimodal molecular weight distribution, with peaks at  $M_w$  of  $2.0 \times 10^6$  g/mol and  $1.2 \times 10^5$  g/mol (Blackley, 1983).

The serum or skim latex contains a small amount of rubber particles, 4-10% DRC, with a high amount of non-rubber components, including amino acids, proteins, carbohydrates, organic acids, inorganic salts and nucleotidic materials. The rubber particles in the serum phase are small particles and show a size distribution over a range of 0.005-0.3 mm. The molecular weight distribution is unimodal, with a GPC peak appearing at  $1.0 \times 10^6$  g/mol.

## **1.2 Chemical Modification via Hydrogenation of Diene – Based Polymers**

The chemical modification of polymers has been an interesting method to improve or produce novel polymeric materials, which are inaccessible or difficult to prepare by conventional polymerization processes. Chemical modifications such as crosslinking, grafting, degradation, oxidation, isomerization, and cyclization have been studied for altering and optimizing the physical and mechanical properties of polymers (Bhowmick and Stephens, eds., 1988; McManus and Rempel, 1995). Diene-based polymers e.g., polyisoprene (PI), polybutadiene (PBD), nitrile butadiene rubber (NBR) as well as natural rubber (NR) have carbon – carbon double bond unsaturation in the backbone structure. The residual carbon – carbon double bonds in the polymer structure are susceptible to thermal and oxidative degradation when exposed to harsh environments, resulting in a decline of the structural properties of the polymers.

Hydrogenation, one type of chemical modification of unsaturated polymers, is an important method to reduce the amount of unsaturation; consequently, the structure of the hydrogenated polymer has better resistance to thermal and oxidative degradation. Significant examples of hydrogenated polymer products in the commercial synthetic rubber industry include hydrogenated styrene-butadiene rubber (HSBR) produced by Shell and hydrogenated acrylonitrile-butadiene rubber (HNBR) manufactured by Zeon Chemicals and Lanxess Inc. Both of these hydrogenated rubbers have excellent high temperature stability and resistance to oxygen, ozone and ultraviolet radiation, which are far superior to those of the parent rubbers (McManus and Rempel, 1995).

Hydrogenation can be carried out by both catalytic (homogeneous, heterogenous) and non-catalytic (diimide) processes (Schulz, 1982). Homogeneous catalysts are favored for catalytic hydrogenation of unsaturated polymers in solution because they have higher selectivity and do not involve a macroscopic diffusion problem. In addition, the performance of homogeneous catalysts can be explained and understood at the molecular level (Bhaduri and Mukesh, 2000).

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 followed by addition of catalyst at the desired reaction temperature and hydrogen pressure. In 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 the hydrogenation is carried out under a particular pressure and temperature.



Many natural and synthetic rubbers are produced in latex form or as emulsions such as NR, SBR, and NBR. A more economically feasible approach is to hydrogenate the elastomers in the 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 is of particular interest to investigate hydrogenation of elastomers in the emulsified form (Singha et al., 1997a).

### 1.3 Hydrogenation of Latex Elastomers

#### 1.3.1 Hydrogenation of Latex with an Oil Soluble Catalyst Using an Organic Co-solvent

Wilkinson's catalyst,  $\text{RhCl}(\text{PPh}_3)_3$ , is well known as an effective catalyst with high selectivity for the hydrogenation of the C=C within the rubber materials containing other functional groups such as  $-\text{CN}$  or  $-\text{C}_6\text{H}_5$ . This catalyst can be produced in high yield and is easy to handle because it is stable in air. Therefore, the Wilkinson's catalyst has been assessed from the hydrogenation of rubber as a solid in latex form. Krause and Tex (1997) reported that 99% conversion was achieved for hydrogenation of styrene-butadiene rubber (SBR) latex using Wilkinson's catalyst,  $\text{Rh}(\text{PPh}_3)_3$ . Murrer and Jenkin (1998) also investigated the hydrogenation of acrylonitrile-butadiene-styrene (ABS) emulsion using Wilkinson's catalyst,  $\text{Rh}(\text{PPh}_3)_3$  and the polymer product was found to contain about 20% hydrogenation. When  $\text{RhCl}(\text{PPh}_3)_3$  was replaced by  $[(\text{Ph}_3\text{P})_2\text{RhCOD}]^+[\text{BF}_4]^-$  about 70% hydrogenation was achieved.

Palladium complexes provide another alternative catalyst source for hydrogenation of unsaturated polymer. Kubo and Ohura (1993) studied the hydrogenation of NBR latex using a benzene solution of a palladium acetate catalyst. The benzene solution of the catalyst was added to the aqueous phase and the product was found to be 90% hydrogenated after 6 h.



Ruthenium complexes are attractive for the hydrogenation of unsaturated polymers since the price of Ru is considerably lower than Rh and Pd. Rempel and Guo. (1993) studied the hydrogenation of NBR emulsion. NBR emulsion (containing 33% solid content, 38% acrylonitrile) was hydrogenated using  $\text{RuCl}_2(\text{PPh}_3)_3$  in methyl ethyl ketone (MEK) at 2.5 to 10 MPa hydrogen pressure over the temperature range of 100 to 200°C. When organic additives such as ascorbic acid, acetic acid were added to the reaction, 99% hydrogenation was achieved in 3 h. The additives had a beneficial effect in minimizing the gel content of the final hydrogenated polymer product.

Guo and Rempel (1997) developed two processes for the catalytic hydrogenation of NBR emulsions using an oil soluble catalyst,  $\text{RuCl}_2(\text{PPh}_3)_3$ . 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 types of additives during the hydrogenation process such as ammonium sulfate or a carboxylic acid were found to improve the catalyst activity. The additives had a further 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 which 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 bonds within the NBR latex was achieved in both processes. More recently, Leube et al. (2002) described 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 added to the system.

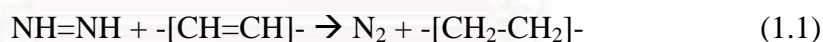
### **1.3.2 Hydrogenation of Latex Using Water Soluble Catalyst**

Hydrogenation of a 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 a water soluble analog of the Wilkinson catalyst,  $\text{RhCl}(\text{DPM})_3$  (DPM = diphenyl phosphino benzene *m*-sulfonate). The reaction was carried out at 75°C and atmospheric hydrogen pressure yielding

more than 60 mole percent 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 apparently significant change in the average particle size of latex as well as particle size distribution. Mudalige et al. (1997) investigated the hydrogenation of a diene-based polymer latex, i.e. PBD, SBR and NBR using water-soluble complexes,  $[\text{RhCl}(\text{HEXNa})_2]_2$  ( $\text{HEXNa} = \text{Ph}_2\text{P}(\text{CH}_2)_5\text{-CO}_2\text{Na}$ ) at  $100^\circ\text{C}$  and 5.5 MPa and compared the activity with  $\text{RhCl}(\text{TPPMS})_3$  ( $\text{TPPMS} = \text{monosulphonated-triphenylphosphine}$ ). It was found that both catalysts hydrogenate 1,2 (vinyl) units and 1,4 (internal) units in all the polymers.

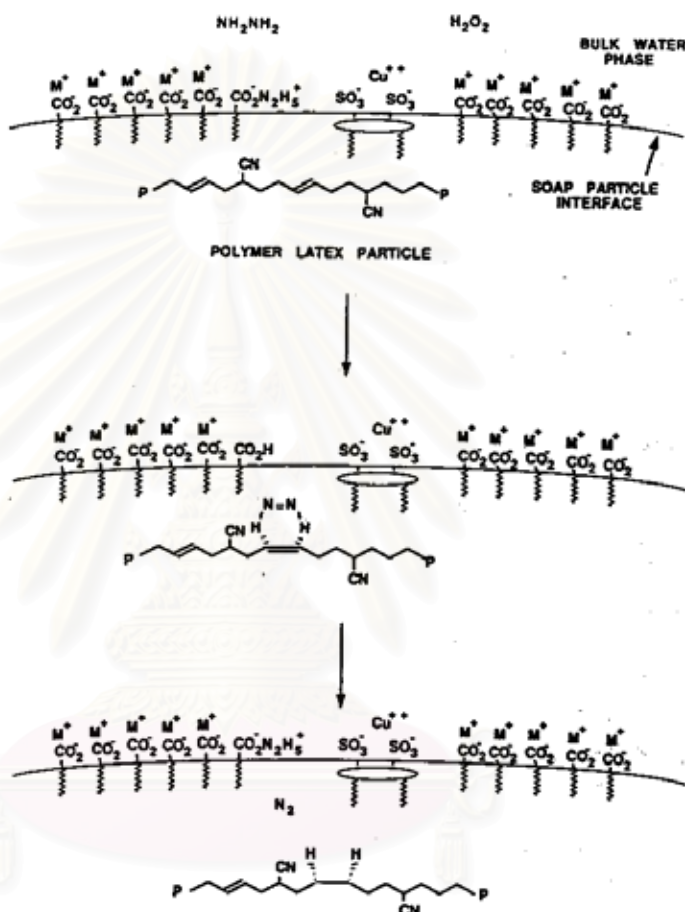
### 1.3.3 Hydrogenation of Latex using Diimide Reduction

The hydrogenation process using diimide, which is generated from the redox reaction between hydrogen peroxide and hydrazine hydrate, is energetically favorable for the catalytic processes. The re-dissolving and solvent-removing steps are eliminated for the diimide process because this process does not use an organic solvent. Moreover, this method can produce a product that is in the latex form. The use of diimide to hydrogenate carbon-carbon double bonds is well known in organic chemistry literature (Parker et al., 1992). The overall reaction is



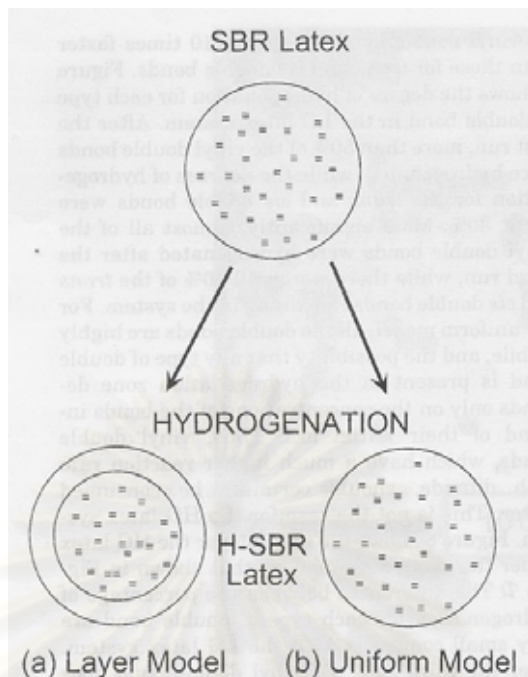
Wideman (1984) introduced the use of the diimide method to hydrogenate NBR latex. The hydrazine hydrate/hydrogen peroxide (or oxygen) redox system was used to produce diimide in situ, and copper ion in terms of cupric sulfate (or ferric sulfate) was used as a catalyst and 80% hydrogenation could be achieved. Based on this patent, Parker et al. (1992, 1995) provided more refined results and a detailed process for the preparation of highly saturated nitrile rubber latex. A mechanism for the hydrogenation reactions was proposed and is shown in Figure 1.5. The anionic soap was indispensable for the hydrogenation because the soap helped to keep the catalytic copper ions at the surface of the rubber particles. Schiessl et al. (1991) suggested that maintaining a large excess of hydrazine helped to reduce crosslinking and provide a gel-free HNBR with a hydrogenation degree of 90%. Belt et al. (2000, 2003) described patents for NBR latex hydrogenation, in which, boric acid was used as

catalyst. It was also claimed that a compound could be added before, during or after the hydrogenation to break crosslinks formed during the hydrogenation. The compound can be chosen from primary, secondary amines, hydroxylamine, imines, azines, hydrazones, oximes and so on. An emulsion form of N-1,4-dimethylphenyl (N'-phenyl)-p-phenylenediamine was also suggested to reduce gel formation.



**Figure 1.5:** Proposed mechanism for hydrogenation (Parker et al., 1992).

He et al. (1997) studied the effect of latex particle sizes on degree of SBR hydrogenation. SBR latex with a diameter of 50 nm could be hydrogenated to 91% using 1 mol hydrazine/hydrogen peroxide per mole double bond. For the latex with a diameter of 230 nm, the hydrogenation degree was 42%. A “Layer model” was proposed to explain the effect of particle size in Figure 1.6. The catalyst, copper ion, was postulated as staying at the surface of the latex particles. By modulating the concentration of copper ions at the particle surface, higher degree of hydrogenation could be attained.



**Figure 1.6:** Two models for the distribution of double bonds in hydrogenated SBR latex particle: (a) layer model; (b) uniform model (He et al., 1997).

Xie et al. (2002) studied the effect of reaction conditions on both hydrogenation and crosslinking. The use of inhibitors both in the rubber phase and in the aqueous phase was suggested to reduce crosslinking. By using sodium N,N-dimethyldithiocarbonate and p-tert-butylpyrocatechol as the inhibitors, the gel content in the final rubber could be reduced to 5%. Similar results were also presented by Sarkar et al., (1997, 2000). Xie et al. (2003) investigated the hydrogenation NBR latex by hydrogen peroxide and hydrazine with copper sulfate as catalyst. 87% hydrogenation was achieved after 6 h at 40°C for a mole ratio of hydrazine to C=C of 1:2.5. Gel formation was a problem for this reaction, and thus p-tert-butylpyrocatechol was used as an inhibitor for the gel formation and it reduced the percent gel from 94.3 to 21.7%. Zhou et al. (2004) also studied the hydrogenation of nitrile butadiene latex (NBRL) by hydrogen peroxide and hydrazine with boric acid as catalyst. Only 81.3% hydrogenation was achieved (6 h, 60°C), 3% gel content was found when hydroquinone was used as inhibitor. Recently, Lin et al. (2004) investigated the hydrogenation process by examining hydrogenation efficiency and hydrogenation degree. It has been found that the hydrogenation efficiency, which is

define as the ratio of amount of hydrogen peroxide consumed for the hydrogenation to total amount of hydrogen peroxide react, varies with both the type of catalyst and degree of hydrogenation. The use of boric acid as promoter, can bring the hydrogenation efficiency to a level of 100% when the degree of hydrogenation below 60%. The decrease of hydrogenation efficiency in range of low hydrogenation degree resulted from side reaction at interphase of latex particles, which modulated by catalyst and the addition rate of hydrogen peroxide; whereas, the decrease in hydrogenation efficiency in the range of high hydrogenation degree which caused by side reaction with polymer phase was also reported. Gel formation in hydrogenated polymer via diimide hydrogenation was investigated (Lin et al., 2005). The result indicated that hydrogen peroxide decomposition, some reaction related to oxygen and the redox reaction between hydrogen peroxide and hydrazine are capable of generating radicals. However, radical generated in the aqueous phase do not appear to initiate the crosslinking of diene-based polymer in latex form. It was proposed that the primary radicals giving rise to crosslinking are generated in polymer phase in situ, and step responsible for generated organic radicals is possibly the diimide disproportionation.

#### **1.4 Hydrogenation of Natural Rubber**

Any polymer with unsaturated hydrocarbon groups, present either in the backbone or within the side chain, can be hydrogenated. The most recent work for polymer hydrogenation has produced excellent products, such as hydrogenated NBR and hydrogenated SBR that have better resistance to thermal and oxidative degradation. In addition, hydrogenation is an alternative way to produce some polymer structures which are difficult to access via conventional polymerization, such as alternating ethylene-propylene copolymer from the hydrogenation of polyisoprene or natural rubber, and hydrogenation of block copolymers such as poly(styrene-co-butadiene-co-styrene), poly(1,4-butadiene-co-1,2-butadiene) and poly(1,4-butadiene-co-1,4-isoprene-co-1,4-butadiene). Hydrogenation of these block copolymers forms thermoplastic elastomers with crystalline and amorphous segments, which are different from those of their unsaturated counterparts (Mark et al., 1994).







### 1.4.1 Hydrogenation of Synthetic *cis*-1,4-Polyisoprene and Natural Rubber

#### a) Homogenous Catalyst

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

Singha et al. (1997b) reported the kinetics for natural rubber hydrogenation. This system reached 88% hydrogenation within 20 h in the presence of 1.18 mM of  $[\text{RhCl}(\text{PPh}_3)_3]$  and toluene under  $30 \text{ kg/cm}^2$  of  $\text{H}_2$  at  $100^\circ\text{C}$ . Hydrogen consumption plots indicated an apparent first-order rate dependence on the concentration of carbon-carbon double bond. The apparent activation energy for this system was calculated to be about 29.1 kJ/mol suggesting that the catalytic process was mass transfer controlled. The rate of hydrogenation increased with hydrogen pressure and then leveled off when the hydrogen pressure was higher than  $40 \text{ kg/cm}^2$ . This system also showed that the extent of hydrogenation increased with catalyst concentration. However, a high concentration of triphenylphosphine was found to decrease the rate of hydrogenation. The effect of solvents on the rate of hydrogenation was also studied. They observed that the extent of hydrogenation of natural rubber decreased as a function of solvent in the order: toluene > chlorobenzene > benzene. The important factors for the catalyst were the nature of solvated rhodium hydride complex and the interaction of solvent with polymer. In addition, the thermal degradation properties of hydrogenated natural rubber were investigated. It was concluded that the hydrogenation enhanced the thermal stability of natural rubber while retaining its glass transition temperature.

Tangthongkul et al. (2004, 2005) studied the kinetics of the hydrogenation of synthetic *cis*-1,4-polyisoprene and natural rubber in the presence of  $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ . It was observed that the hydrogenation rate for these rubbers followed pseudo first order kinetics with respect to the concentration of carbon-carbon double bonds concentration under all sets of reaction conditions studied. The kinetic results suggested that the hydrogenation reaction of isoprene rubbers showed a first-order behavior with respect to total catalyst concentration and hydrogen pressure. An inverse order dependence on added  $\text{PCy}_3$  was also observed. The apparent activation energy of *cis*-1,4-polyisoprene hydrogenation was estimated as 51.1 kJ/mol over the temperature range of 130 to 180°C, whereas it was 25.3 kJ/mol for natural rubber hydrogenation. The addition of a small amount of *p*-toluenesulfonic acid to the system substantially increased the rate of reaction. In addition, the impurities in the natural rubber resulted in a severely reduced catalytic activity. The main polymer chain length and molecular weight decreased during the hydrogenation due to the reaction conditions employed.

Charmondusit (2002) studied the kinetics of homogeneous hydrogenation of *cis*-1,4-polyisoprene catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ . Both catalysts were very effective for hydrogenation of isoprene rubbers leading to high levels of hydrogenation (> 95% hydrogenation) which could be obtained within 20 minutes depending on conditions. This study showed that the hydrogenation of *cis*-1,4-polyisoprene in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  had a first order dependence on the carbon-carbon double bond concentration. A second order behavior with respect to hydrogen concentration at low hydrogen concentration shifted to a zero order dependence as the hydrogen pressure was increased. The apparent activation energy over the temperature range of 115 – 140°C was calculated as 109.3 kJ/mol. The kinetic study of the hydrogenation of *cis*-1,4-polyisoprene catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  differs from the osmium complex with respect to the effect of hydrogen pressure. The hydrogenation catalyzed by the iridium system was first order with respect to hydrogen pressure at low catalyst concentration but at high catalyst concentration tended to produce dimerization or trimerization of the catalyst, which decreased the catalytic activity. An apparent activation energy for hydrogenation in the presence of the iridium catalyst of 79.8

kJ/mol was obtained. The relative viscosity of the hydrogenated rubber catalyzed by both catalysts indicated that no side reaction such as degradation or crosslinking occurred over the range of experimental conditions used. Natural rubber could be quantitatively hydrogenated using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  in the presence of acid added. It was found that the presence of a strong carboxylic acid or that of a higher coordinating power reaction solvent increased the catalytic activity for the hydrogenation process.

Hinchiranan (2004) also studied the kinetics of natural rubber using the 5d metal catalysts  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ . The level of hydrogenation was determined via a  $^1\text{H-NMR}$  spectroscopic technique. Kinetic data were collected using a computer controlled gas-uptake apparatus which measured hydrogen consumption as a function of time. The kinetic results indicated that the hydrogenation of NR catalyzed by both catalysts exhibited a first-order behavior with respect to catalyst concentration and an inverse behavior dependence on rubber concentration due to impurities present in the rubber. A first order behavior with respect to hydrogen concentration at low concentration shifts to a zero order dependence as the hydrogen pressure was increased for NR hydrogenation catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ . In the case of NR hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ , a first order behavior with respect to hydrogen concentration was reported. The apparent activation energies for NR hydrogenation catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  were 122.8 and 75.6 kJ/mol, respectively. It was shown that reaction was under chemical controlled. The addition of some acids and certain nitrogen containing materials exhibited an effect on the hydrogenation rate. The thermal stability of NR was improved by hydrogenation without affecting its glass transition temperature.

#### **b) Using Diimide Generated *in situ***

Diimide, generated *in situ* from *p*-toluenesulphonylhydrazide (TSH), has been extensively studied as a general hydrogenation reagent. Many observations of hydrogenation via diimide reduction of *cis*-1,4- polyisoprene have been reported.

Nang et al. (1976) reported the cyclization of rubber occurred during hydrogenation *cis*-1,4- polyisoprene. 11.7% hydrogenation was obtained after reaction at 140°C for 60 min. The poor physical properties of vulcanized rubber were reported.

Hahn (1992) showed that the suitable ratio of 2 mol of TSH and 2 mol of amine/mol of olefin was necessary to assure >99% hydrogenation for 2% wt butadiene rubber in xylene. In contrast, polymer prepared from isoprene was only partially hydrogenated when treated with TSH in the presence of tri-*n*-propylamine. There was evidence of a slight degradation in the polymer structure.

Phinyocheep et al. (2003) studied hydrogenation of isoprene-styrene diblock copolymer by diimide generated *in situ*. The reaction was carried out in xylene at 135°C. A molar ratio of TSH to double bonds equal to 4:1 was found to be the optimum ratio, which provided the highest percentage of hydrogenation. The percentage of hydrogenation was analyzed by <sup>1</sup>H-NMR, IR spectroscopy, and iodine number value. The thermal stability of hydrogenated products was improved. The glass-transition temperature of hydrogenated products were found to increase to about 10-20 °C above those of the original block copolymer

Samran et al. (2004) also studied the hydrogenation of natural rubber (NR) and epoxidized natural rubber (ENR) by diimide generated *in situ* from thermal decomposition of *p*-toluene sulfonyl hydrazide (*p*-TSH) in xylene solution at 135°C. The 85-95% hydrogenation was obtained with a two fold excess of TSH. *Cis*, *trans* isomerization was also observed. It was also found that the high temperature of the reaction conditions employed to led chain degradation in both NR and ENR.

#### **1.4.2 Hydrogenation of Natural Rubber Latex**

Wideman (1984) patented the hydrogenation process for various latex polymers. Natural rubber latex was also investigated. Diimide was used as a source for hydrogenation. The reaction between hydrazine and hydrogen peroxide or oxygen were used to promote the formation of the diimide species in this system. It was claimed that 27%hydrogenation of high ammonia natural rubber latex hydrogenation was achieved at 100°C in 3 h.

Tangthongkul (2003) also studied the kinetics of the hydrogenation of natural rubber latex in the presence of  $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ . It was observed that the hydrogenation rate of these rubbers followed pseudo first order kinetics in carbon-carbon double bond concentration under all sets of reaction conditions studied. The kinetic results suggested that the hydrogenation reaction of isoprene rubbers showed first-order rate behavior with respect to total catalyst concentration and hydrogen pressure. An inverse dependence on added  $\text{PCy}_3$  was also observed. The apparent activation energy of natural rubber latex was estimated as 29.2 kJ/mol over the temperature range of 140 to 160°C. The addition of a small amount of *p*-toluenesulfonic acid to the system substantially increased the rate of reaction but impurities in the natural rubber severely reduced the catalytic activity.

### 1.5 Objectives and Scope

Natural rubber latex is a useful material for industrial applications but still has a disadvantage relative to some synthetic elastomers due to as low ozone resistance and degradation on long term heating. Thus, natural rubber latex requires improvement of some of its properties in order to be used for a wider range of applications in the rubber product. Chemical modification of diene-based polymers is an alternative method to modify polymers to obtain the desired properties. Direct hydrogenation of rubber in latex form is a challenging method to reduce the time involved with the coagulation process after polymerization and the dissolution of the coagulated product in a solvent. The method for hydrogenation of the rubber in latex form was studied in this investigation. The objectives of this research are:

- To investigate the kinetics of hydrogenation of natural rubber latex, propose the reaction mechanism of catalytic cycle of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and study the effect of parameters on the hydrogenation rate
- To study the hydrogenation of natural rubber latex using diimide reduction.
- To study the physical and thermal properties of the hydrogenated natural rubber



Chapter 1 of this thesis provides a review of relevant literature. Details of materials, experimental procedures and analytical methods are given in Chapter 2. Chapter 3 and Chapter 4 summarize the results obtained for the hydrogenation of natural rubber using homogeneous catalysts. Two homogeneous catalytic systems,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ , were investigated for the catalytic hydrogenation of natural rubber latex. The kinetics of both systems were studied using an automatic gas uptake apparatus. The influence of reaction parameters were evaluated by using a two-level factorial design in order to find the main and interacting effects of these systems. Univariate experiments were used to study the effect of each parameter on the hydrogenation rate. Plausible reaction mechanisms for both catalytic systems have been suggested based on the kinetic data. In Chapter 3 the hydrogenation study of fresh natural rubber latex was also studied. These experiments were carried out in a high pressure Parr reactor. The hydrogenated natural rubber was characterized using FTIR,  $^1\text{H-NMR}$  spectroscopy.

Noncatalytic hydrogenation of natural rubber latex using diimide generated *in situ* as another alternative for hydrogenation natural rubber latex is presented in Chapter 5. Noncatalytic hydrogenation is the hydrogenation process without the use of any catalyst and hydrogen gas. This method was carried out in a glass reactor. The diimide source of this method was generated from thermal decomposition of p- toluene sulfonyl hydrazide (p-TSH). The hydrogenated natural rubbers were characterized using FTIR and  $^1\text{H-NMR}$  spectroscopy. Two-level factorial design was also applied to examine the interaction behavior of all parameters. Then, univariate experiments were carried out to demonstrate the effect of various reaction parameters on the degree of hydrogenation.

The following two chapters (Chapter 6 and Chapter 7) described the hydrogenation of natural rubber latex by using diimide hydrogenation. Diimide reduction is one alternative for a hydrogenation process without the use of any organic solvent. The influence of reaction parameters were evaluated by using a two-level factorial design in order to find the main interaction effects of these systems. Univariate experiments were carried out to study the effect of each parameter on the degree of hydrogenation.



In Chapter 8, the change in the polymer structure after the hydrogenation was investigated in terms of the molecular weight and the molecular weight distribution. In addition, the thermal properties such as glass transition temperature and decomposition temperature were determined. The results were compared with the properties for the parent polymer. Vulcanization of hydrogenated NR was also investigated. Physical properties of vulcanized hydrogenated natural rubber in terms of ozone resistance were also studied and are described in this chapter. In Chapter 9, the important conclusions of this study are summarized and recommendations for possible future are provided.



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## CHAPTER II

### EXPERIMENTAL AND DATA ANALYSIS

#### 2.1 Materials

##### a) Rubber

Commercial *cis*-1,4-polyisoprene with 97% *cis* configuration (Natsyn) having a molecular weight of approximately 800,000 was obtained from Bayer, Inc. (Sania, Canada). Natural rubber (STR 5L) was provided from Chalong Latex Industry Co., Ltd. (Songkhla, Thailand). Natural rubber latex (60% dry rubber content) was supplied by Thai Rubber Latex Co., Ltd. (Bangkok, Thailand). The overall compositions of STR 5L and NRL are summarized in Appendix A, Table A-1 and Table A-2, respectively. Ethylene-propylene rubber (EPDM) of grade Keltan 509 x 100 (100 parts paraffinic extender oil with 8.7% diene content) and Keltan 314 obtained from DSM Elastomer (Sittard, Netherlands) and were used for properties comparison. The physical properties for these EPDMs are summarized in Appendix A (Table A-3). In all cases, these starting polymers were used as received.

##### b) Catalyst and Chemicals for Catalytic Hydrogenation Experiments

Reagent grade monochlorobenzene (MCB) and methylene chloride were purchased from Fisher Scientific Ltd., (Fair Lawn, NJ, USA). Toluene, xylene, triethylamine, hexane, and 2-methoxyethanol from EM Science (Darmstadt, Germany), tetrahydrofuran and pyridine from Caledon Laboratories Ltd. (Georgetown, ON, Canada) were all reagent grade and used as received. All solvents were used without further purification. The 99.99% oxygen-free hydrogen gas for the hydrogenation experiment was supplied by Praxair Inc. (Kitchener, ON, Canada).

$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  were prepared according to the procedures outlined in the literature (Esteruelas et al. 1986, 1988). Osmium (III) chloride ( $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ ) and tricyclohexylphosphine ( $\text{PCy}_3$ ) were purchased from Strem Chemicals (Newburyport, MA, USA).  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$  were also prepared according to literature methods with  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{RhCl}_3$

3H<sub>2</sub>O supplied by Engelhard Industries Inc (Newark, NJ, USA). The Crabtree's catalyst, [Ir(cod)(PCy<sub>3</sub>)(py)]PF<sub>6</sub>, was also purchased from Strem Chemicals. Phenylacetylene, 3-chloropropionic acid, succinic acid, and *p*-toluenesulfonic acid (*p*-TSA) were obtained from Aldrich Chemical Co. Inc. (Milwaukee, WI, USA). Hexylamine was purchased from BDH Chemicals (Toronto, ON, Canada). Hexadecylacrylamide was prepared from the reaction of acryloyl chloride and hexadecylamine supplied from Aldrich Chemical Co. Inc. (Milwaukee, WI, USA). Ammonium hydroxide was purchased from Fischer Scientific Co. Ltd. (Fair Lawn, NJ, USA).

c) Chemicals for Diimide Hydrogenation Experiments

Hydrazine hydrate (> 99%) was purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI, USA). Sodium n-dodecyl sulfate (SDS) (99%) an anionic surfactant was purchased from BDH Chemicals (Toronto, ON, Canada). Gelatin was purchased from J. T. Baker Chemical Co. Ltd. (Fairmont, NJ, USA) Hydrogen peroxide (30% aqueous solution) was purchased from VWR Chemical (Toronto, ON, Canada). Catalysts (cupric sulfate, cupric acetate, cupric chloride, ferric sulfate, cobalt sulfate, magnesium sulfate) were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI, USA).

d) Chemicals for Diimide generated in situ Hydrogenation Experiment

*p*-toluenesulfonylhydrazide (*p*-TSH), 2,4,6 -Tri-isopropylbenzenesulfonyl hydrazide (TPSH) and 2,4,6 -Trimethylbenzenesulfonyl hydrazide (MSH) were purchased from Aldrich Chemical Co. Inc. (Steinheim, Germany). Nitrogen gas, with purity of 99.9% was obtained from Praxair, Inc. (Kitchener, ON, Canada).

e) Chemicals for Vulcanization

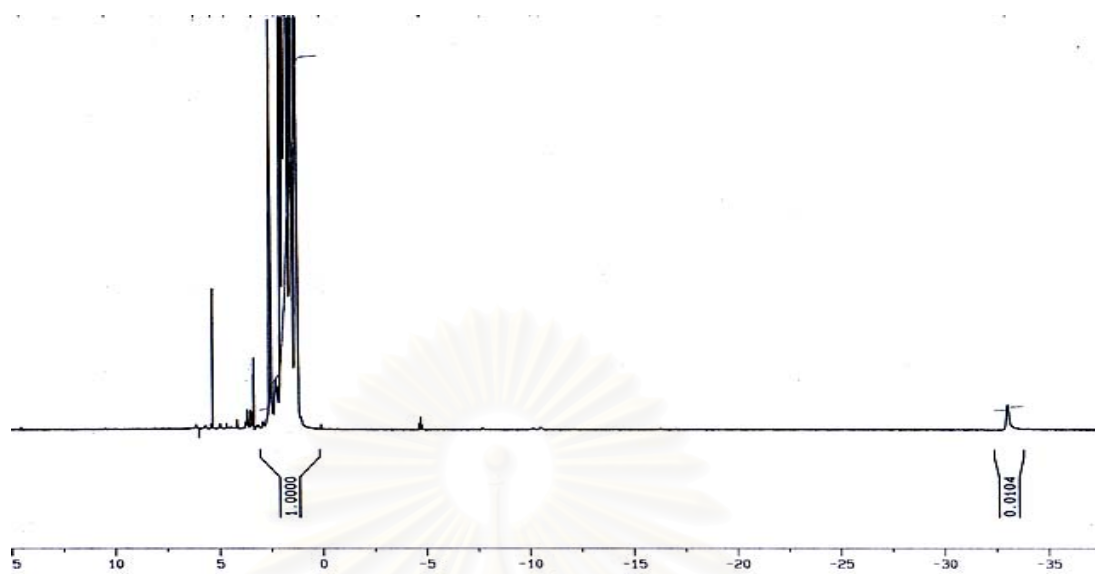
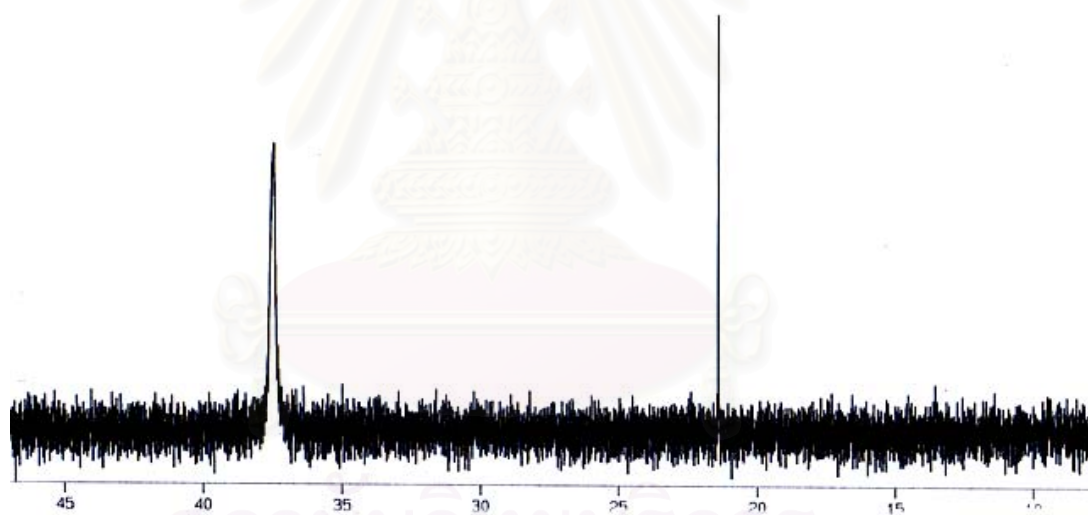
The rubber chemicals for the vulcanization process, such as zinc oxide from Utids Enterprise Co. Ltd. (Bangkok, Thailand), stearic acid from Imperial Industrial Chemicals Co. Ltd. (Pathumthani, Thailand), and sulfur from Siam Chemical Industry Co. Ltd. (Samutprakarn, Thailand) were used as received. *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS) from Flexsys (Monsanto) (Antwerp,

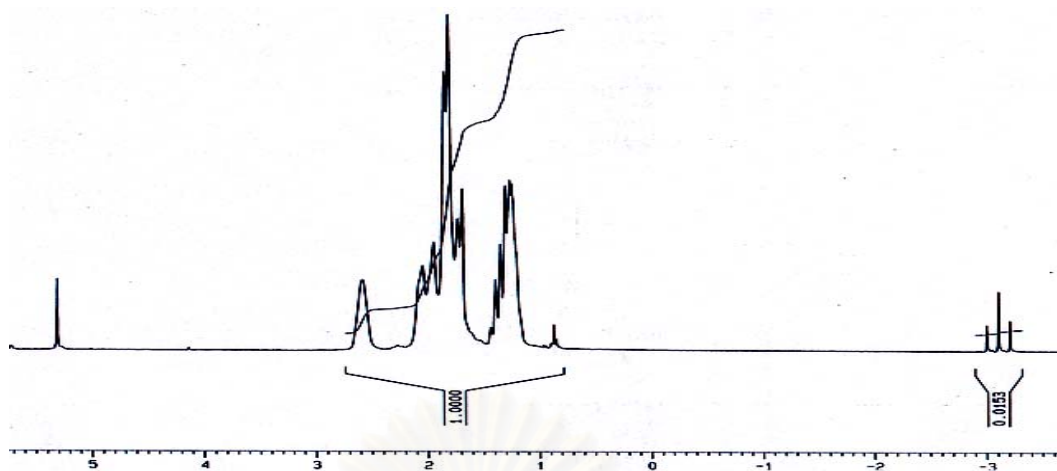
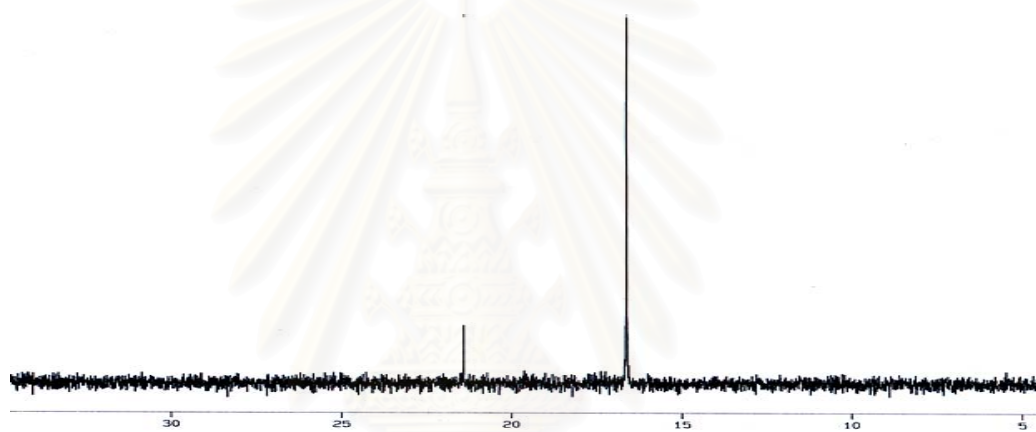
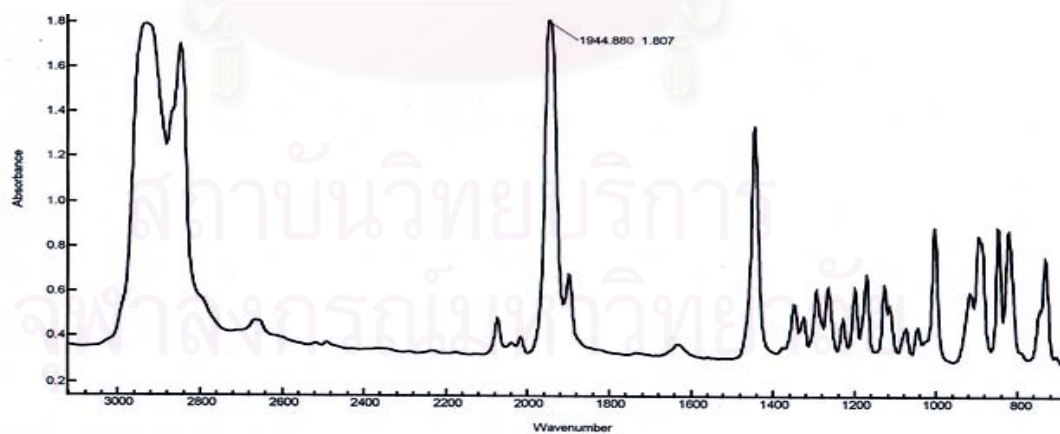
Belgium), tetramethylthiuram disulfide (TMTD) from Flexsys (Monsanto) (Cologne, Germany), 2-mercaptobenzothiazole (MBT) from Kawaguchi Chemicals (Tokyo, Japan) and paraffinic oil (grade Diana process oil PS 32 T) from Apollo Co. Ltd. (Bangkok, Thailand) were all commercial grade.

## 2. 2 Catalyst Preparation

$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was prepared by refluxing  $\text{OsCl}_3 \cdot \text{H}_2\text{O}$  (1 g) with tricyclohexylphosphine (5 g) in degassed 2-methoxyethanol (100 mL) in a 500 mL round bottom flask with a gas inlet tube under a nitrogen atmosphere for 24 h and then cooled down to room temperature. After that, the red-orange crystalline product,  $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$ , was collected and washed twice with degassed methanol (15 mL).  $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$  was dried and kept under a nitrogen atmosphere.

$\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$  was analyzed by NMR spectroscopy and the spectra are shown in Figure 2.1:  $^1\text{H}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -33.06 (br.),  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  37.5 (s).  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was synthesized by exposing a degassed hexane (50 mL) suspension of the species  $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$  to pure oxygen gas until the white product.  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  formed which was filtered by normal filtration since this osmium complex was air-stable. This oxygen complex was then washed with hexane and dried in vacuum for overnight. The NMR and FTIR spectra of the final product are shown in Figure 2.2:  $^1\text{H}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -2.99 (t),  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  16.63 (s), IR:  $\nu(\text{CO})$  1945  $\text{cm}^{-1}$ . The spectrum obtained from  $^1\text{H}$ -NMR spectroscopy showed a triplet, attributed to the metal-hydride peaks at -2.99 ppm, and the peaks of various cyclohexyl protons of the complex appeared in the region from 2.5 to 0.8 ppm. The integration of the hydride and cyclohexyl protons gave a ratio of approximately 66 to 1 in close accord with the molecular formula.

(a)  $^1\text{H}$ -NMR(b)  $^{31}\text{P}\{^1\text{H}\}$  NMR**Figure 2.1**  $^1\text{H}$ -NMR and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$ .

(a)  $^1\text{H-NMR}$ (b)  $^{31}\text{P}\{^1\text{H}\}$  NMR

(c) FTIR

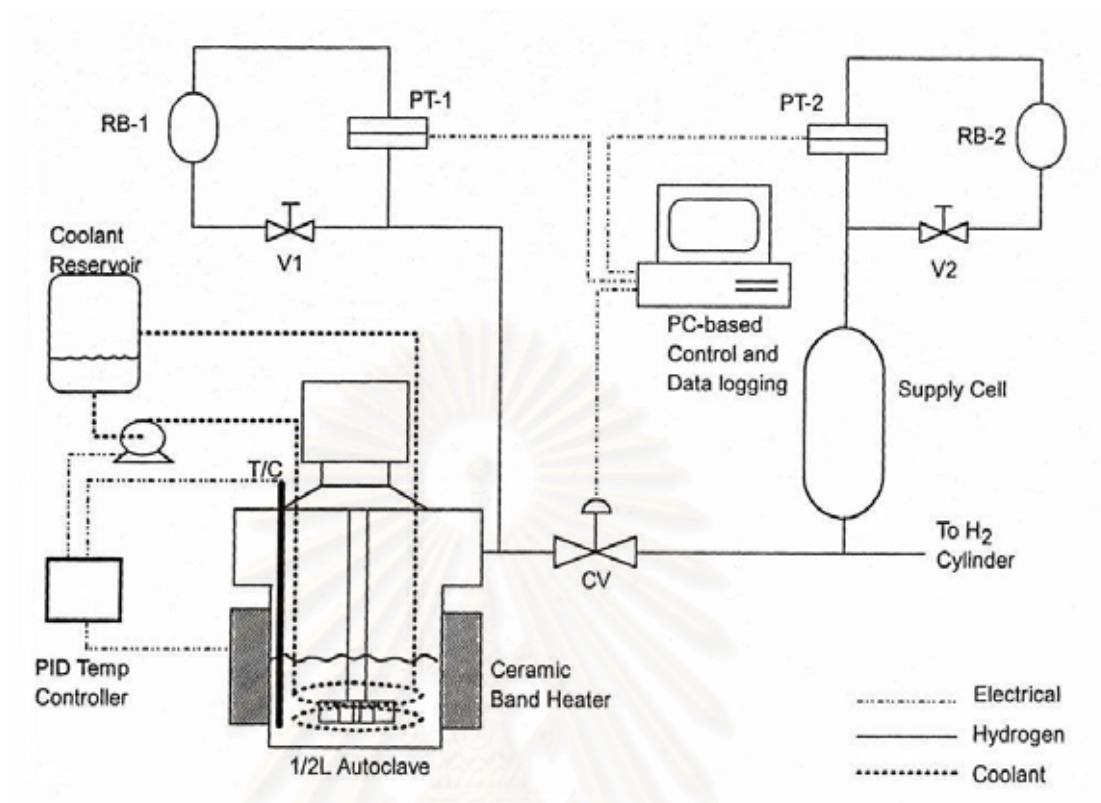
**Figure 2.2**  $^1\text{H-NMR}$ ,  $^{31}\text{P}\{^1\text{H}\}$  NMR and FTIR spectra of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ .



### 2. 3 Hydrogenation in Gas Uptake Apparatus

The gas uptake apparatus utilized in this investigation is a computer controlled batch reactor system that was developed by Mohammadi and Rempel (1987b). Reliable kinetic studies for gas consuming catalytic reactions were carried out in the apparatus that was designed to maintain a constant pressure and temperature while monitoring  $H_2$  consumption as a function of real time. Figure 2.3 illustrates the operational schematic of the equipment. A drop in the autoclave pressure relative to the reference bomb RB-1 was detected by the differential pressure transducer (PT-1). This error signal functioned as the input for the control algorithm residing within a personal computer. Via an i/p converter, the PC activated the pneumatic control valve to permit  $H_2$  from the supply cell to recharge the autoclave. This control system maintained the autoclave pressure to no less than 0.3 psi below its set point.

PT-2 monitored pressure drop in the supply cell relative to RB-2 and the amount of  $H_2$  lost during the reaction is an integrated measure of the hydrogenation rate. PT-2 converted the signal to millimoles of  $H_2$  by calibrating its output voltage against the conversion of a known amount of substrate. This technique assumed that a change in pressure was linearly proportional to the  $H_2$  loss from the supply cell. Ideal gas behavior was maintained for  $H_2$  at 1250 psi and 295 K.



**Figure 2.3 Schematic of gas uptake apparatus.**

#### 2.4 Typical Hydrogenation in a Parr Reactor

Hydrogenation reactions were carried out in a 300 ml Parr pressure reactor. In a typical experiment, a specific amount of the natural rubber latex was weighed and dissolved in 130 ml of the solvent. The rubber mixture was transferred into the reactor. The catalyst was added via a catalyst addition bucket. The autoclave was purged with hydrogen gas. Subsequently, the reactor was pressurized to 32 bar before being heated up to the required reaction temperature. When thermal equilibrium was reached in the reactor (vapor/liquid), the catalyst bucket was dropped by pressurized hydrogen gas and the hydrogen pressure was adjusted to the required reaction pressure. During hydrogenation, the mixture was stirred at a constant speed of 600 rpm. This reaction was maintained at the desired temperature and pressure for a given time. After hydrogenation, hydrogenated rubber was precipitated in ethanol and finally dried under vacuum at room temperature for subsequent analysis.

## 2. 5 Kinetic Experiment Procedure

The kinetic data for the hydrogenation of natural rubber latex in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  were obtained by measuring the hydrogen consumed as a function of time using a gas uptake apparatus. The hydrogenation conditions can be controlled at a constant temperature  $\pm 1^\circ\text{C}$  and pressure  $\pm 0.02$  bar from the target point throughout the reaction. Typically, natural rubber latex was prepared by dissolving the desired mass in monochlorobenzene within a 100 mL volumetric flask. This flask was placed in the dark. Then, this rubber mixture was transferred into the autoclave and the flask was rinsed with 50 mL of chlorobenzene to provide a total solution volume of 150 mL. The required mass of catalyst precursor was weighed into a small glass bucket and then it was loaded into a catalyst chamber on the reactor head. The autoclave, containing the rubber mixture and catalyst bucket, was then assembled.

Due to the sensitivity of the catalyst to air when in solution form, the system was required to have eliminated air by rigorously purging with hydrogen gas ( $\text{H}_2$ ). Three cycles of charging the reactor with the  $\text{H}_2$  at 14 bar and venting were performed without agitation. Then, the agitator was started at 200 rpm and the autoclave was immersed in an ice-water bath until the temperature inside the autoclave dropped to below  $10^\circ\text{C}$  in order to reduce the vapor pressure of the solvent. Subsequently, the reactor pressure was vented and recharged with  $\text{H}_2$  continuously at 14 bar for ca. 20 min while the agitation speed was changed to 1,200 rpm to ensure that the oxygen in the reactor was removed. After that, the ceramic band heater was installed. To achieve the desired reaction conditions, the reactor was pressurized to approximately 80% of the target value of the  $\text{H}_2$  pressure and the desired initiated through the temperature controller. The increase in the temperature of the sealed autoclave provided the pressure reach the set point. Once the system reached the desired conditions, it was allowed a minimum of 45 min to equilibrate.

The  $\text{H}_2$  uptake monitoring program employed two user-specified, data logging intervals. The first was of short duration and was designed to monitor the reaction during its initial stages where the reaction rates are greatest. The second interval was initiated by the operator to avoid the unnecessary collection of data

during periods of slow hydrogenation. Once activated, the program waited one logging interval before starting to record the time, reaction temperature and amount of H<sub>2</sub> consumed. At this point, the reference isolation valves V1 and V2 were closed and the catalyst bucket was dropped. For dispersing the catalyst powder in the rubber solution, the agitator speed was adjusted to 1,200 rpm.

After the reaction of each experiment terminated, the reactor was cooled down to below 50°C using the cooling unit and blowing with air before releasing the pressure of the reactor. Then, the autoclave was disassembled and the hydrogenated product was precipitated with ethanol and dried under vacuum. Then, the residue of product in the reactor was removed by using toluene. Then, the reactor containing toluene was reassembled and heated at ca. 120°C with 200 rpm of agitation speed. After the rinse, the reactor was blown dry with air before starting the next batch. The final degree of olefin conversion obtained from gas uptake was confirmed by <sup>1</sup>H-NMR spectroscopy.

## 2.6 Kinetic Study Experimental Design

Several studies were necessary to determine the basic kinetic dependencies of the system. In each study, the dependence of the pseudo first order rate constant  $k'$  on a different parameter was determined. The rate of hydrogenation is known to be influenced by factors such as the catalyst concentration, hydrogen pressure, double bond concentration, and temperature.

Experiments within each of the basic kinetic dependencies were performed in random order to avoid the accumulation of systematic error. Replicate experiments at a base set of conditions were performed periodically to ensure that no systematic trend, such as catalyst degradation, was not convoluting the measurement. Factor combinations of NRL hydrogenation experiments have been assigned. This consists of a two level factorial design coupled with univariate experiments which inspect the influence of factors acting alone or in combination. Of principle interest were the influences of the concentrations of catalyst, polymer and H<sub>2</sub> pressure on the rate of reaction. Of secondary interest were the effects of varying solvents, and the reaction temperature. A two-level factorial design was employed for principle factors

to identify joint interactions. The influences of various solvents, temperature and added acid have been investigated by univariate experiments alone.

Selection of concentrations and temperatures considered weighing precision, polymer solution viscosities as well as limitations on the reaction rates that the apparatus could control and monitor effectively. The univariate factor combinations have been duplicated for hydrogenation of natural rubber and natural rubber latex to gain a fundamental understanding of the kinetic behavior of this system.

### **2.7 Diimide Generated *in situ* Hydrogenation Procedure**

Hydrogenation of natural rubber latex via noncatalytic hydrogenation via diimide generated *in situ* was carried out under nitrogen gas in a 250 mL glass reactor. A specific amount of the natural rubber latex was weighed and dissolved in 50 mL of solvent. The rubber mixture was transferred into the glass reactor. Various amounts of TSH were added into the reactor. The solution was refluxed at the desired temperature for 3 h under nitrogen gas. The product was filtered with filter paper to remove residua; of TSH and then precipitated within ethanol and dried under vacuum.

### **2.8 Diimide Hydrogenation Procedure**

The natural rubber latex was diluted with water added to a 250 mL three-necked flask. After stirring for 15 min, a catalyst such as cupric sulfate or zinc sulfate or cupric acetate and hydrazine hydrate was added and then stirred for 30 min. The mixture was then heated to 55 °C. Hydrogen peroxide was added dropwise at a rate so that the temperature of the mixture did not increase. During the addition of hydrogen peroxide, if too many bubbles formed, one drop of Dow Corning silicone oil or a antifoaming agent was added. After completing the addition of the hydrogen peroxide, the reaction mixture was kept at the reaction temperature for 1 h.



## 2.9 Blending and Vulcanization Process of Rubbers

To study the ozone resistance properties of the hydrogenated natural rubber latex (HNRL) compared with natural rubber latex (NRL) and ethylene-propylene rubber (EPDM), all rubbers (15 g/batch) were blended with the desired amount of ingredients in a Brabender Plasticorder with 30 rpm of rotor speed at mixing temperature of 70°C for blending of NRL and compounds of NRL/HNRL in order to avoid the overcure of NR in rubber mixtures and 100°C for blending of pure HNR and EPDM. In the vulcanization process, zinc oxide and stearic acid were both used as the activator. The curing agents used for this step were composed of sulfur and accelerators such as tetramethylthiuram disulfide (TMTD) and 2-mercaptobenzothiazole (MBT) which were added to reduce the cure time for the vulcanization step. The recipe of blending will be given in Chapter 10. Then, these compounds were left at room temperature overnight and vulcanized in an electrically heated compression mould at 150°C for NR and 160°C for HNRL, EPDM and NRL/HNRL. The optimum cure time could be investigated using an oscillating disk rheometer (ODR) before vulcanizing the rubber compounds.

To study mechanical properties of hydrogenated rubber latex (HNRL), natural rubber latex compared with natural rubber latex (NRL), ethylene-propylene rubber (EPDM), and mixed rubber of NRL/HNRL, all rubbers (100 g/batch) were blended with the desired amount of ingredients in a two-roll mill at 70°C for blending of NRL and compounds of NRL/HNRL and 100°C for blending of pure EPDM. The recipe of blending will be given in Chapter 8. Then, these compounds were left at room temperature overnight and vulcanized in an electrically heated compression mould at 150°C.

## 2.10 Characterization Methods

### 2.10.1 Fourier Transform Infrared Spectroscopic Analysis

Infrared spectra were collected on a Bio-Rad FTS 3000X spectrometer. For the catalytic hydrogenation and diimide generated in situ experiment, the rubber samples were prepared by casting thin films on a sodium chloride disk. For the diimide hydrogenation experiment, the latex film was cast on a Zn-Sn plate and dried at room temperature.

### 2.10.2 $^1\text{H}$ -NMR and $^{13}\text{C}$ -NMR Analysis

The final degree of olefin conversion was quantified by NMR spectroscopic analysis.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on 3% w/v solutions of the rubber in  $\text{CDCl}_3$  using an Avance 300 MHz spectrometer, Bruker.

### 2.10.3 Molecular Weight Measurement

Molecular weights were obtained using a GPC system which consisted of a Waters 1515 Isocratic HPLC pump and a Waters 2414 refractive index detector (RID). Breeze software was used for data collection and processing. A Styragel HR 3,4,6 THF column were used for separation. Tetrahydrofuran at a flow rate of 1 mL/min was used as the mobile phase. The samples of 0.1% (w/v) rubber solutions were filtered through a 0.45  $\mu\text{m}$  pore size filter and then 200  $\mu\text{L}$  of the filtrated samples was injected in to the mobile phase. The measurements were carried out at 40°C.

### 2.10.4 Viscosity Measurement

The relative viscosity of the solutions of the hydrogenated natural rubber samples were also measured.  $0.125000 \pm 0.00015$  g of HNRL samples were dissolved in 25 ml of toluene at 35°C and then transferred to an Ubbelohde capillary viscometer through a coarse, sintered – glass filter to separate the insoluble gel in the rubber solution. The relative viscosity data ( $\eta_{\text{rel}}$ ) was reported as the viscosity relative to pure solvent.

### **2.10.5 Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis (TGA) of the sample was performed on a Perkin-Elmer Pyris Diamond TG/DTA. The temperature was raised under a nitrogen atmosphere from room temperature to 700°C at a constant heating rate of 10°C/min. The flow rate of nitrogen gas was 50 ml/min. The initial decomposition temperature ( $T_{id}$ ) and the temperature at the maximum of mass loss rate ( $T_{max}$ ) were evaluated.

### **2.10.6 Differential Scanning Calorimetry (DSC)**

Differential scanning calorimetry (DSC) of the sample was carried out on a Mettler Toledo DSC 822. The instrument signal is derived from the temperature difference between sample and the reference. The rubber samples were cooled to –100°C with liquid nitrogen and then heated at a constant rate of 20°C/min to 25°C. The glass transition temperature ( $T_g$ ) was calculated from the midpoint of the baseline shift of DSC thermogram.

### **2.10.7 Morphological Study**

The morphology of the sample was observed on a JEOL JEM 2010 transmission electron microscope (TEM). A small amount of sample was dispersed in water and dropped on the grid. The sample was then stained with  $OsO_4$  vapor for 24 h before observation. The TEM micrograph was taken by using a 15 kV electron beam with a magnification of 200 –1000 K.

### **2.10.8 Cure Characterization**

The optimum cure time for vulcanization of rubbers was investigated using a Monsanto Rheometer MDR 2000. The test specimen size was approximately 1.5 cm x 1.5 cm x 5 mm. The test temperature was 150°C for the natural rubber latex and 160°C for the hydrogenated natural rubber latex and the EPDM rubber.

### 2.10.9 Mechanical Properties

The mechanical properties in terms of tensile strength and hardness of vulcanized rubber were evaluated. The tensile strength of all vulcanized rubber samples was carried out on a Universal Testing Machine (LLOYD model LR5K) at 500 mm/min of the cross-head speed. This test method followed the standard method ASTM D 412. The elongation of specimens was obtained from the extensometer. The testing specimens were cut using a die C and the average of three specimens was considered as the representative value.

### 2.10.10 Ozone Resistance Test

The test of ozone resistance followed the standard method ISO 1431/1 – 1980 (E) for vulcanized rubber samples. The specimens were cut to a size of 2.5 cm x 8.0 cm x 2.7 mm. Samples of rubbers were exposed in an ozone cabinet (HAMPDEN, Northampton, England) at 40°C to an ozone atmosphere of 50 pphm (part per hundred million). Before exposure to ozone, the specimens were stretched by 20% using a specimen holder for 48 h in the absence of light and ozone. The results of ozone cracking were observed at 3, 6, 24, 27 and 48 h. The cracking on rubber surfaces was examined by using an optical microscope and a CCD camera.

### 2.11 Degree of Hydrogenation Determination

The final degree of hydrogenation of each experiment was evaluated using <sup>1</sup>H-NMR spectroscopy. The lump peak area for the saturated protons (-CH<sub>2</sub>- and -CH<sub>3</sub>) in the range of 0.8 – 2.3 ppm and the unsaturated protons peak area at 5.2 ppm were measured in order to calculate the %hydrogenation using eq. (2.1):

$$\% \text{Hydrogenation} = \frac{A - 7B}{A + 3B} \times 100 \quad (2.1)$$

where A is the lump peak area of saturated protons and B is peak area of unsaturated protons. An example for the %hydrogenation calculation is illustrated in Appendix B.

The data obtained from the automated gas uptake apparatus consisted of three columns: reaction time in seconds, total gas uptake in millimoles, and reaction temperature. Data files were exported to a Microsoft Excel program for calculation. The total degree of hydrogenation measured by  $^1\text{H-NMR}$  spectroscopy was compared to the total hydrogen uptake. The gas uptake data were converted to the percent double bond conversion ( $x$ ) using the known maximum extent of reaction. The plot of  $\ln(1-x)$  versus time was constructed. An apparent reaction rate constant ( $k'$ ) was provided from the slope of a plot of  $\ln(1-x)$  versus time. The slope of the plot was determined by linear regression.



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## CHAPTER III

### HYDROGENATION OF NATURAL RUBBER LATEX IN THE PRESENCE OF $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$

Natural rubber latex (NRL) is a milk like substance which is produced from rubber trees: *Hevea Brasilliensis*. Natural rubber latex (NRL) contains a rubber part, a non-rubber part and water. NRL is known chemically as polyisoprene. The rubber chain has oligopeptide and fatty acid ester group at the unidentified initiating and chain end, respectively. The high resilience, tear resistance, excellent dynamic properties and fatigue resistance are main advantages of natural rubber believed to result from the proteins in the rubber structure. Due to the unsaturation of carbon-carbon double bonds within the isoprene backbone, natural rubber is subject to degradation when exposed to sunlight, ozone, and oxygen. Chemical modification of natural rubber has been an active field of research because of the technological importance of the modified products. Hydrogenation is one of the important methods for improving and changing the properties of unsaturated elastomers toward greater stability against thermal, oxidative, and radiation- induced degradation (Singha et al., 1997).

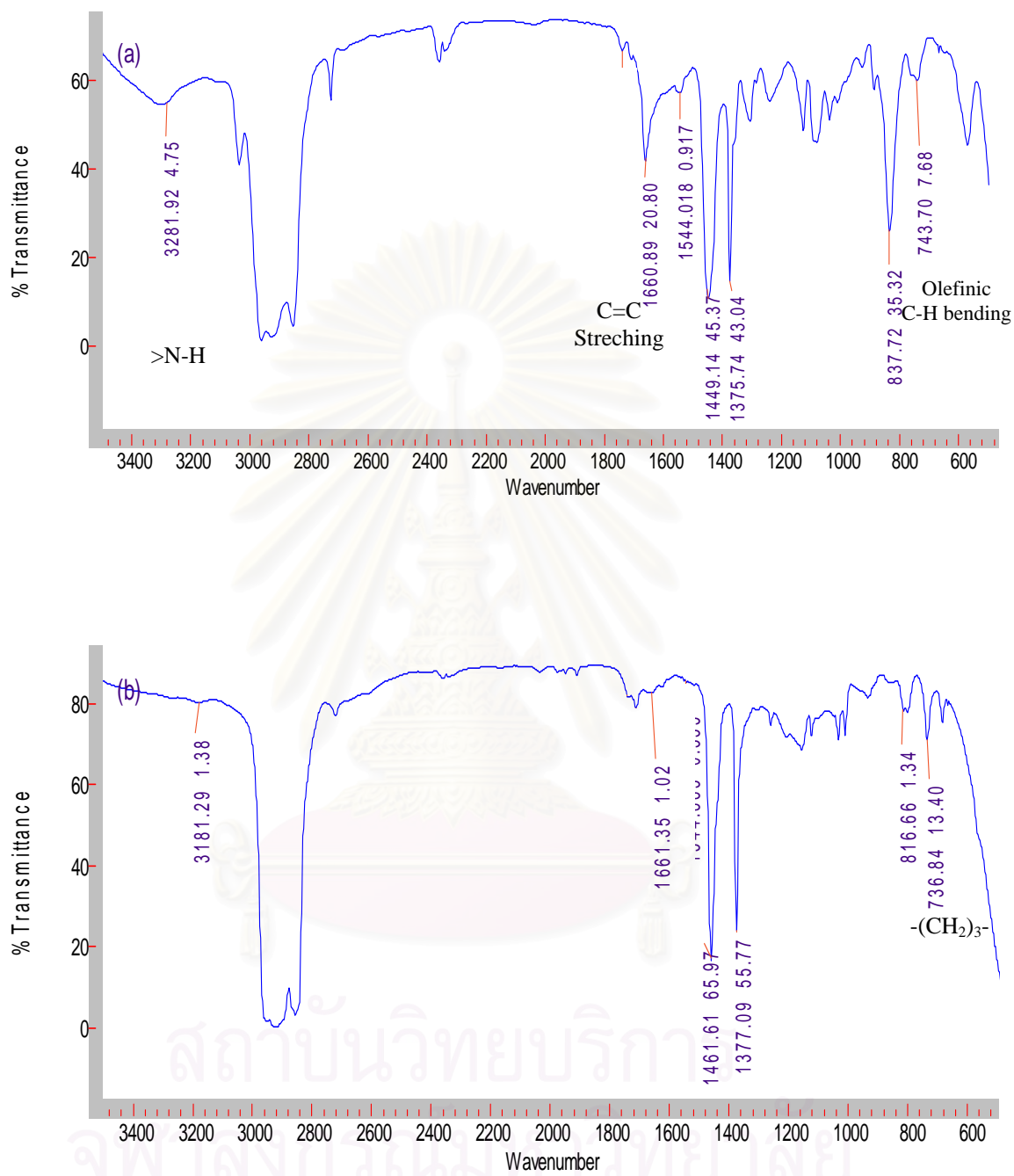
Hydrogenation of synthetic *cis*-1,4-polyisoprene (PIP) ( Charmondusit et al., 2003) and natural rubber (NR) (Hinchiranan, 2004) in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was reported to provide up to 99 % conversion of the carbon-carbon double bonds within 15-30 minutes for PIP and up to 94 % conversion within 20 minutes for NR under moderate reaction conditions. Whereas, the quantitative hydrogenation of NR in presence of  $\text{RhCl}(\text{PPh}_3)_3$  (Singha et al., 1997) required 22 h. Thus, the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst appears to be an extremely effective catalyst for NR hydrogenation.

The objective of the present work was to study the kinetics of NRL hydrogenation catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ . The effect of catalyst concentration ( $[\text{Os}]$ ), rubber concentration based on C=C concentration ( $[\text{C}=\text{C}]$ ), hydrogen pressure ( $P_{\text{H}_2}$ ), *p*-toluenesulfonic acid concentration ( $[p\text{-TSA}]$ ), and

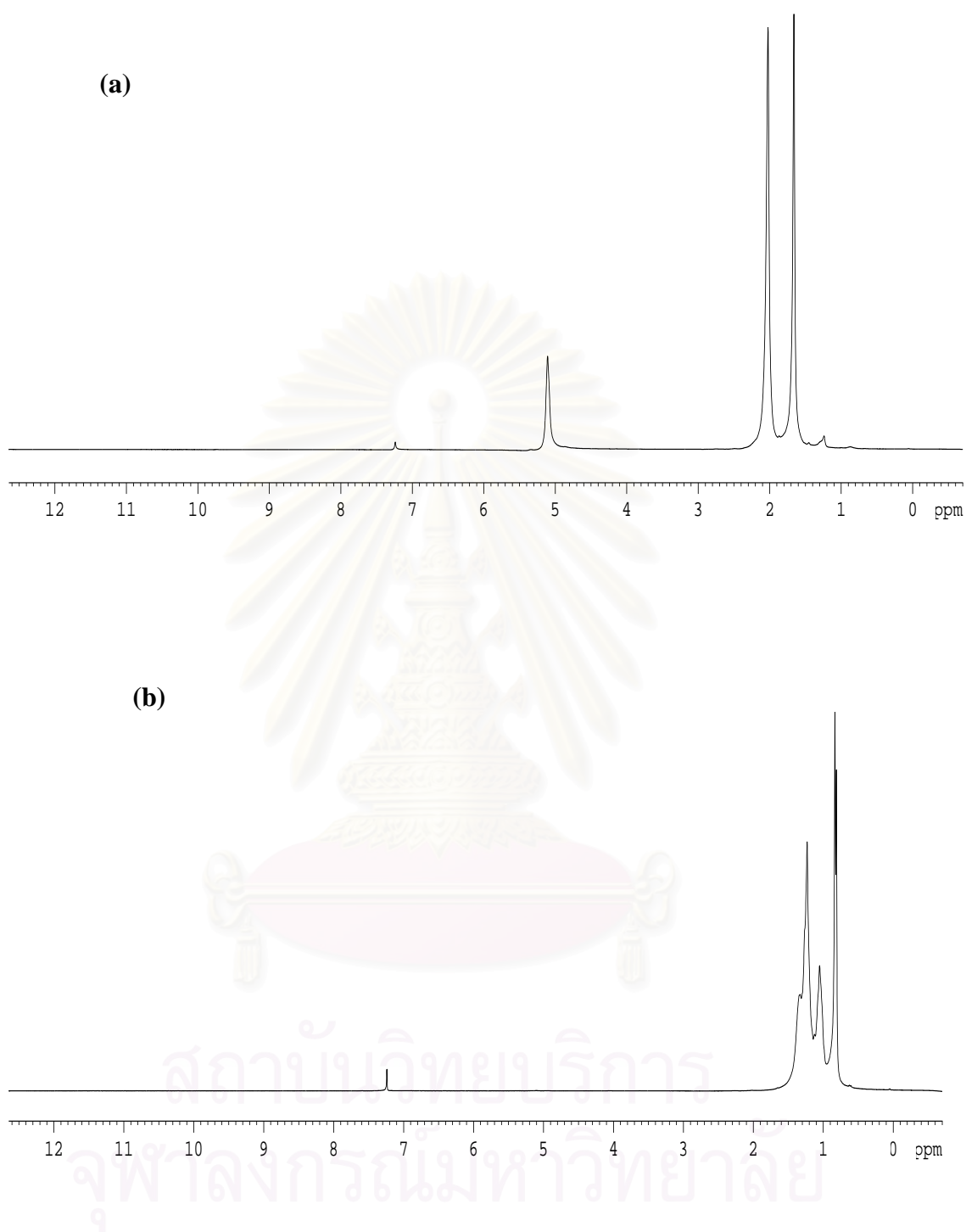
reaction temperature were studied using a two-level factorial design and univariate kinetic experiments. The results obtained were used to propose a catalytic mechanism. The effects of impurities present in the NRL system on the hydrogenation rate and the thermal properties of the hydrogenated natural rubber latex (HNRL) were also investigated

### 3.1 Structure Characterization Using FTIR and NMR Spectroscopy

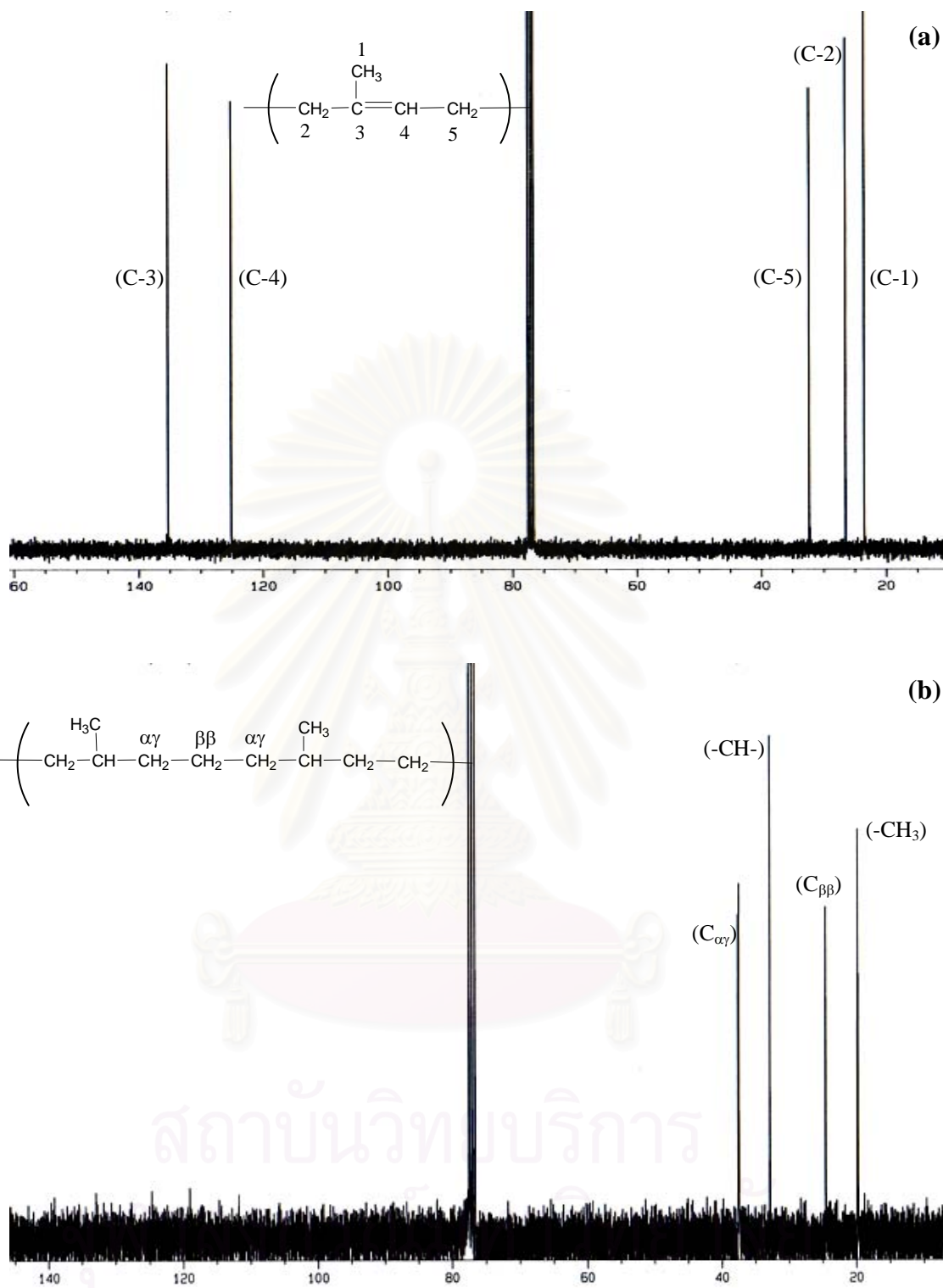
The FTIR spectrum of the starting natural rubber latex (NRL) and the hydrogenated natural rubber latex (HNRL) are shown in Figure 3.1a and 3.1b, respectively. The most apparent change in the FTIR spectra are the reduction in the bands at  $1660$  and  $837\text{ cm}^{-1}$  due to C=C stretching and olefinic bending. The augmentation in the band at  $735\text{ cm}^{-1}$  attributed to the  $-(\text{CH}_2)-$  species increases, as the extent of hydrogenation of C=C increases. FTIR spectra indicated that the transmittance at  $3280\text{ cm}^{-1}$  and  $1544\text{ cm}^{-1}$  which represents N-H stretching and  $>\text{N}-\text{C}=\text{O}$  amide II vibration (an impurity in NRL) (Aik-Hwee et al., 1992) remained unchanged. The final degree of hydrogenation was determined by  $^1\text{H-NMR}$ . A comparison between the  $^1\text{H-NMR}$  spectrum of NRL and HNRL are shown in Figure 3.2a and 3.2b respectively. The hydrogenation led to the reduction in the intensity of the peaks at 1.67, 2.03 and 5.14 ppm which are assigned to  $-\text{CH}_3$ ,  $-\text{CH}_2$ , and olefinic protons, respectively and the appearance of new peaks at 0.8 and 1.2 are attributed to saturated  $-\text{CH}_2$ ,  $-\text{CH}_3$  of the ethylene – propylene hydrogenation product. The actual degree of hydrogenation for each experiment could be calculated from the peak area at 5.1 ppm and the summation of peak areas between 0.8 and 2.0 ppm as described in Chapter 2 and Appendix B. Confirmation was obtained from  $^{13}\text{C-NMR}$  spectrum as shown in Figure 3.3a and 3.2b. The polymer product is a strictly alternating copolymer of ethylene propylene. The peak areas at 135.4 and 125.2 ppm decrease with an increase in the reduction of the olefinic carbons and four new peaks appear at 37.8, 33.1, 24.8 and 20.0 ppm which are attributed to  $\text{C}_\alpha$ ,  $-\text{CH}$ ,  $\text{C}_\beta$  and  $-\text{CH}_3$  carbons, respectively.



**Figure 3.1** FTIR spectra of (a) NRL and (b) HNRL catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ .



**Figure 3.2**  $^1\text{H-NMR}$  spectra of (a) NRL and (b) HNRL catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ .



**Figure 3.3**  $^{13}\text{C}$ -NMR spectra of (a) NRL and (b) HNRL catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ .



### 3.2 Hydrogenation Catalyzed by Various Catalysts

The catalytic hydrogenation results for NRL using various catalysts with and without acid in a batch reactor, are summarized in Table 3.1.  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$ ,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , and  $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$  were found to be effective for hydrogenation of NRL at 150 °C in monochlorobenzene with acid addition. However,  $\text{RhCl}(\text{PPh}_3)_3$  was not an effective catalyst for NRL hydrogenation, although, Singha et al. (1997) reported that 80% hydrogenation of natural rubber was achieved in 22 h. It is probable that the  $\text{RhCl}(\text{PPh}_3)_3$  formed an inactive complex species with an impurity in the NR latex. These results are consistent with those observed by Charmondusit et al. (2002) for the hydrogenation of synthetic *cis*-1,4- polyisoprene. Therefore,  $\text{OsHCl}(\text{O}_2)(\text{PCy}_3)_2$  was found to be the most effective catalyst for NRL hydrogenation. The rate of hydrogenation was faster than that using  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$  with acid and without acid. In the examples with added acid,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was capable of providing a hydrogenation level of > 90 % of C=C bonds of NRL in 3 h. It is obvious that acid addition played a key role in enhancing the NRL hydrogenation. The effect of acid will be discussed in more detail later.

**Table 3.1** Results of NRL Hydrogenation Catalyzed by Various Catalysts

EXP	Catalyst Type	[p-TSH] (mM)	Time (h)	% Conversion
1	$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$	-	6	25.5
2	$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$	7	3	95.8
3	$[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$	-	6	16.3
4	$[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$	7	3	67.5
5	$\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$	-	6	13.5
6	$\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$	7	3	59.4
7	$\text{RhCl}(\text{PPh}_3)_3$	-	6	5.2
8	$\text{RhCl}(\text{PPh}_3)_3$	7	3	10.0

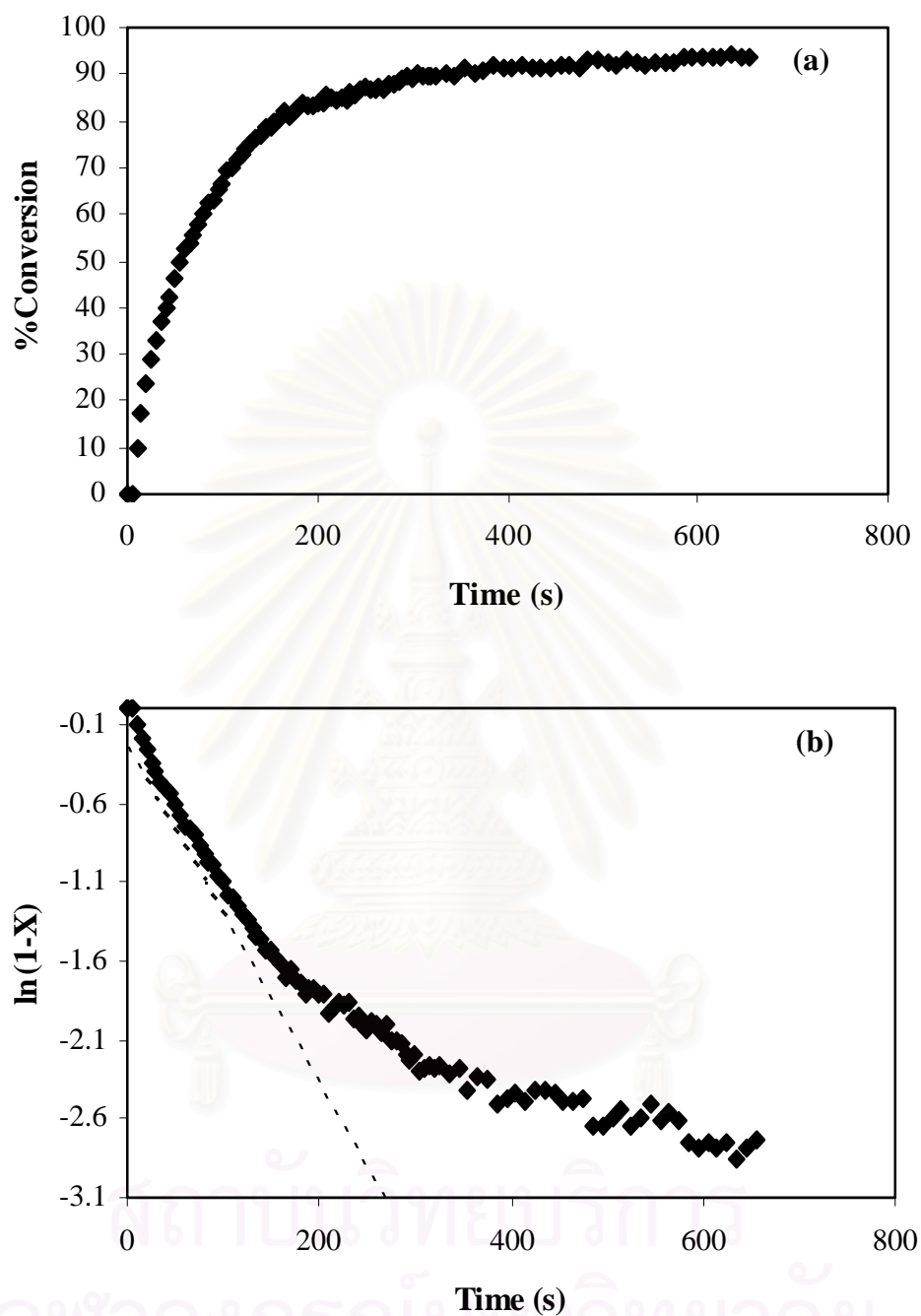
Condition: [Catalyst] = 145  $\mu\text{M}$ ,  $P_{\text{H}_2}$  = 27.6 bar, [C=C] = 180 mM, T = 150°C in Monochlorobenzene.

### 3.3 Kinetics of NRL Hydrogenation in the Presence of OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>

For all the kinetic studies of NRL hydrogenation, OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> functioned as an effective catalyst. The computer control gas uptake apparatus was used to investigate the rate dependence of reaction variables, such as polymer concentration, catalyst concentration, acid concentration, temperature, and hydrogen pressure. A representative hydrogen uptake profile corresponding to the olefin consumption with respect to time is shown in Figure 3.4. The hydrogen consumption plot exhibits an apparent first order dependence for hydrogenation of C=C concentration over the first 75% of the reaction. The first-order rate equation as shown in eq. 3.1 where k' is a pseudo first order rate constant represents the hydrogenation process.

$$\frac{-d[\text{H}_2]}{dt} = \frac{-d[\text{C}=\text{C}]}{dt} = k' [\text{C}=\text{C}] \quad (3.1)$$

Although the ln (1-x) versus time plot deviates from linearity in the latter stage of reaction, k' can still be calculated with a fair degree of confidence for the major part of the conversion. Impurities in the NRL were believed to cause a reduction in catalytic activity as the degree of hydrogenation increased and therefore the ln (1-x) versus time plot data deviates from the linear model.



**Figure 3.4** (a) Olefin conversion of NRL hydrogenation obtained from the gas uptake apparatus; (b)  $\ln(1-x)$  vs time plot (----- model from linear regression).  $[O_s] = 140 \mu\text{M}$ ;  $[C=C] = 150 \text{ mM}$ ;  $P_{H_2} = 6.9 \text{ bar}$ ;  $[p\text{-TSA}] = 9 \text{ mM}$  and  $T = 150^\circ\text{C}$  in monochlorobenzene.

### 3.4 Statistical Analysis Using Two-Level Factorial Design Experiments

To determine the significance of joint factor interactions, a two level factorial design was used (Morntgomery, 2001). Four principal factors, which were considered to have an effect on the NRL hydrogenation rate were concentration of rubber as present in terms of carbon-carbon double bond concentration, concentration of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , hydrogen pressure and concentration of p-toluenesulfonic acid. When a two-level factorial design was applied to calculate the effect of a parameter in the experiment, the level of the factor may be arbitrarily called “low (-)” and “high (+)”. The range of rubber concentration, catalyst concentration, hydrogen pressure and p-toluenesulfonic acid concentration were 150-300 mM, 120-170  $\mu\text{M}$ , 20.7-41.4 bar and 6-12 mM in monochlorobenzene, respectively. The reaction temperature was kept constant at 150  $^\circ\text{C}$ . In Table 3.2, the results for the factorial design experiments are presented. Yate’s algorithm was applied to investigate the main effects and interaction effects on the rate constant derived from the experiment (Mason, 1989). Tables 3.3 and 3.4 represent the results of Yate’s algorithm calculation and the calculation of effects and standard error of a  $2^4$  factorial experiment. The results in Table 3.3 indicated that [Os], [C=C], [p-TSA] and the interaction between [C=C] and [p-TSA] had a very strong influence on the hydrogenation rate whereas the effect of  $\text{P}_{\text{H}_2}$  and other interactions were moderate for the system. The [Os],  $\text{P}_{\text{H}_2}$  and [p-TSA] had a positive effect. This implies that the rate of hydrogenation increased with an increase in [Os],  $\text{P}_{\text{H}_2}$  and [p-TSA]. In contrast, [C=C] and interaction between [C=C] and [p-TSA] showed a large negative effect on the hydrogenation rate constant. It can be postulated that the impurities in NRL have an effect on hydrogenation rate. The other binary interactions, [Os]\*[C=C], [Os]\* $\text{P}_{\text{H}_2}$ , [Os]\*[p-TSA],  $\text{P}_{\text{H}_2}$ \*[C=C],  $\text{P}_{\text{H}_2}$ \*[p-TSA] also affected the hydrogenation rate but the three factor and four factor interactions were not highly significant.

**Table 3.2** Results from 2<sup>4</sup> Factorial Design Experiment for NRL Hydrogenation

EXP	[Os] ( $\mu\text{M}$ )	P <sub>H<sub>2</sub></sub> (bar)	[C=C] (mM)	[p-TSA] (mM)	k' x 10 <sup>3</sup> (s <sup>-1</sup> )
1	120	20.7	150	6	1.77
2	120	20.7	150	6	1.61
3	170	20.7	150	6	4.89
4	170	20.7	150	6	4.84
5	120	41.4	150	6	1.92
6	120	41.4	150	6	1.78
7	170	41.4	150	6	4.99
8	170	41.4	150	6	5.19
9	120	20.7	300	6	0.22
10	120	20.7	300	6	0.33
11	170	20.7	300	6	2.92
12	170	20.7	300	6	3.05
13	120	41.4	300	6	0.24
14	120	41.4	300	6	0.26
15	170	41.4	300	6	2.91
16	170	41.4	300	6	3.07
17	120	20.7	150	12	6.97
18	120	20.7	150	12	6.83
19	170	20.7	150	12	12.13
20	170	20.7	150	12	11.89
21	120	41.4	150	12	7.83
22	120	41.4	150	12	7.67
23	170	41.4	150	12	12.90
24	170	41.4	150	12	13.09
25	120	20.7	300	12	0.94
26	120	20.7	300	12	1.02
27	170	20.7	300	12	3.32
28	170	20.7	300	12	3.42
29	120	41.4	300	12	1.39
30	120	41.4	300	12	1.37
31	170	41.4	300	12	3.83
32	170	41.4	300	12	3.98

Conditions: T = 150°C in monochlorobenzene.



**Table 3.3** Yate's Algorithm Calculation of the 2<sup>4</sup> Factorial Experiment

EXP	[Os] ( $\mu\text{M}$ )	P <sub>H<sub>2</sub></sub> (bar)	[C=C] (mM)	[p-TSA] (mM)	k'average (s <sup>-1</sup> )	1	2	3	4	Divisor	Estimate	Identification
1	-	-	-	-	0.00169	0.00656	0.01349	0.02000	0.06928	16	0.004330	Average
2	+	-	-	-	0.00486	0.00694	0.00650	0.04928	0.02713	8	0.003391	[Os]
3	-	+	-	-	0.00185	0.00326	0.03965	0.01186	0.00312	8	0.000391	PH <sub>2</sub>
4	+	+	-	-	0.00509	0.00324	0.00963	0.01527	0.00035	8	0.000043	[Os]*PH <sub>2</sub>
5	-	-	+	-	0.00027	0.01891	0.00641	0.00036	-0.03702	8	-0.004627	[C=C]
6	+	-	+	-	0.00299	0.02074	0.00545	0.00276	-0.00640	8	-0.000800	[Os]*[C=C]
7	-	+	+	-	0.00025	0.00435	0.01035	0.00009	-0.00131	8	-0.000164	PH <sub>2</sub> *[C=C]
8	+	+	+	-	0.00299	0.00528	0.00492	0.00026	-0.00004	8	-0.000005	[Os]*PH <sub>2</sub> *[C=C]
9	-	-	-	+	0.0069	0.00317	0.00038	-0.00699	0.02929	8	0.003661	[p-TSA]
10	+	-	-	+	0.01201	0.00323	-0.00002	-0.03003	0.00341	8	0.000427	[Os]*[p-TSA]
11	-	+	-	+	0.00775	0.00271	0.00184	-0.00096	0.00240	8	0.000300	PH <sub>2</sub> *[p-TSA]
12	+	+	-	+	0.01299	0.00274	0.00093	-0.00544	0.00017	8	0.000022	[Os]*PH <sub>2</sub> *[p-TSA]
13	-	-	+	+	0.00098	0.00511	0.00006	-0.00040	-0.02303	8	-0.002879	[C=C]*[p-TSA]
14	+	-	+	+	0.00337	0.00524	0.00002	-0.00091	-0.00448	8	-0.000560	[Os]*[C=C]*[p-TSA]
15	-	+	+	+	0.00138	0.00239	0.00013	-0.00004	-0.00051	8	-0.000063	PH <sub>2</sub> *[C=C]*[p-TSA]
16	+	+	+	+	0.0039	0.00252	0.00013	0.00000	0.00004	8	0.000005	[Os]*PH <sub>2</sub> *[C=C]*[p-TSA]

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**Table 3.4** Calculation of Effects and Standard Errors for  $2^4$  Factorial Design Experiment

Effect	Estimate	±	Standard
Average	0.004330	±	3.54E-05
<b>Main Effect</b>			
Catalyst Concentration, [Os]	0.003391	±	1.77E-05
Hydrogen Pressure, $P_{H_2}$	0.000391	±	1.77E-05
Rubber Concentration, [C=C]	-0.004627	±	1.77E-05
Acid Concentration, [p-TSA]	0.003661	±	1.77E-05
<b>Two-Factor Interaction</b>			
[Os]* $P_{H_2}$	0.000043	±	1.77E-05
[Os]*[C=C]	-0.000800	±	1.77E-05
[Os]*[p-TSA]	0.000427	±	1.77E-05
$P_{H_2}$ *[C=C]	-0.000164	±	1.77E-05
$P_{H_2}$ *[p-TSA]	0.000300	±	1.77E-05
[C=C]*[p-TSA]	-0.002879	±	1.77E-05
<b>Three-Factor Interaction</b>			
[Os]* $P_{H_2}$ *[C=C]	-0.000005	±	1.77E-05
[Os]* $P_{H_2}$ *[p-TSA]	0.000022	±	1.77E-05
[Os]*[C=C]*[p-TSA]	-0.000560	±	1.77E-05
$P_{H_2}$ *[C=C]*[p-TSA]	-0.000063	±	1.77E-05
<b>Four-Factor Interaction</b>			
[Os]* $P_{H_2}$ *[C=C]*[p-TSA]	0.000005	±	1.77E-05

### 3.5 Univariate Kinetic Experiments

As mentioned above, factorial design is generally used to explore the effect of factors to study the main effect and joint effects of factors on the response. The factorial design established the significance of joint factor interaction without determining the functional form. The univariate components augment the factorial study by exploring how each variable influences the hydrogenation rate in isolation. The univariate experiment data are presented in Table 3.5.

**Table 3.5** Univariate Kinetic Data of NRL Hydrogenation Catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ 

Exp	[Os] ( $\mu\text{M}$ )	[C=C] (mM)	$P_{\text{H}_2}$ (bar)	Temp ( $^{\circ}\text{C}$ )	[p-TSH] (mM)	%Hydrogenation in 10 min	$k' \times 10^3$ ( $\text{s}^{-1}$ )	$\eta_{\text{rel}}$
1	30	150	27.6	150	9	20.0	0.35	6.32
2	60	150	27.6	150	9	57.8	2.84	6.48
3	80	150	27.6	150	9	70.8 (7.8 min)	4.09	7.63
4	100	150	27.6	150	9	85.5	5.46	8.77
5	140	150	27.6	150	9	95.8 (8min)	8.59	8.95
6	160	150	27.6	150	9	97.0	9.75	8.99
7	30	150	41.4	150	9	35.4	0.88	-
8	60	150	41.4	150	9	56.9	3.13	-
9	80	150	41.4	150	9	73.9	4.66	-
10	100	150	41.4	150	9	88.8	5.95	-
11	140	150	41.4	150	9	96.4 (8.9 min)	8.67	-
12	160	150	41.4	150	9	98.2	10.45	-
13	140	150	2.1	150	9	68.5	1.99	7.11
14	140	150	3.4	150	9	70.9	3.49	7.78
15	140	150	5.2	150	9	80.5	6.77	8.74
16	140	150	6.9	150	9	88.9	7.51	8.86
17	140	150	13.8	150	9	91.2	8.35	8.90
18	140	150	27.6	150	9	96.5	8.61	8.96
19	140	150	27.6	150	9	95.8	8.60	8.96
20	140	150	27.6	150	9	96.9	8.61	-
21	140	150	27.6	150	9	96.8 (8.5min)	8.60	-
22	140	150	41.4	150	9	97.6	8.65	9.00
23	140	150	41.4	150	9	97.7	8.70	-
24	140	65	27.6	150	9	99.1 (7 min)	14.50	5.25
25	140	100	27.6	150	9	98.8 (8.3min)	12.50	6.41
26	140	150	27.6	150	9	95.4 (9.2 min)	8.60	8.95
27	140	150	27.6	150	9	95.5 (8.9 min)	8.60	-
28	140	150	27.6	150	9	96.0	8.61	-
29	140	200	27.6	150	9	77.8	4.06	7.65
30	140	250	27.6	150	9	40.3	1.25	6.48
31	140	400	27.6	150	9	15.4	0.58	6.32
32	140	150	27.6	150	0.0	4.4	0.10	4.80
33	140	150	27.6	150	0.4	10.5	0.25	5.10
34	140	150	27.6	150	2.1	14.7	0.30	5.20
35	140	150	27.6	150	6.0	40.0	1.42	6.48
36	140	150	27.6	150	9.0	97.3 (7.8 min)	8.62	8.96
37	140	150	27.6	150	9.0	95.5	8.60	-
38	140	150	27.6	150	9.0	96.8	8.61	-
39	140	150	27.6	150	11.8	97.7	9.94	5.46
40	140	150	27.6	150	19.8	86.6	6.05	4.82
41	140	150	27.6	150	27.7	85.3	5.49	4.76
42	140	150	27.6	120	9	54.0	2.12	-
43	140	150	27.6	130	9	73.0	3.78	-
44	140	150	27.6	140	9	84.8	6.21	-
45	140	150	27.6	150	9	95.5	8.65	-
46	140	150	27.6	160	9	99.2	10.7	-

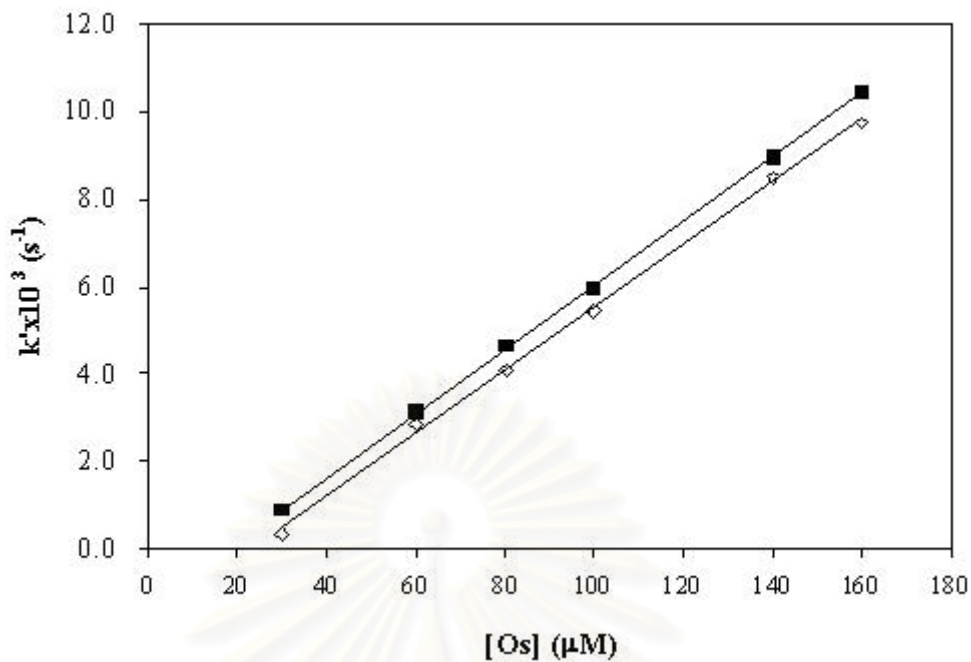
Solvent = Monochlorobezene; Relative viscosity of NRL, NR in toluene ( $\eta_{\text{rel}}$ ) = 4.55, 7.52.

### 3.5.1 Dependence on Catalyst Concentration

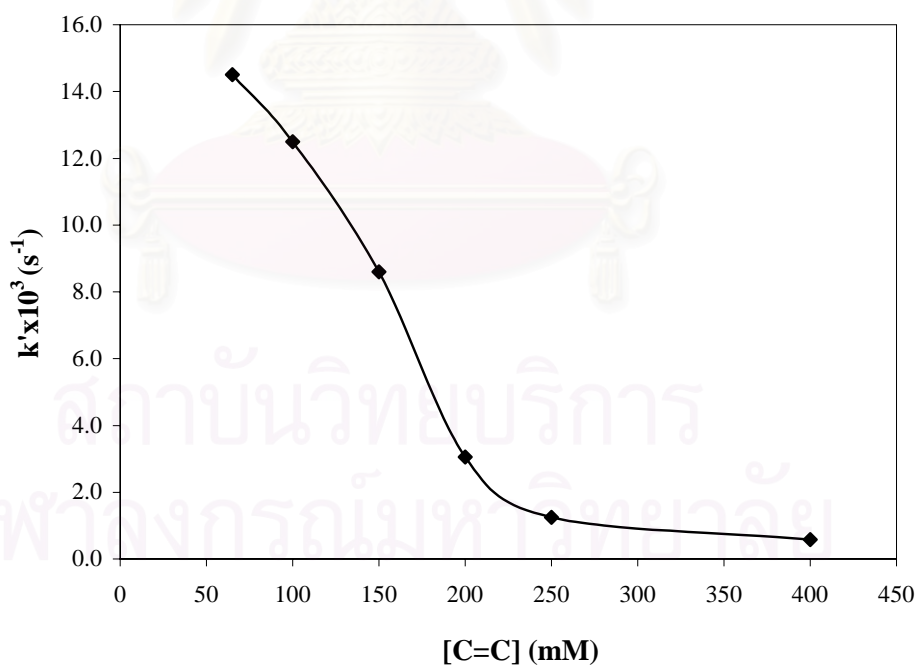
Two sets of experiments were performed to determine the effect of catalyst loading on the rate of hydrogenation. The two sets were carried out under a hydrogen pressure of 27.6 bar and 44.1 bar, respectively. The range of [Os] was between 30 and 160  $\mu\text{M}$ , with  $[\text{C}=\text{C}] = 150 \text{ mM}$ , and  $[\text{p-TSA}] = 9 \text{ mM}$  at  $150^\circ\text{C}$  in monochlorobenzene. The influence of catalyst concentration on the reaction system is illustrated in Figure 3.5. It can be seen that the reaction rate is linearly proportional to the total catalyst concentration at every hydrogen pressure investigated. This indicated that the active species is linearly proportional to catalyst precursor loading. This observation is consistent with the work of Andriollo et al. (1989) It is seen that NRL hydrogenation had a first order dependence with respect to catalyst concentration. It suggested that this catalyst is a mononuclear active complex. On comparing the present data with that obtained by Charmondusit et al. (2003) for hydrogenation of *cis*-1,4- poly isoprene and Parent et al. (1998) for hydrogenation of NBR, the dependence on catalyst concentration is similar. The plots of NRL hydrogenation show an intercept on the x-axis. This suggests that in the NRL some portion of the osmium complex reacts with impurities in the NRL and is therefore inactive.

### 3.5.2 Dependence on Rubber Concentration

A series of experiments was carried out at varying polymer concentration to examine the effect of rubber concentration. The rubber concentration used ranged from 65-400 mM when catalyst concentration (140  $\mu\text{M}$ ), reaction temperature ( $150^\circ\text{C}$ ), hydrogen pressure (27.6 bar) and p-toulenesulfonic acid (9 mM) were kept constant. The results of these experiments are shown in Figure 3.6. The results obtained indicated that the reaction rate decreased with an increase in rubber concentration. In contrast, the hydrogenation rate of PIP is constant when the rubber concentration is increased which is as expected for systems showing a strict first order behavior (Lu et al., 1987). For NBR, a decreasing rate of hydrogenation with an increase in rubber concentration was observed. The nitrile functional group in NBR is known to reversibly coordinate to  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  as the nitrogen lone pair of electrons binds to the metal center (Parent et al., 1998).



**Figure 3.5** Effect of catalyst concentration on the rate of NRL hydrogenation. [C=C] = 150 mM; P<sub>H<sub>2</sub></sub> = 27.6 (◇) and 41.4 (■) bar; [p-TSA] = 9 mM; T = 150°C in monochlorobenzene (MCB).



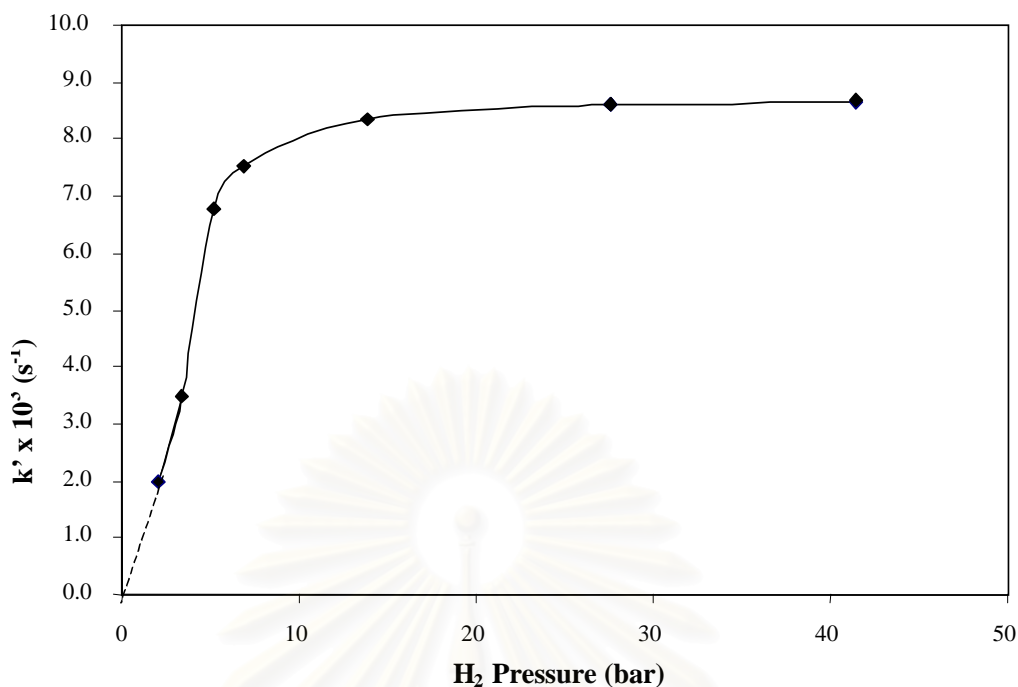
**Figure 3.6** Effect of rubber concentration on the rate of NRL hydrogenation. [Os] = 140 μM; P<sub>H<sub>2</sub></sub> = 27.6 bar; [p-TSA] = 9 mM; T = 150°C in MCB.



This behavior has also been observed for NBR hydrogenation catalyzed by  $[\text{Rh}(\text{diene})(\text{NBD}_2)]^+$  (Mao and Rempel, 1998),  $\text{RhCl}(\text{PPh}_3)_3$  (Parent et al., 1996),  $\text{RhH}(\text{PPh}_3)_4$  (Parent et al., 1996) and  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$  (Matin et al., 1997). The reduction in the NRL hydrogenation rate can be explained by the effect of impurities in the latex. It is generally believed that impurities such as protein in the rubber latex might compete with the olefin for metal coordination sites to form inactive complexes. The effect of impurities is reported in a later section of this chapter.

### 3.5.3 Dependence on Hydrogen Pressure

To investigate the effect of hydrogen pressure, a series of experiments in which the hydrogen pressure was varied over the range 2.1 – 41.4 bar at 150°C in monochlorobenzene was carried out. The concentration of catalyst and rubber were kept constant at 140  $\mu\text{M}$  and 150 mM, respectively. The results shown in Figure 3.7 suggest that the rate of NRL hydrogenation maybe second order to first order with respect to the hydrogen pressure from 2.1 to 6.9 bar and then shifts to a zero order dependence at a pressure higher than 13.8 bar. It might be due to the formation of dihydrogen ligand for active form of catalyst which observed at low hydrogen pressure (Parent et al, 1998, Mao and Rempel, 2000). These results are in agreement with those for NBR and PIP hydrogenation in the presence of the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst system, whereas NBR hydrogenation using the rhodium complex,  $\text{RhCl}(\text{PPh}_3)_3$  is found to shift from a first order to zero order behavior with increasing hydrogen pressure. In the case of NBR hydrogenation in the presence of the ruthenium complex,  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$ , strictly first order behavior is maintained (Matin et al, 1997) irrespective of the hydrogen pressure used.



**Figure 3.7** Effect of hydrogen pressure on the rate of NRL hydrogenation. [Os] = 140  $\mu$ M; [C=C] = 150 mM; [p-TSA] = 9 mM; T = 150°C in MCB.

### 3.5.4 Effect of Acid Concentration

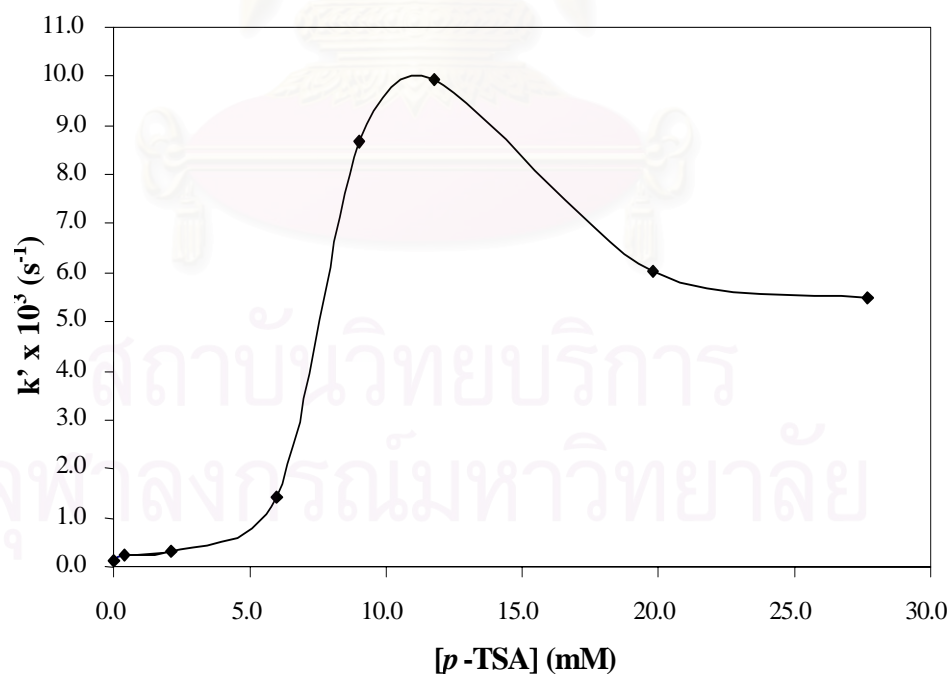
Guo and Rempel (1997) established that carboxylic acid enhanced the catalytic activity of  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$  in the hydrogenation of NBR emulsions. It was suggested that carboxylic acids were very effective in preventing the poisoning of the catalyst. Guo and Rempel (1997) also found that the addition of acid increased the catalytic activity due to the selective entrapment of the dissociated phosphine ligand and the formation of a 14-electron ruthenium-mono species in alkene hydrogenation by  $\text{RuHCl}(\text{CO})(\text{PCy}_3)_2$ . The effect of the acid type was also studied. In this investigation, experiments were carried out at a catalyst concentration of 140  $\mu$ M, rubber concentration of 150 mM, acid concentration of 9 mM, hydrogen pressure of 27.6 bar and temperature of 150 °C in monochlorobenzene. Table 3.6 shows the effect of the acid type. It was found that p-TSA addition led to the highest hydrogenation rate. It is believed that the strong acid increases the hydrogenation rate more than the weaker acids. Also p-TSA is non-coordinating with respect to the osmium complex. The strong acid likely reacts with impurities in the NRL more efficiently than the weaker acid, and therefore the rate of hydrogenation was

increased. From Figure 3.8, it is seen that the rate of hydrogenation increased with increasing acid concentration from 0.03 to 9 mM, then diminished and leveled off at acid concentrations above 9.5 mM.

**Table 3.6** Effect of Acid Types on NRL Hydrogenation Rate

Acid Type	$k' \times 10^3$ (s <sup>-1</sup> )
p-TSA	8.69
3-CPA	7.89
Citric acid	6.77
Succinic acid	6.02
Stearic acid	1.57
-	0.1

Condition: [Os] = 140  $\mu$ M,  $P_{H_2}$  = 27.6 bar, [C=C] = 150 mM, [Acid] = 9 mM at 150<sup>o</sup>C in MCB  
(p-TSA = p-toluenesulfonic acid, 3-CPA = 3-chloropropionic acid).



**Figure 3.8** Effect of acid concentration on the rate of NRL hydrogenation. [Os] = 140  $\mu$ M;  $P_{H_2}$  = 27.6 bar; [C=C] = 150 mM; T = 150<sup>o</sup>C in MCB.

For NRL hydrogenation, it is possible that the acid neutralized the impurity in the NRL and prevented the poisoning of the catalyst. Consequently, the hydrogenation rate was increased. The hydrogenation rate slowly increased over the range of 0.02 to 6 mM. It seems that NRL needs some portion of the acid to react with some main impurities in the system such as ammonia or perhaps the protein. Over the range of 6.0 to 9 mM added acid, the hydrogenation rate was drastically increased. However, at above 10.5 mM added acid, the hydrogenation rate decreased. It is quite likely that at higher acid concentration, free excess p-TSA which does not interact with any further impurities could reduce the hydrogenation rate. There are two possible ways to explain this result. The first maybe due to the fact that p-TSA easily dissociates to  $\text{SO}_4^{2-}$  which may decrease the efficiency of the catalyst by forming an inactive catalyst species. The other reason may possibly result from the residual p-TSA after neutralization of the impurity in NRL may be involved in side reactions such as polymerization, isomerization, or a crosslinking reaction. Consequently, at a acid concentrations above 10.5 mM, the hydrogenation rate may decrease. All side reactions may be competitive with the hydrogenation reaction. Moreover, the dried hydrogenated product at a high acid level was observed to form gel when dissolved in toluene. This implies that crosslinking reactions occurred during the reaction when the added acid concentration was at a high level.

To gain more insight into the effect of added acid on the hydrogenation of NRL, *cis*-1,4- polyisoprene and hexylamine were used. These results are presented in Table 3.7. It was found that the addition of the acid decreased the PIP hydrogenation rate. It is possible that the formation between the complex and  $\text{SO}_4^{2-}$  resulting from the dissociation of p-TSA and other side reactions occurred. Furthermore in the case of *cis*-1,4- polyisoprene, the addition of hexylamine and acid resulted in a higher hydrogenation rate compared to a reaction in which only hexylamine was added. Thus, it definitely appears that the role of the added acid in the NRL hydrogenation was to neutralize impurities in the rubber.

**Table 3.7** Effect of Acid Addition on Hydrogenation Rate of Synthetic *Cis*-1, 4-Polyisoprene (PIP)

[p-TSA] (mM)	[Hexylamine] (mM)	$k' \times 10^3$ (s <sup>-1</sup> )
-	-	7.05
-	1.28	0.97
9	-	2.85
9	1.28	3.74

Condition: [Os] = 140  $\mu$ M,  $P_{H_2}$  = 27.6 bar, [C=C] = 150 mM and T = 150  $^{\circ}$ C in MCB.

### 3.5.5 Effect of Impurity

As mentioned before, the effect of impurities was suspected to reduce the hydrogenation rate. To confirm these ideas, the hydrogenation of deproteinized NRL was examined. The deproteinized rubber was prepared according to the literature method (Tangpakdee and Tanaka, 1997). The experiments were carried out at a catalyst concentration of 140  $\mu$ M, rubber concentration of 150 mM, a p-TSA concentration of 9 mM, a hydrogen pressure of 27.6 bar and a temperature of 150  $^{\circ}$ C. Table 3.8 shows the effect of the impurity. The rate constant measured for the hydrogenation of deproteinized NRL has an appreciably higher rate constant than that of virgin NRL. It was established that the protein content in rubber caused a decrease in activity of the OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub> catalyst. It is possible that the nitrogen group in the protein can coordinate with the active catalyst species in much the same way as the -CN group in NBR as reported in previous work (Parent et al., 1998). To clarify this idea for the effect of the impurity, an experiment was set up using *cis*-1,4-polyisoprene (CPIP) as an analogue of NRL in terms of rubber microstructure. Hexylamine and hexadecylamide which have a nitrogen functional group similar to those of the proteins present in NRL were added in the CPIP hydrogenation to test if the effect would be similar to the protein effect on hydrogenation rate of NRL. The effect of high ammonia content in the latex was also investigated to see if it had an influence on hydrogenation rate. Table 3.9 shows the effect of nitrogen containing additives in the rubber. The reaction conditions were: [C=C] = 150 mM, [Os] = 40

$\mu\text{M}$ ,  $P_{\text{H}_2} = 27.6$  bar and  $T = 150$  °C in monochlorobenzene. It was found that all compounds with nitrogen functional groups reduced the rate constants for hydrogenation of CPIP. Hexylamine and ammonia have an amine group, which is an electron donating species, which can coordinate easily with osmium. For hexadecylacrylamide, the lone pair of electrons of the nitrogen atom can be delocalized between nitrogen and  $-\text{C}=\text{O}$ ; therefore, hexadecylacrylamide does not easily form a complex with osmium. However, the effect seen from the hexadecylacrylamide is in line with that of hexylamine and ammonia.

**Table 3.8** Effect of Impurity on Hydrogenation Rate of Synthetic *Cis*-1,4-Polyisoprene

Substance	$k' \times 10^3$ ( $\text{s}^{-1}$ )
-	7.03
hexylamine	0.98
hexadecylacrylamide	1.24
ammonium hydroxide	1.02

Condition:  $[\text{Os}] = 140$   $\mu\text{M}$ ,  $P_{\text{H}_2} = 27.6$  bar,  $[\text{C}=\text{C}] = 150$  mM and  $T = 150$  °C in MCB.

**Table 3.9** Effect of Nitrogen Content on NRL Hydrogenation Rate

Rubber Type	% Nitrogen Content	$k' \times 10^2$ ( $\text{s}^{-1}$ )
NRL	0.20	0.86
DPNRL	0.02	1.23

Condition:  $[\text{Os}] = 140$   $\mu\text{M}$ ,  $P_{\text{H}_2} = 27.6$  bar,  $[\text{C}=\text{C}] = 150$  mM,  $[\text{p-TSA}] = 9$  mM and  $T = 150$  °C in MCB.



### 3.5.6 Effect of Water Addition

High ammonia natural rubber latex contains 40% water by weight. The rubber particles disperse in water to form an emulsion. Water present in the latex may also possibly reduce the hydrogenation rate of NRL when using the osmium catalyst. Experiments were carried out in which various amounts of water were present in the natural rubber latex in terms of % dry rubber content (DRC) at the base condition ( $[Os] = 140 \mu M$ ,  $P_{H_2} = 27.6 \text{ bar}$ ,  $[C=C] = 150 \text{ mM}$ ,  $[p-TSA] = 9 \text{ mM}$  and  $T = 150 \text{ }^\circ\text{C}$ ). % DRC is the percent of dry rubber content in the natural rubber latex. The range of DRC in this study was between 30 and 60% by weight, corresponding to 70-40% water by weight, respectively. The effect of water content within the NRL on the hydrogenation rate is summarized in Table 3.10. It was found that the rate constant decreased when the amount of water was increased (decrease % DRC). There are some possible explanations for this. The first idea is that the addition of water may induce more impurities in the system by promoting the release of some additional protein part in the rubber particles. The more soluble protein part may form a complex with the catalyst. The second idea is based on the premise that the water may act as an inhibitor in this system to hinder the formation of the catalytic active species. In order to gain more insight about the effect of water on the NRL system, *cis*-1,4-polyisoprene was used as a model. Table 3.10 shows that a lower rate constant was found at 30% DRC in the presence of added water. These results suggest that water acted as an inhibitor to hydrogenation in this system. Thus the presence of water seems to be detrimental to the performance of the Os catalyst.

**Table 3.10** Effect of Dry Rubber Content on NRL and *Cis*-1,4- Polyisoprene Hydrogenation Rate

Rubber Type	DRC %	k'x10 <sup>3</sup> (s <sup>-1</sup> )
NR	60	8.63
	50	6.16
	40	4.62
	30	3.06
<i>Cis</i> -1,4- Polyisoprene	-	7.04
	60	5.00
	50	5.98
	40	4.49
	30	3.79

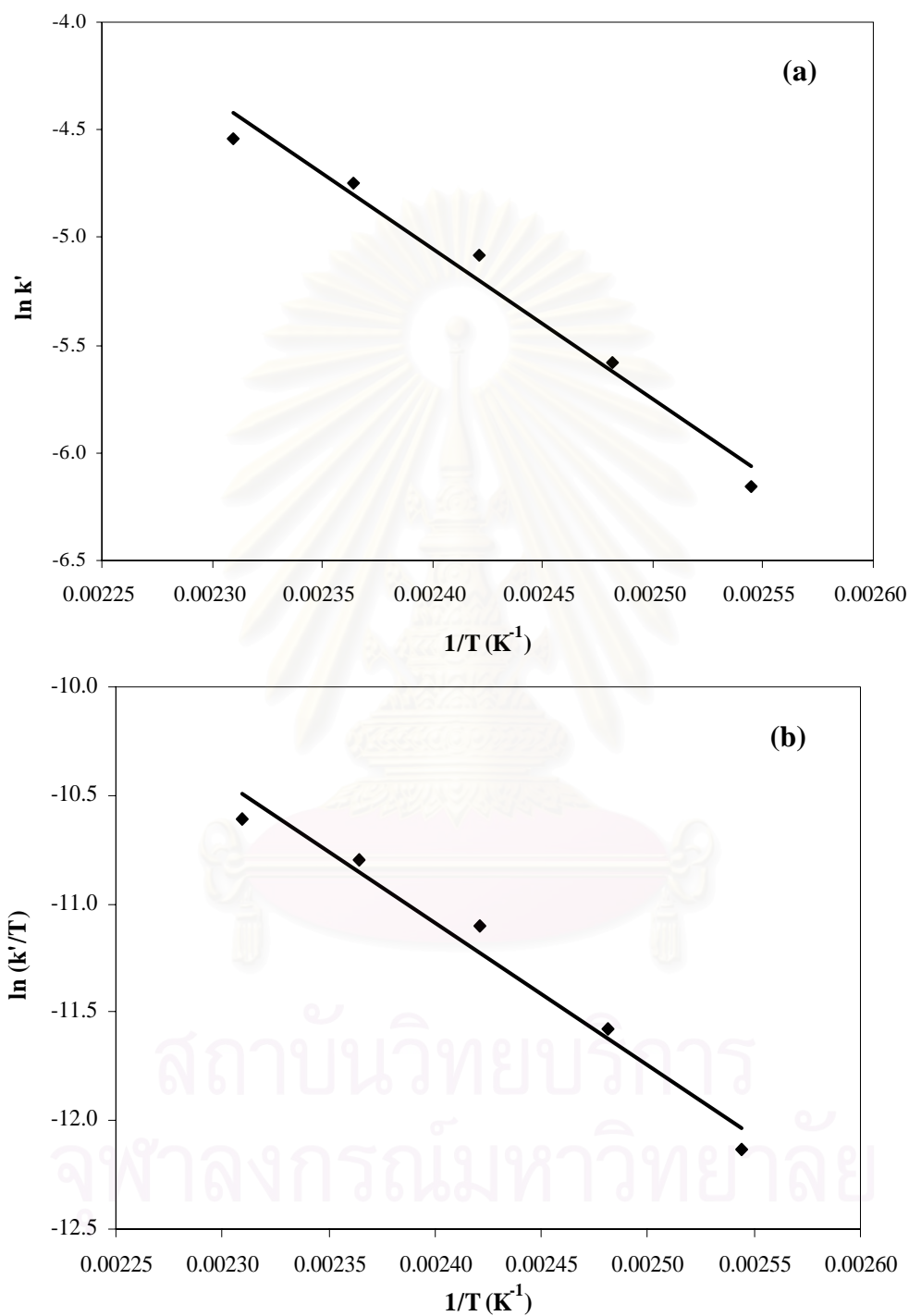
Condition: [Os] = 140 μM, P<sub>H<sub>2</sub></sub> = 27.6 bar, [C=C] = 150 mM, [p-TSA] = 9 mM and T = 150 °C in MCB.

### 3.5.7 Dependence on Reaction Temperature

A series of experiments were carried out over the temperature range of 120-160°C with a catalyst concentration of 140 μM, natural latex rubber concentration of 150 mM, p-TSA concentration of 9 mM and a hydrogen pressure of 27.6 bar. An Arrhenius plot of the acquired data is illustrated in Figure 3.9a. The ln k' versus 1/T plot was linear and yielded a correlation coefficient (R<sup>2</sup>) of 0.98 and a random distribution of residuals. An apparent activation energy of 57.80 kJ/mol was obtained which suggests that the experiments occurred under chemical reaction control and that mass transfer limitation of the reaction is not a rate determining step under the reaction conditions, employed in this study. Based on the corresponding Eyring equation (eq. 3.2 cited in Tangthongkul, 2003), the apparent activation enthalpy and entropy were estimated as 54.4 kJ/mol and -159.2 J/mol K, respectively as shown in Figure 3.9b.

$$k = \frac{k_B T}{h} e^{\frac{-\Delta H^\ddagger}{RT}} e^{\frac{\Delta S^\ddagger}{R}} \quad (3.2)$$

where  $k_B$  is Boltzmann's constant ( $1.381 \times 10^{-23}$  J/K) and  $h$  is Planck constant ( $6.626 \times 10^{-34}$  J/s).



**Figure 3.9** (a) Arrhenius plots and (b) Eyring plot for NRL hydrogenation.  $[Os] = 140 \mu M$ ;  $[C=C] = 150$  mM;  $[p-TSA] = 9$  mM;  $P_{H_2} = 27.6$  bar and  $T = 120$ - $160^\circ C$ .

### 3.5.8 Dependence on Solvents

Several solvents other than chlorobenzene were investigated for NRL hydrogenation at a catalyst concentration of 140  $\mu\text{M}$ , natural rubber concentration of 150 mM, p-TSA concentration of 9 mM, hydrogen pressure of 27.6 bar and at a reaction temperature of 150  $^{\circ}\text{C}$ . When natural rubber latex was added to organic solvents, the rubber particles swelled and an increase in viscosity resulted. The water soluble impurities were believed to be dispersed in the matrix between the rubber particles. Solvents are believed to reduce the interphase between the hydrophobic (organic phase) and hydrophilic (aqueous phase) zone in the rubber particle. The rubber can move to the surface of organic phase so that the hydrogenation reaction can take place. Table 3.11 lists the pseudo first order rate constant for NRL hydrogenation at the base condition. Since the solubility of hydrogen in each solvent was not known, the solvent effect contains several factors: the difference in hydrogen solubility, the homogeneity or inhomogeneity between the solvent and the latex rubber and the actual effect of the solvent on the reaction parameters. Thus, few useful conclusions can be drawn from the solvent dependence. However, from the data, it seems that for a solvent within has stronger polarity a better rate of hydrogenation and higher conversion will result. The hydrogenation rate was higher in a solvent which has sufficient coordinating power to replace the tricyclohexylphosphine ligand in the catalytic cycle of the hydrogenation process. However, its coordination power should not be too strong as to cause the displacement of coordinated alkenes. Solvents in the ketone series such as methyl ethyl ketone (MEK) and butanone were not tried because  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  is not an active hydrogenation catalyst in these solvents (Parent et al., 1998). MEK is also a poor solvent, for NRL and PIP.

The solvent experiments showed that the rate of reaction increased with increasing coordinating power of the solvents in the order: tetrahydrofuran > chlorobenzene > toluene > benzene > *p*-xylene. Low polarity solvents only swelled the rubber particle. The compatibility between the polymer particle and the solvent is one of reasons that the hydrogenation rate decreases when the polarity of the solvent decreases. In such case, the strong polarity such as provided by tetrahydrofuran (THF) may assist in helping the rubbers particle to dissolve in solution. When the rubber can

be dissolved in solution, the rubber can be more easily reacted with the catalyst in solution so as to provide a higher hydrogenation rate.

**Table 3.11** Effect of Solvent on the NRL Hydrogenation Rate

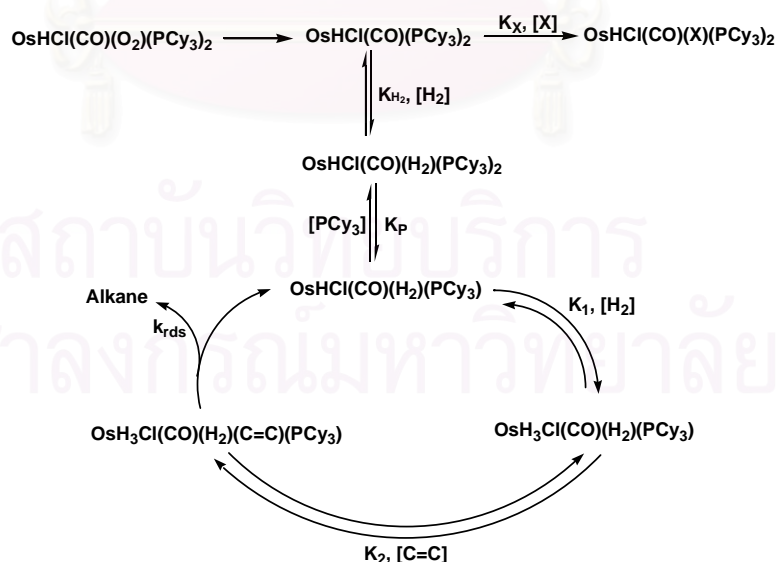
Solvent	$k \times 10^2$ ( $s^{-1}$ )
Tetrahydrofuran	1.49
Monochlorobenzene	0.85
Toluene	0.74
Xylene	0.16

Condition:  $[Os] = 140 \mu M$ ,  $[C=C] = 150 mM$ ,  $[p-TSA] = 9 mM$  and  $P_{H_2} = 27.6 bar$

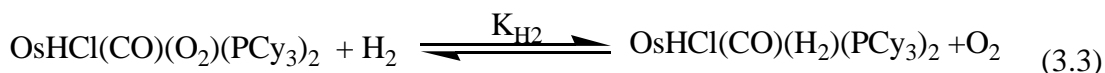
$T = 150^\circ C$ .

### 3.6 Mechanistic Interpretation of Kinetic Data

The catalytic cycle of diene polymer hydrogenation in the presence of  $OsHCl(CO)(O_2)(PCy_3)_2$  has been proposed in previous investigations; PIP and NBR hydrogenation. From the kinetic data, the catalytic cycle for  $OsHCl(CO)(O_2)(PCy_3)_2$  catalyzed hydrogenation of NRL is shown in Figure 3.10. The  $OsHCl(CO)(O_2)(PCy_3)_2$  oxidatively adds molecular hydrogen to form the trihydrido metal complex  $OsHCl(CO)(H_2)(PCy_3)_2$ , as shown by eq. 3.3.



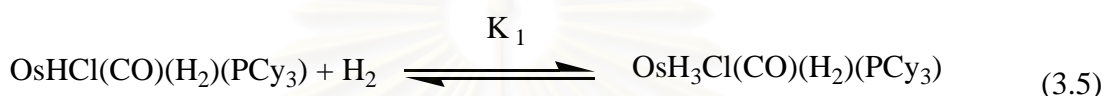
**Figure 3.10** Proposed catalytic mechanism for NRL hydrogenation in presence of  $OsHCl(CO)(O_2)(PCy_3)_2$ . (X = impurity)



The trihydrido complex subsequently dissociates into a monophosphine complex, as shown by eq. 3.4.



The monophosphine complex oxidatively adds a second hydrogen molecule to form  $\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)$  and then interacts with the carbon-carbon double bonds of the natural rubber to form an olefin complex, as shown by eq. 3.5 and 3.6, respectively.



The behavior of impurities and water (X) in natural rubber latex on hydrogenation were similar to that seen for the effect of the nitrile functional group in NBR hydrogenation which can decrease the catalytic activity for the NBR hydrogenation at lower hydrogen pressure. It is possible that impurities in NRL might coordinate with the active species of catalyst to reduce the hydrogenation activity as shown in eq. 3.7



where X represents an impurity.

Parent et al. (1996) proposed that the dihydrogen ligand of  $\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)_2$  does not add oxidatively to the metal in such a manner as to permit either the insertion of olefin or the elimination of an alkyl ligand. While the  $\eta^2\text{-H}_2$  ligand may indeed participate in olefin hydrogenation, it is proposed that it cannot do so in the absence of a second molecule of hydrogen. This unconventional assumption is required to account for the second-order behavior observed for NBR hydrogenation at lower hydrogen pressure. Consequently, a mechanism containing a single rate-determining step cannot be derived without this step.



The observed kinetic isotope effect observed by Parent et al. (1996) implies cleavage of a bond to hydrogen in the rate-limiting reaction. This could result from the insertion of olefin into an Os-H bond or by reductive elimination of an osmium-alkyl to yield the saturated product. The proposed mechanism does not discriminate between these possibilities. Rather, it assumes one of these processes is rapid relative to its rate-determining counterpart. Accordingly, olefin hydrogenation could be governed by the rate expression:

$$\frac{-d[\text{C}=\text{C}]}{dt} = k_{\text{rds}} [\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)(\text{C}=\text{C})] \quad (3.8)$$

A material balance on the osmium charged to the system is given by eq. 3.9.

$$[\text{Os}]_{\text{T}} = [\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)(\text{C}=\text{C})] + [\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{PCy}_3)] + [\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)] \\ + [\text{OsHCl}(\text{CO})(\text{H}_2)(\text{PCy}_3)_2] + [\text{OsHCl}(\text{CO})(\text{PCy}_3)_2] + [\text{OsHCl}(\text{CO})(\text{X})(\text{PCy}_3)_2] \quad (3.9)$$

Applying the equilibrium relations defined in Figure 3.10, the concentration of  $\text{OsH}_3\text{Cl}(\text{CO})(\text{H}_2)(\text{C}=\text{C})(\text{PCy}_3)$  may be substituted into eq. 3.8 to provide the resulting rate law, as shown by eq. 3.10.

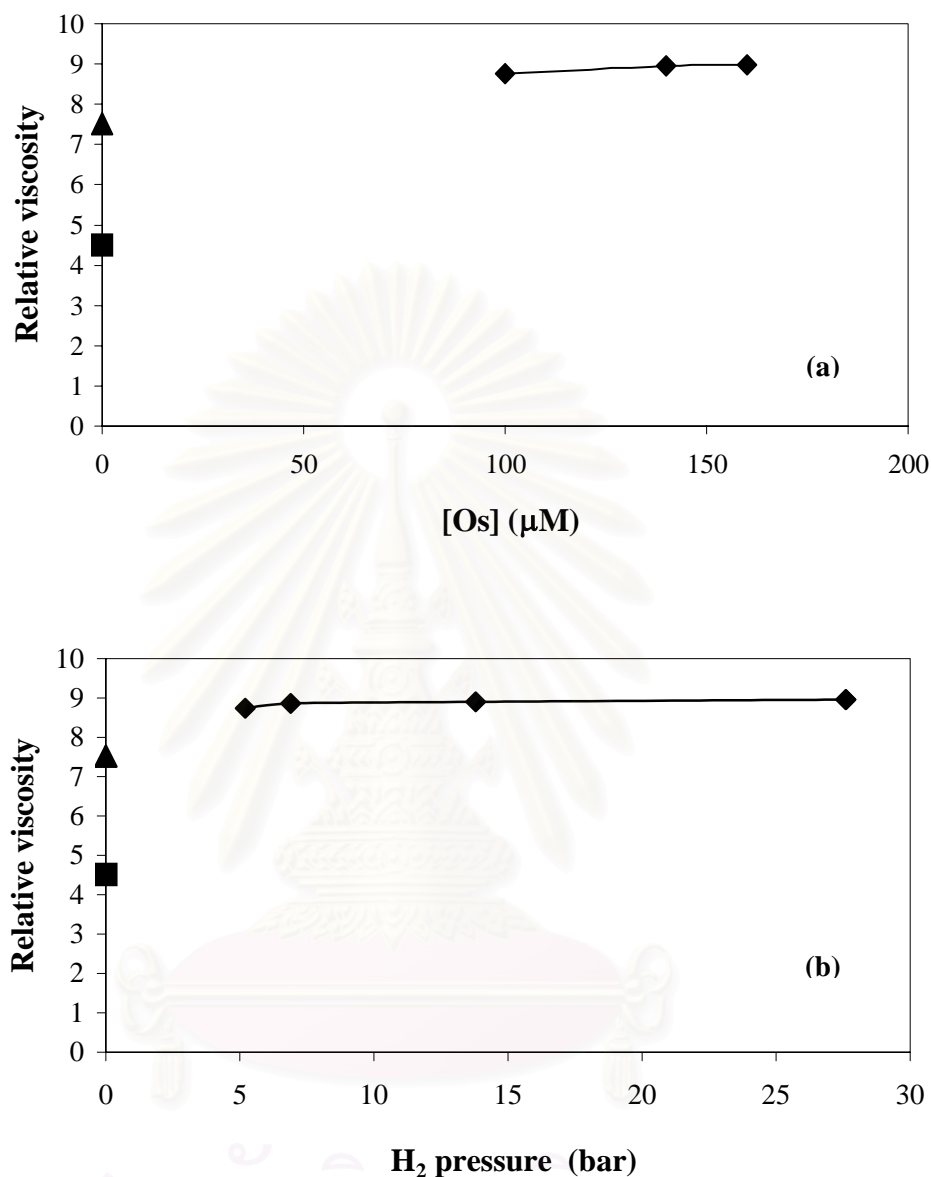
$$\frac{-d[\text{C}=\text{C}]}{dt} = \frac{k_{\text{rds}} [\text{Os}]_{\text{T}} K_{\text{H}_2} K_{\text{p}} K_1 K_2 [\text{C}=\text{C}] [\text{H}_2]^2}{[\text{PCy}_3] + K_{\text{H}_2} [\text{PCy}_3] [\text{H}_2]^2 + K_{\text{X}} [\text{PCy}_3] [\text{X}] + K_{\text{H}_2} K_{\text{p}} [\text{H}_2] + K_{\text{H}_2} K_{\text{p}} K_1 [\text{H}_2]^2 (1 + K_2 [\text{C}=\text{C}])} \quad (3.10)$$

The rate expression derived from the mechanism is consistent with the observed kinetic data. The rate law equation for NRL hydrogenation indicates that the reaction exhibits a first-order dependence on catalyst concentration and exhibits an inverse order behavior with respect to the rubber concentration due to impurities present in the natural rubber latex and the amount of water in the system. At a hydrogen pressure lower than 6.9 bar, second-order response of  $k'$  to hydrogen pressure was observed. The reaction rate however becomes zero order in hydrogen when the hydrogen pressure is more than 13.9 bar.

### 3.7 Relative Viscosity of Hydrogenated Natural Rubber

Although FTIR or NMR spectroscopy are capable of detecting the level of hydrogenation, these techniques are not sensitive enough to investigate side reactions such as degradation and crosslinking during the hydrogenation reaction. Dilute solution viscometry is used to monitor the changes of molecular weight. To investigate side reactions such as degradation and crosslinking during the hydrogenation reactions, dilute solution viscometry can be used to monitor the shifts of molecular weight which is related to the morphology and microstructure of the polymer chains. Nevertheless, the absolute value of molecular weight of the HNRL by gel permeation chromatography (GPC) technique is not as yet available, as the specific refractive index increment of hydrogenated natural rubber has not been determined. Nevertheless, the viscosity of a dilute NRL and HNRL solution relative to the pure solvent ( $\eta_{rel}$ ) provides a simple and effective means of measuring the consequences of crosslinking and degradation of samples. The hydrogenated natural rubber samples used for the measurement of relative viscosity were produced from reactions carried out in the gas uptake apparatus described above for the kinetic study.

Over the range of conditions:  $[Os] = 30 - 160 \mu M$ ,  $P_{H_2} = 2.1 - 41.4 \text{ bar}$ ,  $[C=C] = 65 - 400 \text{ mM}$ ,  $[p-TSA] = 6 - 12 \text{ mM}$ ,  $T = 150 \text{ }^\circ\text{C}$ , the results obtained are shown in Table 3.5. Figure 3.11 (a)-(b) illustrates the effect of  $[Os]$  and  $P_{H_2}$  at high conversion (84.8 - 99.2% hydrogenation), respectively. It was found that it was difficult to determine the relative viscosity of natural rubber latex due to gel formation. The samples prepared for the latex had high gel content, especially in the case where high acid concentration was used and low % hydrogenation occurred (< 40%). In the case of high acid concentration, the crosslinking reaction resulting from the residual acid after removing the impurity in the NRL was believed to be the main factor for gel formation. It is possible that residual acid can protonate radical formation to cause a crosslinking reaction in the system. In the case of low %hydrogenation, the residual high double bond concentration was inferred as the reason for the crosslinking reaction and gel formation in presence of added acid.



**Figure 3.11** Relative viscosity ( $\eta_{\text{rel}}$ ) of HNRL (◆) as a function of (a) total catalyst loading (72.7 - 98.3% hydrogenation):  $P_{\text{H}_2} = 27.6$  bar,  $[\text{C}=\text{C}] = 150$  mM,  $[\text{p-TSA}] = 9$  mM,  $T = 150^\circ\text{C}$ ; (b) hydrogen pressure (95 - 98% hydrogenation):  $[\text{Os}] = 140$  μM,  $[\text{C}=\text{C}] = 150$  mM,  $[\text{p-TSA}] = 9$  mM,  $T = 150^\circ\text{C}$  in toluene (Relative viscosity of NR (■) = 7.54, of NRL (▲) = 4.50).

The relative viscosity of hydrogenated natural rubber latex varied over a wide range from 4.76 - 8.99 depending on the reaction conditions, degree of hydrogenation and extent of gel formation.

The actual concentration of NRL and HNRL in each solvent was not known for cases where gel formation occurred. Thus, few useful conclusions can be drawn from the relative viscosity measurement. However, from the data, it seems that at high conversion and no gel formation, hydrogenated NRL has a higher relative viscosity ( $\eta_{\text{rel}}$  of hydrogenated rubber latex  $\sim$  4.76 - 8.99) than natural rubber latex ( $\eta_{\text{rel}}$  of rubber latex = 4.5) and natural rubber ( $\eta_{\text{rel}}$  of rubber = 7.5) at the same concentration. The relative viscosity results did not change significantly with an increase in [Os] and  $P_{\text{H}_2}$  which is consistent with results obtained for hydrogenated *cis*-1,4-polyisoprene (Lu et al., 1987).

### 3.8 Hydrogenation of Fresh Natural Rubber Latex

Fresh natural rubber latex (FNRL) contains about 30% dry solid content and a high level of water and impurities, proteins and phospholipids. For comparison of FNRL and NRL hydrogenation, this section presents the possibility of catalytic hydrogenation of FNRL. For the initial study, the FNRL hydrogenation was studied in a Parr reactor.

#### 3.8.1 Hydrogenation Catalyzed by Various Catalysts

The FNRL hydrogenation using various catalysts with and without *p*-toluenesulfonic acid are summarized in Table 3.12. The efficient catalysts for NRL hydrogenation, which were present in section 3.2, were investigated.  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$ ,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , and  $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$  were found to be effective for hydrogenation of FNRL at 150°C in tetrahydrofuran with acid addition. The % conversion of FNRL is lower than NRL due to the higher content of impurities in FNRL. The degree of hydrogenation decreased with increasing amount of impurities. From these results, the acid addition in FNRL played a key role in enhancing the degree of hydrogenation as observed in NRL

hydrogenation in the previous section.  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was also found to be the most efficient catalyst for hydrogenation FNRL. For the following experiments, Os catalyst was chosen for the study of the effects of variables on FNRL hydrogenation.

**Table 3.12** Initial Studies of Natural Rubber Hydrogenation in Parr Reactor

Catalyst Type	[p-TSH] (mM)	Time (h)	% Conversion
$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$	-	6	4.5
$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$	7	4	64.4
$[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$	-	6	3.3
$[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$	7	4	43.7
$\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$	-	6	3.1
$\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$	7	4	52.4

Conditions: [Catalyst] = 145 mM;  $P_{\text{H}_2}$  = 27.6 bar; [C=C] = 180 mM and T = 150°C in tetrahydrofuran (THF).

### 3.8.2 Effect of Solvent Type

A series of experiments for the study of the solvent effect were carried out using various solvent types, [Os] = 145  $\mu\text{M}$ ,  $P_{\text{H}_2}$  = 27.6 bar, [C=C] = 180 mM, and T = 150°C. The effects of solvent types on FNRL hydrogenation are summarized in Table 3.13. It was found that the degree of hydrogenation increased with increasing coordination power of the solvent. The reaction rate varied with the nature of solvent in the order: tetrahydrofuran > chlorobenzene > toluene > benzene. The solvent should have sufficient coordinating power to displace the phosphine ligand. Tetrahydrofuran is a strongest coordinating solvent. It can promote the dissociation of the phosphine ligand and formation of a solvated 14 - electron osmiumtrihydride species which may lead to increase in the catalytic activity of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{Pcy}_3)_2$ . Moreover, FNRL, which had more water content in the rubber mixture, requires a higher polarity solvent to dissolve. Therefore, THF is an effective solvent for NRL hydrogenation. It was also found that acid addition is a key factor for FNRL hydrogenation.

**Table 3.13** Effect of Solvent on Degree of Hydrogenation of FNRL

[P-TSH] (mM)	Solvent	Result
0	Toluene	No hydrogenation after 6 h
0	MCB	No hydrogenation after 6 h
0	THF	a little hydrogenation after 6 h
7	Toluene	~50% hydrogenation after 4 h
7	MCB	~55% hydrogenation after 4 h
7	THF	~64% hydrogenation after 4 h

Condition: [Os] = 145  $\mu$ M, [C=C] = 180 mM,  $P_{H_2}$  = 27.6 bar and T = 150  $^{\circ}$ C.

### 3.8.3 Effect of Acid Type

As mentioned above, the acid addition played a main role for hydrogenation of NRL and FNRL. Table 3.14 shows the effect of acid types on the degree of hydrogenation ([Os] = 145 mM,  $P_{H_2}$  = 27.6 bar, [C=C] = 180 mM, [Acid] = 7 mM and T = 150 $^{\circ}$ C in THF). p-Toluenesulfonic acid (p-TSA) was found to be an efficient acid promoter for hydrogenation of FNRL in the presence of OsHCl(CO)(O<sub>2</sub>)(Pcy<sub>3</sub>)<sub>2</sub>.

**Table 3.14** Effect of Acid Type on the FNRL Hydrogenation

Carboxylic Acid	% Conversion in 4 h.
p- TSA	65.0
3- CPA	58.8
Succinic acid	24.6
Citric acid	32.4

Condition: [Os] = 145  $\mu$ M, [Acid] = 7 mM, [C=C] = 180 mM,  $P_{H_2}$  = 27.6 bar and T = 150  $^{\circ}$ C in THF.



### 3.8.4 Effect of Catalyst Concentration, Rubber Concentration and Acid Concentration

From the previous sections (3.5.1, 3.5.2 and 3.5.4), when the rubber concentration was low, a high concentration of catalyst was required to obtain the high level of hydrogenation. The hydrogen pressure chosen was above 13.8 bars. The concentration of p-TSA was over the range of 7-12 mM for 180 mM of [C=C]. The temperature effect was also studied to achieve a high degree of hydrogenation. The result summarized in Table 3.15 indicates that 98.9 % conversion can be achieved within 4 h at the appropriate reaction conditions.

The influence of catalyst concentration on the reaction system is illustrated in Table 3.15 and Figure 3.12. It can be seen that the degree of hydrogenation is linearly proportional to the total catalyst concentration. These results are consistent with NRL hydrogenation. Thus, it is likely that for FNRL hydrogenation, a first order dependence with respect to catalyst concentration occurs. The plots of FNRL hydrogenation show an intercept on the x-axis. It can be presumed that some portion of the osmium complex was sacrificed for impurities present inside the FNRL.

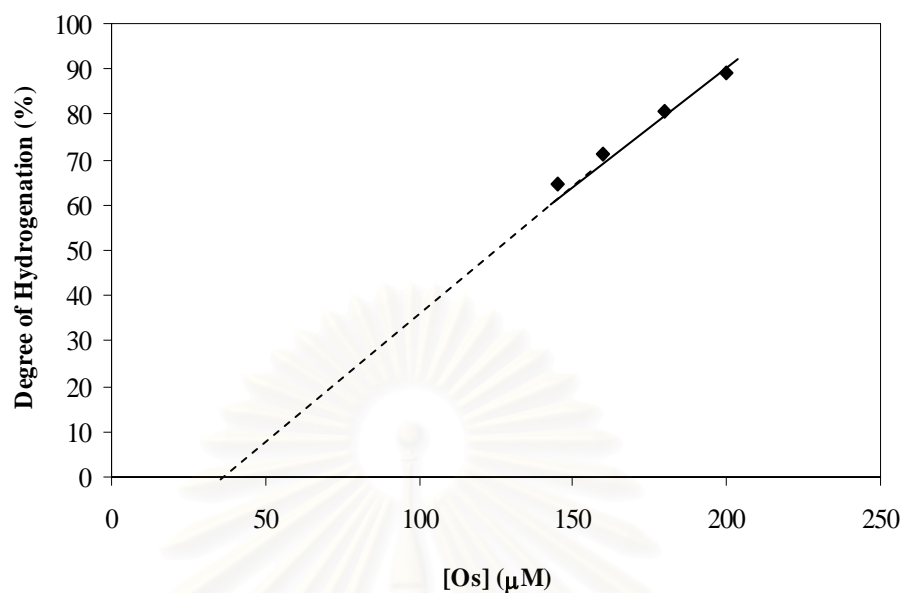
To investigate the effect of rubber concentration, a series of experiments was carried out at three levels of polymer concentration: 120, 150 and 180 mM. The catalyst concentration (145  $\mu$ M), reaction temperature (150°C), hydrogen pressure (27.6 bar) and p-toulenesulfonic acid (7 mM) in THF were kept constant. The results of these experiments are shown in Figure 3.13. The results indicate that the degree of hydrogenation decreased with an increase in rubber concentration. The reduction of the FNRL hydrogenation degree can be explained by the effect of impurities in the latex which has been already explained in the prior section (section 3.5.5).

**Table 3.15** Degree of FNRL Hydrogenation Data Catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$

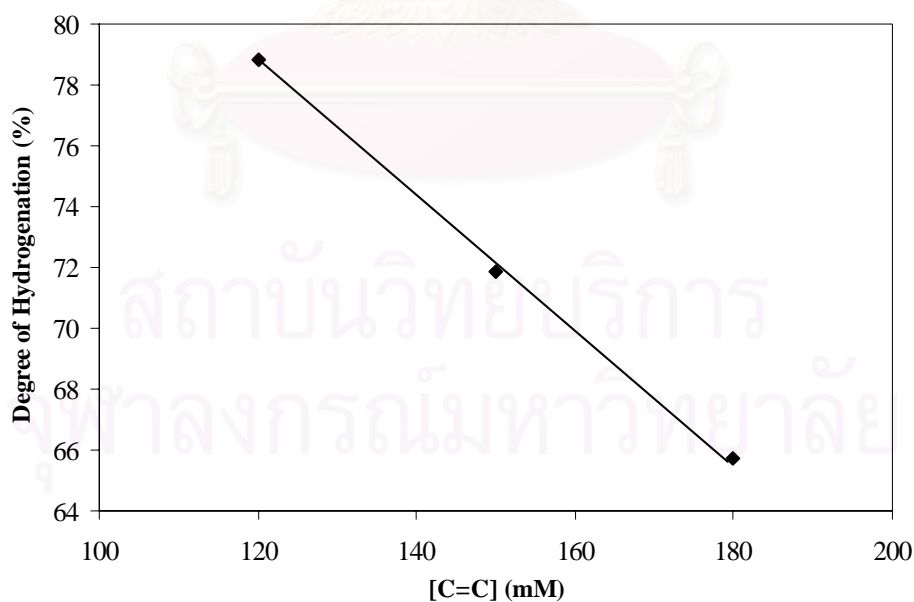
Expt	$P_{\text{H}_2}$ (bar)	Temp ( $^{\circ}\text{C}$ )	[C=C] (mM)	[Os] ( $\mu\text{M}$ )	[P-TSH] (mM)	Time (h)	% Conversion
1	27.6	150	180	145	7	4	64.7
2	27.6	150	150	145	7	4	71.8
3	27.6	150	120	145	7	4	78.8
4	27.6	150	180	160	7	4	71.4
5	27.6	150	180	180	7	4	80.5
6	27.6	150	180	200	7	4	89.0
7	27.6	150	120	180	7	4	92.5
8	6.9	150	180	145	7	4	41.4
9	13.8	150	180	145	7	4	63.3
10	27.6	150	180	145	7	4	65.1
11	41.4	150	180	145	7	4	66.3
12	27.6	150	180	145	0	4	3.7
13	27.6	150	180	145	9	4	72.5
14	27.6	150	180	145	12	4	73.5
15	27.6	150	180	145	15	4	70.5
16	27.6	160	180	145	7	4	70.0
17	41.4	150	180	145	7	4	66.1
18	41.4	160	180	145	7	4	73.8
19	27.6	160	120	180	9	4	97.7
20	41.4	160	120	180	9	4	99.0

Solvent: tetrahydrofuran (THF)

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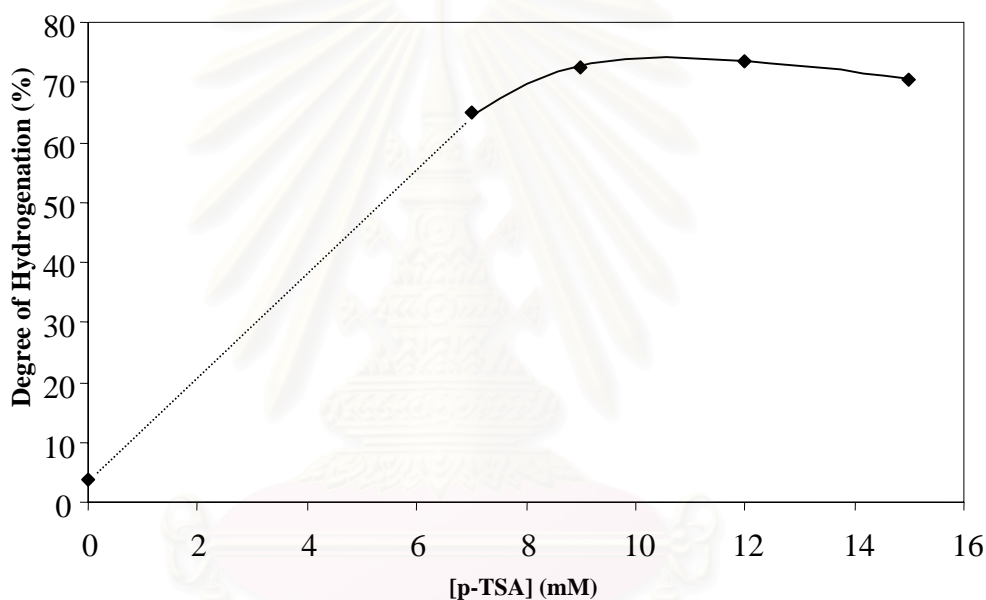


**Figure 3.12** Effect of catalyst concentration on the degree of FNRL hydrogenation. [C=C] = 180 mM;  $P_{H_2}$  = 27.6 bar; [p-TSA] = 7 mM; T = 150°C in tetrahydrofuran (THF).



**Figure 3.13** Effect of rubber concentration on the degree of FNRL hydrogenation. [Os] = 145 μM;  $P_{H_2}$  = 27.6 bar; [p-TSA] = 7 mM; T = 150°C in THF.

Figure 3.14 shows the effect of acid concentration, ( $[\text{Os}] = 145 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 180 \text{ mM}$ ,  $P_{\text{H}_2} = 27.6 \text{ bar}$  and  $T = 150^\circ\text{C}$  in THF). For NRL hydrogenation, it is possible that the acid might neutralize the impurity in the FNRL and prevent additional catalyst from poisoning. The same behavior was also found in NRL hydrogenation. The hydrogenation of FNRL was also studied using p-TSA at more than 7 mM. Over the range of 7 to 12 mM of acid concentration (see Figure 3.14), the degree of hydrogenation was increased. However, at a higher amount of acid ( $>12 \text{ mM}$  of acid concentration) a reduction of hydrogenation degree was observed.



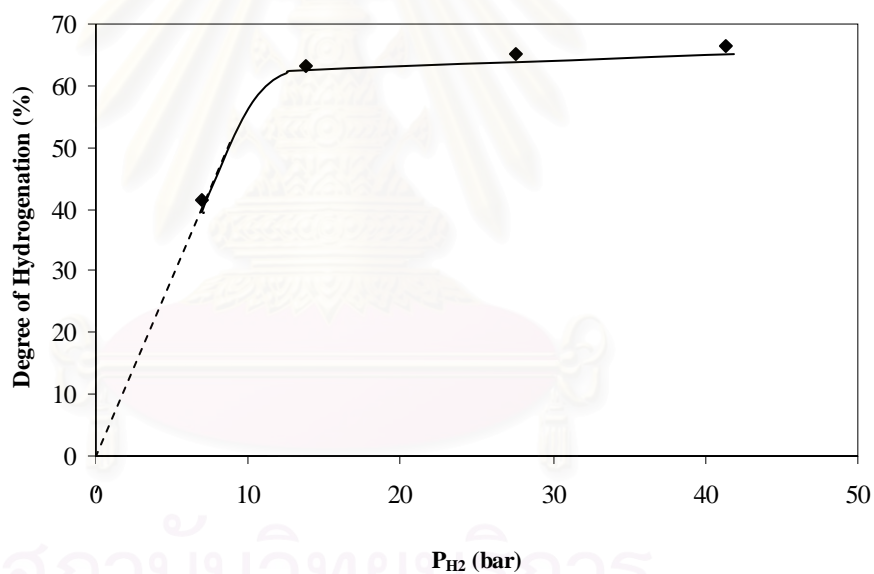
**Figure 3.14** Effect of acid concentration on the degree of FNRL hydrogenation.

$[\text{Os}] = 145 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 180 \text{ mM}$ ;  $P_{\text{H}_2} = 27.6 \text{ bar}$ ;  $T = 150^\circ\text{C}$  in THF.

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### 3.8.5 Effect of Hydrogen Pressure

The effect of hydrogen pressure on the hydrogenation of FNRL using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{Pcy}_3)_2$  was investigated. Hydrogen pressure was varied over the range 6.9 – 41.4 bar at  $150^\circ\text{C}$  in THF. The concentration of catalyst, rubber and p-TSA were kept constant at  $145\ \mu\text{M}$ ,  $180\ \text{mM}$  and  $7\ \text{mM}$  respectively. The results are presented in Table 3.15. Figure 3.15 suggests that the degree hydrogenation of FNRL hydrogenation sharply increased below 6.9 bar and then became insensitive to  $P_{\text{H}_2}$  at a pressure higher than 13.8 bar. These results are in agreement with those observed for NRL hydrogenation in the presence of the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst system (section 3.5.3).



**Figure 3.15** Effect of hydrogen pressure on the degree of FNRL hydrogenation.

$[\text{Os}] = 145\ \mu\text{M}$ ;  $[\text{C}=\text{C}] = 180\ \text{mM}$ ;  $[\text{p-TSA}] = 7\ \text{mM}$ ;  $T = 150^\circ\text{C}$  in THF.

## CHAPTER IV

### **HYDROGENATION OF NATURAL RUBBER LATEX IN THE PRESENCE OF $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$**

The hydrogenation of elastomers in latex form would be of great interest and significant since many diene based polymers are produced in the latex form especially natural rubber. By applying the hydrogenation process to a polymer emulsion, the typical procedures for the polymer hydrogenation, such as the precipitation of polymer from its emulsion, the subsequent drying process, and the redissolution of the polymer into an organic solvent for the hydrogenation, can be avoided. This would represent economic and environmental advantages for the production of hydrogenated polymers. Hydrogenation of latex rubber can be performed by both catalytic and non-catalytic methods. Hydrogenation of polymer via homogenous catalyst is a favorable method. Many of the new developments in the field of catalytic hydrogenation have involved the use of homogeneous catalysts because they have higher selectivity and do not have macroscopic diffusion problems. In addition, the performance of homogeneous catalysts are more easily explained and understood on the molecular level (Bhaduri and Mukesh, 2000).

Many homogeneous hydrogenation catalysts share one shortcoming-hindered olefins are not reduced at efficient rates. Normally, a homogeneous hydrogenation solution contains either coordinating solvents or dissociated ligands which compete with the olefin for catalytically active metal sites, preventing hydrogenation of highly hindered olefins. An exception is the Crabtree's catalyst. Crabtree et al. (1977) discovered that the cationic iridium catalysts,  $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$  and  $[\text{Ir}(\text{cod})\text{L}(\text{py})]\text{PF}_6$ , were effective catalysts for hindered alkene hydrogenation in the presence of noncoordinating chlorinated solvents,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_5\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ . Presumably, they all have high polarity but negligible coordinating power. Normally,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  can oxidize and deactivate the low valent catalysts involved in hydrogenation. Nevertheless, both iridium catalytic precursors were later found to be stable to oxidizing reagents such as  $\text{O}_2$  or ethyl iodide (EtI).

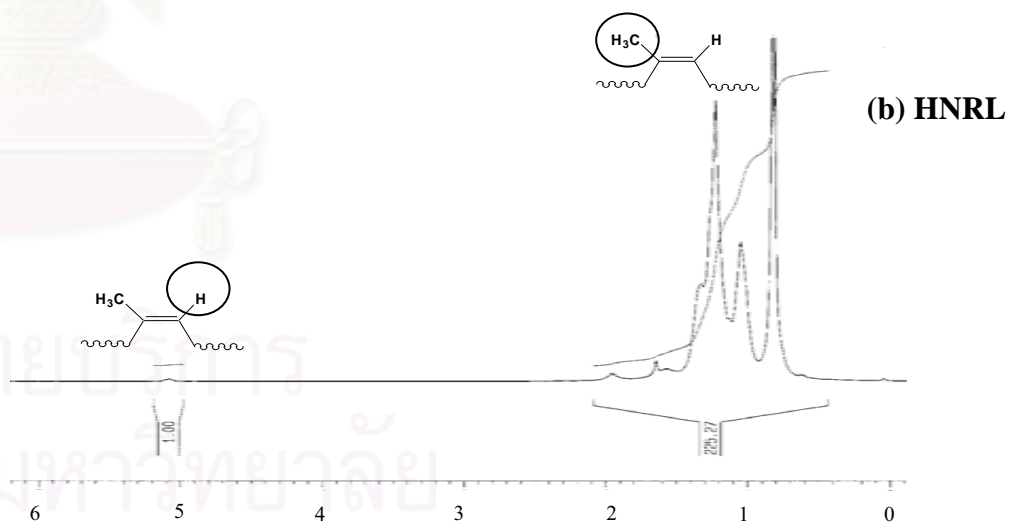
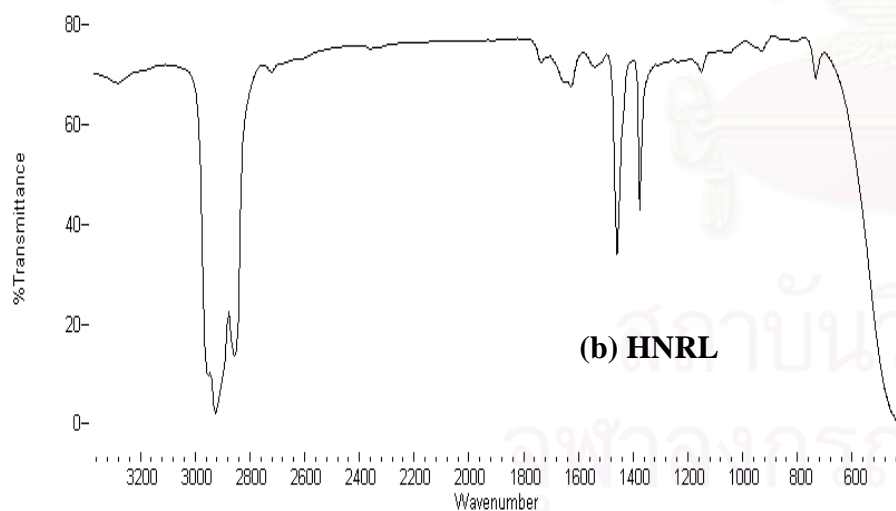
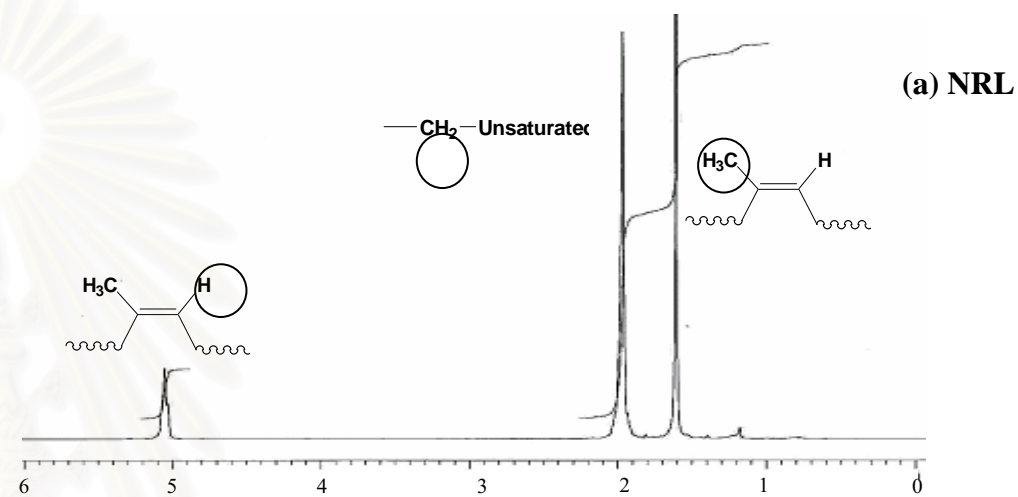
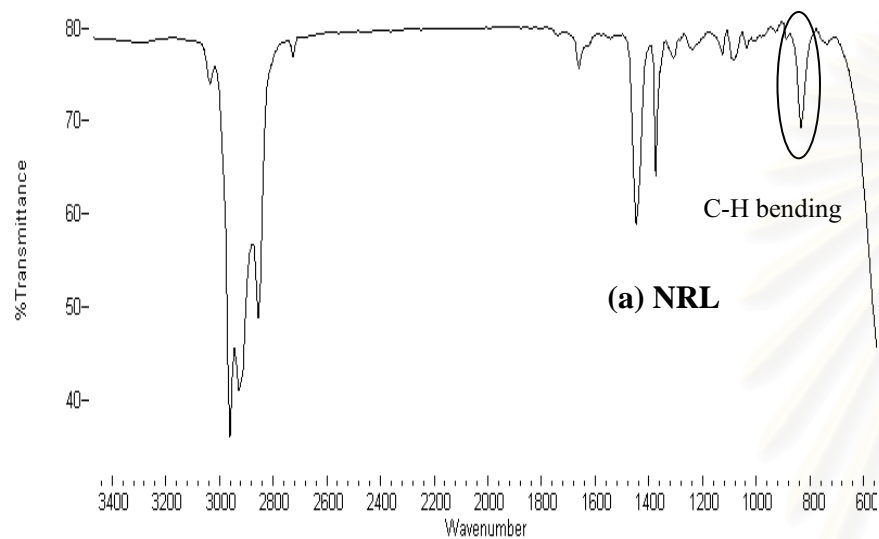


There are some previous works on the hydrogenation of diene - based polymers catalyzed by iridium catalysts. Gilliom (1989) studied the catalytic hydrogenation of polybutadiene and butadiene-styrene triblock copolymer by using polymer entrained  $[\text{Ir}(\text{cod})(\text{PMePh}_2)_2]\text{PF}_6$  as a catalyst in the absence of solvent under moderate conditions. Hu (2000) studied the kinetics of the hydrogenation of nitrile-butadiene rubber using  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  in solution. Charmondusit (2002) and Hinchiranan (2004) have also used this iridium complex to hydrogenate synthetic *cis*-1,4-polyisoprene and natural rubber in solution and proposed a catalytic mechanism for this system.

In this chapter, the goal of the research was to study the hydrogenation of natural rubber latex catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ . The effect of reaction parameters on the hydrogenation rate such as catalyst concentration, rubber concentration, hydrogen pressure, acid concentration and reaction temperature were investigated. The reaction mechanisms of natural rubber latex hydrogenation were proposed.

#### 4.1 Structure Characterization Using FTIR and NMR Spectroscopy

The structure of natural rubber latex (NRL) before and after the hydrogenation process was preliminarily characterized by infrared spectroscopy (FTIR) as shown in Figure 4.1a and 4.1b. The structure of hydrogenated natural rubber latex (HNRL) shows that the absorption bands corresponding to the C=C stretching, olefinic C-H bending and  $-(\text{CH}_2)_3-$  are located at 1664, 836 and 739  $\text{cm}^{-1}$ , respectively. The characteristic signals of unsaturation, 1664 and 836  $\text{cm}^{-1}$ , disappeared in the hydrogenated rubbers while an intense signal appeared at 739  $\text{cm}^{-1}$  due to saturated carbon formed through hydrogenation.  $^1\text{H-NMR}$  spectroscopy was used to examine the actual degree of hydrogenation in each sample. The  $^1\text{H-NMR}$  spectra of NRL before and after the hydrogenation reaction are shown in Figure 4.2a and 4.2b. The olefinic proton signal at 5.2 ppm after the hydrogenation process was reduced, which confirms that the carbon-carbon double bond in NRL was hydrogenated. The aliphatic proton signals at 0.8 and 1.2 ppm, attributed to saturated  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups, show a strong increment due to the chemical transformation of double bonds upon saturation.



**Figure 4.1** FTIR spectra of NRL before and after hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ .

**Figure 4.2** <sup>1</sup>H-NMR spectra of NRL before and after hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ .

The actual degree of hydrogenation could be calculated from the peak area at 5.2 ppm and the summation of peak area between 0.8 and 2.0 ppm as described in Chapter 2.

#### 4.2 Kinetic Experiments of Natural Rubber Latex Hydrogenation

All the kinetic data for NRL hydrogenation in the presence of the homogeneous catalyst,  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ , were obtained using an automated gas-uptake apparatus. The univariate experiments were carried out to investigate the effect of each factor individually. All kinetic data were collected under a constant pressure of hydrogen, with vigorous mixing. Therefore,  $[\text{H}_2]$  was assumed to be in equilibrium with the gaseous pressure and remained constant during the course of the reaction. Consequently, the reaction could be approximated as a pseudo-first-order reaction:

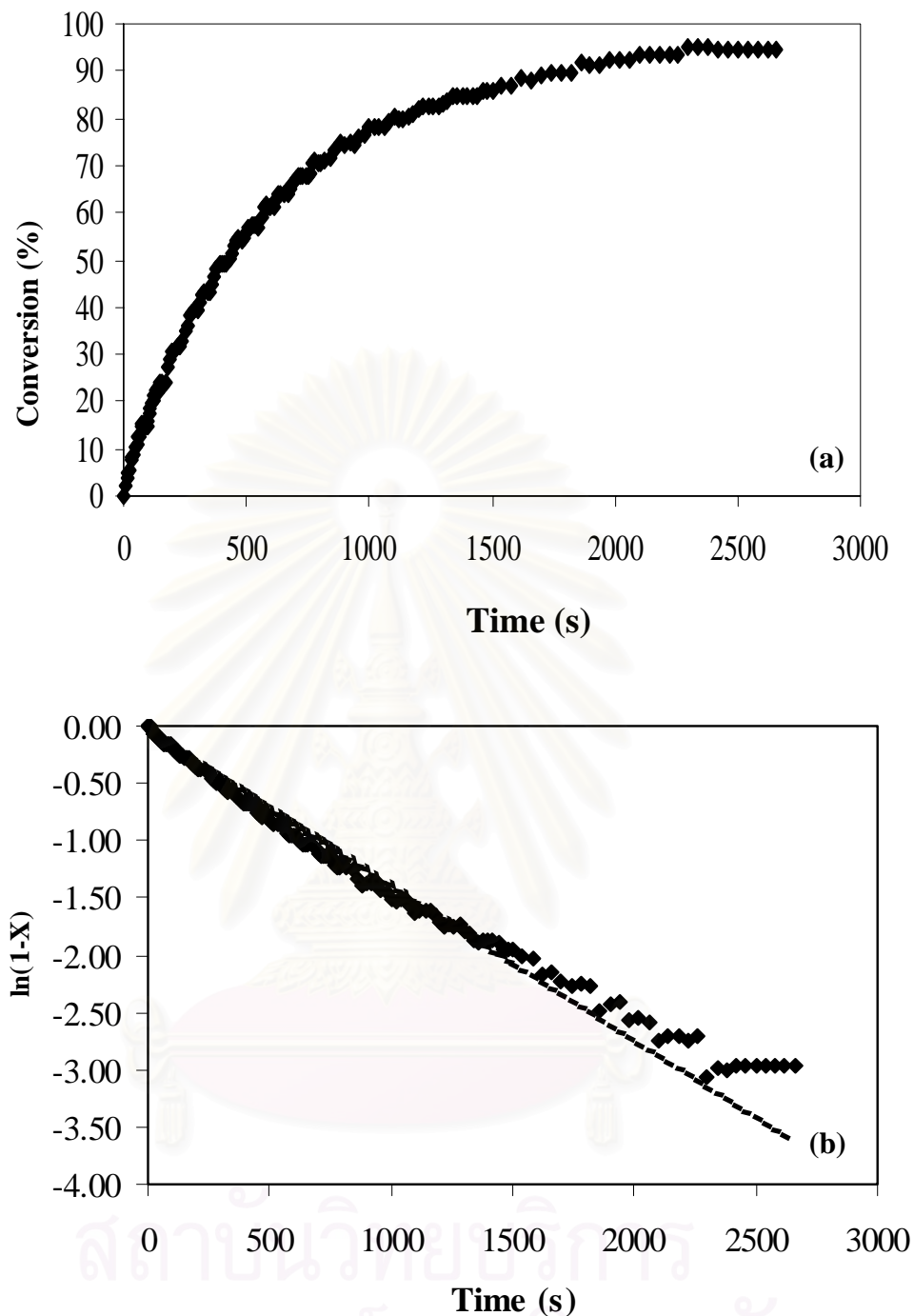
$$-\frac{d[\text{C}=\text{C}]}{dt} = k'[\text{C}=\text{C}] \quad (4.1)$$

where  $k'$  is the pseudo-first-order rate constant. Figure 4.3a shows the plot of conversion versus time for the NRL hydrogenation reaction. The hydrogen consumption plot indicates that the reaction was apparently first-order in the olefinic substrate, which according to eq. 4.1 can be expressed in terms of the conversion of unsaturated double bonds (extent of hydrogenation),  $x$ , as

$$\ln(1 - x) = -k't \quad (4.2)$$

where  $t$  is the reaction time. Figure 4.3b shows a linear plot of  $\ln(1-x)$  versus time ( $t$ ) for the NRL hydrogenation. The pseudo-first-order rate constant is then readily determined from the slope of the corresponding curve. A summary of results for the effect of hydrogenation variables on the rate constant is presented in Table 4.1.

The effect of reaction parameters on the degree of hydrogenation such as catalyst concentration, rubber concentration, acid concentration and hydrogen pressure were studied. The kinetic results for the NRL hydrogenation is presented in Table 4.1.



**Figure 4.3** NRL Hydrogenation profile obtained from gas uptake apparatus. (a) olefin conversion profiles and (b) first-order  $\ln$  plot (----- model from linear regression) of NRL hydrogenation.  $[\text{Ir}] = 120 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[\text{p-TSA}] = 10 \text{ mM}$ ;  $T = 150^\circ\text{C}$  in monochlorobenzene.

**Table 4.1** Kinetic Results of Univariate Experiments for NRL Hydrogenation Catalyzed by  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$

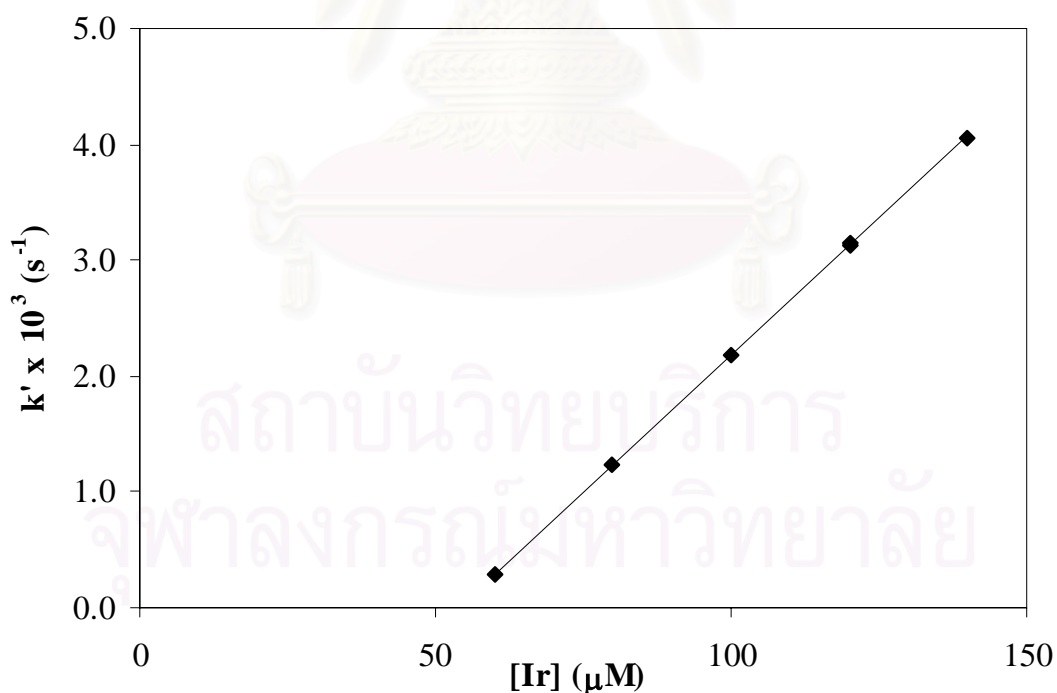
Expt.	[Ir] ( $\mu\text{M}$ )	[C=C] (mM)	$P_{\text{H}_2}$ (bar)	Temp ( $^\circ\text{C}$ )	[Acid] (mM)	$k' \times 10^3$ ( $\text{sec}^{-1}$ )	% Hydrogenation at 30 min	$\eta_{(\text{rel})}$
1	60	100	41.4	150	10	0.29	22.5	-
2	80	100	41.4	150	10	1.23	52.6	8.23
3	100	100	41.4	150	10	2.19	79.4	8.41
4	120	100	41.4	150	10	3.13	89.9	8.67
5	120	100	41.4	150	10	3.14	90.1	8.69
6	140	100	41.4	150	10	4.06	95.4	8.82
7	120	80	41.4	150	10	4.56	97.6 (25.5 min.)	-
8	120	100	41.4	150	10	3.14	90.0	8.67
9	120	100	41.4	150	10	3.15	90.0	8.68
10	120	120	41.4	150	10	2.30	66.5	8.41
11	120	150	41.4	150	10	1.56	46.9	8.13
12	120	200	41.4	150	10	1.02	21.5	7.73
13	120	100	6.9	150	10	0.89	25.4	-
14	120	100	13.8	150	10	1.35	48.7	8.56
15	120	100	27.6	150	10	2.27	66.7	8.67
16	120	100	41.4	150	10	3.12	89.9	8.70
17	120	100	41.4	150	10	3.11	90.0	8.68
18	120	100	55.1	150	10	3.85	93.7 (28.6 min.)	8.72
19	120	100	69.2	150	10	4.48	92.4 (25.5 min.)	8.73
20	120	100	41.4	150	0	0.02	4.5	-
21	120	100	41.4	150	3	0.09	15.9	-
22	120	100	41.4	150	5	0.42	34.6	-
23	120	100	41.4	150	7	2.65	63.6	8.56
24	120	100	41.4	150	10	3.13	90.0	8.69
25	120	100	41.4	150	12	2.96	80.7	6.05
26	120	100	41.4	150	15	2.65	70.6	5.12
27	120	100	41.4	120	10	1.55	45.8	-
28	120	100	41.4	130	10	2.06	56.9	-
29	120	100	41.4	140	10	2.78	76.7	-
30	120	100	41.4	150	10	3.23	88.4	-
31	120	100	41.4	160	10	3.79	90.3(23.7 min.)	-

Solvent: Monochlorobenzene (150 ml).

Relative viscosity ( $\eta_{\text{rel}}$ ) of NR and NRL in toluene = 7.42, 4.45, respectively.

#### 4.2.1 Effect of Catalyst Concentration

To investigate the influence of catalyst concentration on NRL hydrogenation, the catalyst concentration was varied. The range of catalyst concentration was 60 to 140  $\mu\text{M}$  in monochlorobenzene. The hydrogen pressure (41.4 bar) and temperature (150°C) were kept constant for all experiments. The results suggest a first-order dependence on catalyst concentration, which implied that the active complex is a mononuclear species. The NRL hydrogenation system required a higher loading of catalyst. It can be presumed that impurities in NRL might reduce the catalytic activity; thus, some portion of catalyst about 50  $\mu\text{M}$  appeared to be sacrificed due to the impurities. This behavior with respect to catalyst concentration is similar to that observed for the NRL hydrogenation catalyzed by  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  which also exhibited a decrease in catalytic activity with an increase in the rubber concentration (see section 3.5.1). This behavior was also reported for hydrogenation of NR using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  (Hinchiranan, 2004).

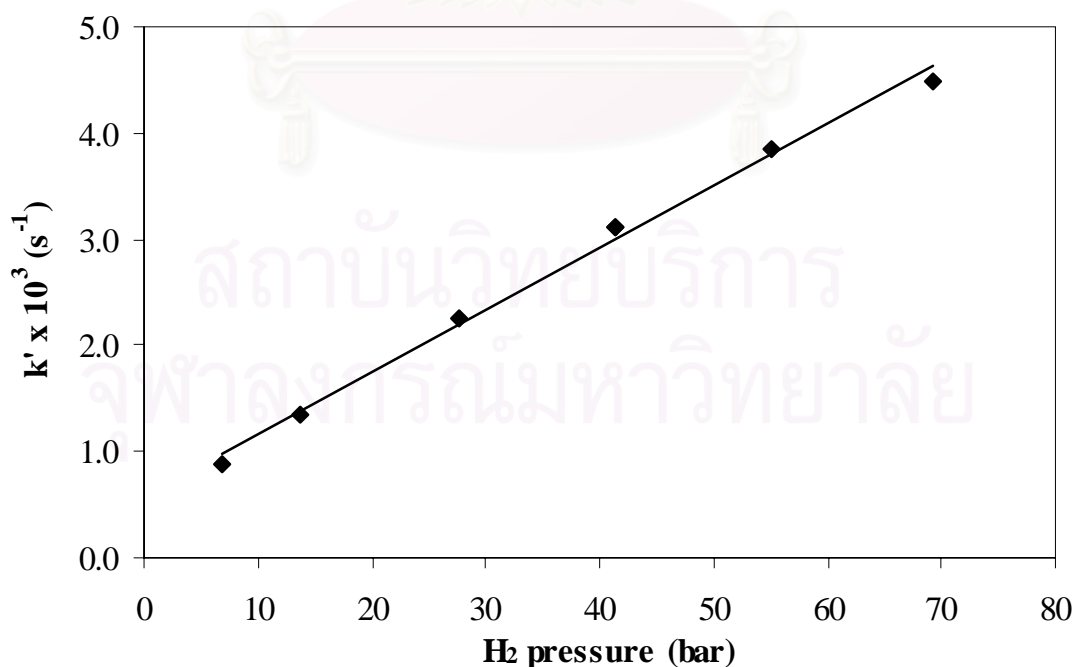


**Figure 4.4** Effect of catalyst concentration on hydrogenation rate.  $P_{\text{H}_2} = 41.4$ . bar;  
 $[\text{C}=\text{C}] = 100$  mM;  $[\text{p-TSA}] = 10$  mM;  $T = 150^\circ\text{C}$ .



#### 4.2.2 Effect of Hydrogen Pressure

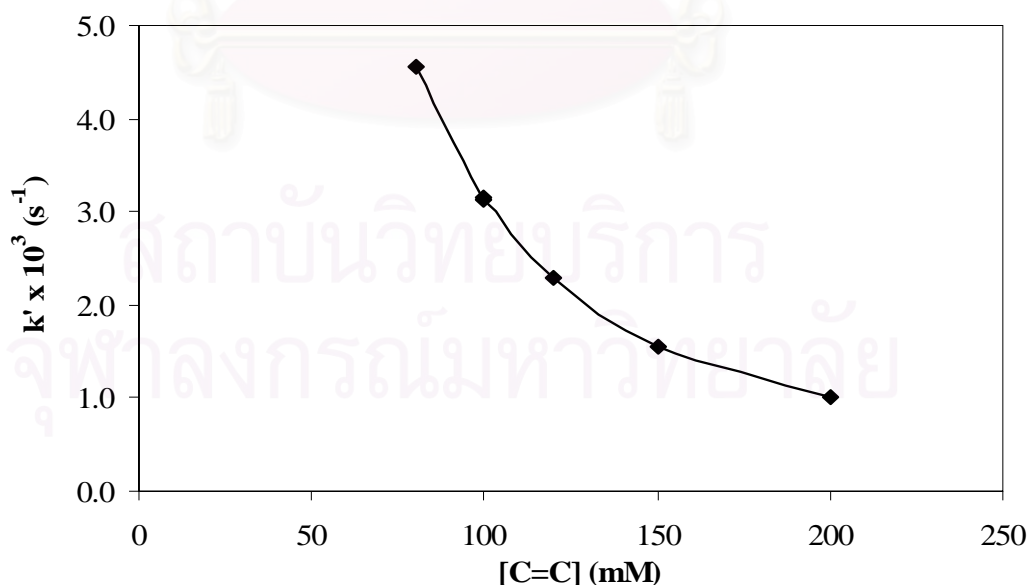
A series of experiments was carried out over the hydrogen pressure range of 6.9 to 69.2 bar ( $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $[\text{p-TSA}] = 10 \text{ mM}$ ) at  $150^\circ\text{C}$  in monochlorobenzene. Figure 4.5 shows a linear plot of the rate constant versus hydrogen pressure, which suggested that the rate of hydrogenation was first-order with respect to the hydrogen pressure. The first order rate dependence implies that primarily a single reaction pathway is probably involved in the reaction of the unsaturation of the polymer with hydrogen. If more than one process were involved, the relative contribution of each pathway should change with varying hydrogen pressure, and thus the dependence might deviate from the first order behavior observed. A similar behavior of first-order rate dependence on hydrogen pressure was also observed in the NBR hydrogenation using this iridium complex (Hu, 2000). Hinchiranan (2004) reported that the first-order rate dependence on hydrogen pressure was also observed in the hydrogenation of NR using this iridium complex. In contrast, the hydrogenation of natural rubber latex (NRL) in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  showed a second- to zero-order dependence as the system pressure increased (section 3.5.3).



**Figure 4.5** Effect of hydrogen pressure on hydrogenation rate.  $[\text{Ir}] = 120 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $[\text{p-TSA}] = 10 \text{ mM}$ ;  $T = 150^\circ\text{C}$ .

### 4.2.3 Effect of Rubber Concentration

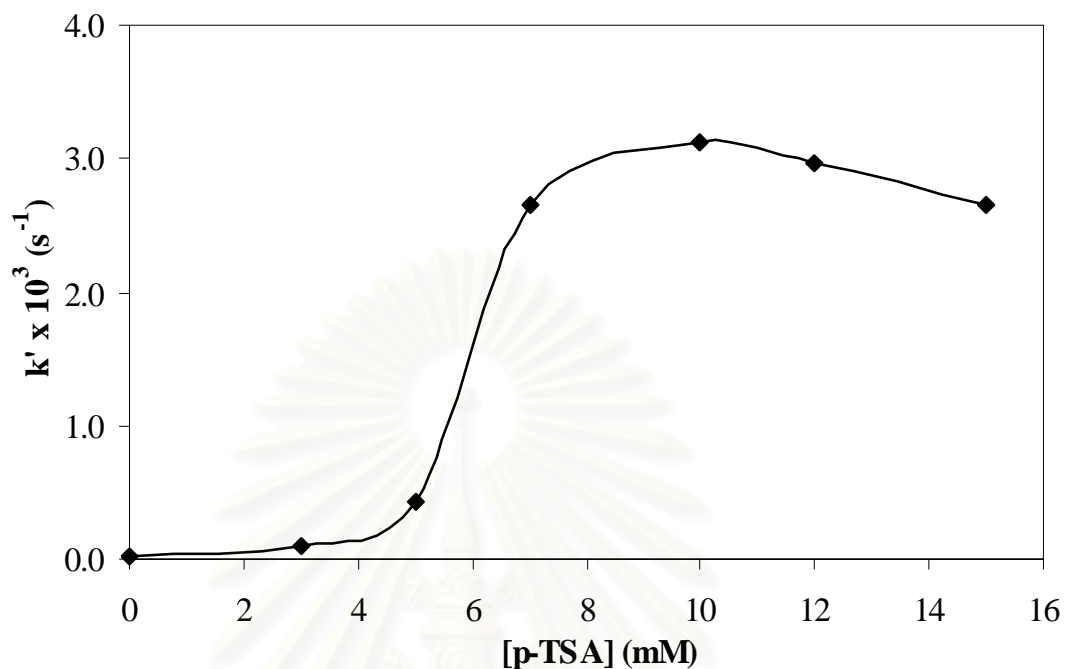
The effect of rubber concentration on the hydrogenation rate was studied over the range of 80-200 mM ( $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{p-TSA}] = 10 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$  in monochlorobenzene). The results are shown in Figure 4.6. It indicates that the reaction rate has an inverse rate behavior with an increase in the rubber loading. The iridium complexes,  $[\text{Ir}(\text{cod})\text{L}(\text{py})]\text{PF}_6$  and  $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$ , were sensitive to a number of functional groups such as amines, which totally deactivate the catalysts via deprotonation reactions (Crabtree et al., 1977). Proteins in NRL likely lower the catalytic activity of  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  due to the amine content in the protein structure. The influence of impurities in NRL drastically decreased the efficiency of the Ir complex. The effect of rubber concentration on the reaction rate of NRL hydrogenation was similar to the hydrogenation of natural rubber and rubber with an interacting functional group such as the nitrile group in NBR. There are a number of reports showing that the activity of rhodium, ruthenium, osmium and iridium complexes were inhibited by coordination of the nitrile functional group with the metal center of the complexes (Hinchiranan, 2004; Hu, 2000; Parent et al., 1998b; Parent et al., 1996; Martin et al., 1997).



**Figure 4.6** Effect of rubber concentration on NRL hydrogenation rate:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[\text{p-TSA}] = 10 \text{ mM}$ ;  $T = 150^\circ\text{C}$ .

#### 4.2.4 Effect of Acid Concentration

Acid addition in the hydrogenation system improved the catalytic activity of the olefinic hydrogenation catalysts. Guo et al. (1997) established that carboxylic acids increased the catalytic activity for the hydrogenation of an NBR emulsion using  $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$ . They reported that the carboxylic acids were very effective in preventing the poisoning of the catalyst by impurities in the emulsion system. Yi et al. (2000) also found that the addition of acids increased the rate of alkene hydrogenation catalyzed by  $\text{RuH}(\text{CO})(\text{Cl})(\text{PCy}_3)_2$ . They suggested that the increase in catalytic activity of this Ru catalytic species might be due to the selective entrapment of the phosphine ligand and the formation of a highly active 14-electron ruthenium-monophosphine species. The effect of acid addition on increasing the NRL hydrogenation rate was also reported. Tangthongkul (2000) studied the effect of acid addition in the presence of  $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ . The results showed that the NRL hydrogenation rate can be increased by adding some acid. For the system of NRL hydrogenation catalyzed by  $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]\text{PF}_6$ , the role of acid on the NRL hydrogenation was studied and the results obtained are presented in Figure 4.7. The effect of acid addition on the NRL hydrogenation rate in the presence of Crabtree's catalyst was carried out at base conditions:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $P_{\text{H}_2} = 41.4$  bar,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $T = 150^\circ\text{C}$ . It was found that the acid addition could slightly increase the rate of NRL hydrogenation. Therefore, it is possible that the acid addition might promote the catalytic activity of  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  by preventing the poisoning of the catalyst due to proteins present in NRL. Hu (2000) reported that a peak for free  $\text{PCy}_3$  ligand dissociated from the catalyst precursor at 10 ppm was not present in the  $^{31}\text{P}$ -NMR spectrum at  $70^\circ\text{C}$ , which indicated that no appreciable dissociation of the  $\text{PCy}_3$  ligand occurred and it can be implied that the role of acid addition was not the entrapment of the  $\text{PCy}_3$ . However, the carboxylic acids have been known to increase the catalytic activity of the catalyst for the NRL hydrogenation as presented in the section 3.5.4. Charmondusit (2002) and Hinchiranan (2004) also report the effect of acid addition. An overload of these acids in the system might partially or totally deactivate Ir complexes, presumably by coordination (Crabtree et al., 1977).

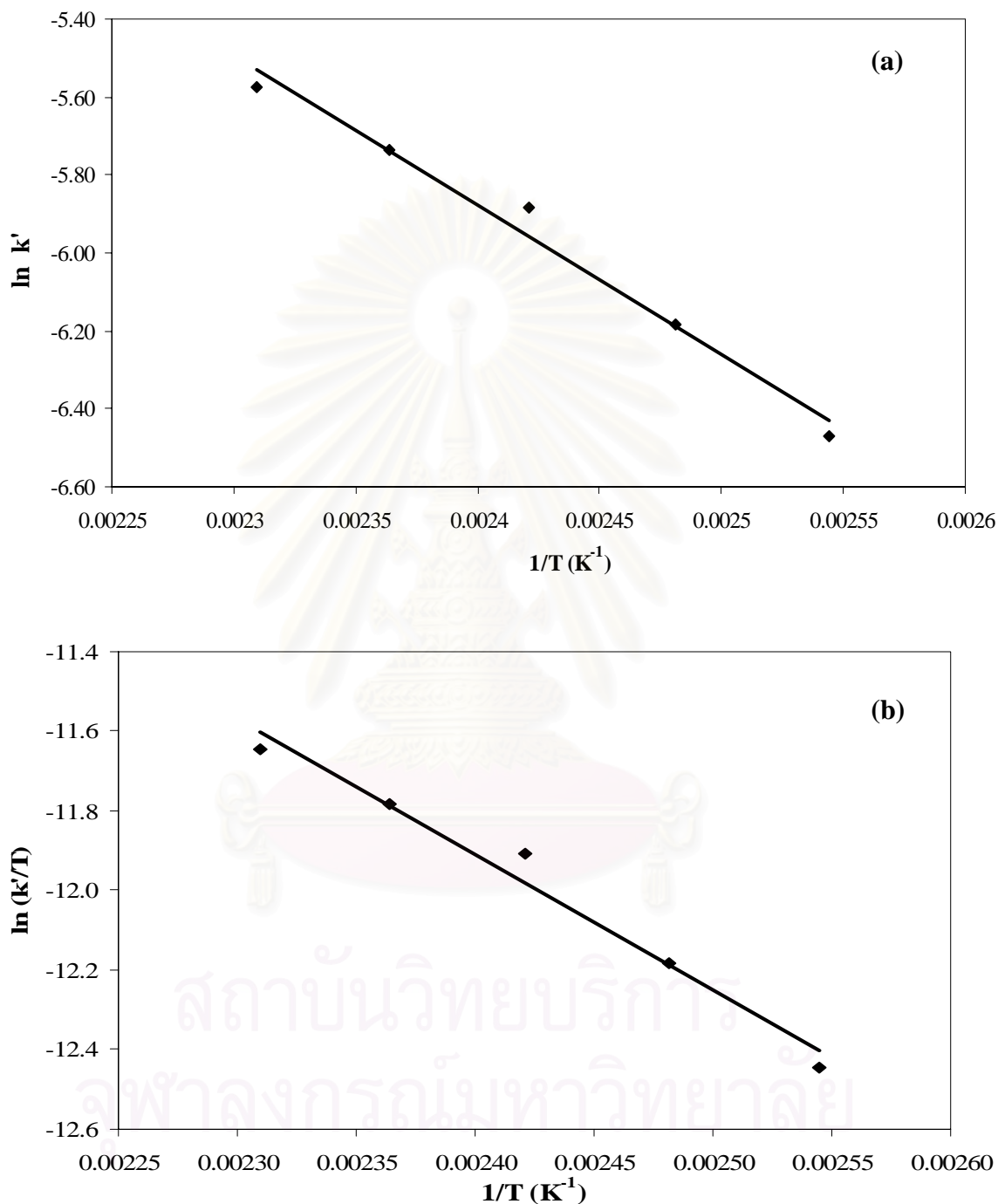


**Figure 4.7** Effect of acid concentration on NRL hydrogenation rate: [Ir] = 120  $\mu$ M;  $P_{H_2}$  = 41.4 bar; [C=C] = 100 mM; T = 150°C.

#### 4.2.5 Effect of Reaction Temperature

A series of experiments were carried out over the temperature range of 120 to 160°C ([Ir] = 120  $\mu$ M, [C=C] = 100 mM and  $P_{H_2}$  = 41.4 bar in monochlorobenzene). The effect of temperature on the rate constant for the hydrogenation of both rubbers can be represented by an Arrhenius plot as shown in Figure 4.8a. The linear plot indicates that a single rate-determining step is observed within the kinetic mechanism. The activation energy calculated from least squares regression analysis of  $\ln(k')$  versus  $1/T$  was 31.79 kJ/mol. This provides further evidence that the kinetic data were obtained without severe mass transfer limitation and the diffusion of the reactants was not the main rate-determining factor under these conditions. Hydrogenation at higher temperature exhibited a faster reaction rate and led to a higher efficiency. The Eyring equation was used to calculate the apparent activation enthalpy and entropy for the reaction. The Eyring plot presented in Figure

4.8b shows the enthalpy and entropy for NRL hydrogenation as 28.4 kJ/mol and – 228.5 J/mol K respectively



**Figure 4.8** (a) Arrhenius plot and (b) Eyring plot for NRL hydrogenation.  $[\text{Ir}] = 120 \mu\text{M}$ ;  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $[\text{p-TSA}] = 10 \text{ mM}$ ;  $T = 120\text{-}160^\circ\text{C}$ .

#### 4.2.5 Effect of Solvents

The effect of different solvents on the hydrogenation rate of NRL in the presence of Crabtree's catalyst was investigated at base conditions:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$ . The effect of solvent on the hydrogenation is summarized in Table 4.2. It seems that chlorinated solvents are viable solvents for catalytic hydrogenation with this cationic iridium catalyst. Toluene, hexane and xylene were not used as solvents since they could not completely dissolve the cationic iridium catalyst. Crabtree et al. (1979) studied alkene hydrogenation catalyzed by  $[\text{Ir}(\text{cod})\text{L}_2]\text{PF}_6$  and  $[\text{Ir}(\text{cod})\text{L}(\text{py})]\text{PF}_6$  where (cod) was 1,5-cyclooctadiene and L was a tertiary phosphine and found that noncoordinating solvents such as toluene, benzene or hexane also were inappropriate solvents since only catalytically inactive precipitates were formed under a hydrogen atmosphere. However, these Ir complexes were very active in solvents containing a chlorine atom except for 1,1-dichloroethylene and carbon tetrachloride since they failed to dissolve the Ir catalysts under a hydrogen atmosphere (Crabtree et al., 1977). The strong coordinating solvent (tetrahydrofuran) was found to be an efficient solvent for the hydrogenation of CPIP and NR using the Os catalyst, but it was not a good solvent for the hydrogenation of CPIP and NR using Crabtree's catalyst (Hinchiranan, 2004). Thus, higher activity of Crabtree's catalyst was obtained in non-coordinating solvents. This is consistent with the hydrogenation of acrylonitrile-butadiene copolymers using Crabtree's catalyst (Hu, 2000). In addition, the results shown in Table 4.2 indicate that the hydrogenation of NRL showed a slight difference in reaction rate with a different amount of chlorine atoms in the chlorinated solvents.



**Table 4.2** Effect of Solvent on NRL Hydrogenation Rate

Solvent	NRL Hydrogenation	
	$k' \times 10^3$ ( $s^{-1}$ )	Final %Hydrogenation
Tetrahydrofuran	1.23	69.8 (~1.3h)
Chlorobenzene	3.14	95.8 (~ 1 h)
Dichlorobenzene	3.26	96.8 (~1.2 h)
Trichlorobenzene	3.54	97.7 (~1 h)

Condition:  $[Ir] = 120 \mu\text{M}$ ,  $P_{\text{H}_2} = 41.1 \text{ bar}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $[\text{p-TSA}] = 10 \text{ mM}$ ,  
 $T = 150^\circ\text{C}$ .

#### 4.2.6 Effect of Impurity

The presence of impurities in NRL was suspected to decrease the hydrogenation rate. To support this the hydrogenation of deproteinized NRL was investigated. The deproteinized rubber latex (DPNRL) was prepared using a proteolytic enzyme method (Tangpakdee and Tanaka, 1997b). The experiments were carried out in a Parr reactor for 4 h:  $[Ir] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $[\text{p-TSA}] = 10 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ,  $T = 150^\circ\text{C}$  in monochlorobenzene. Table 4.3 shows the effect of impurity on the degree of hydrogenation. For comparison between DPNRL and NRL, DPNRL exhibited a higher degree of hydrogenation than NRL. This is attributed to the lower amount of impurity in the system. A similar result was obtained for NRL hydrogenation using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  (section 3.5.5).

**Table 4.3** Effect of Impurity on Degree of NRL Hydrogenation

Rubber Type	% Nitrogen Content	% Conversion (4 h)
NRL	0.20	91.2
DPNRL	0.02	98.9

Condition:  $[\text{Ir}] = 120 \mu\text{M}$ ,  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $[\text{p-TSA}] = 10 \text{ mM}$ ,  $P_{\text{H}_2} = 41.1 \text{ bar}$ ,  
 $T = 150 \text{ }^\circ\text{C}$  in monochlorobenzene.

#### 4.2.7 Effect of Dry Rubber Content

Since the Crabtree's catalyst is sensitive to moisture, the effect of water in the system was studied. The hydrogenation at varying water content in system was performed in a Parr reactor under the base condition:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ,  $P_{\text{H}_2} = 41.4 \text{ bar}$ ;  $[\text{p-TSA}] = 10 \text{ mM}$ ,  $T = 150 \text{ }^\circ\text{C}$  in monochlorobenzene. The range of %DRC was varied between 60 and 40%. From Table 4.4, it can be seen that the degree of hydrogenation decreased with decreasing dry rubber content (or increasing water content). This might be due to the presence of water in system acting as an inhibitor during hydrogenation.

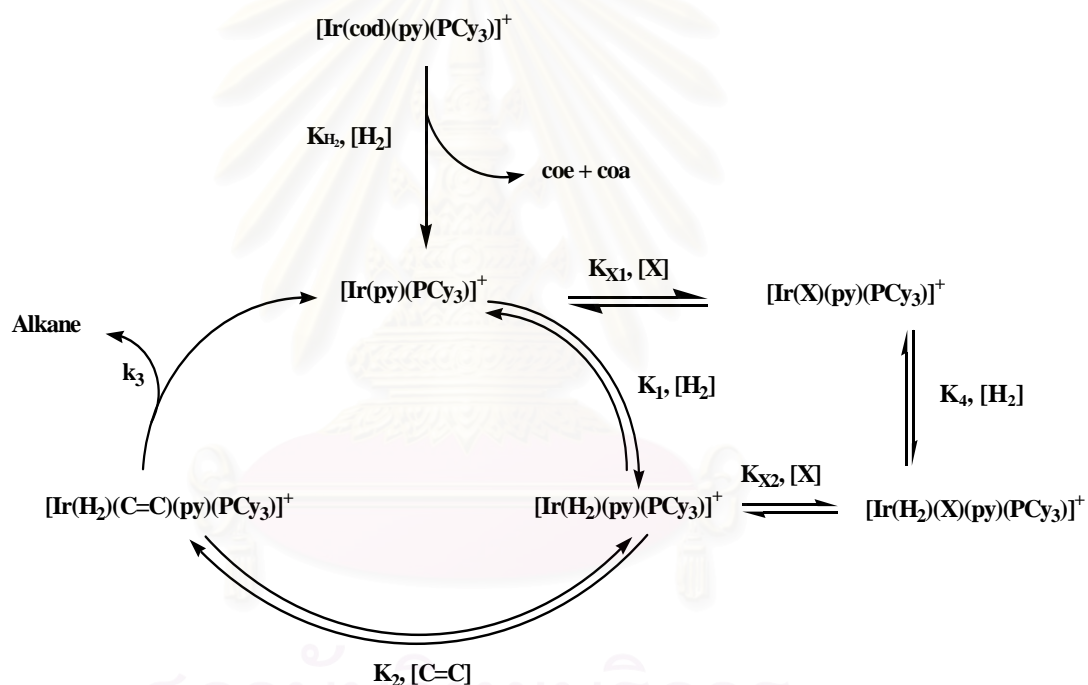
**Table 4.4** Effect of Dry Rubber Content on Degree of NRL Hydrogenation

DRC %	% Conversion (4 h)
60	91.3
50	57.6
40	44.5
30	38.7

Condition:  $[\text{Ir}] = 120 \mu\text{M}$ ;  $P_{\text{H}_2} = 41.1 \text{ bar}$ ;  $[\text{C}=\text{C}] = 100 \text{ mM}$ ;  $[\text{p-TSA}] = 10 \text{ mM}$ ;  
 $T = 150 \text{ }^\circ\text{C}$  in monochlorobenzene.

### 4.3 Reaction Mechanism and Rate Law

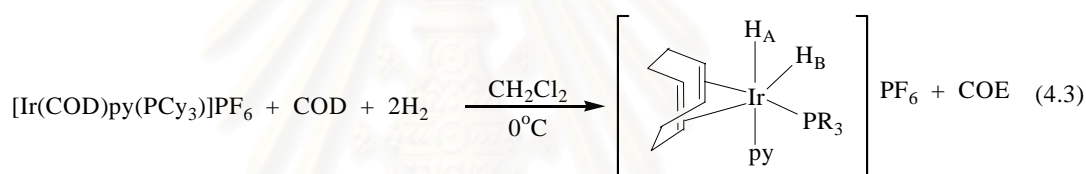
Previous studies of Crabtree's catalyst and its analogues have provided plausible pathways involved in the catalytic hydrogenation of olefins. Hydrogenation of diene polymers catalyzed by homogeneous catalysts consist of many intermediate complexes. Thus, the preferred catalytic pathway is developed from inferences from the kinetic data and electron counting schemes. The plausible catalytic cycles of  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  for the NRL hydrogenation are illustrated in Figure 4.9.



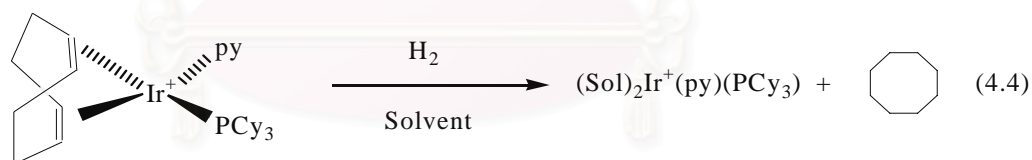
**Figure 4.9** Proposed catalytic mechanism for NRL hydrogenation in the presence of  $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]\text{PF}_6$ .

X = impurity

Crabtree et al. (1979) reported that  $[\text{Ir}(\text{cod})(\text{PR}_3)(\text{py})]\text{PF}_6$  ( $\text{PR}_3 = \text{PCy}_3$ ,  $\text{P-}i\text{-Pr}_3$ ) reacts with  $\text{H}_2$  at  $0^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  in the presence of excess cyclooctadiene (cod) to produce the *cis*-dihydrido-diolefin complexes. Their stereochemistry is shown in eq. 4.3. They had no evidence that  $[\text{IrH}_2(\text{cod})(\text{PR}_3)(\text{py})]\text{PF}_6$  can be formed by the direct activation of  $\text{H}_2$  by  $[\text{Ir}(\text{cod})(\text{PR}_3)(\text{py})]\text{PF}_6$  in the absence of excess (cod) since pyridine, a donor ligand, inhibited  $\text{H}_2$  addition to  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  which was different from other donor ligands that favored  $\text{H}_2$  addition to the metal center. However, the active catalyst can be formed in the presence of  $\text{H}_2$  and a noncoordinating solvent, presumably via reduction of the cyclooctadiene to cyclooctene (coe) and ultimately to cyclooctane (coa) as shown in eq. 4.4. The system is particularly effective for the reduction of highly substituted alkenes since the  $[\text{Ir}(\text{py})(\text{PCy}_3)]^+$  fragment is not very bulky (Dickson, 1985; Crabtree, 2001).



(COE = cyclooctene; R = Cy, *P-}i\text{-Pr})*



This 12-electron active species,  $[\text{Ir}(\text{py})(\text{PCy}_3)]^+$ , reacts with the  $\text{H}_2$  molecule to generate the dihydrido iridium complex,  $[\text{Ir}(\text{H}_2)(\text{py})(\text{PCy}_3)]^+$ . The substrate double bond coordinates to the dihydrido catalyst. Then, the hydrogen is transferred to the pi-olefin complex to obtain an alkyl complex. The alkyl complex is cleaved by transferred hydride to form the hydrogenated polymer and to regenerate the cationic active species.

According to the proposed reaction mechanism, the NRL hydrogenation catalyzed by iridium complex may be represented by the following rate expression:

$$-\frac{d[C=C]}{dt} = k_3[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]^+ \quad (4.5)$$

The effect of impurities (X) in NRL on the hydrogenation rate can be compared to the effect of the nitrile functional group, which inhibits the catalytic activity in NBR hydrogenation (Hu, 2000) and NR hydrogenation (Hinchiranan, 2004). It is possible that impurities in NRL might coordinate with unsaturated active species of the catalyst to reduce the hydrogenation activity. A material balance on the active species of the Ir catalyst is expressed in eq. 4.6.

$$[\text{Ir}]_T = [\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{H}_2)(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{X})(\text{py})(\text{PCy}_3)]^+ + [\text{Ir}(\text{H}_2)(\text{X})(\text{py})(\text{PCy}_3)]^+ \quad (4.6)$$

All the iridium complex species within the concentration terms in eq. 4.6 can be expressed in terms of  $[\text{Ir}(\text{H}_2)(\text{C}=\text{C})(\text{py})(\text{PCy}_3)]^+$  using the equilibria defined in Figure 4.9 and then can be substituted into eq.4.5 to provide the resulting rate law:

$$-\frac{d[C=C]}{dt} = \frac{k_3 K_1 K_2 [\text{Ir}]_T [\text{C}=\text{C}] [\text{H}_2]}{1 + K_{X1} [\text{X}] + K_1 [\text{H}_2] (1 + K_2 [\text{C}=\text{C}] + K_{X2} [\text{X}])} \quad (4.7)$$

The rate expression is consistent with the behavior of the iridium system observed throughout the kinetic investigations. Although the rate expression would show that the hydrogenation rate should have a zero order dependence on  $[\text{H}_2]$ , the kinetic observation indicated that the hydrogenation rate was first order with respect to hydrogen pressure. Thus it can be assumed that  $K_1$ ,  $K_2$  and  $K_{X2}$  are very small and then the term in which they appear in eq 4.7 are negligible for the range of the reaction conditions and substrate concentration used in this study. The reaction was found to exhibit a first order response of  $k'$  to  $[\text{Ir}]$ . In the case of NR and PIP hydrogenation, Hinchiranan (2004) reported that the reaction was found to exhibit a first order response of  $k'$  to  $[\text{Ir}]$  at low catalyst concentration and shift to zero order at a high level of catalyst concentration due to the possible dimerization of the catalyst. The rate of NRL hydrogenation decreased with increasing rubber concentration due to an increase in the amount of impurities in the NRL.

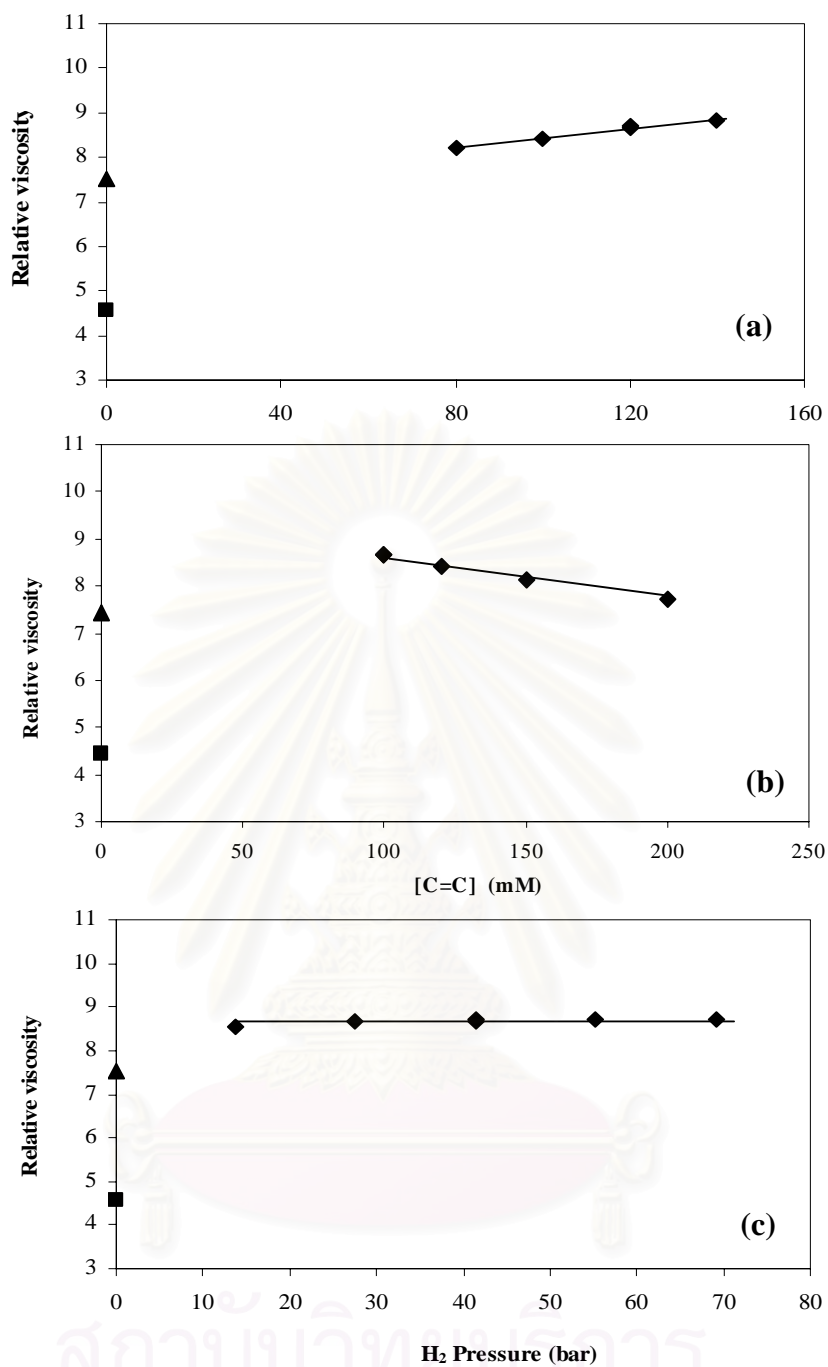
#### 4.4 Relative Viscosity of Hydrogenated Rubbers

Side reactions such as crosslinking and chain scission are some of the problems associated with polymer modification NRL. IR and NMR spectroscopies can confirm only the degree of hydrogenation; these techniques lack the sensitivity required to detect the presence of side reactions, which cause the undesirable properties. Therefore, the degree of polymer crosslinking must be inferred indirectly from molecular weight measurements. Dilute solution viscosity has been used to monitor the shifts in molecular weight that are created by crosslinking, branching or degradation. The viscosity of a dilute NRL solution before and after the hydrogenation process relative to pure solvent ( $\eta_{\text{rel}}$ ) was undertaken to investigate the effect of side reactions on the NRL hydrogenation using Crabtree's catalyst.

The effect of catalyst concentration, polymer concentration, and hydrogen pressure on the relative viscosity of NRL after the hydrogenation process is shown in Table 4.1 and Figure 4.10. Over the range of conditions investigated, (NRL ( $\eta_{\text{rel}} = 4.45$ ) and NR ( $\eta_{\text{rel}} = 7.42$ ):  $[\text{Ir}] = 60\text{-}140 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 80\text{-}200 \text{ mM}$  and  $P_{\text{H}_2} = 6.9\text{-}69.2 \text{ bar}$ ;  $T = 150^\circ\text{C}$ ), the relative viscosity of the hydrogenated rubbers was higher than NR. The increase in the relative viscosity suggests that no degradation occurred during the catalytic hydrogenation reaction.

Figure 4.10 shows that the relative viscosity of hydrogenated natural rubber latex (HNRL) varies over the range of 7.73 – 8.73, and is dependent on the reaction conditions, degree of hydrogenation and reaction time. The relative viscosity of HNRL samples was higher when samples were hydrogenated at high catalyst loading or low rubber concentration (Figure 4.10a – 4.10b). This might be explained on the basis that when the catalyst loading is relatively high compared with the amount of polymer, it is possible to attain a higher degree of crosslinking or branching within the polymer chain. Similar results were observed for NBR hydrogenation catalyzed by this Ir complex (Hu, 2000). For the effect of hydrogen pressure (Figure 4.10c), it was found that the relative viscosity of HNRL did not change.





**Figure 4.10** Relative viscosity ( $\eta_{rel}$ ) of HNRL as a function of (a) total catalyst loading:  $P_{H_2} = 41.4$  bar,  $[C=C] = 100$  mM,  $[p-TSA] = 10$  mM,  $T = 150^\circ C$ ; (b) polymer loading:  $[Ir] = 120$   $\mu M$ ,  $[p-TSA] = 10$  mM,  $P_{H_2} = 41.4$  bar,  $T = 150^\circ C$ ; (c) hydrogen pressure:  $[Ir] = 120$   $\mu M$ ;  $[C=C] = 100$  mM,  $[p-TSA] = 10$  mM,  $T = 150^\circ C$  in toluene (Relative viscosity of NR (■) = 7.54, of NRL (▲) = 4.50).

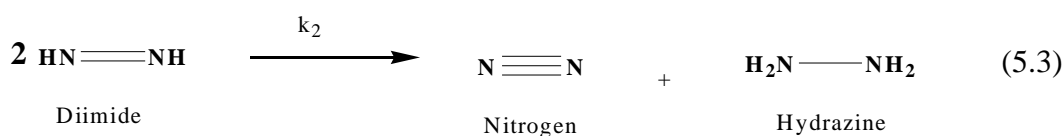
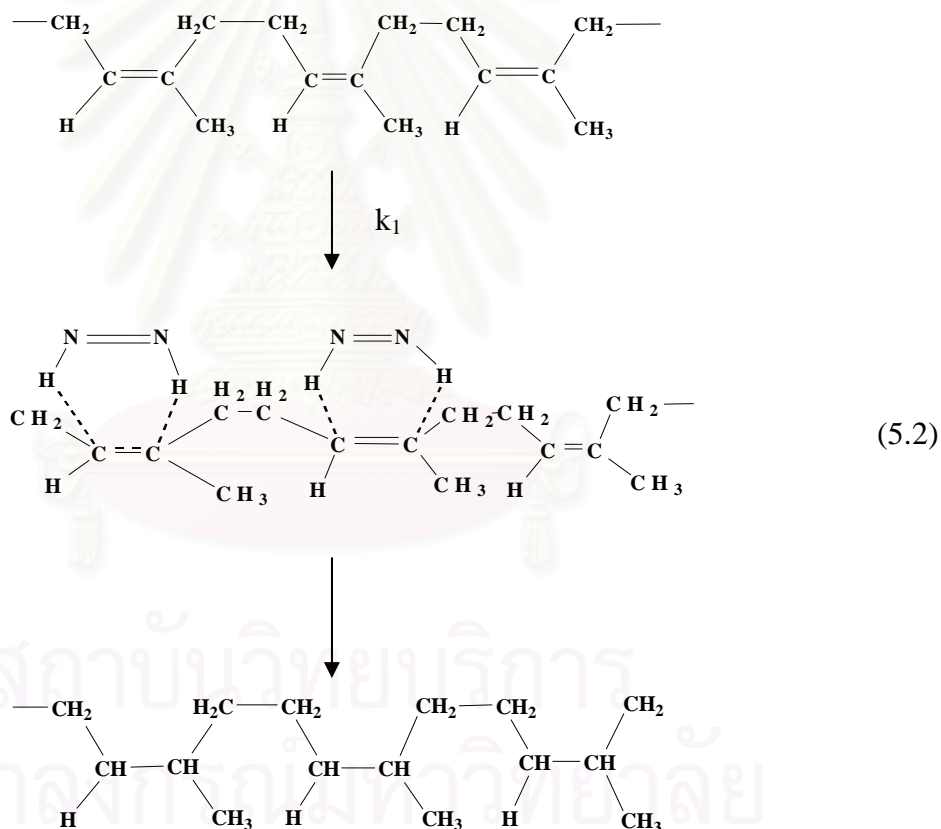
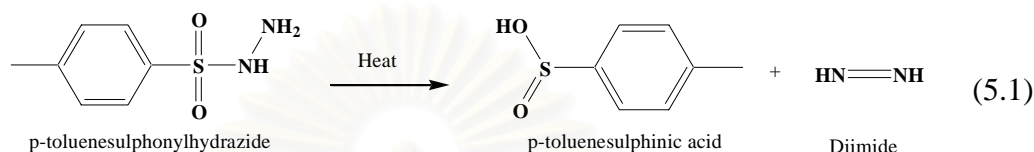
## CHAPTER V

### NONCATALYTIC HYDROGENATION OF NATURAL RUBBER LATEX

Catalytic and noncatalytic hydrogenation of diene based polymers has been widely studied. Classical catalytic hydrogenation, which is a reaction of unsaturated substrates with transition-metal-activated hydrogen, is usually quite expensive. It requires special equipment because the reaction is normally carried out under a high pressure of hydrogen and at a high temperature. The noncatalytic technique using a hydrogenation reagent has been extensively studied over the past 20 years. The reaction is homogeneous and generally performed under nitrogen gas at atmospheric pressure with a relatively simple apparatus. Diimide has been generated for use as a hydrogenation reagent via oxidation of hydrazine, decarboxylation of potassium azodicarboxylate, photochemical irradiation of 1-thia-3, 4-diazolidine-2, 5-dione and from thermolysis of arylsulfonylhydrazide (Schulz et al., 1982). Among these hydrogen-releasing agents, the thermal decomposition of *p*-toluenesulfonylhydrazide (*p*-TSH) has been successful. Mango and Lenz (1973) reviewed the use of diimide for hydrogenation of unsaturated polymers. Hanh (1992) improved the method for diimide hydrogenation of butadiene and isoprene by adding tri-*n*-propyl amine to eliminate side reactions in the butadiene polymer. Phinyocheep et al. (2003) studied diimide hydrogenation of a isoprene-styrene diblock copolymer. The solution 2% (w/v) of polymer in *o*-xylene was hydrogenated at 1:4 mole ratio between isoprene double bond and TSH, under 1 atm of nitrogen pressure at 135°C; 98.4% conversion was achieved within 4 hour. Samran et al. (2005) reported 80-85% hydrogenation for a 1% solution (w/v) of polymer in *o*-xylene solvent (100 ml), with 1 mole of C=C in the rubber per 2 moles of TSH under 1 atm of nitrogen pressure at 135°C for 8 h.

Noncatalytic hydrogenation technique involves *in situ* generation of diimide by heating *p*-TSH in a high boiling aromatic solvent such as xylene. Product of the thermal decomposition of *p*-TSH is *p*-toluenesulphinic acid and diimide (eq. 5.1). *p*-Toulenesulfonic acid is believed to cause the cyclization of polyisoprene and the acceleration of thermal decomposition of polymer (Luo, 1995). The transitory

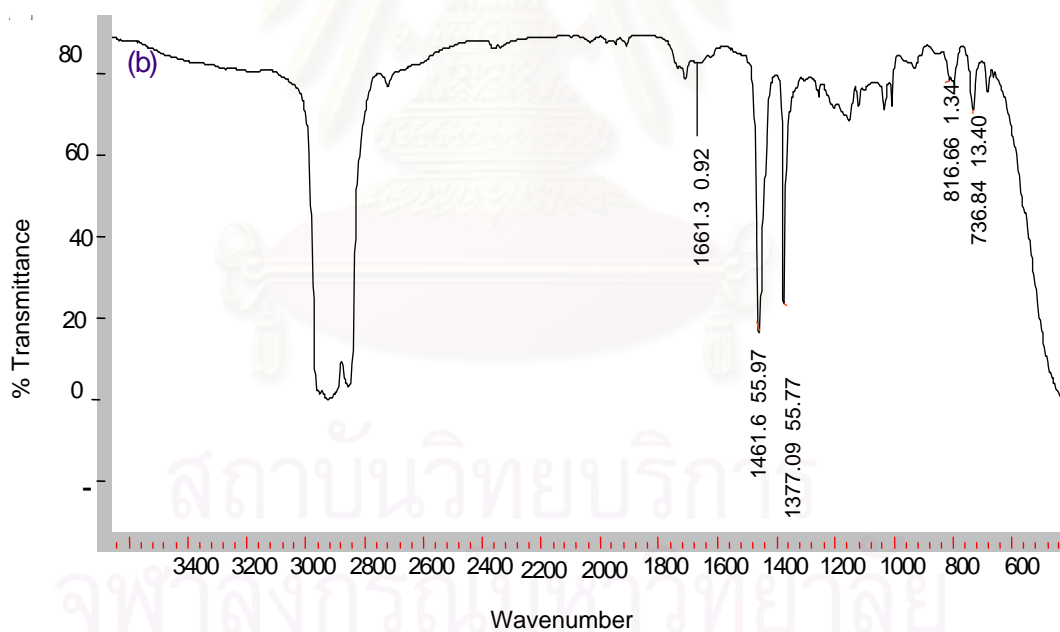
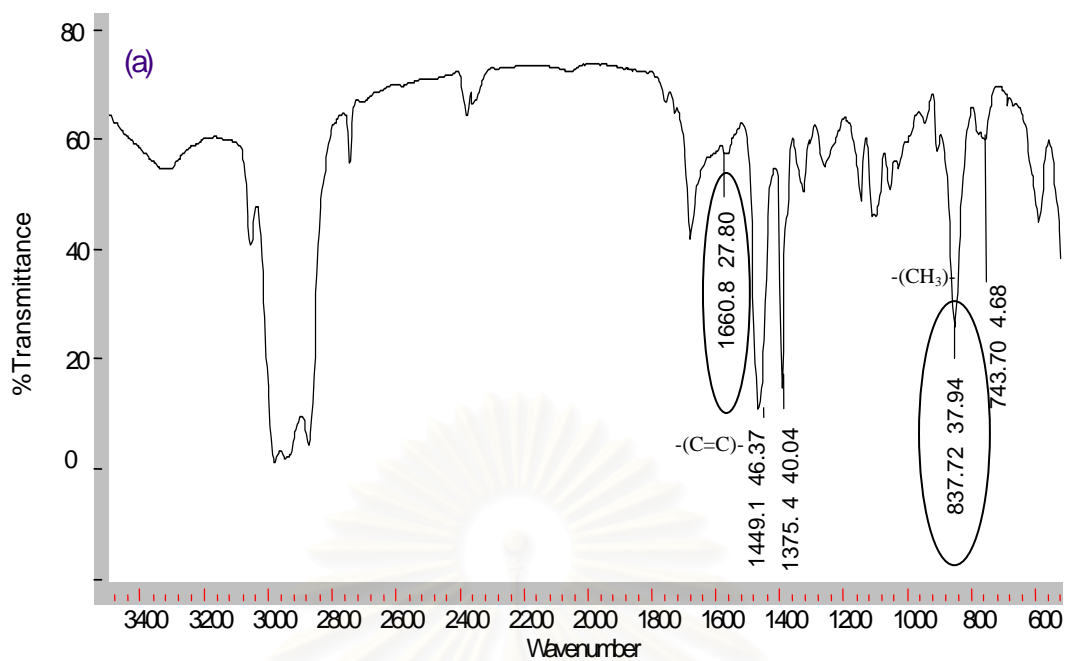
diimide could hydrogenate natural rubber latex *in situ* in solution. This reaction is homogenous and conducted at normal pressure. Syn addition of diimide on the carbon-carbon double bond in the polymer structure is presented (eq. 5.2). The hydrogenated latex product is an alternate ethylene propylene copolymer. The disproportionation reaction, also occurred and yields nitrogen and hydrazine, according to eq. 5.3



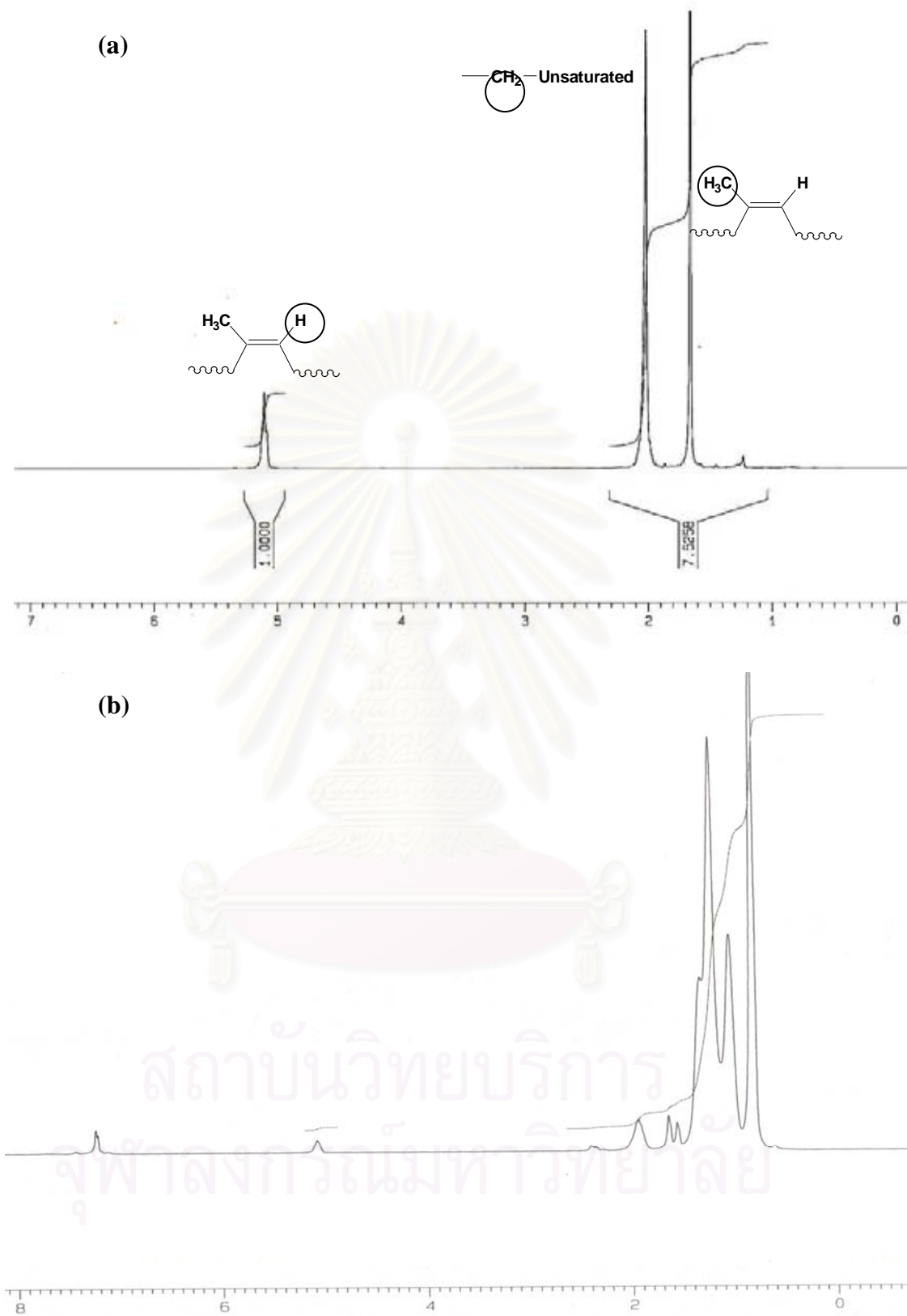
The objectives of this chapter were to study the hydrogenation of natural rubber latex by using diimide as an *in situ* reagent. Effect of rubber concentration ( $[C=C]$ ), diimide concentration, solvent type, source of diimide reagent and temperature were investigated. The diimide for this study was mainly derived from *p*-toluenesulfonylhydrazide ([*p*-TSH]). Conversion profiles and effect of impurities are also discussed.

### 5.1 Structure Characterization Using FTIR and NMR Spectroscopy

The FTIR spectrum for the starting natural rubber latex (NRL) and for the hydrogenated natural rubber latex (HNRL) are shown in Figure 5.1 (a) and 5.1 (b); respectively. The most apparent change in the FTIR spectra was the reduction of bands at 1660 and 837  $\text{cm}^{-1}$  attributed to C=C stretching and olefinic bending. The augmentation in the band at 735  $\text{cm}^{-1}$  for the  $-(\text{CH}_2)-$  species increased, as the extent of hydrogenation of C=C increased. The final degree of hydrogenation was determined by  $^1\text{H-NMR}$ . The comparison between the  $^1\text{H-NMR}$  spectrum of NRL and HNRL is shown in Figure 5.2 (a) and 5.2 (b), respectively. The hydrogenation led to peak intensity at 1.67, 2.03 and 5.14 ppm which was assigned to  $-\text{CH}_3$ ,  $-\text{CH}_2$ , and olefinic protons, respectively and the appearance of new peaks at 0.8 and 1.2 ppm attributed to saturated  $-\text{CH}_2$  and  $-\text{CH}_3$  of the ethylene – propylene of the hydrogenation product. Confirmation was obtained from  $^{13}\text{C-NMR}$  spectrum as shown in Figure 5.3 (a) and 5.3 (b). The polymer product is a strictly alternating copolymer of ethylene and propylene. The peak areas at 135.4 and 125.2 ppm decreased with an increase in the reduction of the olefinic carbon double bonds and four new peaks appear at 37.8, 33.1, 24.8 and 20.0 ppm which are attributed to  $\text{C}_\alpha$ ,  $-\text{CH}$ ,  $\text{C}_\beta$  and  $-\text{CH}_3$ , respectively.

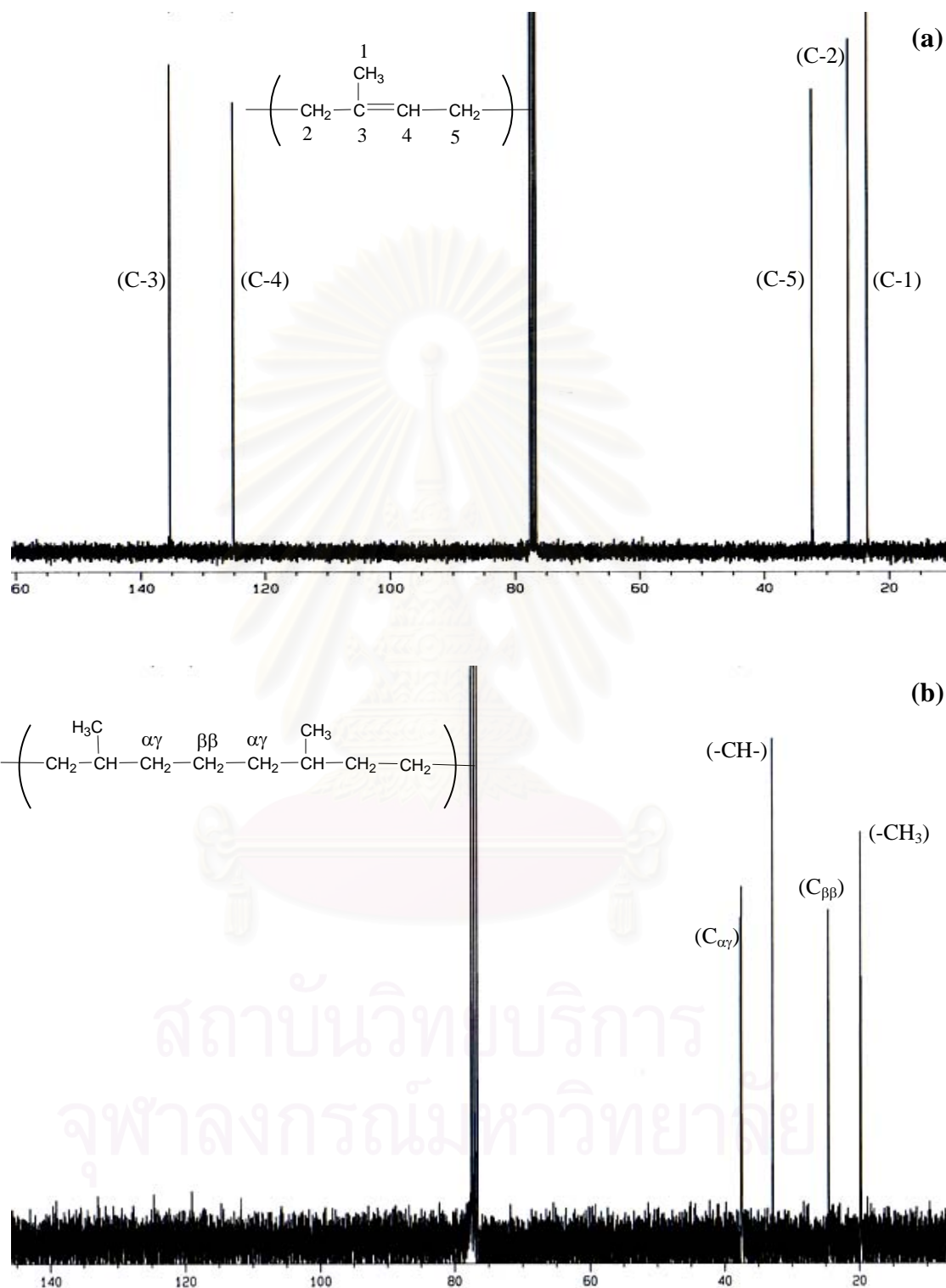


**Figure 5.1** FTIR spectra of (a) NRL and (b) HNRL obtained from diimide hydrogenation *in situ*.



**Figure 5.2**  $^1\text{H}$ -NMR spectra of (a) NRL and (b) HNRL obtained from diimide hydrogenation *in situ*.





**Figure 5.3**  $^{13}\text{C}$ -NMR spectra of (a) NRL and (b) HNRL obtained from diimide hydrogenation *in situ*.

## 5.2 Statistical Analysis Using Two-Level Factorial Design Experiments

Factorial designs are generally used for experimental systems involving several factors in order to study the main effects and joint effects of factors on the response (Montgomery, 2001). Two-level factorial design experiments are widely used to screen the influence of each reaction factor. In this work, the principal factors, which had an effect on the degree of hydrogenation were [p-TSH], [C=C] and temperature. When two-level factorial design was applied to calculate the effect of parameters in the experiment, the levels of factors may be arbitrarily called “low (-1)” and “high (+1)”. The range of [p-TSH], [C=C] and temperature were 88 - 256 mM, 64 - 180 mM and 125 - 145 °C, respectively. In Table 5.1, the results of factorial design experiments are presented. Yate’s algorithm was applied to investigate the main effects and interaction effects on % hydrogenation derived from the experiment.

Tables 5.2 and 5.3 present the results of Yate’s algorithm calculation and the calculation of effects and standard error of the  $2^3$  factorial experiment. The results in Table 5.3 indicated that [p-TSH], [C=C], and temperature had an influence on the degree of hydrogenation. [p-TSH] and temperature had positive effects which imply that the degree of hydrogenation increased with increasing p-TSH concentration and temperature. In contrast, C=C concentration showed a large negative effect on the degree of hydrogenation. The binary interactions and three-factor interactions were not highly significant.

**Table 5.1** Results from 2<sup>3</sup> Factorial Design Experiment for NRL Hydrogenation

Run	Temp (°C)	[p-TSH] (mM)	[C=C] (mM)	Degree of Hydrogenation (%)
1	125	64	88	65.5
2	145	64	88	78.5
3	125	180	88	83.5
4	145	180	88	90.0
5	125	64	256	50.2
6	145	64	256	56.1
7	125	180	256	67.4
8	145	180	256	72.4
9	125	64	88	63.5
10	145	64	88	80.2
11	125	180	88	81.5
12	145	180	88	88.9
13	125	64	256	50.1
14	145	64	256	54.1
15	125	180	256	69.4
16	145	180	256	71.6

Conditions: T = 135°C in o-xylene (100 ml), time = 4 h.

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**Table 5.2** Yate's Algorithm Calculation of the  $2^3$  Factorial Experiment

EXP	Design Matrix Variables			Average. Degree of Hydrogenation (%)	Algorithm			Divisor	Estimate	Identification
	Temp	[p-TSH]	[C=C]		(1)	(2)	(3)			
1	-1	-1	-1	64.5	143.8	315.7	561.5	8	70.2	Average
2	1	-1	-1	79.3	171.9	245.7	30.3	4	7.9	Temp
3	-1	1	-1	82.5	105.3	21.8	63.2	4	15.8	[p-TSH]
4	1	1	-1	89.5	140.4	8.5	-9.2	4	-2.3	Temp*[p-TSH]
5	-1	-1	1	50.2	14.8	28.0	-70.0	4	-17.5	[C=C]
6	1	-1	1	55.1	7.0	35.1	-13.3	4	-3.3	Temp*[C=C]
7	-1	1	1	68.4	4.9	-7.8	7.0	4	1.8	[p-TSH]*[C=C]
8	1	1	1	72.0	3.6	-1.4	6.4	4	1.6	Temp*[C=C]*[p-TSH]

Conditions: T = 135°C in o-xylene (100 ml), time = 4 h.

**Table 5.3** Calculation of Effects and Standard Errors for  $2^3$  Factorial Design Experiment

Effect	Estimate		Standard Error
Average	70.18	±	0.285
<b>Main Effects</b>			
Temp	7.58	±	0.571
[p-TSH]	15.81	±	0.571
[C=C]	-17.50	±	0.571
<b>Two-Factor Interaction</b>			
[p-TSH]*Temp	-2.30	±	0.571
Temp*[C=C]	-3.33	±	0.571
[p-TSH]*[C=C]	1.76	±	0.571
<b>Three-Factor Interaction</b>			
Temp*[C=C]*[p-TSH]	1.614	±	0.571

### 5.3 Effect of Parameters

The statistical experiments described above provide only information on the significance of the factors. In order to determine how each variable affects the hydrogenation degree, univariate experiments of the parameters were carried out individually in order to determine their influence on the degree of hydrogenation as shown in Figure 5.4 – 5.6. The univariate experimental results are presented in Table 5.4

**Table 5.4** Results of Hydrogenation of NRL by noncatalytic hydrogenation

Run	Temp (°C)	[p-TSH] (mM)	[C=C] (mM)	Degree of Hydrogenation (%)
1	135	32	88	29.6
2	135	64	88	71.0
3	135	81	88	94.4
4	135	161	88	94.1
5	135	161	88	94.2
6	135	161	88	94.4
7	135	180	88	94.7
8	135	180	88	94.6
9	135	322	88	93.6
10	135	430	88	91.9
11	135	161	44	97.8
12	135	161	88	94.7
13	135	161	88	94.7
14	135	161	132	90.5
15	135	161	176	82.8
16	135	161	221	74.5
17	135	161	265	65.0
18	135	161	353	48.6
19	135	161	441	38.0
20	115	161	88	47.3
21	125	161	88	70.0
22	135	161	88	94.8
23	145	161	88	90.8
24	155	161	88	81.3

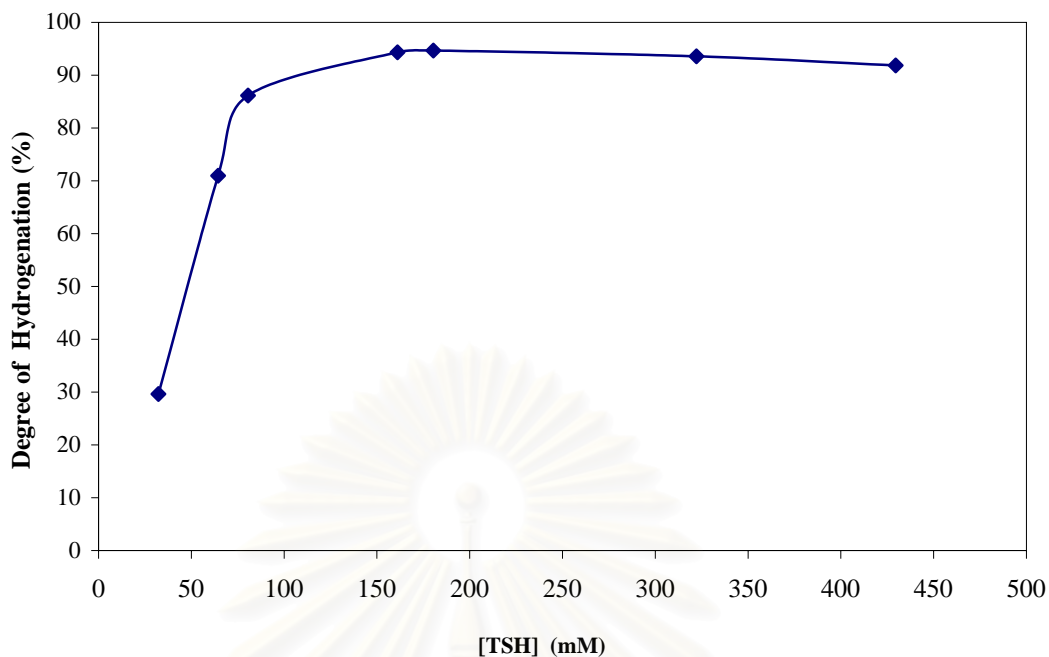
Condition: solvent = o- xylene (100 ml), time = 4 h

### 5.3.1 Effect of p-TSH Concentration

p-TSH is one of the most popular reagents for releasing a diimide ( $N_2H_2$ ) intermediate under thermal decomposition reaction (Hung et al., 1965). TSH was only slightly soluble in xylene at room temperature, however, it could be totally dissolved after heating to the reaction temperature. As the reaction proceeded, the reaction mixture changed from colorless to deep yellow with the release of the diimide molecule. The diimide then underwent hydrogen addition to the double bonds in the polymer structure. The diimide could undergo reactions as shown in eq. 5.1 – 5.3.  $k_1$  and  $k_2$  are the rate constants for hydrogenation of NRL and diimide disproportionation, respectively.

In order to investigate the effect of TSH concentration on the degree of hydrogenation, TSH was varied from 32 to 430 mM. The reaction condition was 88 mM of rubber concentration in o-xylene at  $135^\circ C$  for 4 h. The effect of p-TSH concentration on latex hydrogenation is shown in Figure 5.4. Theoretically, a 1:1 molar ratio should give complete hydrogenation. Harwood et al. (1973) reported that approximately 5 moles of hydrazide per mole of butadiene or isoprene unit were required to complete the hydrogenation. Samran et al. (2005) showed that 2 moles of p-TSH per mole of double bond in NR were used to achieve 85% hydrogenation in 8 h. In this work, it was found that the degree of hydrogenation was low at low level of p-TSH concentration. However, 161 mM of p-TSH concentration (the mole ratio of  $C=C:TSH = 1:1.8$ ) was used to attain 95% hydrogenation. As expected, the degree of hydrogenation increased at high level of p-TSH concentration due to the large amount of diimide generated. Mango and Lenz (1973) reported that the rate of hydrogenation depended on the microstructure of polyisoprene segments. They found that the vinyl segments were hydrogenated at a greater rate than either the cis or trans 1,4 units ( $k_{\text{vinyl}} > k_{\text{cis}} \sim k_{\text{trans}}$ ).



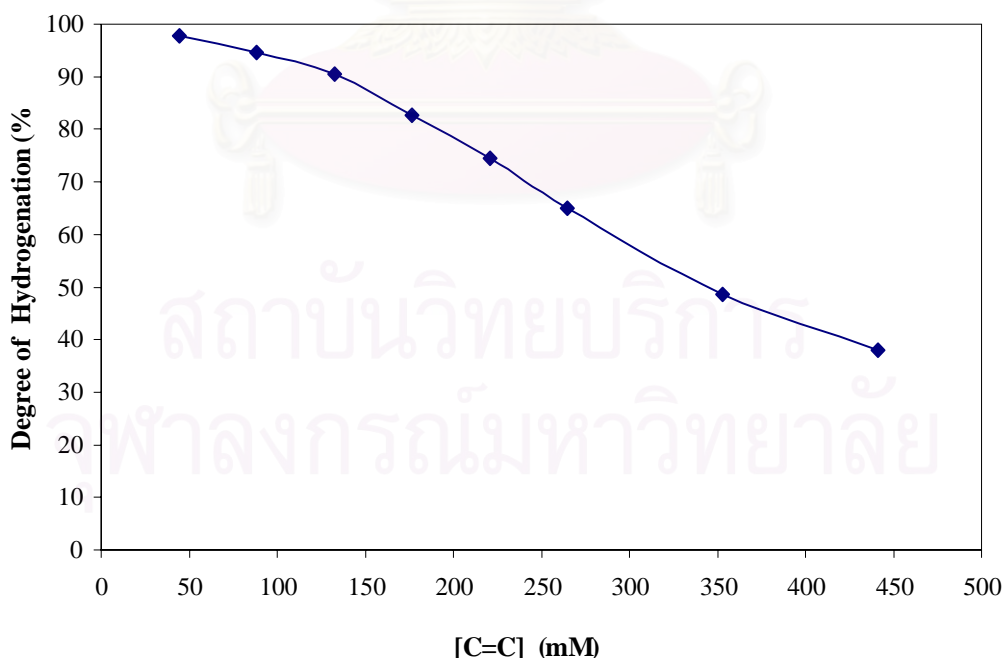


**Figure 5.4** Effect of p-TSH concentration on NRL hydrogenation.  $[C=C] = 88$  mM;  $T = 135$  °C in o-xylene (100 ml); time = 4 h.

The rate of disproportionation ( $k_2$ ) was reported to be faster than that of reaction between diimide and double bonds of diene polymers ( $k_1$ ). At 161 mM of TSH concentration, the mole ratio of the substrate and diimide concentration appeared to be high enough to prevent the disproportionation reaction that in the later stage of the hydrogenation resulted in wasteful side reactions (Harwood et al., 1973).

### 5.3.2 Effect of Rubber Concentration

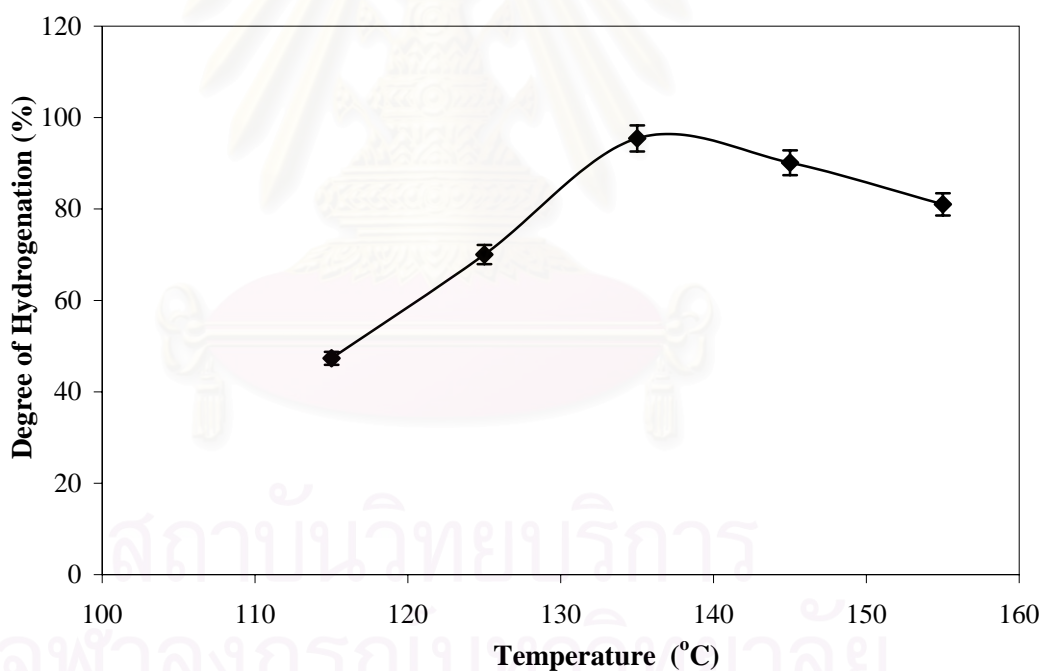
The effect of rubber concentration on the degree of hydrogenation was investigated over the range of 44 – 441 mM at [p-TSH] = 161 mM in o-xylene. The hydrogenation condition was at 135°C for 4 h. Figure 5.5 shows that the increase in rubber concentration caused a reduction in degree of hydrogenation. It is possible that the active diimide species from TSH was not adequate for complete removal of carbon-carbon double bonds in the system. Thus, the degree of hydrogenation declined with increasing rubber concentration. At high rubber concentration, the disproportionation rate of diimide was faster than that of hydrogenation rate. Since rubber solution at high rubber concentration was more viscous than at low rubber concentration, it was possible that for the high rubber concentration system, it was difficult for the diimide to diffuse and react with C=C in the rubber structure, and thus, the degree of hydrogenation was decreased. Moreover, impurities such as lipid and water in NRL might cause the reduction of the hydrogenation level. In contrast to the present results, Nang et al. (1976) reported that rate of hydrogenation increased with increasing rubber concentration.



**Figure 5.5** Effect of rubber concentration on NRL hydrogenation. [p-TSH] = 161 mM; T = 135 °C in o-xylene (100 ml); time = 4 h.

### 5.3.3 Effect of Reaction Temperature

Experiments were carried over the temperature range of 115 - 155°C with 161 mM of p-TSH concentration and 88 mM of rubber concentration in o-xylene. The results shown in Figure 5.6 indicate that the degree of hydrogenation increased with increasing temperature and then slightly decreased when temperature was above 135°C. The higher temperature caused an increase in the rate of decomposition, which relates to an increase in the amount of diimide in the system. At high temperature, the rate of disproportionation ( $k_2$ ) was faster than that of reaction between diimide and carbon-carbon double bonds of diene polymers ( $k_1$ ) (Hahn 1992). It was believed that the diimide species were suddenly degraded at high temperature and caused the increase in the  $k_2$  value which retarded the degree of hydrogenation.



**Figure 5.6** Effect of Temperature on NRL hydrogenation. [C=C] = 88 mM; [p-TSH] = 161 mM; T= 115-155°C in o-xylene (100 ml); time = 4 h.

### 5.3.4 Effect of Solvents

The specific choice of solvent for a given polymer was dependent upon the ease of product isolation. It is most convenient to use a low boiling point solvent consistent with dissolving all components of the reaction system (Harwood et al., 1973). A series of experiments were undertaken using different solvents for NRL hydrogenation under the base condition: [p-TSH] = 161 mM, [C=C] = 88 mM at 135°C. The effect of solvent type on the hydrogenation of NRL is shown in Table 5.5. The NRL was dissolved to a greater extent in polar solvents than in non-polar solvents whereas, p-TSH was more soluble in the non-polar solvents. The results show that o-xylene was the best solvent for hydrogenation of NRL using p-TSH diimide generated *in situ*. It is probable that TSH was dissolved in o-xylene to a greater extent than in other solvents and it is easier to produce the diimide species which could react with carbon-carbon double bonds to achieve a higher degree of hydrogenation.

**Table 5.5** Effect of Solvent on the NRL Hydrogenation

Solvent	% Hydrogenation
Tetrahydrofuran	62.3
Monochlorobenzene	82.9
Touelene	84.6
Benzene	89.0
o-Xylene	95.2
Cyclohexane	79.9
Hexane	77.1

Condition: [p- TSH] = 161 mM, [C=C] = 88 mM, T = 135 °C, time = 4 h.

### 5.3.5 Effect of Diimide Source

Hydrogenation of natural rubber latex via diimide generated *in situ* depended on the concentration of diimide as presented in section 5.3.1. Therefore, the source of diimide was investigated. Diimide source was selected based on thermal analysis of hydrazine species. Diimide concentration was related with the decomposition rate of the diimide source. A series of experiments were undertaken using different diimide sources for NRL hydrogenation at the base condition:  $[N_2H_2] = 64 \text{ mM}$ ,  $[C=C] = 88 \text{ mM}$  at  $135^\circ\text{C}$ . The effect of diimide source types on hydrogenation of NRL is summarized in Table 5.6. TPSH and MSH were also found to be a source of diimide for hydrogenation of natural rubber latex. Cusack et al. (1976) found that the thermal decomposition rate of TPSH and MSH was 380 and 24 times greater compared to TSH; respectively. Under these conditions, TPSH was the best diimide source for NRL hydrogenation due to its high decomposition rate and high stability of the diimide species.

**Table 5.6** Effect of Source of Diimide on the NRL Hydrogenation

Source of Diimide	% Hydrogenation
TSH	70.9
MSH	75.0
TPSH	84.4

Condition:  $[p\text{-TSH}] = 88 \text{ mM}$ ,  $[C=C] = 64 \text{ mM}$ ,  $T = 135^\circ\text{C}$  in *o*-xylene (100 ml) for 4 h.

TSH = *p*-Toluene sulfonyl hydrazide

MSH = 2,4,6-Trimethylbenzenesulfonyl hydrazide

TPSH = 2,4,6-Tri-isopropylbenzenesulfonyl hydrazide

### 5.3.6 Effect of Impurity

The effect of impurities was suspected to reduce the hydrogenation rate of NRL hydrogenation catalyzed by the osmium catalyst. To study the effect of impurity on the degree of hydrogenation of NRL using diimide with an *in situ* reagent method, the hydrogenation of deproteinized NRL (DNRL) prepared according to the previous literature (Tangpakdee and Tanaka, 1997b) was examined. The experiments were carried out at 161 mM of [p-TSH], 88 mM of [C=C] at 135°C in *o*-xylene for 4 h. Table 5.7 shows the effect of nitrogen content in the rubber. The degree of hydrogenation of DPNRL was at the same level as that obtained from NRL hydrogenation. It is possible that the protein content in the rubber does not cause the decrease in the activity of the diimide reagent. It can be explained that the nitrogen group in the protein structure cannot coordinate with the active species or prohibit the diimide generation. To clarify this idea for the effect of the possible impurity, an experiment was set up using *cis*-1,4-polyisoprene (CPIP) as an analogue of NRL in terms of rubber microstructure. Hexylamine and hexadecylacrylamide which have nitrogen functional groups similar to those in proteins were added in the CPIP hydrogenation to test if the effect would be similar to the protein effect on degree of NRL hydrogenation.

The effect of high ammonia content in the latex was also investigated on the degree of hydrogenation as shown in Table 5.8. The reaction conditions were: [C=C] = 88 mM, [p-TSH] = 161 mM at 135 °C in *o*-xylene. It was found that all experiments with nitrogen functional groups increase the degree of hydrogenation for diimide hydrogenation of CPIP. It was believed that the nitrogen group could produce the base condition in the reaction, which reacts with *p*-toluenesulfonic acid in the system with *p*-toluenesulfonic acid produced from thermal decomposition as shown in eq 5.3. The addition of base species into the system may increase the reaction rate by assisting in the deprotonation of TSH. One such attempt to hydrogenate the synthetic polyisoprene with TSH in the presence of an amine base (pyridine) has been reported. The addition of tertiary amine, tri-*n*-propyl amine, was believed to cause protonation of amine instead of an olefin which should greatly decrease the propensity of the *p*-toluenesulfinate anion, which is an excellent nucleophile, to react the polymer backbone (Mango and Lenz, 1973).



**Table 5.7** Effect of Nitrogen Content on Degree of NRL Hydrogenation

Rubber Type	% Nitrogen Content	% Hydrogenation
NRL	0.20	94.5
DPNRL	0.02	90.5

Condition: [p- TSH] = 161 mM, [C=C] = 88 mM, T = 135 °C in o-xylene, time = 4 h

NRL = Natural Rubber Latex

DPNRL = Deproteinized Natural Rubber Latex

**Table 5.8** Effect of Impurity on Hydrogenation of Synthetic *Cis*-1, 4-Polyisoprene

Substance	% Hydrogenation
-	41.0
hexylamine	45.3
hexadecylacrylamide	70.3
ammonium hydroxide	75.0

Condition: [p- TSH] = 161 mM, [C=C] = 88 mM and impurity 0.25% by weight at 135 °C in o-xylene (100 ml), time = 4 h

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### 5.3.7 Effect of Water Addition

High ammonia natural rubber latex contains 40% water by weight. The rubber particles disperse in water to form an emulsion. Water present in the latex may also possibly reduce the degree of NRL hydrogenation using diimide generated *in situ*. Experiments were carried out with various amounts of water present in the natural rubber latex in terms of % dry rubber content (DRC) at the base condition [p-TSH] = 161 mM, [C=C] = 88 mM at 135°C. The range of DRC in this study was between 30 and 60% by weight, corresponding to 70 - 40% water by weight. The effect of water content within the NRL on the degree of hydrogenation is summarized in Table 5.9. It was found that the degree of hydrogenation was not significantly decreased with an increase in the amount of water (the lower % DRC).

**Table 5.9** Effect of Dry Rubber Content on the Degree of NRL Hydrogenation

DRC %	% Hydrogenation
60	94.7
50	93.5
40	92.5
30	91.8

Condition: [p-TSH] = 161 mM, [C=C] = 88 mM at 135 °C in o-xylene for 4 h.

#### 5.4 Kinetics for Natural Rubber Latex Hydrogenation

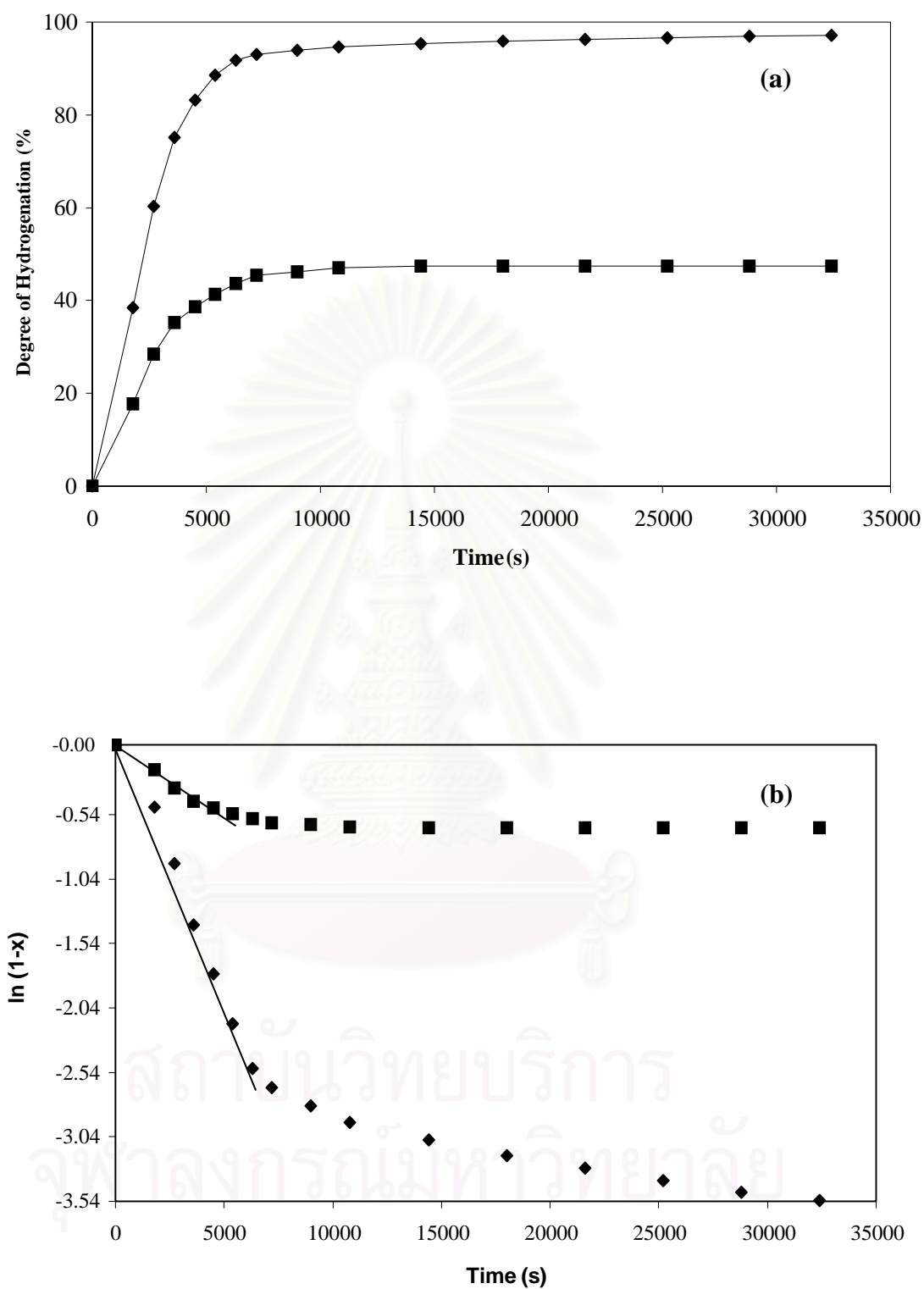
For the kinetic studies of NRL hydrogenation by diimide generated *in situ*, samples collected during hydrogenation were used to investigate the rate dependence of reaction. A conversion profile is shown in Figure 5.7. Nang et al (1976) proposed that the kinetics for the reaction are as shown in eq. 5.4. The second order rate equation was proposed. In this work, the conversion profile exhibits an apparent first order dependence for hydrogenation of C=C. The pseudo first-order rate equation as shown in eq.5.5 where  $k'$  is a pseudo first order rate equation which represents the hydrogenation process when TSH was present in excess.

$$\frac{-d[\text{C}=\text{C}]}{dt} = k [\text{C}=\text{C}][\text{TSH}] \quad (5.4)$$

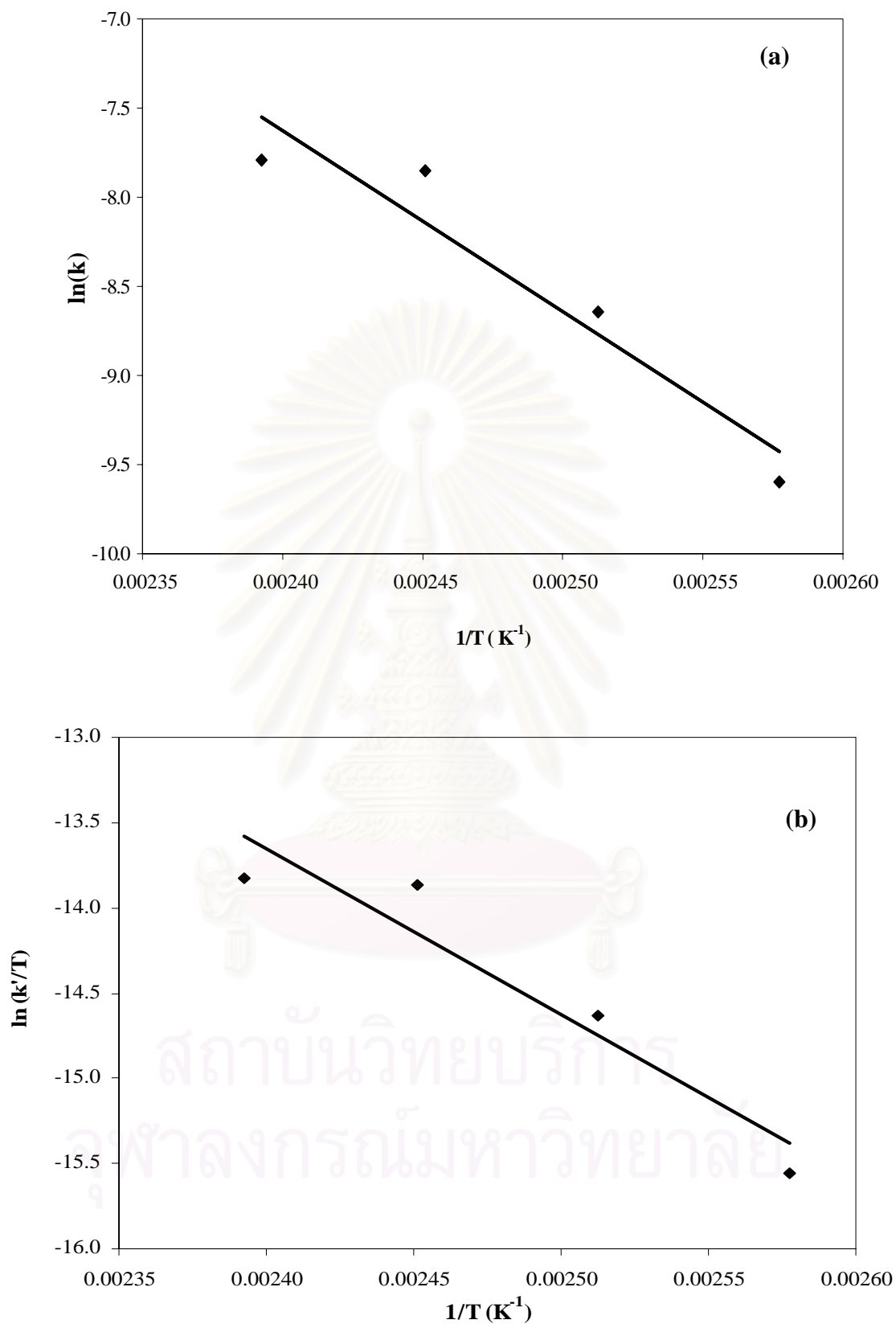
$$\frac{-d[\text{C}=\text{C}]}{dt} = k' [\text{C}=\text{C}] \quad (5.5)$$

Although the  $\ln(1-x)$  versus time plot deviates from linearity in the latter stages of reaction,  $k'$  can be calculated with a fair degree of confidence. The rate constant ( $k'$ ) for the overall reactions of NRL hydrogenation was about  $1.9 \times 10^{-4} \text{ s}^{-1}$ . It was postulated that the deviations of the  $\ln(1-x)$  versus time plot might result from the side reactions of diimide which becomes dominate once a higher degree of hydrogenation is achieved.

The activation energy for the hydrogenation of NRL by diimide generated *in situ* was investigated as shown in Figure 5.8a. The results from the Arrhenius plots for NRL hydrogenation by diimide generated *in situ* indicate that the activation energy of this system was about 84.2 kJ/mol. The apparent activation enthalpy and entropy were estimated as 80.9 kJ/mol and -117.0 J/mol K, respectively as shown in Figure 5.8b



**Figure 5.7** (a) Olefin conversion profiles and (b) first-order  $\ln$  plot of NRL hydrogenation.  $[p\text{-TSH}] = 161 \text{ mM}$ ;  $[\text{C}=\text{C}] = 88 \text{ mM}$ ; (◆)  $T = 135^\circ\text{C}$ , (■)  $T = 115^\circ\text{C}$  in *o*-xylene.



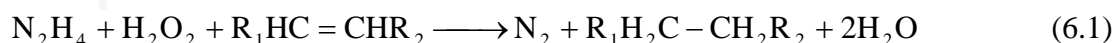
**Figure 5.8** (a) Arrhenius plots and (b) Eyring plot for NRL hydrogenation by diimide generated *in situ*.  $[\text{C}=\text{C}] = 88 \text{ mM}$ ;  $[\text{p-TSH}] = 161 \text{ mM}$ ;  $T = 115\text{-}135^\circ\text{C}$  in *o*-xylene (100 ml).

## CHAPTER VI

### DIIMIDE HYDROGENATION OF NATURAL RUBBER LATEX IN THE PRESENCE OF CUPRIC IONS

Hydrogenation of diene –based rubbers helps to improve the thermal and oxidative stability of these polymer when the radical-susceptive C=C are replaced by saturated hydrocarbon bonds. Natural rubber latex (NRL) could be hydrogenated to a strictly alternating ethylene-propylene copolymer using a diimide reduction system. As a potential alternative to conventional hydrogenation technology, the diimide hydrogenation is a method, in which gaseous hydrogen, organic solvents and precious transition-metal catalysts are not necessary. This is especially advantageous when hydrogenated natural rubber in latex form is demanded. The diimide hydrogenation process is more attractive for the hydrogenation of polybutadiene-based rubbers in latex form (Parker et. al., 1994). The reaction between hydrogen peroxide and hydrazine may be employed to hydrogenate rubber in latex form. Different catalysts, different procedures of reactant addition and different additives are used to achieve the efficient hydrogenation. Cupric ion has been found to be an effective catalyst (Parker et. al, 1991). Diimide reduction technique of NRL was accomplished by using hydrazine hydrate/hydrogen peroxide and  $\text{Cu}^{2+}$  as catalyst.

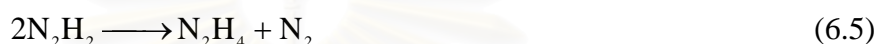
The overall reaction for diimide hydrogenation of polymer is presented in eq. 6.1 (Lin, 2004). Diimide hydrogenation is divided into two steps: (1) the reaction between hydrazine and hydrogen peroxide to produce diimide and (2) the reaction between diimide and carbon-carbon double bonds to form hydrogenated polymer, as given by the following equations ( eq. 6.2 and eq. 6.3 )







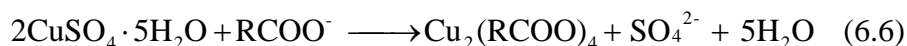
However, according to the reactivity of diimide, two side reactions possibly accompany the hydrogenation reaction. One is the further reaction of diimide with hydrogen peroxide to generate nitrogen, which most likely occurs on the interface as the hydrogen peroxide resides in the water phase. The other side reaction is the reaction between two diimide molecules to produce one molecule of hydrazine and to release one nitrogen molecule, which most likely occurs in the rubber phase.



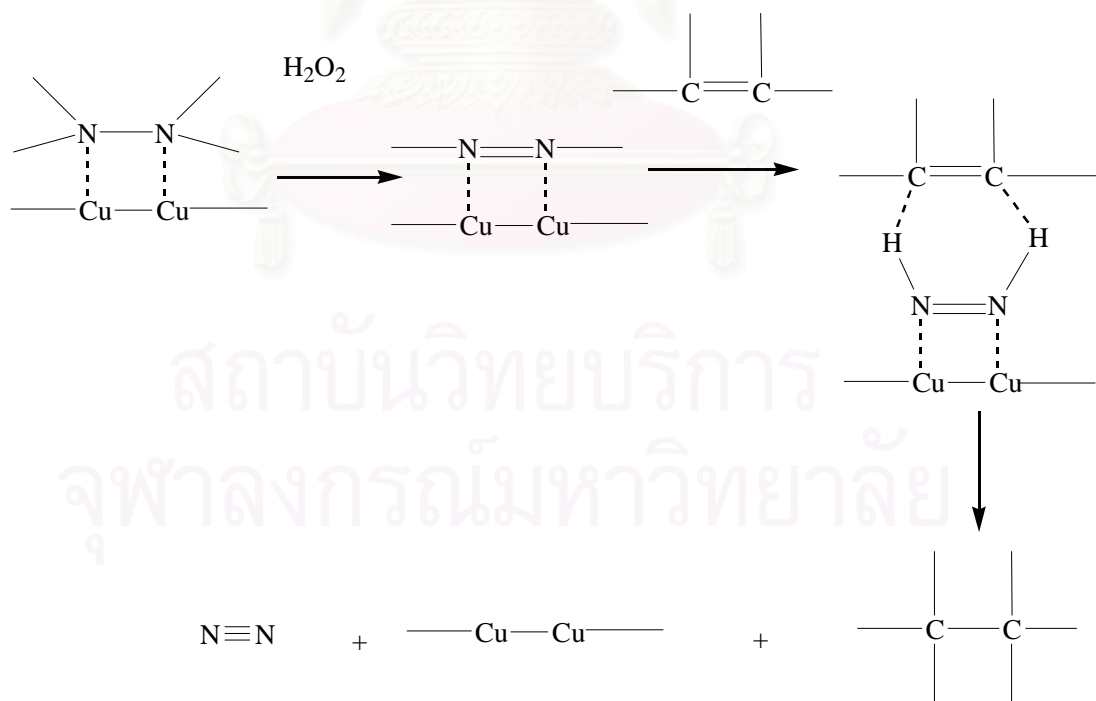
The four reactions represented by eq. 6.2, 6.3, 6.4 and 6.5 comprise the framework of the diimide hydrogenation of latex. Equation 6.2 may occur at the interface of rubber particles and also at the bulk aqueous phase. Diimide may get consumed by way of eq. 6.4 either at the interface or in the aqueous phase before it actually diffuses into the rubber particles. Equation 6.5 is the radical source for crosslinking. There are three competing parallel processes in the reaction mechanism

- 1) The reaction of eq. 6.2 may occur at the interface and also in the bulk aqueous phase. Diimide generated in the aqueous phase would not be available for the hydrogenation reaction in the organic phase. Thus, this competition influences the efficiency of the diimide utilization in the aqueous phase.
- 2) The reaction of eq. 6.4 competes with the diimide diffusion process for diimide before it diffuses into the rubber particles. This competition influences the efficiency of diimide utilization at the interface.
- 3) The reactions eq. 6.5 and eq. 6.2 compete with each other for diimide. This competition influences the diimide utilization efficiency in the rubber phase, and also sets up the platform for radical generation and crosslinking.

The copper ion is able to greatly accelerate the formation of diimide from the  $N_2H_4/H_2O_2$  redox system. Copper ion when added to the system can be distributed over the surface of latex particles by means of a strong complex with carboxylate group ( $RCOO^-$ ) at outer surface (Sarkar et al., 2000). The reaction can be represented as



From the above equation, it is seen that the active site is actually bimetallic copper which resides within the surface layer of polymer particle as the bridge species (Parker et al., 1992). As copper resides at the latex particle surface, where it comes across a large excess of hydrazine in aqueous phase, it is likely that hydrazine bound between copper centers through lone electron pairs on nitrogen. Subsequent oxidation of bound hydrazine with hydrogen peroxide then directly produces diimide and water while the active copper site is regenerated. Diimide is the actual hydrogenating species which reduces the double bond. The overall process is shown in eq. 6.7.

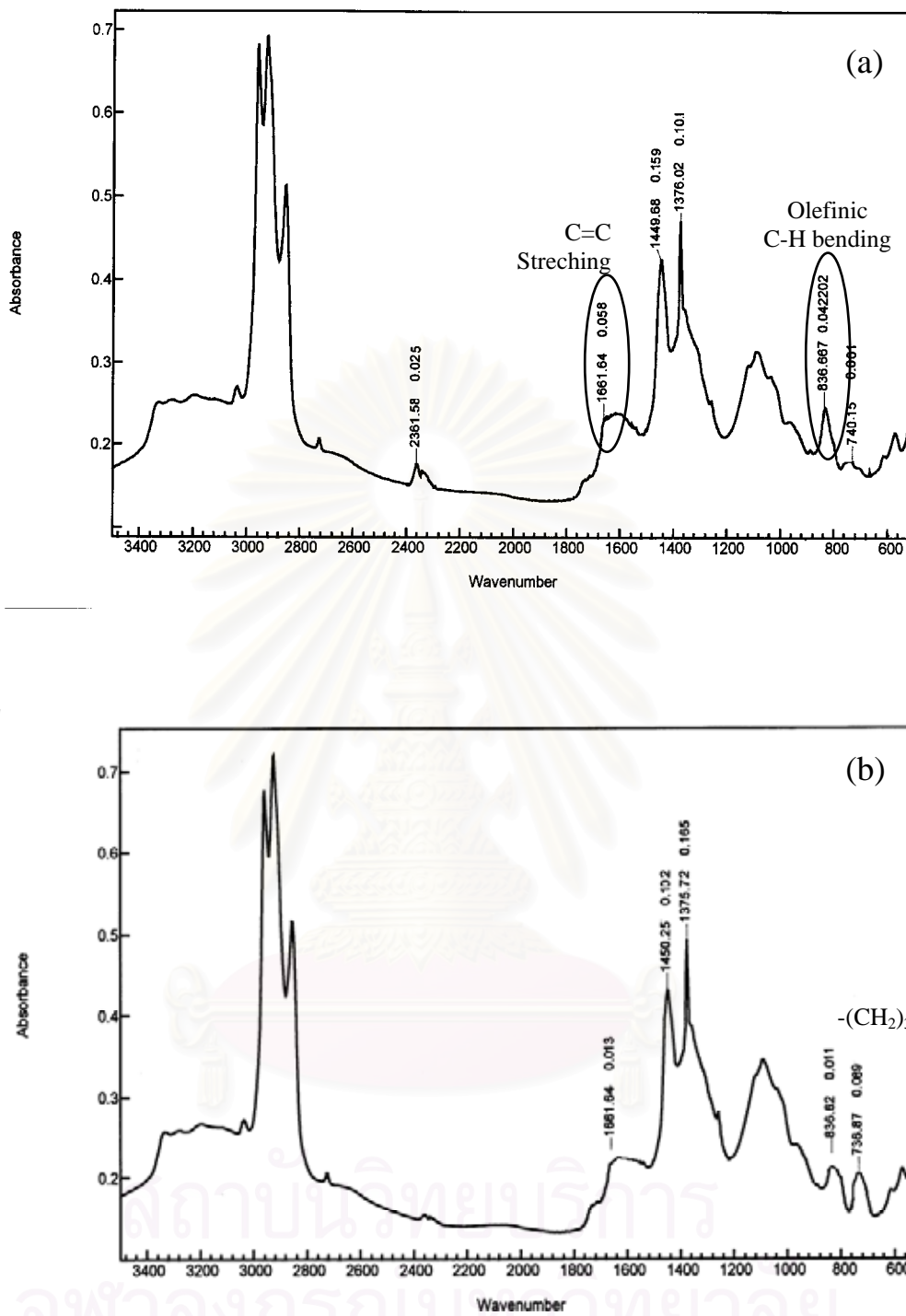


(6.7)

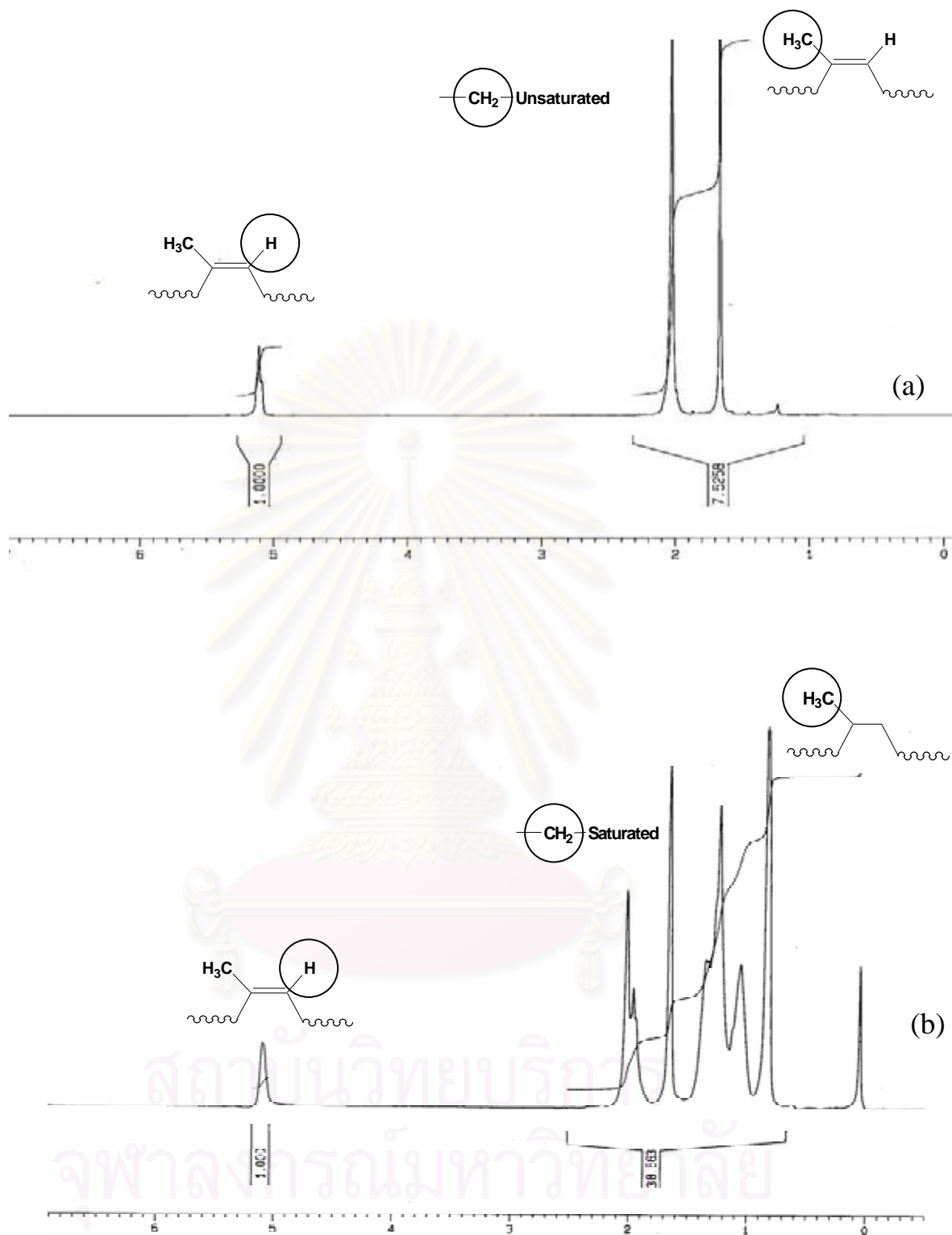
The purpose of the work presented in this chapter was to study the hydrogenation of natural rubber latex via metal ion diimide hydrogenation. The effects of reaction parameters such as catalyst concentration, rubber concentration, hydrazine concentration, hydrogen peroxide concentration and reaction temperature were investigated. The effect of catalyst type was also discussed.

### 6.1 FTIR and NMR Spectroscopic Characterization

Figure 6.1 illustrates the IR spectra of both NR latex (NRL) and 67.8% hydrogenated NR latex (HNRL). The nonhydrogenated latex spectrum shows distinct peaks for the C=C unsaturation, i.e. at  $1663\text{ cm}^{-1}$  (C=C stretching) and  $836\text{ cm}^{-1}$  (trisubstituted olefinic C-H bending). It can be noted that the absorbance peaks for the C=C unsaturation decrease after the hydrogenation.  $^1\text{H-NMR}$  spectra for the nonhydrogenated NR latex and 67.8 % hydrogenated NR latex are provided in Figure 6.2. Major peaks are obtained in the aliphatic (1.7 and 2.2 ppm) regions. The signals of *cis* olefinic protons are centered at 5.2 ppm. As the hydrogenation progresses, the olefinic peak area considerably decreases, and new peaks appear at 0.8 – 1.8 ppm attributed to  $-\text{CH}_3$  and saturated  $-\text{CH}_2-$  units. The extent of hydrogenation has been calculated from the  $^1\text{H-NMR}$  spectra by noting the change in the integral of the peaks representing protons for the hydrogenated rubber latex.



**Figure 6.1** FTIR spectra of (a) NRL and (b) HNRL. C=C = 84 mmol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; CuSO<sub>4</sub> = 8 μmol; H<sub>2</sub>O = 1.67 mol; total volume = 90 ml; T = 55°C.



**Figure 6.2**  $^1\text{H-NMR}$  spectra of (a) NRL and (b) HNRL.  $\text{C}=\text{C} = 84$  mmol;  $\text{N}_2\text{H}_4 = 0.336$  mol;  $\text{H}_2\text{O}_2 = 0.437$  mol;  $\text{CuSO}_4 = 8$   $\mu\text{mol}$ ;  $\text{H}_2\text{O} = 1.67$  mol; total volume = 90 ml;  $T = 55^\circ\text{C}$ .

## 6.2 Factorial Design Experiment

NRL hydrogenation via diimide reduction in the presence of metal ions was studied using the hydrogenation procedure described in section 2.6. The degree of hydrogenation was calculated by NMR spectroscopy as mentioned in section 2.10 for investigating the effect of reaction parameters on the degree of hydrogenation. To determine the significant reaction factors and the significance of joint factor interactions in the hydrogenation of the latex, a  $2^k$  factorial experimental design was used (Montgomery, 2001). Three principal factors considered to have an effect on the hydrogenation degree of NRL, are the amount of hydrazine ( $N_2H_4$ ), hydrogen peroxide ( $H_2O_2$ ) and rubber as present in terms of carbon- carbon double bond concentration ( $C=C$ ). A two-level factorial design was applied to calculate the effect of a given parameter. In this experiment, the level of the factor may be subjectively called “ low (-)” and “high (+)”. The ranges of hydrazine, hydrogen peroxide, and rubber ( $C=C$ ) were 100 – 250 mmol, 80 - 250 mmol, and 50 – 180 mmol, respectively as shown in Table 6.1. Total volume of the mixture was varied due to the amount of hydrazine and hydrogen peroxide supplied under the different conditions. Thus, the total reaction volume was varied over the range of 49 – 90 ml. The reaction temperature was kept constant at 55°C. The amount of cupric sulfate and water were also kept constant at 8  $\mu$ mol and 1.67 mol, respectively. Yate’s algorithm was applied to investigate the main effects and interaction effects on the degree of hydrogenation derived from the experimental data. Tables 6.2 and 6.3 show the results of the Yate’s algorithm calculation and the calculation of effects and standard errors for the  $2^3$  factorial design, respectively. The results in Table 6.3 indicate that ( $N_2H_4$ ), ( $H_2O_2$ ) and ( $C=C$ ) had a profound influence on the degree of hydrogenation. The ( $N_2H_4$ ) and ( $H_2O_2$ ) had a positive effect which implied that the degree of hydrogenation increased with an increase in ( $N_2H_4$ ) and ( $H_2O_2$ ). In contrast, ( $C=C$ ) showed a negative effect on the degree of hydrogenation. The degree of hydrogenation decreased with increase in ( $C=C$ ). Other interactions were moderate for the system. These observations indicated that the interaction does not give rise to a significant factor affecting the reaction.



**Table 6.1** Results from  $2^3$  Factorial Design Experiment for NR Hydrogenation

Run	N <sub>2</sub> H <sub>4</sub> (mmol)	H <sub>2</sub> O <sub>2</sub> (mmol)	C=C (mmol)	Degree of Hydrogenation (%)
1	100	80	50	38.0
2	250	80	50	51.5
3	100	250	50	46.4
4	250	250	50	69.9
5	100	80	180	24.5
6	250	80	180	31.9
7	100	250	180	27.2
8	250	250	180	42.0
9	100	80	50	37.2
10	250	80	50	50.5
11	100	250	50	47.2
12	250	250	50	70.1
13	100	80	180	23.7
14	250	80	180	32.1
15	100	250	180	26.9
16	250	250	180	42.0

Conditions: H<sub>2</sub>O= 1.67 mol, CuSO<sub>4</sub> = 8 μmol, total volume = 49 - 90 ml,

T= 55°C, reaction time = 6 h.

**Table 6.2** Yate's Algorithm Calculation of the  $2^3$  Factorial Experiment

Experiment	Design Matrix Variables			Avg. degree of Hydrogenation (%)	Algorithm				Identification	
	N <sub>2</sub> H <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	C=C		(1)	(2)	(3)	DivisorEstimate		
1	-1	-1	-1	37.6	88.5	205.4	330.5	8	41.3	Average
2	1	-1	-1	51.0	116.8	125.1	59.3	4	14.8	N <sub>2</sub> H <sub>4</sub>
3	-1	1	-1	46.8	56.1	36.5	41.2	4	10.3	H <sub>2</sub> O <sub>2</sub>
4	1	1	-1	70.0	69.0	22.8	16.8	4	4.2	N <sub>2</sub> H <sub>4</sub> *H <sub>2</sub> O <sub>2</sub>
5	-1	-1	1	24.1	13.4	28.1	-80.2	4	-20.1	C=C
6	1	-1	1	32.0	23.2	12.9	-13.7	4	-3.4	N <sub>2</sub> H <sub>4</sub> *C=C
7	-1	1	1	27.1	7.9	9.8	-15.3	4	-3.8	H <sub>2</sub> O <sub>2</sub> *C=C
8	1	1	1	42.0	14.9	7.0	-2.8	4	-0.7	H <sub>2</sub> O <sub>2</sub> *C=C*N <sub>2</sub> H <sub>4</sub>

Conditions: H<sub>2</sub>O= 1.67 mol, CuSO<sub>4</sub> = 8 μmol, total volume = 49 - 90 ml,

T= 55°C, reaction time = 6 h.

**Table 6.3** Calculation of Effects and Standard Errors for  $2^3$  Factorial Design Experiment

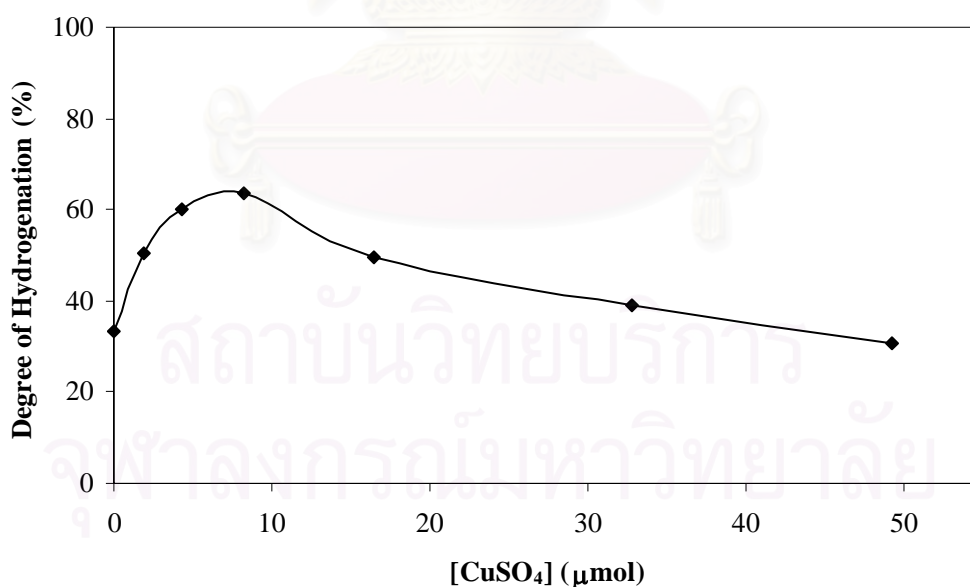
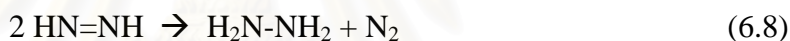
<b>Effect</b>	<b>Estimate</b>	<b>Standard Error</b>
<b>Average</b>	41.3	$\pm 1.10E-01$
<b>Main Effects</b>		
N <sub>2</sub> H <sub>4</sub>	14.8	$\pm 2.20E-01$
H <sub>2</sub> O <sub>2</sub>	10.4	$\pm 2.20E-01$
C=C	-20.1	$\pm 2.20E-01$
<b>Two-Factor Interaction</b>		
N <sub>2</sub> H <sub>4</sub> *H <sub>2</sub> O <sub>2</sub>	4.2	$\pm 2.20E-01$
N <sub>2</sub> H <sub>4</sub> *C=C	-3.4	$\pm 2.20E-01$
H <sub>2</sub> O <sub>2</sub> *C=C	-3.8	$\pm 2.20E-01$
<b>Three-Factor Interaction</b>		
H <sub>2</sub> O <sub>2</sub> *C=C*N <sub>2</sub> H <sub>4</sub>	-0.7	$\pm 2.20E-01$

### 6.3 Effect of Process Parameters

NRL hydrogenation via diimide reduction in the presence of a metal ion was carried out under the condition that organic solvent, hydrogen gas and high reaction temperature were not necessary. The diimide species in this system was produced via a redox mechanism between hydrogen peroxide and hydrazine. Hydrogenation of NRL was studied in a glass reactor. The effect of different parameters on NRL hydrogenation was studied by varying the amount of water, catalyst concentration, rubber concentration, hydrazine concentration, hydrogen peroxide concentration, and temperature. All details are described below.

### 6.3.1 Effect of Cupric Sulfate Concentration

The effect of cupric sulfate concentration on diimide hydrogenation was carried out over a range of 0 to 49  $\mu\text{mol}$ . The hydrogenation reaction was carried out at  $55^\circ\text{C}$ ,  $\text{C}=\text{C} = 84 \text{ mmol}$ ,  $\text{N}_2\text{H}_4 = 0.252 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.328 \text{ mol}$  and  $\text{H}_2\text{O} = 1.67 \text{ mol}$  (total volume 77.5 ml). Figure 6.3 demonstrates the effect of cupric sulfate concentration and indicates that the copper ion was able to accelerate the formation of diimide from the  $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$  redox system. The copper ion in this system can be presented in three locations depending on the concentration: (a) in the water medium; (b) at the polymer surface; (c) inside the latex particle (He et al., 1997). At high cupric sulfate concentration, copper ion may be present in these 3 locations. On the other hand, copper ion at low cupric sulfate concentration may be present at only the polymer surface or in the water media. Localizing copper ion in the water phase will lead only to decomposition reactions of diimide as shown in eq. 6.8 and 6.9. The disproportionation/decomposition reaction of diimide involves (Sarkar et al., 2000):

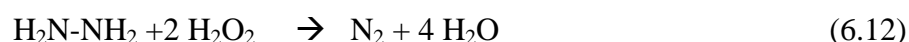


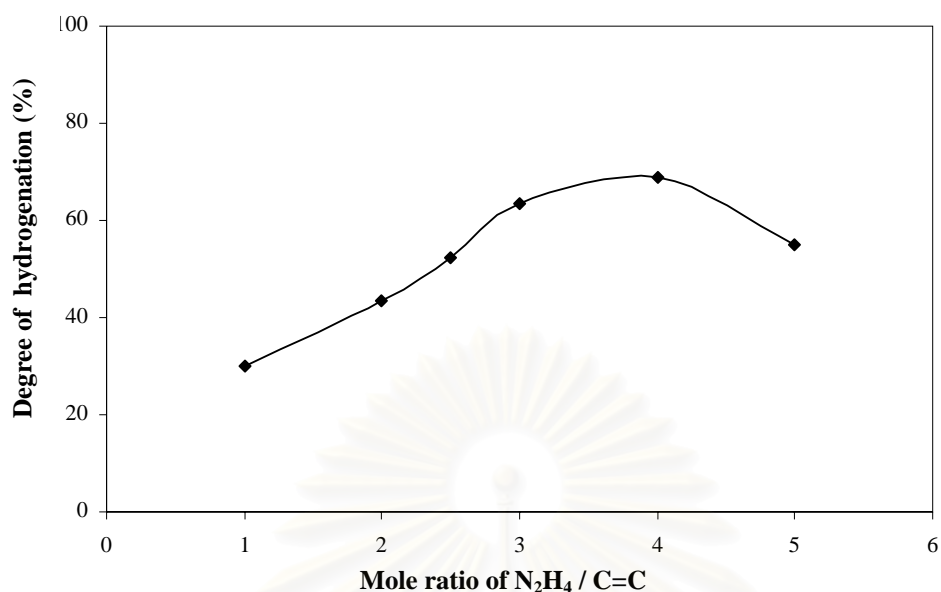
**Figure 6.3** Effect of cupric sulfate concentration on NRL hydrogenation.  $\text{C}=\text{C} = 84 \text{ mmol}$ ;  $\text{N}_2\text{H}_4 = 0.252 \text{ mol}$ ;  $\text{H}_2\text{O}_2 = 0.328 \text{ mol}$ ;  $[\text{H}_2\text{O}] = 1.67 \text{ mol}$ ; total volume 77.5 ml;  $T = 55^\circ\text{C}$ ; time = 6 h.

Copper ion added into this system can be distributed over the surface of latex particles by means of a strong complex with the carboxylate soap anions of the surfactant (Parker et al., 1992). Thus the concentration of copper ion at the particle surface is a key factor, which needs to be controlled. In order to reach a high degree of hydrogenation, the copper ion should reside only at the surface of the latex particle. In this work, the degree of hydrogenation increased with increasing cupric sulfate concentration up until 8  $\mu\text{mol}$  where thereafter the degree of hydrogenation decreased. The rate of formation of diimide would be faster at higher concentration of the catalyst, which in turn may result in an increase in diimide disproportionation as compared to its use for the hydrogenation process. At higher copper ion concentration, some free copper ions may also be present in the water medium. This would also cause the  $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$  reaction (decomposition) to mostly occur in the aqueous phase resulting in a reduction in the hydrogenation level of NRL.

### 6.3.2 Effect of Hydrazine Concentration

The mole ratio of  $\text{N}_2\text{H}_4/\text{C}=\text{C}$  has been varied over the range of 1 to 5. The hydrogenation reaction was carried out at  $55^\circ\text{C}$ ,  $\text{C}=\text{C} = 84 \text{ mol}$ , mole ratio of  $\text{H}_2\text{O}_2/\text{N}_2\text{H}_4 = 1.3$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$  and  $\text{H}_2\text{O} = 1.67 \text{ mol}$  (total volume = 54 – 108 ml). The effect of  $\text{N}_2\text{H}_4/\text{C}=\text{C}$  mole ratio is shown in Figure 6.4. It was found that the degree of hydrogenation increased with increasing  $\text{N}_2\text{H}_4$ . It was possible that the amount of diimide, the active species for the hydrogenation process, was increased when hydrazine was in excess. The rate of the interaction of the diimide species with  $\text{C}=\text{C}$  was expected to result in an increase in the degree of hydrogenation. The three possible reactions between hydrazine and hydrogen peroxide as shown in eq. 6.10 - 6.12 are consistent with this idea.





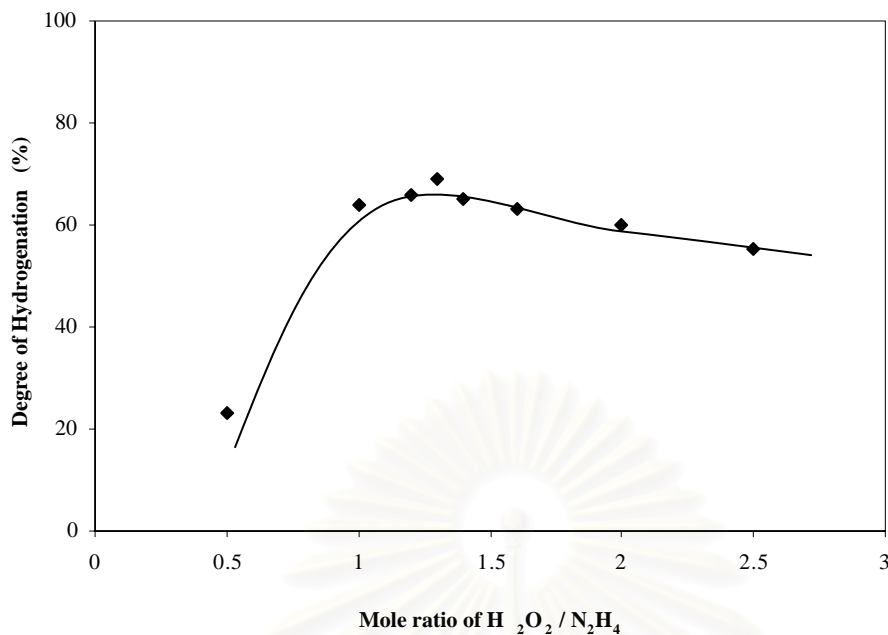
**Figure 6.4** Effect of hydrazine concentration on NRL hydrogenation.  $CuSO_4 = 8 \mu mol$ ;  $C=C = 84 mmol$ ; mole ratio of  $H_2O_2 / N_2H_4 = 1.3$ ;  $H_2O = 1.67 mol$ ;  $T = 55^\circ C$ ; total volume = 54 – 108 ml; time = 6 h.

In the presence of carbon – carbon double bonds of isoprene segments in NRL and a metallic ion as a catalyst, eq. 6.11 was predominant. Diimide species were produced and then reacted with  $C=C$  to increase the level of hydrogenation. When the amount of  $C=C$  was decreased and the amount of hydrogen peroxide was increased, eq 6.12 predominated and produced a large amount of nitrogen gas. The higher the amount of added  $N_2H_4$ , the more diimide was produced, which then increased the degree of hydrogenation. In contrast, the degree of hydrogenation began to slowly decrease when  $N_2H_4/C=C$  was higher than 4. It can be explained that this behavior results from the diimide species self reacting at high concentration levels of diimide to cause a decrease in hydrogenation efficiency. Another possible reason to explain the lower hydrogenation efficiency is that the excess content of diimide in this system may also disperse into the aqueous phase. Xie et al. (2002) claimed that the higher ratio between rubber and hydrazine is helpful for the decrease in gel formation when higher degrees of hydrogenation of NBRL were attained.

### 6.3.3 Effect of Hydrogen Peroxide Concentration

The hydrogenation reaction was carried out by varying the ratio between hydrogen peroxide and hydrazine over the range of 0.5 to 2.5,  $C=C = 84$  mmol,  $N_2H_4/C=C$  mol ratio = 4,  $CuSO_4 = 8 \mu mol$  and  $H_2O = 1.67$  (total volume = 66 – 129 ml) The reaction temperature was  $55^\circ C$ . Figure 6.5 shows that the degree of hydrogenation dramatically increased at low  $H_2O_2/N_2H_4$  ratio. Above a  $H_2O_2/N_2H_4$  mol ratio = 1.4, the degree of hydrogenation tended to decrease. This occurrence may be attributed from the competitive reaction between hydrazine and  $H_2O_2$  (eq. 6.11 and eq. 6.12). When  $H_2O_2/N_2H_4$  was higher than 1.6, the degree of hydrogenation decreased due to a possible crosslinking reaction, which reduces the number of free carbon – carbon double bonds for diimide reduction (Sakar et al., 1997). Moreover, some hydrazine may be consumed by the side reaction as shown in eq. 6.12 at high hydrogen peroxide concentration resulting in a decrease in the degree of hydrogenation. Based on the reaction stoichiometry as shown in eq. 6.10, the suitable ratio for generation of the diimide species was 1:1 of hydrogen peroxide: hydrazine. Parker and Purdon (1991) found the suitable ratio for diimide species in the hydrogenation of NBR latex was 2:1, which was similar to the results for hydrogenation of SBR latex reported by He et al. (1997). Sakar et al. (2000) found the suitable ratio for diimide species to hydrogenate XSBR (carboxylic styrene butadiene rubber latex) was 2:1. In this experiment, the optimum ratio of hydrogen peroxide and hydrazine was between 1:1 and 1.4:1. It was believed that the hydrogen peroxide was easily decomposed, so it was necessary to have an in excess hydrogen peroxide for effective production of diimide under the present reaction conditions used.

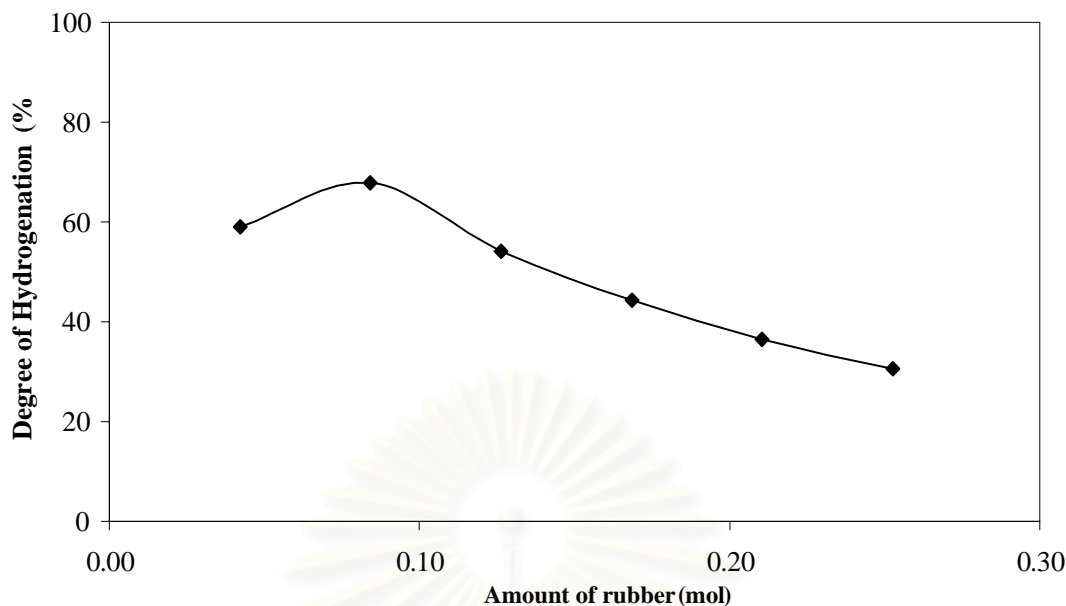




**Figure 6.5** Effect of hydrogen peroxide concentration on NRL hydrogenation.  $\text{CuSO}_4 = 8 \mu\text{mol}$ ;  $\text{C}=\text{C} = 84 \text{ mmol}$ ; mole ratio of  $\text{N}_2\text{H}_4/\text{C}=\text{C} = 4$ ;  $\text{H}_2\text{O} = 1.67 \text{ mol}$ ; total volume = 66 - 129 ml;  $T = 55^\circ\text{C}$ ; time = 6 h.

#### 6.3.4 Effect of Rubber Concentration

The effect of rubber concentration was studied in terms of the rubber volume over the range of 20 ml (0.042 mol) - 100 ml (0.252 mol) of rubber containing 14 % DRC in the presence of  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ,  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$  and  $\text{CuSO}_4 = 8 \mu\text{mol}$ , total volume = 67 - 167 ml. The hydrogenation was carried out at  $55^\circ\text{C}$  for 6 h. The results of these experiments are shown in Figure 6.6. These results indicate that the degree of hydrogenation decreased with an increase in rubber volume since it affected the efficiency of the diimide species in this system. At high volume of rubber, the diimide species may be self decomposed during the hydrogenation process resulting in a low degree of hydrogenation. In contrast, at a lower volume of rubber (low rubber concentration), it is possible that the diimide hydrogenation reaction occurred in the rubber phase rather than self decomposition of diimide. The diimide species was in excess when compared to the rubber species in system. Therefore, the degree of hydrogenation increased at low volume of rubber.

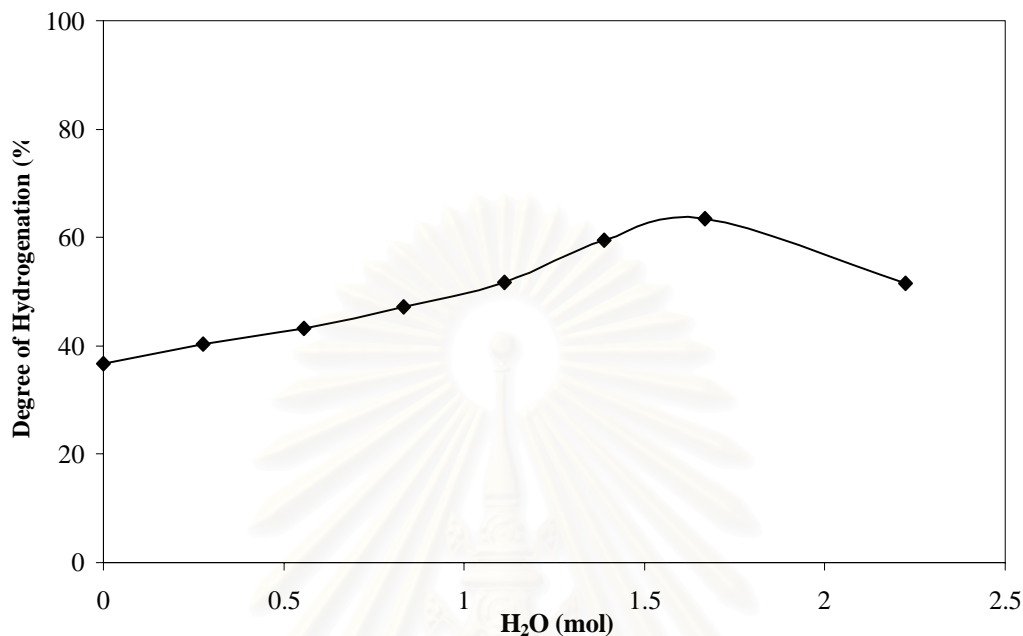


**Figure 6.6** Effect of rubber concentration on NRL hydrogenation. 14.3% DRC of latex;  $\text{CuSO}_4 = 8 \mu\text{mol}$ ;  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ;  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ;  $T = 55^\circ\text{C}$ ; total volume = 67 – 167 ml; time = 6 h.

### 6.3.5 Effect of Water Addition

The effects of water addition were studied over the range of 0 - 2.2 mol of distilled water. The hydrogenation condition was carried out at  $55^\circ\text{C}$ ,  $\text{C}=\text{C} = 84 \text{ mmol}$ ,  $\text{N}_2\text{H}_4 = 0.252 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.328 \text{ mol}$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$  with a total reaction volume from 47.5 to 87.5 ml. The different added water amounts caused a variation in the total volume. The effect of water addition is shown in Figure 6.7. The result showed that the hydrogenation conversion increased with an increase in the amount of water up until a level of 1.67 mol water after which the hydrogenation conversion decreased. The presence of a small amount of added water in the NRL system reduced the viscosity of latex and provided for ease of mixing of the latex with other reaction substances. It was believed that the cupric ion dispersed in the aqueous phase had more space to move around the rubber particle to provide active sites for the occurrence of the hydrogenation reaction. Moreover, water addition in the system also diluted the impurities in the system by removing some water-soluble protein, which may surround the rubber particles. When the added water was higher than 1.67 mol it was found that the degree of hydrogenation decreased due to the easier dispersion of cupric ion in the aqueous phase than in contact with rubber particle. Thus, the number

of active sites for the hydrogenation reaction were reduced. This result was similar to that provided in Wideman's patent (1998).

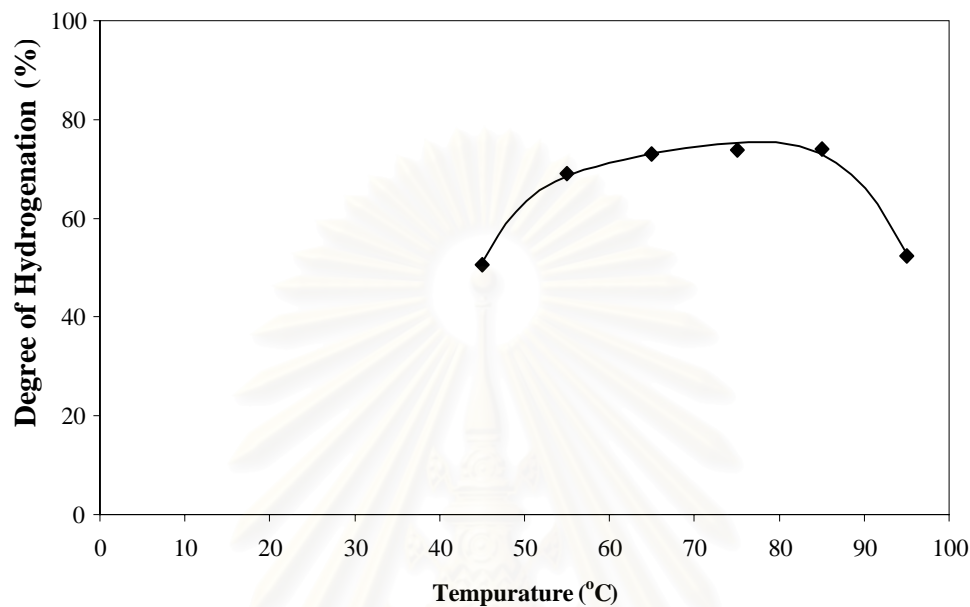


**Figure 6.7** Effect of water concentration on NRL hydrogenation. C=C = 84 mmol; N<sub>2</sub>H<sub>4</sub> = 0.252 mol; H<sub>2</sub>O<sub>2</sub> = 0.328 mol; CuSO<sub>4</sub> = 8 μmol; total volume = 47.5 – 87.5; T = 55°C; time = 6 h.

### 6.3.6 Effect of Reaction Temperature

The effect of hydrogenation temperature was studied over the range of 45°C to 95°C in the presence of C=C = 84 mmol, N<sub>2</sub>H<sub>4</sub> = 0.336 mol, H<sub>2</sub>O<sub>2</sub> = 0.437 mol, CuSO<sub>4</sub> = 8 μmol and H<sub>2</sub>O = 1.67 mol (total volume = 90 ml). The results of the temperature dependence on the hydrogenation of NRL are shown in Figure 6.8. The degree of hydrogenation increased initially with increasing temperature. When the temperature was lower than 55°C, the degree of hydrogenation was quite low. After increasing the reaction temperature to higher than 55°C, the hydrogenation degree increased. These results can be explained on the basis that the diimide reactant was not effective at low reaction temperature due to low collision probability with the particle. As the reaction temperature increased, both the probability of collision and activity of the reactant molecules increased, resulting in enhancement of the hydrogenation degree of NRL. On the other hand, H<sub>2</sub>O<sub>2</sub> tended to more readily

decompose and produce free radicals at higher reaction temperature. When the temperature reached 95°C, the degree of hydrogenation was drastically decreased. A suitable temperature for the reaction was in the range of 55 - 80°C (Lin, 2004), at which 67.8% - 78% hydrogenation was achieved within 6 h.



**Figure 6.8** Effect of temperature on NRL hydrogenation. C=C = 84 mmol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; [H<sub>2</sub>O] = 1.67 mol; CuSO<sub>4</sub> = 8 μmol; total volume = 90 ml; time = 6 h.

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### 6.3.7 Effect of Catalyst Type

The effect of catalyst type on the degree of hydrogenation was also investigated. Various types of catalysts were examined in the presence of  $C=C = 84$  mmol,  $N_2H_4 = 0.336$  mol,  $H_2O_2 = 0.437$  mol,  $[Catalyst] = 8 \mu\text{mol}$ , and  $1.67$  mol of  $H_2O$  (total volume = 90 ml). The reaction was carried out at  $55^\circ\text{C}$  for 6 h. The results are presented in Table 6.4. These results indicate that the cation and the anion of the catalyst affect the degree of hydrogenation. Table 6.4 shows that the cupric ion and the zinc ion were suitable metallic ions for catalyzing the diimide hydrogenation of NRL. The degree of hydrogenation increased according to the following order of cations used as catalyst:  $Mg^{2+} < Fe^{2+} < Cu^{2+}, Zn^{2+}$ . For hydrogenation of XSBR latex, Xie et al. (2002) claimed that  $Fe^{2+}$  was the best catalyst for diimide hydrogenation. The effect of the counter anion has also been studied for a given fixed cationic species such as cupric eg., cupric sulfate, cupric acetate and cupric chloride. The results are shown in Table 6.4. The acetate anion was found to be the most effective anion for the diimide hydrogenation of NRL. The catalytic activity of the cupric complexes was dependent upon two properties of the catalyst: the basicity of the ligand, and the strength of the metal ligand interaction. The catalytic activity of these complexes increased in the same order as the basicity of the ligand;  $Cl^- < SO_4^{2-} < CH_3COO^-$ . The same result was also reported for diimide hydrogenation of SBR latex (Sakar et al., 2000).

**Table 6.4** Effect of Catalyst Types on NRL Hydrogenation

Catalyst	Degree of Hydrogenation (%)
Cupric chloride ( $CuCl_2$ )	50.2
Cupric sulfate ( $CuSO_4$ )	67.7
Cupric acetate ( $Cu(OAC)_2$ )	75.8
Magnesium sulfate ( $MgSO_4$ )	47.4
Ferric sulfate ( $FeSO_4$ )	52.5
Zinc sulfate ( $ZnSO_4$ )	67.0

Condition: Catalyst =  $8 \mu\text{mol}$ ,  $C=C = 84$  mmol,  $N_2H_4 = 0.336$  mol,  $H_2O_2 = 0.437$  mol,  $H_2O = 1.67$  mol, total volume = 90 ml,  $T = 55^\circ\text{C}$ , time = 6 h.

### 6.3.8 Effect of Impurity

The effect of impurities in the rubber was studied by comparing the degree of hydrogenation between natural rubber latex (NRL) and deproteinized natural rubber latex (DPNRL). The reaction was performed in the presence of  $C=C = 84$  mmol,  $N_2H_4 = 0.336$  mol,  $H_2O_2 = 0.437$  mol,  $CuSO_4 = 8$   $\mu$ mol and  $H_2O = 1.67$  mol total volume = 90 ml. The hydrogenation condition was at  $55^\circ C$  for 6 h. The results are shown in Table 6.5 which indicates that the degree of hydrogenation changed slightly from 67.8% to 69.2% after treating NRL by deproteinization. This implies that impurities such as protein, ammonia or other nitrogen content in the NRL probably do not effect or only slightly affect the degree of hydrogenation. To confirm this hypothesis, the addition of an impurity such as hexylamine, hexadecylamide, ammonium hydroxide and amino acid was added into NRL to increase the potential impurity level before hydrogenation as shown in Table 6.6. It shows that such an additive does not have any significant effect on the hydrogenation via diimide reduction. Since  $H_2O_2$  is a strong oxidant, it probably oxidizes the added impurities. In contrast the effect of such impurities have a significant effect on the hydrogenation of natural rubber latex catalyzed by  $OsHCl(CO)(O_2)(PCy_3)_2$  in the presence of molecular hydrogen (see section 3.5.5). This is probably due to complexation of the amine with the active osmium center.

**Table 6.5** Effect of Nitrogen Content on the Degree of Hydrogenation

Rubber Type	% Nitrogen Content	Degree of Hydrogenation (%)
NRL	0.2	67.8
DPNRL	0.02	69.2

Condition:  $C=C = 84$  mmol,  $N_2H_4 = 0.336$  mol,  $H_2O_2 = 0.437$  mol,  $CuSO_4 = 8$   $\mu$ mol,  $H_2O = 1.67$  mol, total volume = 90 ml,  $T = 55^\circ C$ , time = 6 h.

NRL = Natural Rubber Latex

DPNRL = Deproteinized Natural Rubber Latex



**Table 6.6** Effect of Nitrogenous Substances on Degree of Hydrogenation

Substance	Degree of Hydrogenation (%)
-	67.8
Hexylamine	66.5
Hexadecylamide	65.7
Ammonium hydroxide	65.4
Amino acid	64.6

Condition: C=C = 84 mmol, N<sub>2</sub>H<sub>4</sub> = 0.336 mol, H<sub>2</sub>O<sub>2</sub> = 0.437 mol, CuSO<sub>4</sub> = 8 μmol, H<sub>2</sub>O = 1.67 mol, substance = 0.23 mol, T = 55°C, total volume = 90 ml, time = 6 h.

#### 6.4 Conversion Profile for NRL Hydrogenation

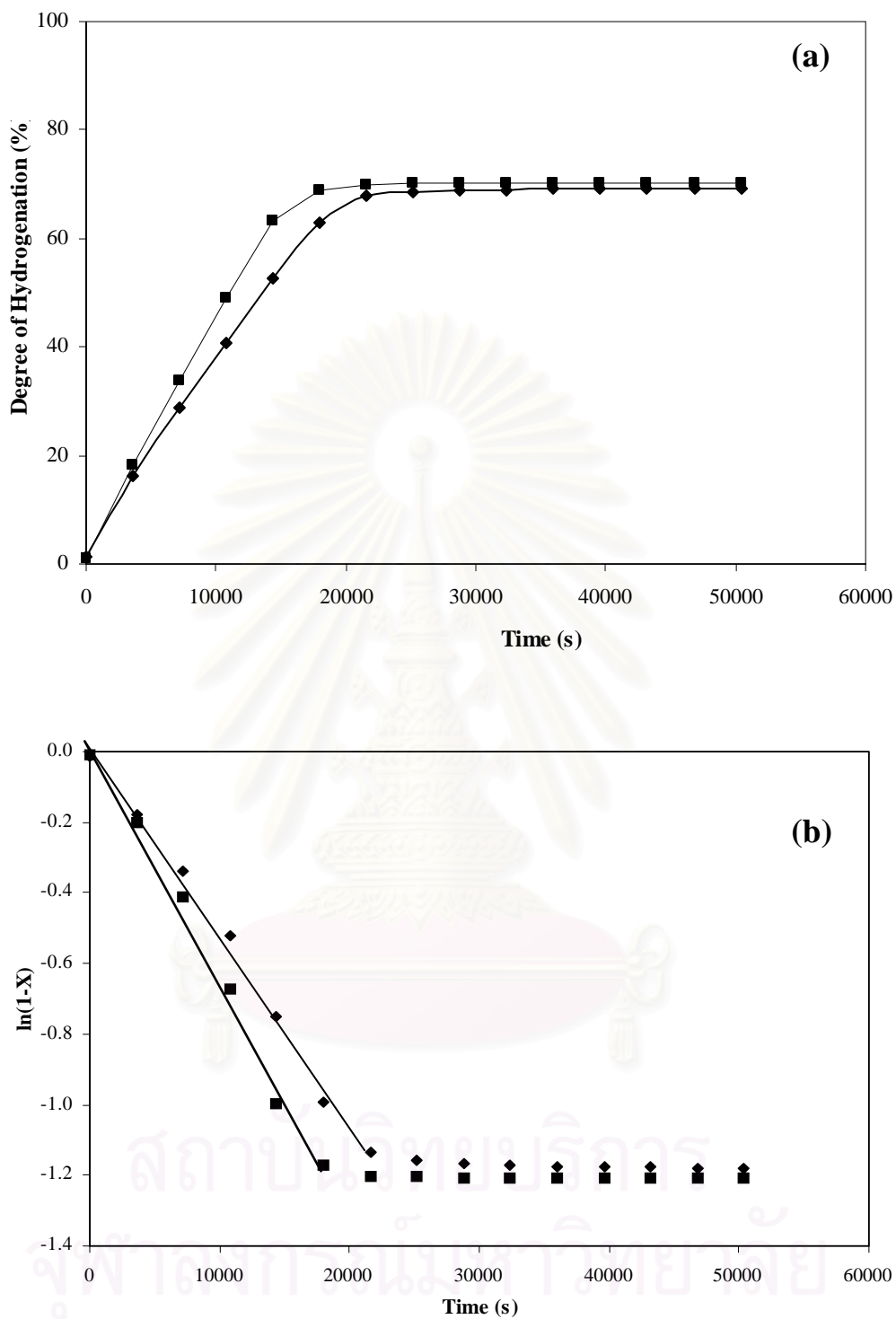
The conversion profile for NRL was studied at 55 °C in the presence of carbon-carbon double bond at 84 mmol, hydrazine 0.336 mol, hydrogen peroxide 0.437 mol, water 1.67 mol, (after addition of water the rubber has about 14% DRC) using 8 μmol cupric sulfate (CuSO<sub>4</sub>) as a catalyst, total volume 90 ml. The reaction was studied over a time range of 0 to 8 h. Figure 6.9a shows that the degree of hydrogenation increased with an increase in reaction time. Maximum conversion, 67.8%, was achieved after 6 h. During the first 6 h, the degree of hydrogenation was sharply increased and then leveled off (67% conversion). The hydrogenation rate slightly increased, which is possibly due to that diimide was formed as an active species at the surface and then diffused into the outer layer (hydrogenated layer) of the latex particle. This concept was also used to explain the degree of hydrogenation after 7 h. At this period (7-12 h), the conversion was quite stable (68.5 - 69.3%) due to the long reaction time which caused a mass transfer limitation of diimide into C=C inside the latex particle. In addition, the decomposition of diimide during long reaction time might have occurred. Conversion plots exhibit an apparent first order dependence for hydrogenation with respect to C=C concentration. The rate constant (k') has been calculated from the slope of the linear plot of ln (1-x) versus time

(Figure 6.9b). A first-order rate equation as shown in eq. 6.13, where  $k'$  is a pseudo first order rate constant, represents the hydrogenation process.

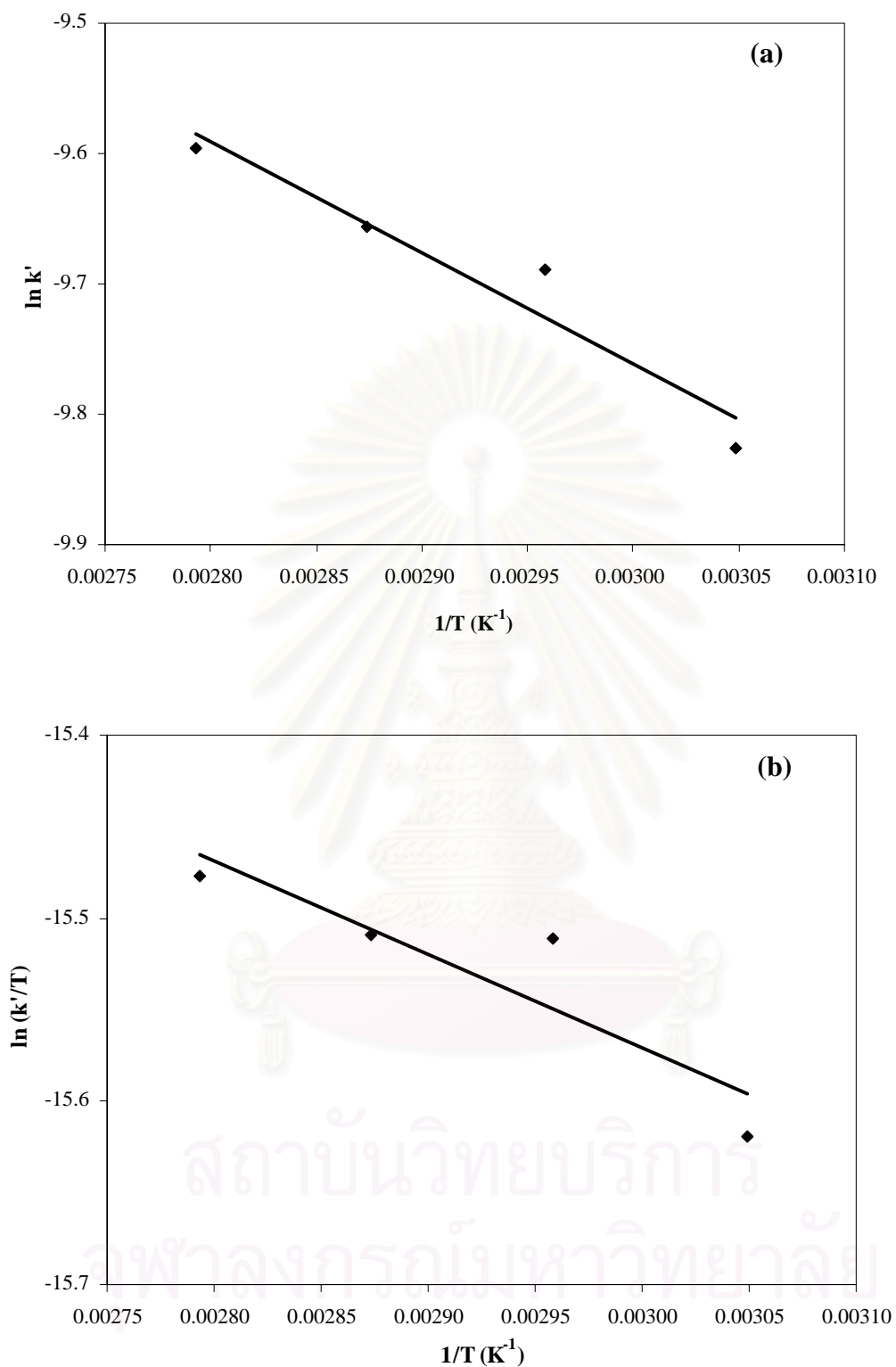
$$\frac{-d[C=C]}{dt} = k' [C=C] \quad (6.13)$$

Although the  $\ln(1-x)$  versus time plot deviates from linearity in the latter stage of reaction,  $k'$ , can still be calculated with a fair degree of confidence. The rate constant, ( $k'$ ) for hydrogenation of NRL was about  $5.4 \times 10^{-5} \text{ s}^{-1}$ .

The Arrhenius plot illustrated the temperature influence on the rate of hydrogenation as provided in Figure 6.10a. The apparent activation energy was 7.10 kJ/mol. Low activation energy provided the evidence that the experiments were performed with mass-transfer limitation. The activation energy of NRL hydrogenation is lower than that of SBR latex hydrogenation (9.5 kJ/mol) (Sakar et al., 1997). It implied that diimide reduction with low activation energy is relatively temperature-insensitive whereas homogeneous catalytic hydrogenation which has a higher activation energy is more temperature sensitive. The Eyring equation was used to estimate the apparent activation enthalpy and entropy for the reactions. Figure 6.10b is the Eyring plot from the temperature dependence data. The enthalpy of activation was 4.26 kJ/mol and the entropy of activation was  $-314.2 \text{ J/mol K}$ .



**Figure 6.9** Hydrogenation profile of NRL. (a) conversion profiles and (b) first-order ln plot.  $C=C = 84$  mmol;  $N_2H_4 = 0.336$  mol;  $H_2O_2 = 0.437$  mol;  $CuSO_4 = 8$   $\mu$ mol;  $H_2O = 1.67$  mol; total volume = 90 ml;  $T = 55^\circ C$  (◆),  $85^\circ C$  (■).



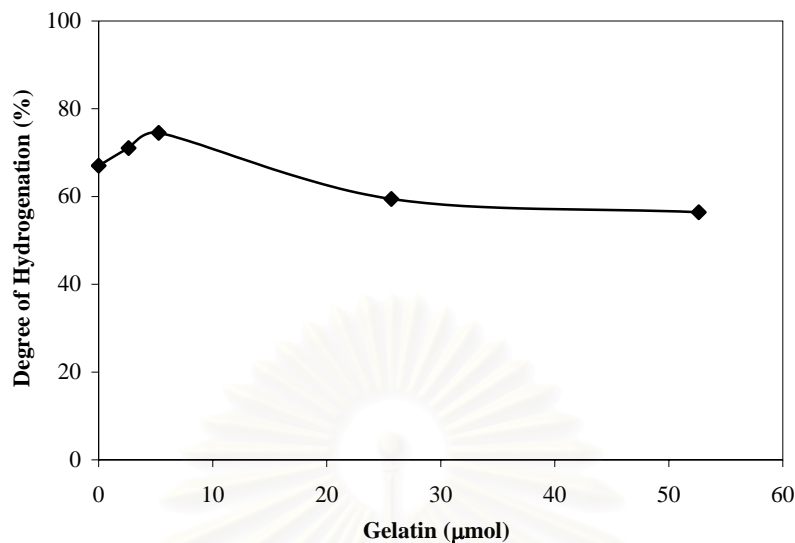
**Figure 6.10** (a) Arrhenius plot (b) Eyring plot for the NRL hydrogenation.  $C=C = 84$  mmol;  $N_2H_4 = 0.336$  mol;  $H_2O_2 = 0.437$  mol;  $H_2O = 1.67$  mol;  $CuSO_4 = 8 \mu\text{mol}$ ; total volume = 90 ml;  $T = 45^\circ\text{C} - 85^\circ\text{C}$ .

## 6.5 Improvement of Redox System

To improve the degree of NRL hydrogenation, the addition of gelatin surfactant (sodium dodecyl sulfate), and inhibitor (hydroquinone) was studied. It was believed that the limitation of NRL hydrogenation by using diimide reduction was caused by the low efficiency of diimide which reacted with the carbon- carbon double bonds. The addition of surfactant, emulsifier and inhibitor into the system was believed to increase the degree of hydrogenation of NRL.

### 6.5.1 Effect of Gelatin

The effect of gelatin addition was studied over the range of 0 - 53  $\mu\text{mol}$  in the presence of  $\text{C}=\text{C} = 84 \text{ mmol}$ ,  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$ ,  $\text{H}_2\text{O} = 1.67 \text{ mol}$ , total volume = 90 ml. The hydrogenation was carried out at  $55^\circ\text{C}$  for 6 h. Figure 6.11 shows that the degree of hydrogenation increased when a small amount of gelatin was added into this system. 74.5% Hydrogenation was achieved after adding 5  $\mu\text{mol}$  of gelatin. It is possible that the addition of gelatin into the system helped in stabilization of cupric ion on the rubber particle surface. It may produce a suitable level of diimide species within 6 h resulting in an increased degree of hydrogenation. When gelatin was added above 5  $\mu\text{mol}$ , the degree of hydrogenation was found to decrease. At such higher levels of gelatin, gelatin inhibited the active site of the cupric ion at the surface of rubber particle.

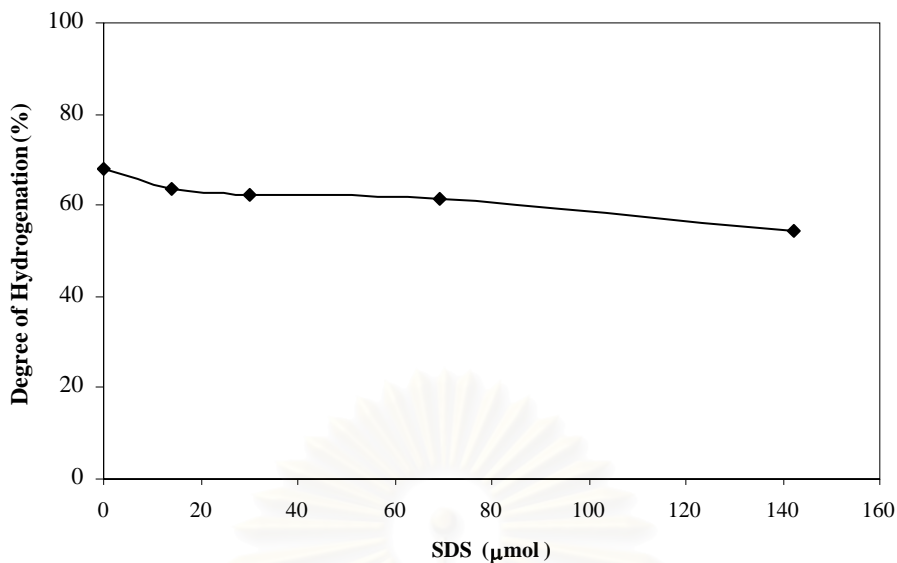


**Figure 6.11** Effect of gelatin concentration on NRL hydrogenation.  $\text{C}=\text{C} = 84 \text{ mmol}$ ;  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ;  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ;  $\text{CuSO}_4 = 8 \mu\text{mol}$ ;  $\text{H}_2\text{O} = 1.67 \text{ mol}$ ; total volume = 90 ml;  $T = 55^\circ\text{C}$ ; time = 6 h.

### 6.5.2 Effect of Sodium Dodecyl Sulfate (SDS)

The surfactant SDS was used as a stabilizer for the rubber particle and cupric ion in the system. Parker et al. (1992) studied the role of surfactant on the diimide hydrogenation process. It was found that the surfactant played a role in stabilizing the cupric ion on the rubber particle. The effect of SDS concentration has been studied from 0 to 142  $\mu\text{mol}$  in the presence of  $\text{C}=\text{C} = 84 \text{ mmol}$ ,  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$ ,  $\text{H}_2\text{O} = 1.67 \text{ mol}$ , total volume = 90 ml. The hydrogenation was carried out at  $55^\circ\text{C}$  for 6 h. It was found that the increase in the SDS concentration decreased the degree of hydrogenation as shown in Figure 6.12. It is possible that the surfactant formed a micelle trap for cupric sulfate which led to a reduction of the amount of diimide species produced. This caused a decrease in the degree of hydrogenation. Moreover, the rubber latex particle had a phospholipid as outer layer (Verhaar, 1959). It was believed that phospholipid in conjunction with the latex particle stabilized the rubber particle and the cupric ion. However the high concentration of surfactant was found to decrease the degree of diimide hydrogenation of NRL.



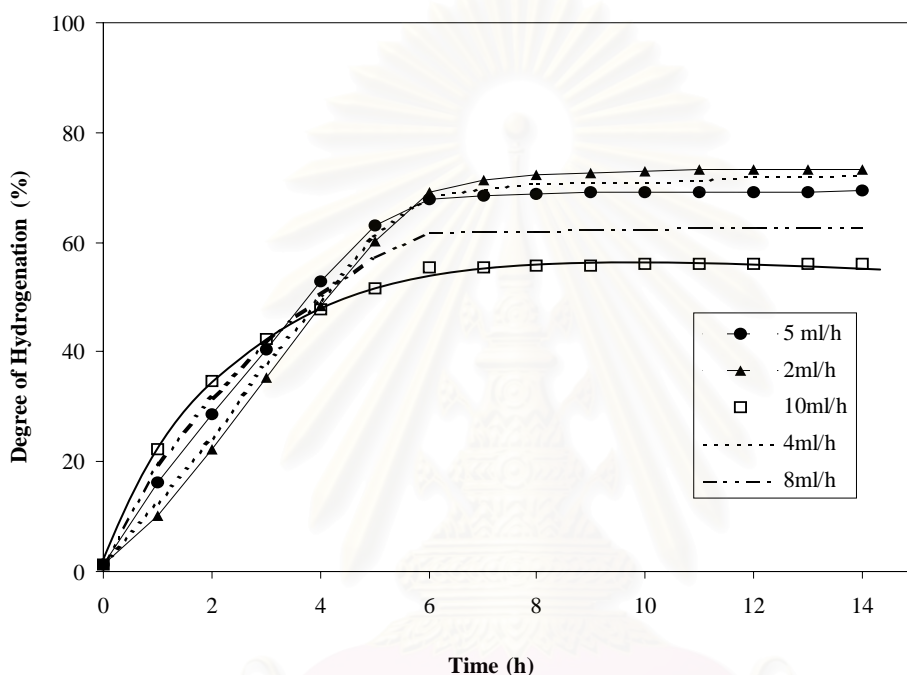


**Figure 6.12** Effect of SDS concentration on NRL hydrogenation. C=C = 84 mmol;  $\text{N}_2\text{H}_4$  = 0.336 mol;  $\text{H}_2\text{O}_2$  = 0.437 mol;  $\text{CuSO}_4$  = 8  $\mu\text{mol}$ ;  $\text{H}_2\text{O}$  = 1.67 mol; total volume = 90 ml; T = 55°C; time = 6 h.

### 6.5.3 Effect of Addition Rate of Hydrogen Peroxide

Some experiments were carried out to investigate the degree of NRL hydrogenation at different addition rate of  $\text{H}_2\text{O}_2$ . The  $\text{H}_2\text{O}_2$  addition rate was varied from 2 - 10 ml/h. This additional one hour reaction time is called the aging period in this work. The hydrogenation was carried out in the presence of: C=C = 84 mmol,  $\text{N}_2\text{H}_4$  = 0.336 mol,  $\text{H}_2\text{O}_2$  = 0.437 mol,  $\text{CuSO}_4$  = 8  $\mu\text{mol}$ ,  $\text{H}_2\text{O}$  = 1.67 mol, total volume = 90 ml. The reaction temperature was 55°C. The reaction system was run for an additional 1h after the final  $\text{H}_2\text{O}_2$  addition point under otherwise similar conditions as used in the previous experiment. The degree of hydrogenation was monitored every hour and is illustrated in Figure 6.13. It was found that the degree of hydrogenation did not increase detectably during the aging period following the  $\text{H}_2\text{O}_2$  addition, which suggest that the  $\text{H}_2\text{O}_2$  was consumed immediately when added into the system. The accumulation of  $\text{H}_2\text{O}_2$  is not significant in the semi- batch operation as long as a suitable addition rate of hydrogen peroxide is chosen. Thus, the number of moles of  $\text{H}_2\text{O}_2$  reacted can be considered to be equal to the added  $\text{H}_2\text{O}_2$  amount. The degree of hydrogenation curve at a fast addition rate for  $\text{H}_2\text{O}_2$  failed to reach a high degree of

hydrogenation. It is possible that the hydrogenation efficiency for a fast addition rate is lower than that for a slow addition rate. The slow addition rate yield 73.0% conversion at 10 h. This comparison demonstrates that a faster addition rate of  $\text{H}_2\text{O}_2$  tends to give lower hydrogenation efficiency, which is consistent with the postulated mechanism above. The same result was found for hydrogenation of NBRL (Lin et al., 2004 and Zhou, et al., 2004).



**Figure 6.13** Effect of hydrogen peroxide addition rate on conversion profile.  $\text{C}=\text{C} = 84 \text{ mmol}$ ;  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ;  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ;  $\text{CuSO}_4 = 8 \mu\text{mol}$ ;  $\text{H}_2\text{O} = 1.67 \text{ mol}$ ; total volume = 90 ml;  $T = 55^\circ\text{C}$  (  $\blacktriangle = 2 \text{ ml/h}$ ,  $\bullet = 5 \text{ ml/h}$ ,  $\square = 10 \text{ ml/h}$ ,  $\cdots = 4 \text{ ml/h}$ ,  $-\cdot-\cdot- = 8 \text{ ml/h}$  ).

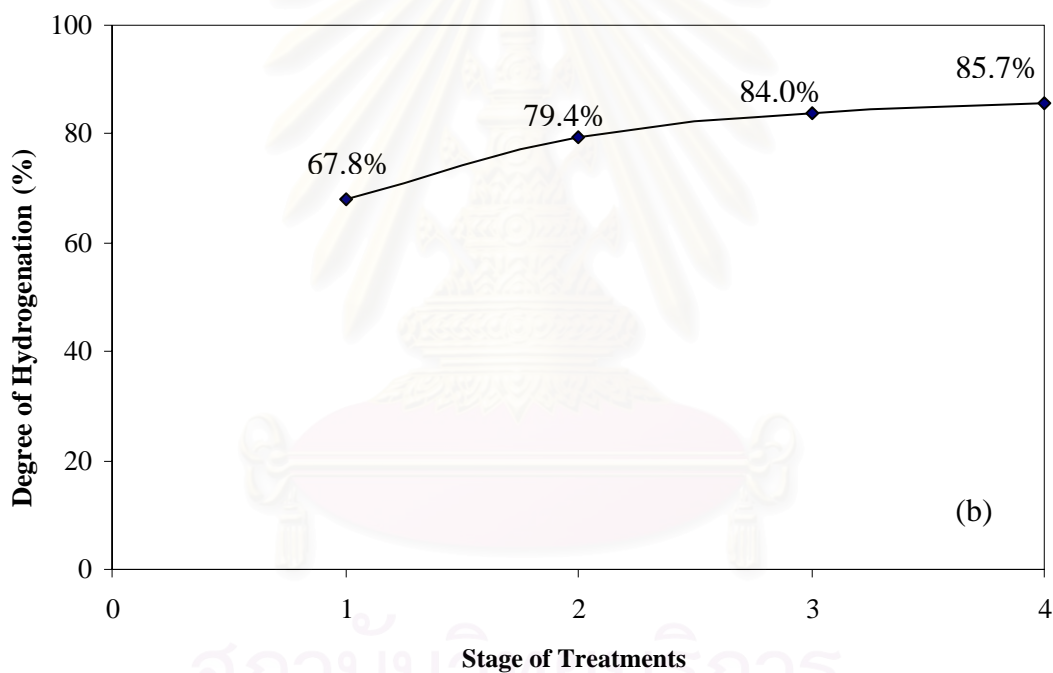
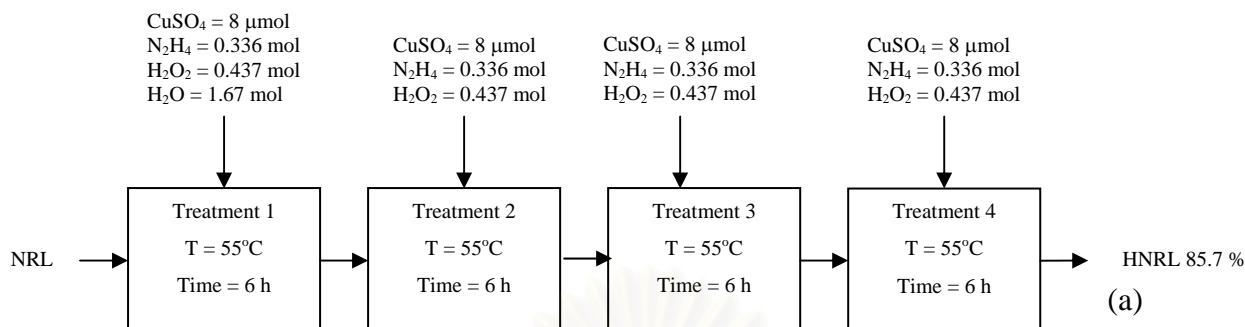
### 6.6 Distribution of Carbon – Carbon Double Bonds in HNRL Particles

The distribution of carbon–carbon double bonds within the natural rubber latex particle during diimide hydrogenation was studied. The condition in the first treatment was  $\text{C}=\text{C} = 84 \text{ mmol}$ ,  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$ ,  $\text{H}_2\text{O} = 1.67 \text{ mol}$ , total volume = 90 ml at  $55^\circ\text{C}$  for 6 h. The product from the previous treatment was used as the starting material for the next treatment under the same reaction conditions:  $\text{H}_2\text{O}_2 = 0.328 \text{ mol}$ ,  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$ , at  $55^\circ\text{C}$  for 6 h (after the fourth treatment the total volume is 278 ml). Figure 6.14a,b

shows the treatment effect on the degree of hydrogenation after each treatment. It was found that the degree of hydrogenation slightly increased after each treatment. It can be calculated that the increasing percentage of hydrogenation between treatments is 11.6., (the difference in percentage hydrogenation between the first and second treatment), 4.6 (the difference between second and the third treatments) and 1.7 (the difference between third and the fourth treatments). The differences in the hydrogenation level between the treatments reduced with successive treatment.

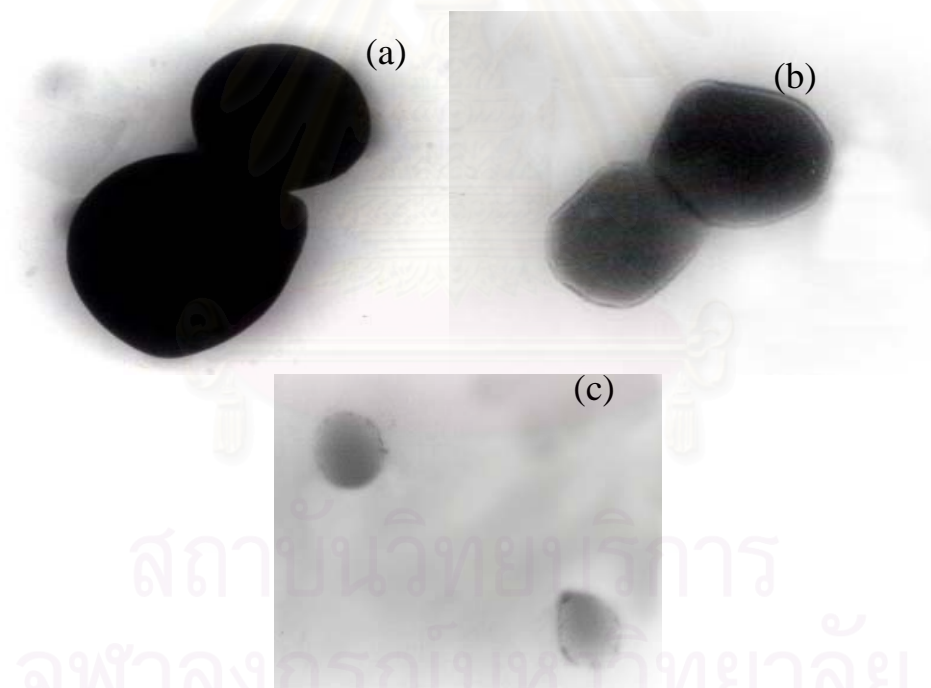
Two models used to explain the distribution of carbon – carbon double bonds in the polymer latex during diimide hydrogenation are an uniform model and a layer model (See Figure 1.6). For the uniform model, the difference of the hydrogenation level between the first and the second treatment, the second and the third, and the third and fourth treatments are very close to the same value. For the layer model the differences in the level of hydrogenation between the first and second treatment, the second and the third treatment, and the third and fourth treatment are very different.

The layer model can be used in explaining the distribution of carbon–carbon double bonds of rubber latex particles during diimide hydrogenation. Moreover, this result suggests that the layer model represents the surface of the particle and resulted in a relatively higher degree of hydrogenation because a lower mobility of highly crosslinked polymer may exist. The concentration of carbon–carbon double bonds in this layer was lower than that of the inner portion of the particle after the first treatment. As a result, the disproportionation reaction among diimide molecules became more competitive in this layer and consequently, resulted in the lower degree of hydrogenation after the second and third treatments. An alternative explanation for this observation may be that the diimide remained bound to the cupric ion. The same result was also found for hydrogenation of SBR latex (He et al., 1997).



**Figure 6.14** Treatment effect on degree of hydrogenation: a) Diagram of treatment procedure. b) Effect of treatment number on NRL hydrogenation. first treatment  $C=C = 84$  mmol;  $N_2H_4 = 0.336$  mol;  $H_2O_2 = 0.437$  mol;  $CuSO_4 = 8$   $\mu$ mol;  $H_2O = 1.67$  mol; total volume = 90 ml;  $T = 55^\circ C$ ; time = 6 h; second, third and fourth treatment  $CuSO_4 = 8$   $\mu$ mol;  $N_2H_4 = 0.336$  mol;  $H_2O_2 = 0.437$  mol;  $T = 55^\circ C$ ; time = 6 h for 2<sup>nd</sup> 3<sup>rd</sup> and 4<sup>th</sup> treatment (total volume = 137, 184, and 278 ml respectively).

Figure 6.15 shows a TEM micrograph of the NRL latex particles before hydrogenation (a), hydrogenation after the first treatment (b) and after the fourth treatment (c). Since the  $\text{OsO}_4$  staining agent can only stain on carbon-carbon double bonds, the lightly colored domain indicates the region of lower carbon-carbon double bond concentration. For the comparison, NRL and HNRL degree of hydrogenation at 67.8% (first treatment) and 85.7% (fourth treatment) are shown in this figure. NRL showed relatively sharp particle edges because the concentration of the  $\text{OsO}_4$  inside the particle was high. On the other hand, 85.7% hydrogenated latex exhibited much lighter color due to the small amount of carbon-carbon double bonds for  $\text{OsO}_4$  staining. For 67.8% hydrogenated rubber, the contrast between the center and the surface of hydrogenated rubber particle was quite different. The rubber particle seemed to be hydrogenated from the outer surface to the center rubber particle according to the layer model.



**Figure 6.15** TEM micrographs of (a) NRL (b) 67.8% HNRL (1<sup>st</sup> treatment) and (c) 85.7% HNRL(4<sup>th</sup> treatment) (x 2000).

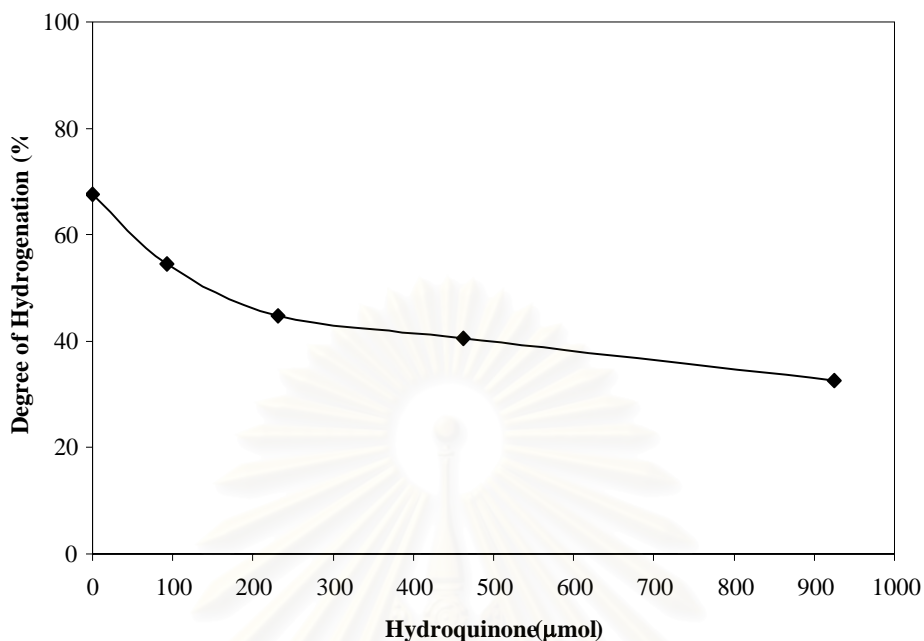
## 6.7 Inhibitor Addition and Gel Behavior

Inhibitor was added to the diimide hydrogenation system in an attempt to capture the free radicals and reduce gel content and increase degree of hydrogenation (Xie et al., 2000). Xie et al (2003) used p-tert-butyl-procathecol as an inhibitor for gel formation. The results indicated that the presence of this inhibitor reduced % gel from 94.3% to 21.7% for hydrogenation of NBR latex. Zhou et al. (2004) also found that the inhibitor (hydroquinone) could reduce gel content from 80% to 3% and provided high conversion of hydrogenation of NBR latex (80% conversion). Hydroquinone seems to be a suitable inhibitor for NBRL hydrogenation. Hydroquinone was also applied in this current investigation in an attempt to improve the hydrogenation of NRL. The amount of hydroquinone was varied from 0 to 925  $\mu\text{mol}$  in the presence of  $\text{C}=\text{C} = 84 \text{ mmol}$ ,  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ,  $\text{CuSO}_4 = 8 \mu\text{mol}$ ,  $\text{H}_2\text{O} = 1.67 \text{ mol}$ , total volume = 90 ml. The hydrogenation was carried out at  $55^\circ\text{C}$  for 6 h. Figure 6.16 shows the effect of hydroquinone on the degree of hydrogenation. It was found that the degree of hydrogenation decreased with an increase in hydroquinone concentration. It is likely that the hydroquinone captured the diimide species in this system and caused the reduction in the NRL hydrogenation level. The presence of this inhibitor did not reduce gel content of NRL. It might imply that the gel behavior of NRL hydrogenation was different from NBRL hydrogenation. Thus, gel behavior for NRL hydrogenation was studied.

Gel formation is generally observed for the diimide hydrogenation both for the diimide generated in situ and for the diimide hydrogenation. The mechanism for crosslink bond formation has not been clearly identified. The disproportionation of diimide may cause the crosslinking of rubber backbones (Gangadhar et al., 1989).





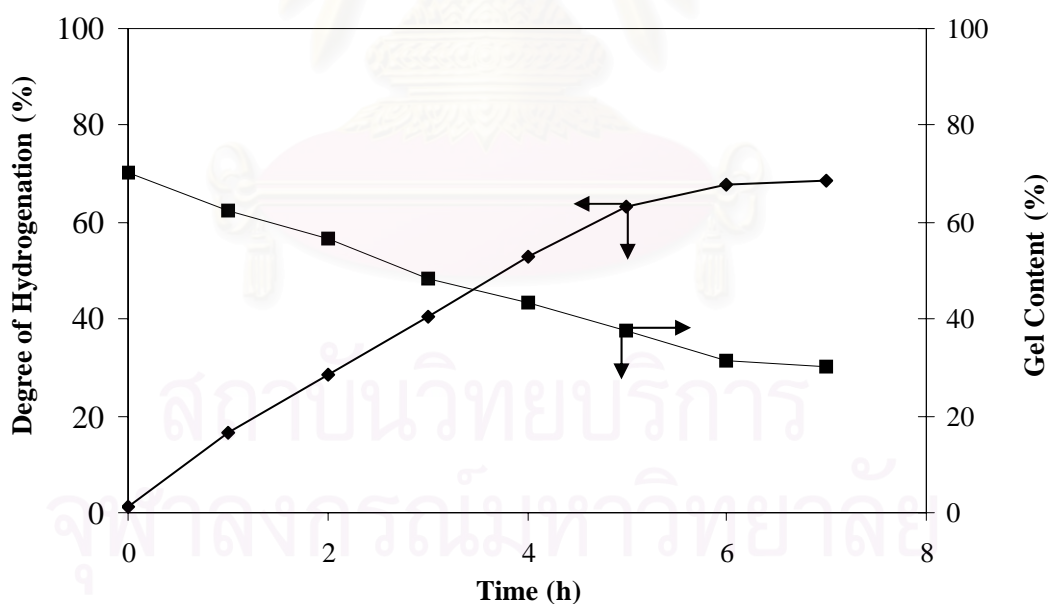


**Figure 6.16** Effect of hydroquinone on NRL hydrogenation. C=C = 84 mmol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; CuSO<sub>4</sub> = 8 μmol; H<sub>2</sub>O = 1.67 mol; total volume = 90 ml; T = 55°C; time = 6 h.

Generally, gel content increases together with the reduction in unsaturation, which deteriorates the mechanical properties of the rubbers. Further reduction in unsaturation and increased gel content would render the rubber useless. On the other hand, in order to improve the oxidation resistance of a rubber, the saturation of the polymer must be elevated to a level such that the residual unsaturation is only enough for vulcanization. To deal with this behavior, Parker et al. (1995) tried to hydrogenate a rubber emulsion to a moderate level of saturation, and then used antioxidants to balance the performance of the material over the degree of crosslinking and oxidation resistance. It was found that HSBRs containing a bound amine-type antioxidant with moderate hydrogenation levels can greatly outperform HSBRs with similar saturation levels without the bound antioxidant with regard to property retention on under thermal and photolytic aging conditions, and that the HSBRs with a bound antioxidant with modest hydrogenation levels can approach the thermal resistance of even very highly saturated HSBR without the presence of an antioxidant. The other route suggested by Parker et al. (1995) was comprised of

treating the resulting mixture from the hydrogenation with ozone to react with residual polymer unsaturation to form ozonated latex of the elastomeric polymer, and then treating the ozonated latex with hydroxylamine to convert aldehyde end groups of the elastomeric polymer to oxime end groups to form oximated polymer latex. This treatment of the resultant latex from diimide hydrogenation generated a soluble, hydrogenated elastomeric polymer in latex form having a reduced level of residual hydrazine therein.

Few conclusions can be drawn from the effect of gel during the diimide hydrogenation, since NRL has a relatively high gel content before hydrogenation. The gel content of NRL was about 70 % and after hydrogenation the gel content was reduced to about 30%. Figure 6.17 shows the plot between gel content and degree of hydrogenation. It is seen that as the degree of hydrogenation increased the gel content decreased. This might be due to the fact that the structures of HNRL change during and after hydrogenation which reduces the carbon – carbon crosslinks in the NRL.

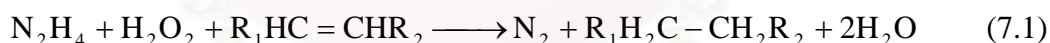


**Figure 6.17** Gel content of HNRL.  $[\text{CuSO}_4] = 114 \mu\text{M}$ ;  $[\text{C}=\text{C}] = 1.17 \text{ M}$ ;  $[\text{N}_2\text{H}_4] = 4.67 \text{ M}$ ;  $[\text{H}_2\text{O}_2] = 4.55 \text{ M}$ ;  $[\text{H}_2\text{O}] = 23.15 \text{ M}$ ;  $T = 55^\circ\text{C}$ .

## CHAPTER VII

### DIIMIDE HYDROGENATION OF NATURAL RUBBER LATEX IN THE PRESENCE OF BORIC ACID

Hydrogenation of elastomers in latex form with diimide provides advantages in that gaseous hydrogen, organic solvents and an expensive transition metal catalyst are not necessary. Chapter 6 presented the diimide hydrogenation of natural rubber latex using an inexpensive base metal ion as catalyst. This chapter will present the diimide hydrogenation without using an added metal ion. The overall reaction for diimide hydrogenation of polymer is presented in eq. 7.1. Boric acid is an alternative material to help in promote diimide hydrogenation. Boric acid is believed to act as a promoter for diimide generation (Lin et al, 2005). Lin (2004) also reported that the promoting ability of boric acid is unique and is not shared with other weak acids. Boric acid provides a higher and more stable rate for the reaction, which makes boric acid the most suitable choice in the latex system for promoting diimide formation. It was suggested that boric acid served to lower and mediate the concentration of hydrogen peroxide. The equilibrium according to eq.7.2 was proposed:



The formation of hydrogen bonds increases the activity of hydrogen peroxide toward hydrazine oxidation. The diimide production was stable after this reaction occurred which control the reproducibility of NBRL hydrogenation (Lin, 2004).

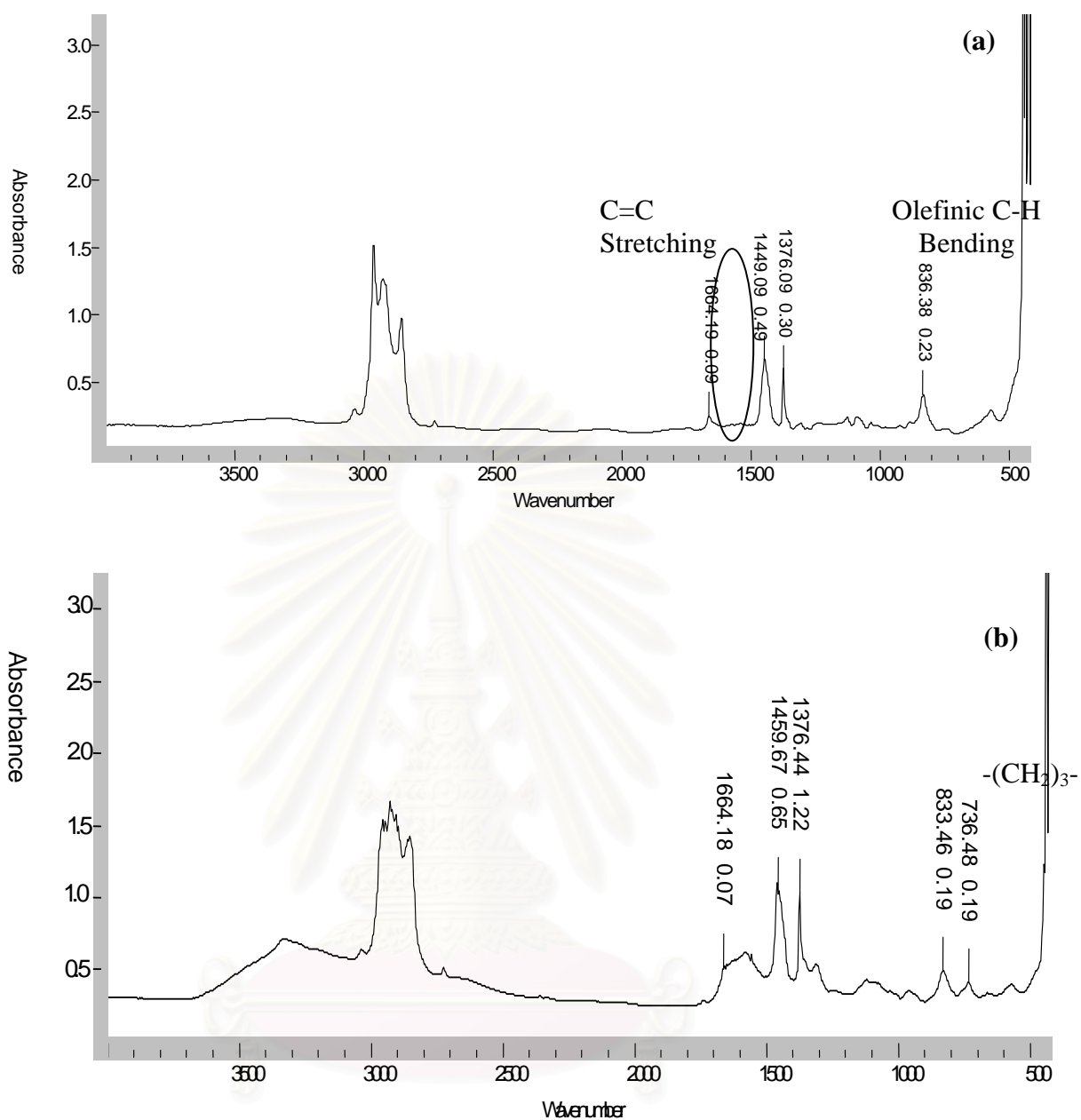
There are some previous research reports for the diimide hydrogenation by using boric acid as a promoter. Belt et al. (2000, 2003) showed that a higher degree of hydrogenation and less cross-linking of the polymer occurred when boric acid was used. This method is better than the metal ion system in which radical generation occurred during diimide formation, which caused gel after hydrogenation process. A suitable boric acid concentration ( $[\text{H}_3\text{BO}_3]$ ), hydrazine concentration

([N<sub>2</sub>H<sub>4</sub>]), reaction temperature, mole ratio of H<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>H<sub>4</sub> and mole ratio of N<sub>2</sub>H<sub>4</sub>/C=C for NBRL have been reported by Zhou et al. (2004). Lin et al. (2005) also report the high efficiency NBRL hydrogenation via diimide hydrogenation in the presence of boric acid.

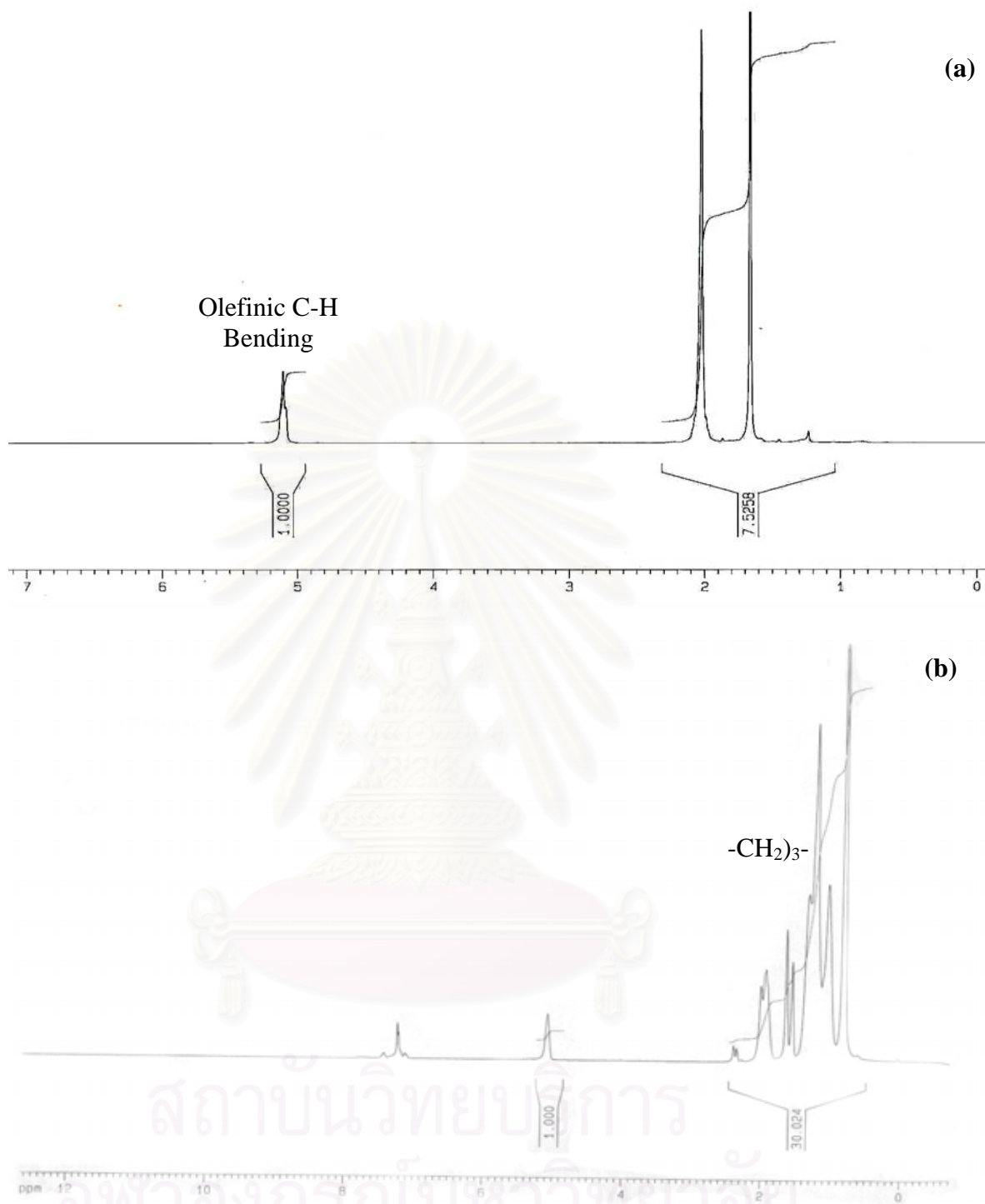
In this chapter, the goal of the research was to study the diimide hydrogenation of natural rubber latex via diimide hydrogenation in the presence of boric acid. The effect of reaction parameters such as boric acid concentration, mole ratio of H<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>H<sub>4</sub>, mole ratio of N<sub>2</sub>H<sub>4</sub>/C=C and reaction temperature were investigated.

### 7.1 Structure Characterization Using FTIR and NMR Spectroscopy

The IR spectra of both natural rubber latex (NRL) and hydrogenated natural rubber latex (HNRL) are shown in Figure 7.1(a) and (b). The nonhydrogenated latex spectrum shows individual peaks for the C=C unsaturation, i.e. at 1663 cm<sup>-1</sup> (C=C stretching) and 836 cm<sup>-1</sup> (trisubstituted olefinic C-H bending). It can be seen that peaks of the C=C unsaturation and peak of olefinic C-H bending decrease after the hydrogenation. The peak around 720 cm<sup>-1</sup> appeared after hydrogenation due to the presence of -(CH<sub>2</sub>)<sub>3</sub>-. <sup>1</sup>H-NMR spectra for the NRL and HNRL are provided in Figure 7.2 (a) and (b). Major peaks are obtained in the aliphatic (1.7 and 2.2 ppm) regions. The signals of *cis* olefinic protons are centered at 5.2 ppm. As the hydrogenation progresses, the olefinic peak area considerably decreases, and new peaks appear at 0.8 – 1.8 ppm attributed to -CH<sub>3</sub> and saturated -CH<sub>2</sub>- units. The extent of hydrogenation has been calculated from the <sup>1</sup>H-NMR spectra by noting the change in the integral of the peaks representing protons for the hydrogenated rubber latex.



**Figure 7.1** FTIR spectra of (a) NRL and (b) HNRL. C=C = 84 mol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; H<sub>3</sub>BO<sub>3</sub> = 10 mmol; H<sub>2</sub>O = 1.67 mol; total volume = 90 ml; T = 55°C; time = 6 h



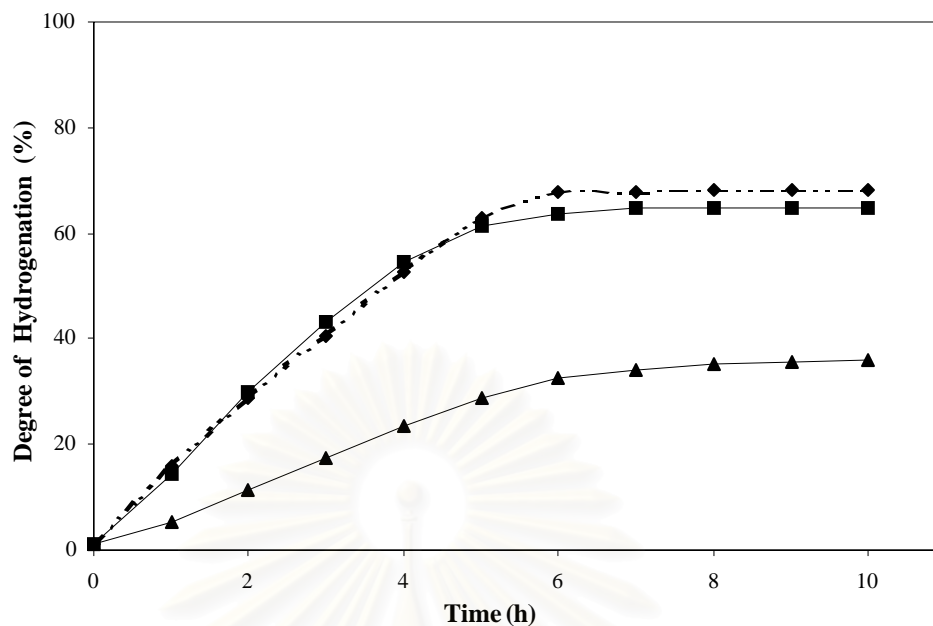
**Figure 7.2** NMR spectra of (a) NRL and (b) HNRL.  $\text{C}=\text{C} = 84$  mol;  $\text{N}_2\text{H}_4 = 0.336$  mol;  $\text{H}_2\text{O}_2 = 0.437$  mol;  $\text{H}_3\text{BO}_3 = 10$  mmol;  $\text{H}_2\text{O} = 1.67$  mol; total volume = 90 ml;  $T = 55^\circ\text{C}$ ; time = 6 h.



## 7.2 Effect of Process Parameters

### 7.2.1 Efficiency of Hydrogenation and Selectivity of Catalyst

Experiments were carried out to study the effect of catalyst type on the degree of hydrogenation. Three systems were studied to compare this effect on the degree of hydrogenation: metal ion (cupric ion), boric acid and no added catalyst. The reaction was performed in the presence of carbon-carbon double bonds 84 mmol, hydrazine 0.336 mol, hydrogen peroxide 0.437 mol and water 1.67 mol. Total volume was 90 ml and the reaction temperature was 55°C. The mole ratio of  $N_2H_4/C=C$  and mole ratio of  $H_2O_2/N_2H_4$  were 4 and 3 respectively. The metal ion and boric acid were 8  $\mu$ mol and 10 mmol, respectively. Figure 7.3 shows degree of hydrogenation curves for diimide hydrogenation under various conditions. Without catalyst, the slope of the degree of hydrogenation curve was comparatively low. It also exhibited a lower final conversion (36.0 %) than the case in which metal ion (68.1%) or boric acid (64.7%) was added to the system. Therefore, the low degree of hydrogenation in this case suggests that the inherent catalytic system has lower selectivity for hydrogenation than the system with added metal ion catalyst or boric acid. Magnesium ion was found in the natural rubber latex after a concentration process (see Table A-2, Appendix A). Therefore, magnesium may act as a catalyst in the case when no catalyst is added. Diimide hydrogenation in presence of cupric ion provides a similar curve to that in presence of boric acid for the degree of hydrogenation with respect to reaction time. However, the boric acid system provides a lower degree of hydrogenation than the cupric ion system at final conversion. Among the above three methods, the reaction with metal ion (cupric ion) provides the highest degree of hydrogenation.

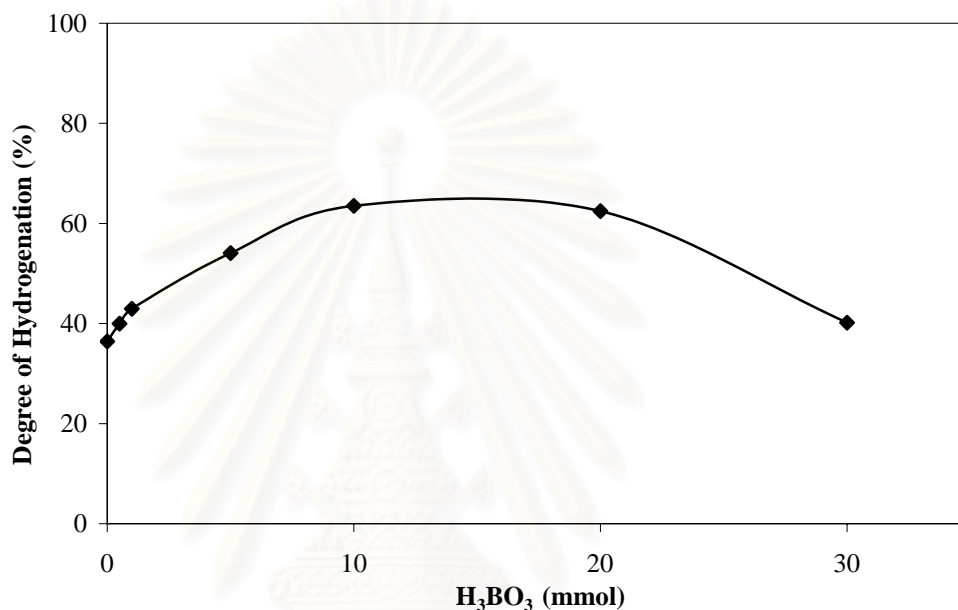


**Figure 7.3** Conversion profile of NRL hydrogenation. (◆) metal ion ( $\text{CuSO}_4 = 8 \mu\text{mol}$ ), (■) boric acid ( $\text{H}_3\text{BO}_3 = 10 \text{ mmol}$ ), (▲) no catalyst at  $\text{C}=\text{C} = 84 \text{ mmol}$ ;  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ;  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ;  $\text{H}_2\text{O} = 1.67 \text{ mol}$ ; total volume = 90 ml;  $T = 55^\circ \text{C}$ .

### 7.2.2 Effect of Boric Acid Concentration

Boric acid, which is not a transition metal, would not be expected to provide a catalytic effect upon the reactions. It was proposed once that boric acid may provide a buffer effect upon which the hydrogenation reaction is promoted (Lin et al., 2005). However, the use of sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) which provides a similar buffer effect compared to boric acid failed to provide the same promotion effect upon the hydrogenation reaction (Lin, 2004). A possible explanation is that boric acid is capable of forming hydrogen bonds with the hydrogen peroxide. This formation of hydrogen bonds stabilizes hydrogen peroxide and reduces the activity of hydrogen peroxide in the system. As a result, side reactions are retarded. The effect of the amount of boric acid in diimide hydrogenation was investigated. The effect of boric acid on the degree of hydrogenation was studied over the range of 0 – 30 mmol. The reaction was carried out in the presence of  $\text{N}_2\text{H}_4 = 0.336 \text{ mol}$ ,  $\text{H}_2\text{O}_2 = 0.437 \text{ mol}$ ,  $\text{C}=\text{C} = 84 \text{ mmol}$  (rubber 14.3% DRC). The hydrogenation condition was at  $55^\circ\text{C}$  for 6 h. Total volume was 90 ml. Figure 7.4 indicates that the degree of hydrogenation

increased up until about 10 mmol of boric acid, then the degree of hydrogenation remained relatively constant and then decreased at boric acid concentration above 20 mmol. It might be possible that the high level of boric acid resulted in a side reaction which decreased the hydrogenation level. Moreover, the stability of NRL might be reduced when a high level of boric acid was added.

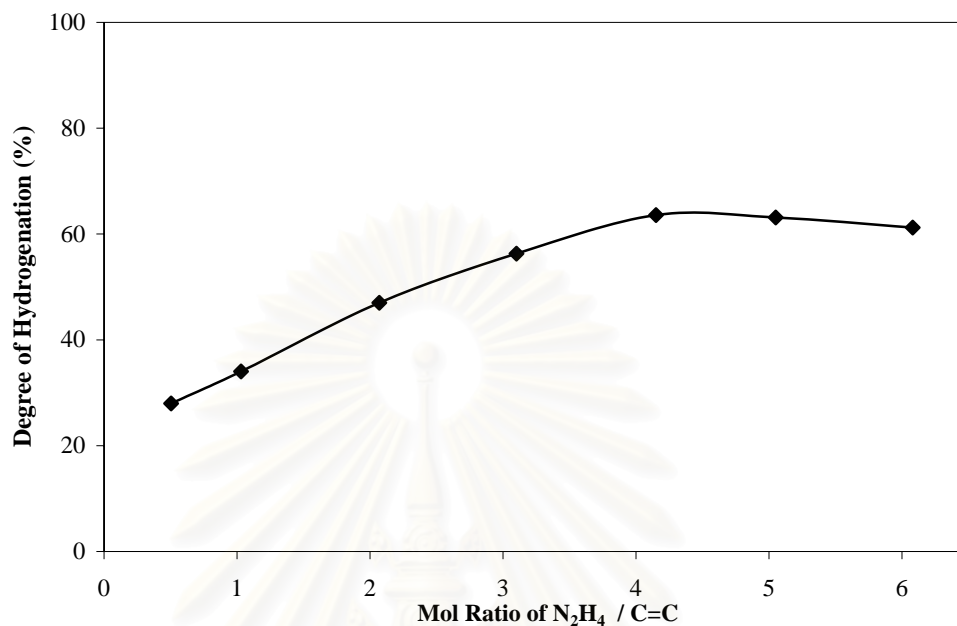


**Figure 7.4** Effect of boric acid concentration on degree of hydrogenation. C=C = 84 mmol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; H<sub>2</sub>O = 1.67 mol; total volume = 90 ml; T = 55°C; time = 6 h.

### 7.2.3 Effect of Hydrazine Concentration

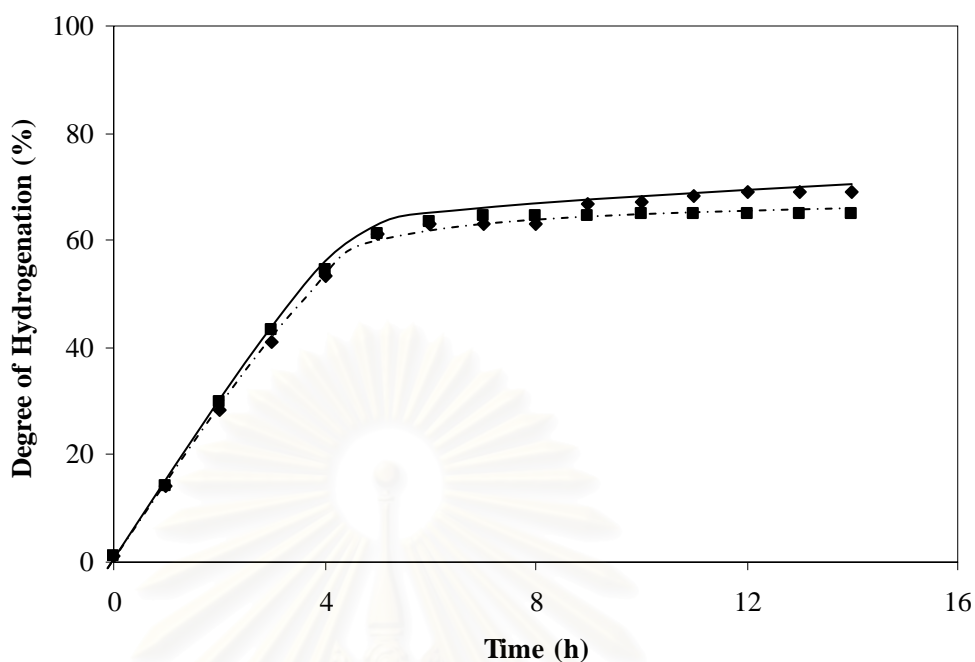
The hydrogenation performance at different concentrations of hydrazine are presented in Figure 7.5. The reaction was carried out in the presence of a mole ratio of hydrazine to carbon-carbon double bonds = 0.5 - 6 (C=C = 84 mmol), mole ratio of (H<sub>2</sub>O<sub>2</sub> / N<sub>2</sub>H<sub>4</sub>) = 1.3, H<sub>3</sub>BO<sub>3</sub> = 10 mmol, H<sub>2</sub>O = 1.67 ml, total volume = 47 - 108 ml. The hydrogenation was carried out at 55°C for 6 h. It was found that the degree of hydrogenation increased with increasing mole ratio of hydrazine to carbon-carbon double bonds. In contrast, the degree of hydrogenation began to slowly decrease at a mole ratio above 5. It can be explained that this behavior results from

the diimide species self reacting at a high level of diimide which causes a decrease in the hydrogenation efficiency. This similar behavior was also observed in the case of using a metal ion as catalyst (Chapter 6).



**Figure 7.5** Effect of ( $N_2H_4/C=C$ ) on degree of hydrogenation.  $H_3BO_3 = 10$  mmol; Rubber 14.3% DRC ( $C=C = 84$  mmol); mole ratio of ( $H_2O_2 / N_2H_4$ ) = 1.3; total volume = 47 - 108 ml;  $T = 55^\circ C$ ; time = 6 h.

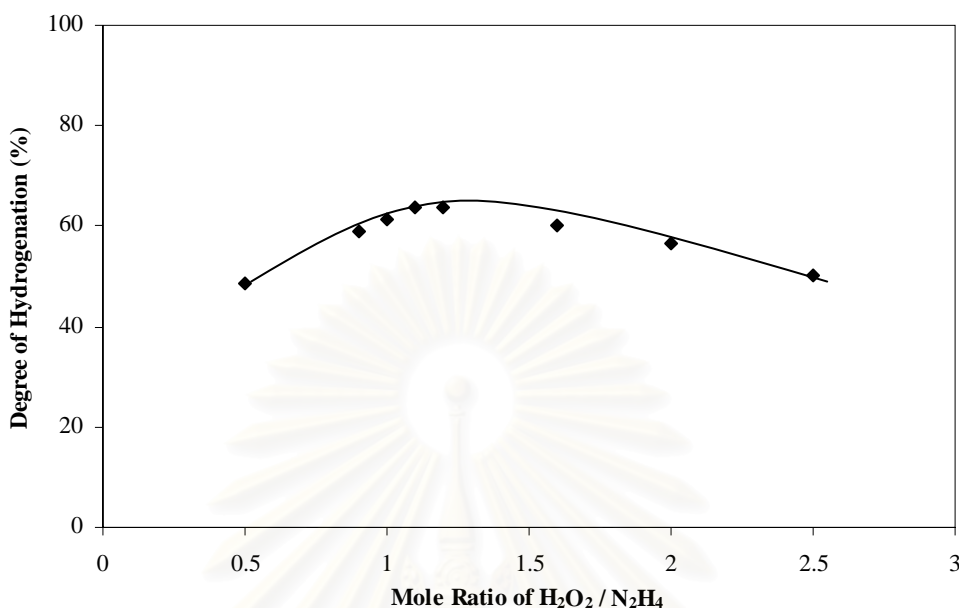
To maintain the hydrazine concentration constant during the hydrogenation reaction, additional hydrazine was added. Stepwise addition was used to maintain the hydrazine concentration level. Amount of hydrazine was divided into 3 parts and each part was added every 2 h. It means that 3 step addition hydrazine was performed. The supplement of hydrazine that was added during the reaction was also investigated due to the postulation that keeping the hydrazine concentration at a high level maintained diimide generation in the system. The result is shown in Figure 7.6. The hydrogenation curve with hydrazine addition during the reaction was the same as that without hydrazine addition during the reaction, which indicated that it was ineffective to provide  $N_2H_2$  at a high level throughout the reaction.



**Figure 7.6** Conversion profile of NRL hydrogenation for one-step addition (■) and three – step addition (◆) of hydrazine.  $\text{H}_3\text{BO}_3 = 10$  mmol; Rubber 14.3% DRC ( $\text{C}=\text{C} = 84$  mmol); mole ratio of ( $\text{H}_2\text{O}_2 / \text{N}_2\text{H}_4$ ) = 1.3; mole ratio of ( $\text{N}_2\text{H}_4/\text{C}=\text{C}$ ) = 4; total volume = 90 ml;  $T = 55^\circ\text{C}$ .

#### 7.2.4 Effect of Hydrogen Peroxide Concentration

The hydrogenation performance of latex with varied hydrogen peroxide/ hydrazine ratio (0.5 - 2.5) was investigated. The diimide hydrogenation was carried out at rubber of 14.3% DRC ( $\text{C}=\text{C} = 84$  mmol), mole ratio of ( $\text{N}_2\text{H}_4 / \text{C}=\text{C}$ ) = 4,  $\text{H}_3\text{BO}_3 = 10$  mmol, total volume = 71 – 129 ml. The reaction condition was carried out at  $55^\circ\text{C}$  for 6 h. Figure 7.7 shows that the degree of hydrogenation was low at low mole ratio of hydrogen peroxide to hydrazine. On the other hand, at a mole ratio above 1.3, the hydrogenation level was decreased. It might be possible that the excess  $\text{H}_2\text{O}_2$  in the system caused a side reaction resulting in a decrease in the degree of hydrogenation. A similar behavior of this hydrogen peroxide effect was observed for diimide hydrogenation in presence of cupric ion (Chapter 6). It might imply that the reaction proposed in eq. 7.2 might not actually be occurring during NRL hydrogenation.

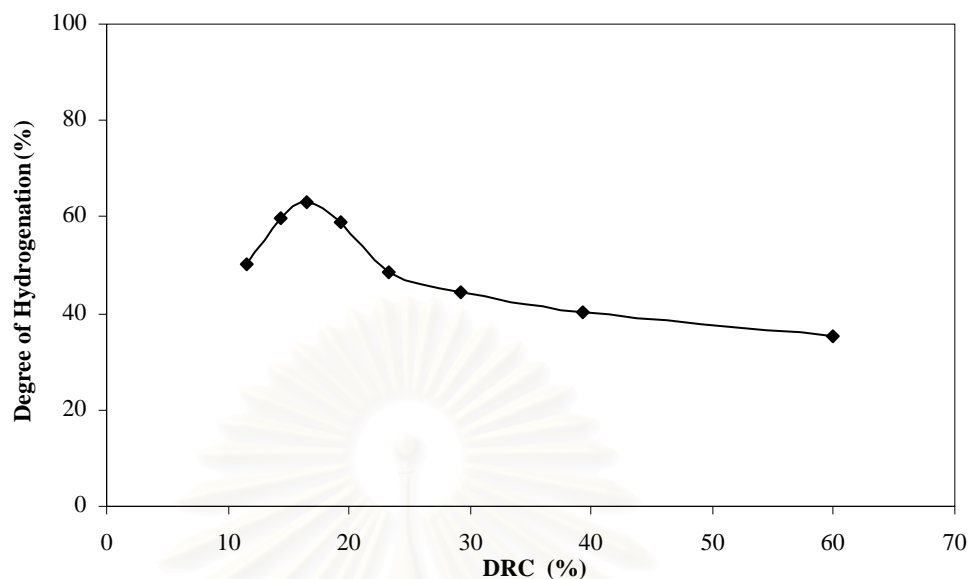


**Figure 7.7** Effect of mole ratio of H<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>H<sub>4</sub> on degree of hydrogenation. H<sub>3</sub>BO<sub>3</sub> = 10 mmol; Rubber 14.3% DRC (C=C = 84 mmol); mole ratio of (N<sub>2</sub>H<sub>4</sub> / C=C) = 4; total volume = 66 – 129 ml; T = 55°C; time = 6 h.

### 7.2.5 Effect of Solid Content

The effects of water addition were studied over the range of 11.5 – 60% dry rubber content. The hydrogenation was carried out at 55°C, C=C = 84 mmol, N<sub>2</sub>H<sub>4</sub> = 0.336 mol, H<sub>2</sub>O<sub>2</sub> = 0.437 mol, H<sub>3</sub>BO<sub>3</sub> = 10 mmol with a total reaction volume from 47.5 to 87.5 ml. The effect of solid content is shown in Figure 7.8. The result shows that the hydrogenation conversion increased with a decrease in the rubber content (increased amount of water in the system) up until 14.3% DRC after which the hydrogenation conversion decreased. It might imply that a small amount of added water in the NRL system (decreased % DRC) reduced the viscosity of latex and provided for ease of mixing of the latex with hydrazine and hydrogen peroxide. At solid content below 14.3%, the hydrogenation level was low. The reason might be due to diimide being more soluble in the water phase than in the rubber phase, which caused a decrease in degree of hydrogenation.





**Figure 7.8** Effect of solid content on the degree of hydrogenation.  $\text{H}_3\text{BO}_3 = 10$  mmol;  $\text{C}=\text{C} = 84$  mmol;  $\text{H}_2\text{O}_2 = 0.437$  mol;  $\text{N}_2\text{H}_4 = 0.336$  mol; total volume = 47.5 - 87.5 ml;  $T = 55^\circ\text{C}$ ; time = 6 h.

### 7.3 Conversion Profile for NRL Hydrogenation

The conversion profile for NRL hydrogenation was studied at  $45^\circ\text{C}$ ,  $55^\circ\text{C}$  and  $75^\circ\text{C}$  in the presence of  $\text{C}=\text{C} = 84$  mmol,  $\text{N}_2\text{H}_4 = 0.034$  mmol,  $\text{H}_2\text{O}_2 = 0.44$  mmol, and  $\text{H}_2\text{O} = 1.67$  mol. Boric acid was 10 mmol. Total volume was 90 ml. The hydrogenation was studied over a time range of 0 to 14 h. Figure 7.9(a) shows that the degree of hydrogenation increased with an increase in reaction time. It also suggests that boric acid promotes this reaction with a high selectivity. Side reactions of diimide become significant when the degree of hydrogenation rises above 55%. Maximum conversion, 63.5%, was achieved after 6 h. During the first 4 h, the rate of hydrogenation was fairly constant and then started to level off. The reason for the reduction of the hydrogenation rate after the first period is possibly due to diimide being formed as an active species at the surface and then diffusing into the outer layer of the latex particle. Then, the diimide decomposed before it could react with residual  $\text{C}=\text{C}$  in the core of the particle.

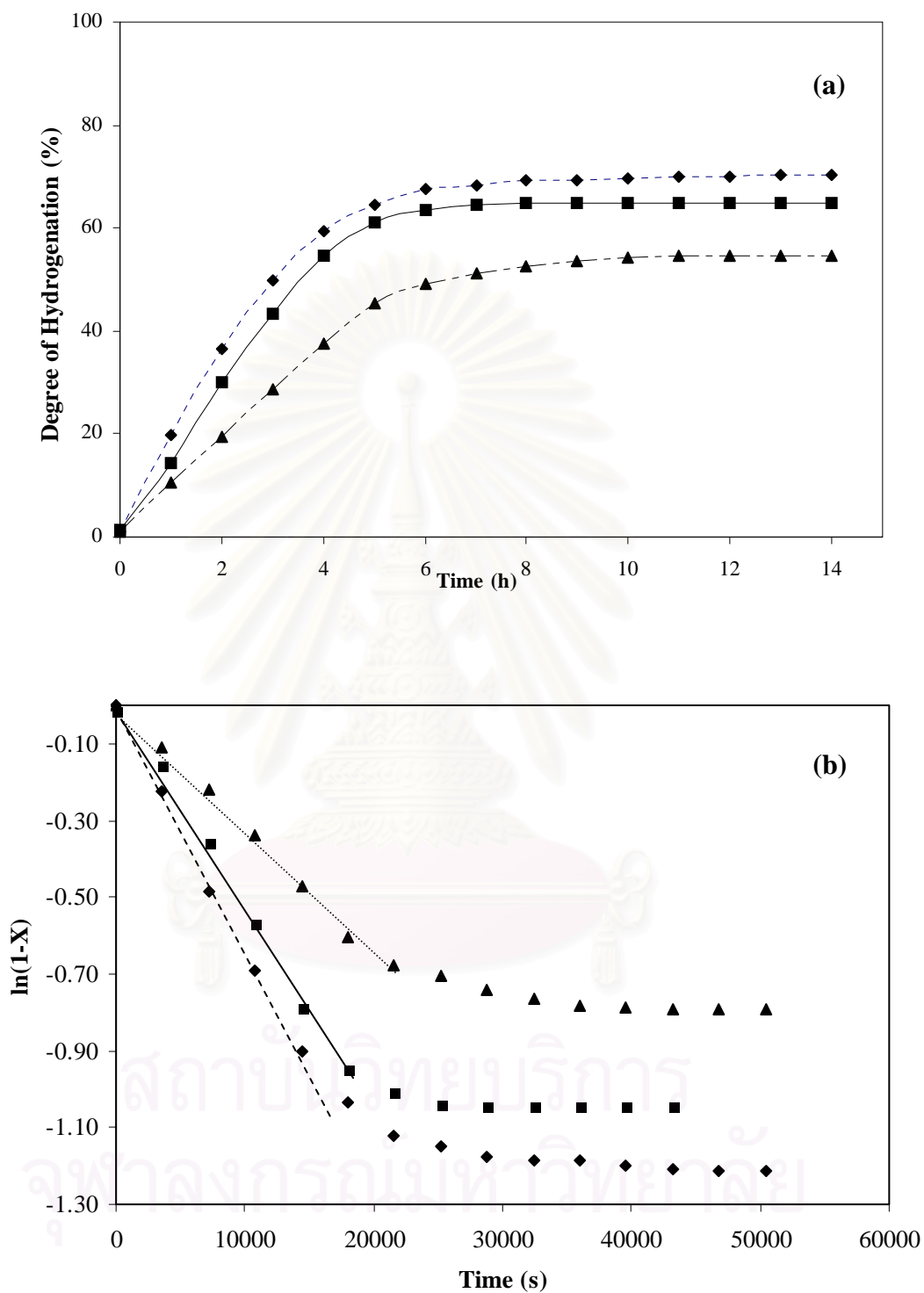
At this point, the conversion was quite stable due to the long reaction time which caused a mass transfer limitation of diimide into the latex particle. Conversion plots exhibit an apparent first order dependence for hydrogenation with respect to C=C concentration. The rate constant ( $k'$ ) was calculated from slope of the linear plot of  $\ln(1-x)$  versus time (Figure 7.9(b)). A first-order rate equation as shown in eq.7.3 where  $k'$  a pseudo first order rate constant represents the hydrogenation process.

$$\frac{-d[C=C]}{dt} = k' [C=C] \quad (7.3)$$

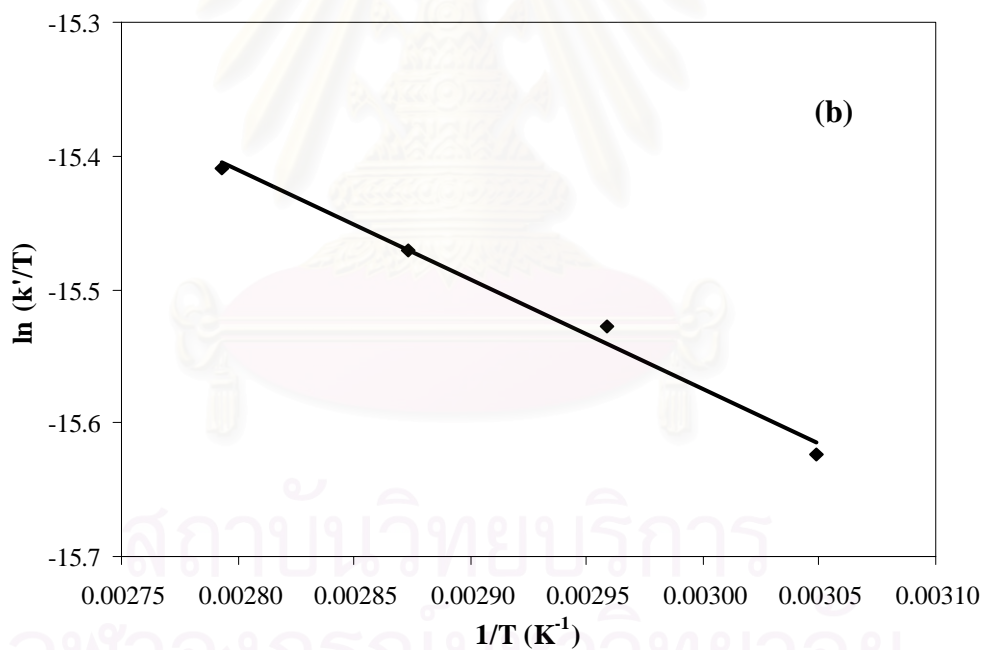
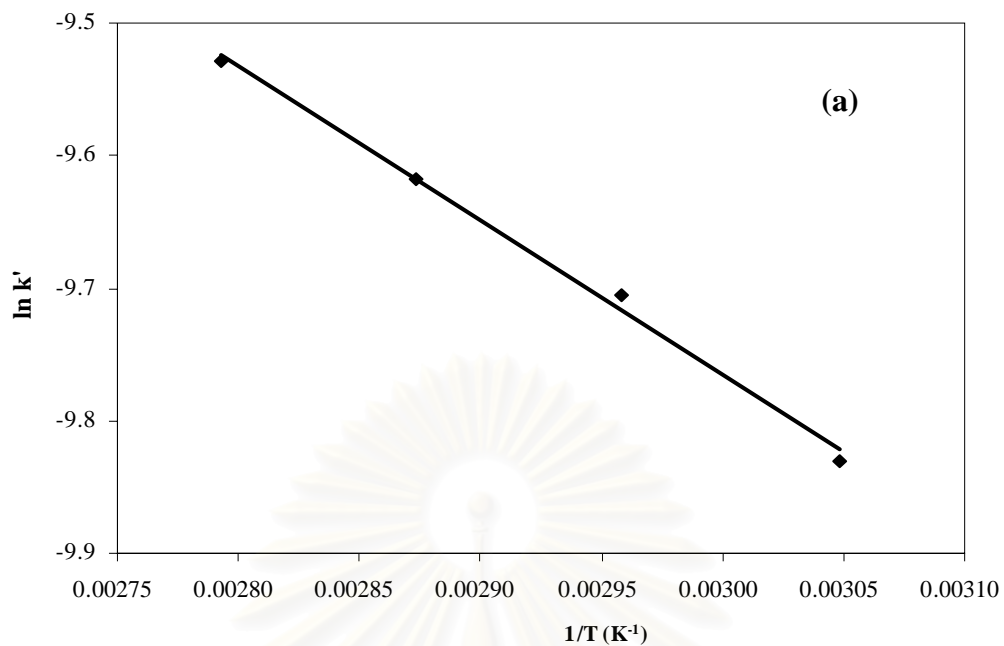
Although the  $\ln(1-x)$  versus time plot deviates from linearity in the latter stage of reaction,  $k'$ , can still be calculated with a fair degree of confidence. The rate constant, ( $k'$ ) for hydrogenation of NRL was about  $5.3 \times 10^{-5} \text{ s}^{-1}$  at  $55^\circ\text{C}$ .

The effect of hydrogenation temperature on the conversion profile shows that the degree of hydrogenation increased with an increase in reaction temperature. An Arrhenius plot is shown in Figure 7.10(a). The apparent activation energy calculated from a least squares regression analysis of  $\ln(k')$  versus  $1/T$  was 9.7 kJ/mol providing evidence that the experiments were performed with mass-transfer limitation. The activation energy of NRL hydrogenation by diimide reduction in the presence of boric acid is higher than that in presence of metal ion ( $E_a = 7.1 \text{ kJ/mol}$ ). It might imply that the boric acid system is more temperature-sensitive than the cupric sulfate system. The Eyring equation was used to estimate the apparent activation enthalpy and entropy for the reactions. Figure 7.10(b) is the Eyring plot from the temperature dependence data. The enthalpy of activation was 6.38 kJ/mol and the entropy of activation was  $-306.6 \text{ J/mol K}$

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**Figure 7.9** Conversion profile of NRL hydrogenation. (a) conversion profiles and (b) first-order ln plot: C=C = 84 mol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; H<sub>3</sub>BO<sub>3</sub> = 10 mmol; H<sub>2</sub>O = 1.67 mol; total volume = 90 ml; T = 75°C (◆), 55°C (■), 45°C (▲).



**Figure 7.10** (a) Arrhenius plot (b) Eyring plot for the NRL hydrogenation. C=C.  $\text{H}_3\text{BO}_3 = 10$  mmol; C=C = 84 mmol;  $\text{H}_2\text{O}_2 = 0.437$  mol;  $\text{N}_2\text{H}_4 = 0.336$  mol;  $\text{H}_2\text{O} = 1.67$  mol; total volume = 90 ml;  $T = 45^\circ\text{C} - 85^\circ\text{C}$ .

## CHAPTER VIII

### PHYSICAL PROPERTIES OF HYDROGENATED NATURAL RUBBER

Chemical modification of C=C unsaturated polymers via hydrogenation techniques changes the physical properties of the elastomers because of changes in thermal properties such as glass transition temperature and thermal stability which are the inherent properties of each elastomer. Hydrogenation improved the thermal stability of natural rubber (NR) by reducing the carbon double bond content in its structure (Singha, 1998). A study of thermal properties, vulcanization behavior and basic mechanical properties of hydrogenated natural rubber (HNR) is required to understand its performance for commercial utilization.

The measurement of mechanical properties of HNR in the earlier research work was precluded due to the limited scale of its preparation (Bhowmick and Stephens, ed., 1988). Consequently, in order to measure such properties in the current study, hydrogenation of natural rubber latex (NRL) in a scaled up reactor was carried out to produce a sufficient quantity of HNR for determination of the mechanical properties. The molecular weight and molecular weight distribution of HNR were investigated. The thermal properties of hydrogenated natural rubber (HNR) is also considered in this chapter. Differential scanning calorimetry (DSC) provided the low temperature properties of the hydrogenated natural rubber (glass transition temperature,  $T_g$ ). The thermal degradation of the hydrogenated natural rubber samples were investigated using thermogravimetric analysis (TGA). The physical and mechanical properties of hydrogenated natural rubber was also investigated. The mechanical properties such as tensile strength and the ozone resistance of vulcanized HNR were studied and compared with vulcanized NR and commercial EPDM rubber. Addition of carbon black as a reinforcing filler in HNR was also explored.

## 8.1 Comparison of Hydrogenation Process

Hydrogenation of natural rubber latex was studied using various catalyst systems. Chapter 3 and 4 reported the hydrogenation of natural rubber latex using homogeneous catalysts. The osmium catalyst ( $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ ) was found to be most efficient catalyst for NRL hydrogenation when compared with the iridium catalyst ( $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{Py})]\text{PF}_6$ ). Although high conversion was achieved in a short period of time, the homogenous catalyst still remained in the rubber and was difficult to separate. Thus, the noncatalytic hydrogenation of natural rubber latex in presence of diimide generated in situ was studied (Chapter 5). Diimide that reacted with carbon double bond in polymer was produced from the thermal degradation of p-toluenesulfonylhydrazide (p-TSH). It was found that the noncatalytic hydrogenation also gave a high degree of hydrogenation within 4 h. This hydrogenation method also used solvent.

In Chapter 6, the diimide reduction for NRL hydrogenation was reported. A metal ion was used as a catalyst to accelerate the diimide generation from hydrazine and hydrogen peroxide. The metal ion may remain in the system after the reaction. The hydrogenation of natural rubber latex in the presence of boric acid was also studied. Boric acid was used as a promoter for this system. Table 8.1 shows a comparison of NRL hydrogenation using various systems. It was found that for HNR via diimide reduction, high conversion was not achieved. The reason for that is that the diimide reduction was controlled by mass transfer effect. Noncatalytic hydrogenation using p-TSH as the reducing agent resulted in the highest activation energy. Diimide reduction in presence of cupric ion exhibited the lowest activation energy. This implied that diimide reduction with low activation energy was relatively temperature-insensitive while homogeneous catalytic hydrogenation with high activation energy was temperature sensitive. The Eyring equation was used to calculate the apparent activation enthalpy and entropy for the reaction. The entropy of activation for all NRL hydrogenation methods had a negative value which implied that the system tried to change from a less ordered state to a more ordered state (Transition state theory [online], 2005).



**Table 8.1** Comparisons of NRL Hydrogenation Processes

Hydrogenation Type	Acid	Solvent	NRL (g)	Condition		Product form	Degree of hydrogenation (%)	Ea kJ/mol	$\Delta H$ kJ/mol	$\Delta S$ J/mol K
<b>Homogenous catalytic</b>										
OsHCl(CO)(O <sub>2</sub> )(PCy <sub>3</sub> ) <sub>2</sub> (140 $\mu$ M)	p- TSA (9 mM)	MCB (150 ml)	2.55 (150 mM)	150°C	27.6 bar (H <sub>2</sub> )	solid	96.0 (10 min)	57.8 (120-160°C)	54.4	-159.2
[Ir(cod)(PCy <sub>3</sub> )(py)]PF <sub>6</sub> (120 $\mu$ M)	p- TSA (10 mM)	MCB (150 ml)	1.7 (100 mM)	150°C	41.4 bar (H <sub>2</sub> )	solid	90.0 (30 min)	31.8 (120-160°C)	28.4	-228.5
<b>Noncatalytic</b>										
p-TSH (161 mM) as reducing agent	-	o-xylene (100 ml)	1 (88 mM)	135°C	1 bar (N <sub>2</sub> )	solid	94.2 (4 h)	84.2 (115-135°C)	80.9	-117.0
<b>Diimide reduction</b>										
CuSO <sub>4</sub> (8 $\mu$ mol) as a catalyst N <sub>2</sub> H <sub>4</sub> :H <sub>2</sub> O <sub>2</sub> (17ml:25ml)	-	-	9.78	55°C	1 bar (Air)	liquid	67.8 (6 h)	7.1 (55-85°C)	4.26	-314.2
Boric acid( 10 mmol) as a promoter N <sub>2</sub> H <sub>4</sub> :H <sub>2</sub> O <sub>2</sub> (17ml:25ml)	-	-	9.78	55°C	1 bar (Air)	liquid	63.5 (6 h)	9.7 (55-85°C)	6.38	-306.5

p-TSA = p-toluenesulfonic acid

p-TSH = p-toluenesulfonylhydrazide

MCB = monochlorobezene

## 8.2 Molecular Weight and Molecular Weight Distribution of Hydrogenated Natural Rubber Latex

Molecular weight and molecular weight distribution are fundamental characteristics of a polymer material. Gel permeation chromatography (GPC) is a useful separation method for polymers and provides a measure of relative molecular weight (Sandler et al., 1998). Generally, rubber from *Hevea brasiliensis* has a high molecular weight with a broad molecular weight distribution. It also has been confirmed to have a bimodal distribution from GPC analysis (Tanaka, 1989).

The molecular weight and molecular weight distribution of NRL and HNRL are presented in Table 8.2. The Mw and polydispersity (Mw/Mn) of HNR obtained from homogenous catalytic hydrogenation was the same as NR. It can also be noticed that the Mw and Mw/Mn did not change with degree of hydrogenation. It might be implied that hydrogenation does not have an effect on molecular weight or that the polymer may form branching after the hydrogenation reaction and retained high molecular weight. A similar result was also found for NR hydrogenation in presence of Ru(CH=CH(Ph))Cl(CO)(PCy<sub>3</sub>)<sub>2</sub> (Tangthogkul et al., 2005). Table 8.2 also indicates that the hydrogenation method had an effect on the molecular weight distribution.

Mw of HNR prepared by diimide generated in situ ( $M_w = 0.81 \times 10^6$ ) was lower than that of NR ( $M_w = 1.09 \times 10^6$ ). The reason for decrease in mW of HNR was due to the high reaction temperature and long reaction time. Thermal degradation of p-TSH was believed to cause the decrease in molecular weight after hydrogenation via side reaction. Thus, molecular weight slightly changed after hydrogenation for homogeneous catalytic and diimide hydrogenation. Even homogenous catalytic hydrogenation was performed at high temperature (150°C) which may caused the degradation of rubber (Tangthogkul, 2003) the reaction time was shorter than diimide hydrogenation.

Crosslink gel was found in the case of hydrogenation via diimide hydrogenation using a metal ion. Mn was increased drastically (from  $4.12 \times 10^5$  to  $5.4 \times 10^5$ : Table 8.2), which be might due to the crosslink gel in hydrogenated product

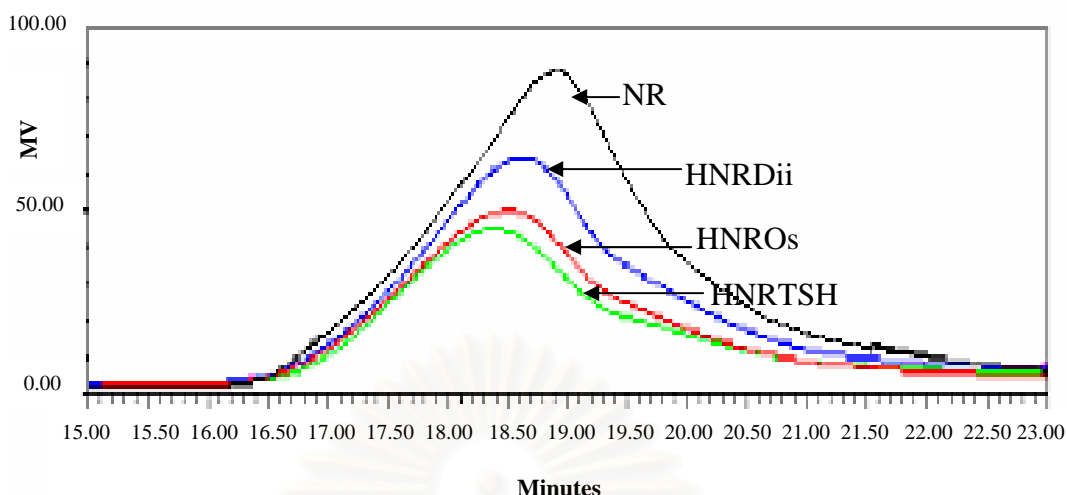
(Lin, 2004). In case of noncatalytic hydrogenation via diimide generated *in situ*, Mn decreased, it might be explained that the polymer chain was changed due to a side reaction of thermal degradation. Figure 8.1 also confirms that HNR obtained from noncatalytic hydrogenation using p-TSH as reducing agent exhibited lower molecular weight than that from the other methods. The level of hydrogenation did not have any significant effect on Mw. This indicates that the highly saturated structure of the rubber has more resistance to thermal degradation than the unsaturated form.

**Table 8.2.** Molecular Weight and Molecular Weight Distribution of Natural Rubber and Hydrogenated Natural Rubber Prepared from Various Hydrogenation Methods

Sample	% Hydrogenation	Mn x 10 <sup>-5</sup> Mw x 10 <sup>-6</sup>		
		Dalton	Dalton	Mw/Mn
NRL	-	4.12	1.09	2.65
HNROs <sup>1</sup>	50.4	4.15	1.08	2.60
	65.6	4.17	1.07	2.57
	99.5	4.24	1.07	2.52
HNRTSH <sup>2</sup>	52.5	3.20	0.81	2.54
	95.7	3.10	0.81	2.61
HNRDi <sup>3</sup>	67.8	6.09	1.08	1.77
	85.7*	5.44	1.08	1.99

- 1 HNR from hydrogenation using OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>.  
Condition: [Os] = 140 μM, [C=C] = 150 mM and [p-TSA] = 9 mM at 27.6 bar of P<sub>H<sub>2</sub></sub> and 150°C for 30 min in gas uptake apparatus
- 2 HNR from noncatalytic hydrogenation.  
Condition: [C=C] = 81mM, [p-TSH] = 161 mM at 1 bar of P<sub>N<sub>2</sub></sub> and 135°C for 4 h in glass reactor.
- 3 HNR from diimide hydrogenation in presence of cupric ion.  
Condition: C=C = 84 mmol, CuSO<sub>4</sub> = 8 μmol, H<sub>2</sub>O = 1.67 mol, N<sub>2</sub>H<sub>4</sub> = 0.336 mol, H<sub>2</sub>O<sub>2</sub> = 0.437 mol at 1 bar of air and 55°C for 6 h. under glass reactor (total volume = 90 ml)

\* Sample from 4<sup>th</sup> treatment in chapter 6 (section 6.6)



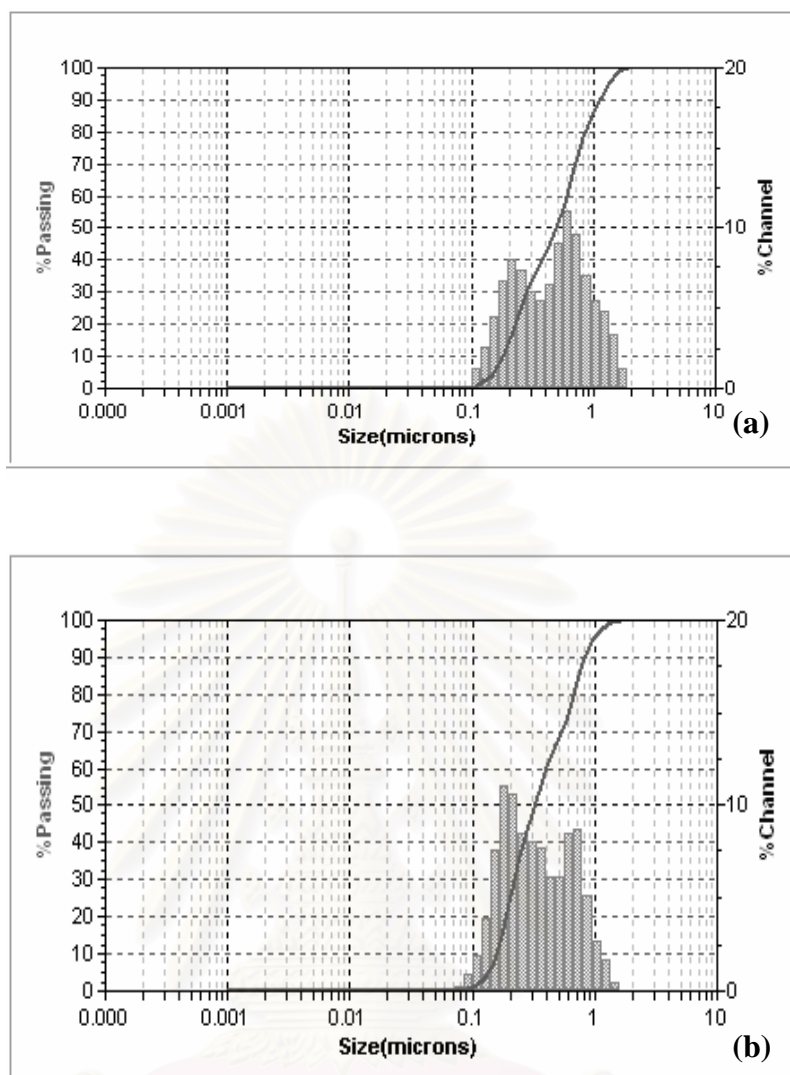
**Figure 8.1** GPC chromatograms of natural rubber samples before and hydrogenated NR obtained from various hydrogenation methods.

HNROs (99.5%):  $[Os] = 140 \mu\text{M}$ ;  $[C=C] = 150 \text{ mM}$ ;  $[p\text{-TSA}] = 9 \text{ mM}$ ;  $P_{H_2} = 27.6 \text{ bar}$ ;  $T = 150^\circ\text{C}$ ; time = 30 min in MCB.

HNRDii (85.7%):  $C=C = 84 \text{ mmol}$ ;  $CuSO_4 = 8 \mu\text{mol}$ ;  $N_2H_4 = 1.34 \text{ mol}$ ;  $H_2O_2 = 1.75 \text{ mol}$ ;  $H_2O = 1.67 \text{ mol}$ ;  $T = 55^\circ\text{C}$ ; time 24 h (total volume = 278 ml).

HNRTSH (95.7%):  $C=C = 81 \text{ mM}$ ;  $[p\text{-TSH}] = 161 \text{ mM}$ ;  $T = 135^\circ\text{C}$ ; time = 4 h in o-xylene.

To investigate the effect of diimide reduction on particle size distribution of hydrogenated natural rubber latex, the particle size of NRL before and after hydrogenation was determined using a particle size analyzer (Microtrac Nanotrac TM150 from Batek INC, USA). Figure 8.2 shows that the particle sizes before and after hydrogenation were not of a narrow size distribution. The rubber particle size of both rubbers was between 0.1 and 1 micron. The particle size before and after hydrogenation did not significantly change. This implies that the degradation of polymer did not occur during or after diimide hydrogenation using the  $N_2H_4/H_2O_2/Cu^{2+}$  system.



**Figure 8.2** Particle analysis of (a) NRL (b) HNRL (67.8% Hydrogenation). C=C = 84 mmol; N<sub>2</sub>H<sub>4</sub> = 0.336 mol; H<sub>2</sub>O<sub>2</sub> = 0.437 mol; CuSO<sub>4</sub> = 8 μmol; H<sub>2</sub>O = 1.67 mol; total volume = 90 ml; T = 55°C; time = 6 h.

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### 8.3 Thermal Properties

The structure of hydrogenated NRL was changed from *cis* -1,4-polyisoprene to an alternating ethylene propylene copolymer which is believed to have high thermal stability. Glass transition temperature and decomposition temperature can be evaluated from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The advantages of these methods are that the samples in the various forms, solid, liquid or gel, can be studied over a wide range of temperature programs and they require a small amount of sample (ca. 0.1  $\mu$ g – 10 mg). Moreover, the sample can be investigated under any atmosphere such as air, helium or nitrogen.

Some researchers (Singha, 1998; Parker, 1994 and Kubo, 1993) have employed thermal analysis to investigate the thermal properties of hydrogenated polymers. The degradation temperature of hydrogenated natural rubber increases with an increasing in the degree of hydrogenation (Singha, 1998). Hydrogenated nitrile rubbers resulting from nitrile butadiene rubber hydrogenation in the presence of  $\text{RhCl}(\text{PPh}_3)_3$  have improved low temperature resistance and improved tensile stress properties (Bhattacharjee et al., 1991). The oxidative resistance and the thermal stability of NBR has been improved by the hydrogenation process (Kubo, 1993). Cassano et al. (1998) studied the thermal stability of hydrogenated polybutadiene and the heat of fusion. It was found that both properties increased as the degree of hydrogenation increased from 0 to 89% conversion. Charmondusit (2001), Tangthongkul (2003) and Hinchiranan (2004) reported the thermal properties of HNR compared to that of NR. The results showed that high temperature properties of HNR were much better than those of NR.

#### 8.3.1 Glass Transition Temperature

Differential scanning calorimetry is a technique for determining the glass transition temperature ( $T_g$ ) of elastomers. The glass transition is a phenomenon observed in amorphous polymers (Sandler et al., 1998). The state of polymer whether it is glassy or rubbery depends on whether its application temperature is above or



below its glass transition temperature (Rosen, 1993). It is determined from the midpoint of the base-line shift of the DSC thermogram. Generally, below the  $T_g$ , an amorphous polymer can be said to have characteristics of a glass, while it becomes more rubbery above the  $T_g$ .

In this work, the glass transition temperature of NR and HNR was determined and compared with synthetic *cis*-1,4-polyisoprene (PIP), and ethylene-propylene copolymer (EPDM: Sumitomo 505A). The hydrogenated natural rubber latex was prepared using homogeneous catalytic hydrogenation, noncatalytic hydrogenation and diimide reduction. The thermal properties and DSC thermograms of hydrogenated natural rubber (HNR) samples at various degrees of hydrogenation are presented in Table 8.3 and Figure 8.3. For the HNR samples prepared by homogeneous catalytic hydrogenation (HNROs) and HNR samples prepared by noncatalytic hydrogenation, (HNRTSH), the DSC thermogram exhibited a one step base-line shift (see Figure 8.3a and 8.3b). This suggests that the HNR samples have a single glass transition temperature. In contrast, for HNR samples prepared by diimide reduction in presence of cupric ion (HNRDii), the DSC thermogram exhibited a two step base-line shift (see Figure 8.3c). The first step was at  $-62^\circ\text{C}$  and the second step was at  $-44^\circ\text{C}$ . It may be implied that two different structures of rubber occurred after the hydrogenation process. As mentioned in Chapter 6, the rubber was hydrogenated via a layer model, having a hydrogenated outer layer and a non-hydrogenated core (see Figure 8.4). For the hydrogenated outer layer, the glass transition temperature ( $T_g$ ) of the amorphous rubber phase was increased by  $15^\circ\text{C}$  which is close to the  $T_g$  of EPDM, (ethylene/propylene = 50/50, diene = 9.5%). It is possible that the amorphous segments were gradually being replaced by the crystalline units in the HNR. For the non-hydrogenated core, the glass transition temperature was the same as that of NR. Moreover, the glass transition temperature of HNR did not increase with an increase in the level of hydrogenation. It can be concluded that the hydrogenation does not affect the glass transition temperature of NR. A similar observation was also made by Charmondusit (2001) and Hinchiranan (2004) for HNR obtained using the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalytic hydrogenation system.

**Table 8.3.** Analysis of Glass Transition Temperature and Decomposition Temperature of Rubber Samples under a Nitrogen Atmosphere

Rubber	%Hydrogenation	T <sub>g</sub> (°C)	T <sub>id</sub> (°C)	T <sub>max</sub> (°C)
NR	-	-62.9	357.2	380.9
NRL	-	-61.3	347.2	373.2
HNROs <sup>1</sup>	39.9	-60.9	366.5	392.5
	50.4	-60.5	390.4	423.3
	79.1	-59.2	420.5	451.2
	99.5	-58.1	447.5	469.2
HNRIr <sup>2</sup>	50.2	-61.4	389.5	421.6
	91.5	-60.8	431.7	460.8
HNRTSH <sup>3</sup>	50.3	-60.2	390.6	422.3
	95.7	-58.4	441.1	469.1
HNRDii <sup>4</sup>	37.9	-44.4, -61.2	368.6	403.5
	67.8	-43.9, -60.7	390.4	423.3
	85.7	-43.3, -58.9	420.5	451.2
HNRBo <sup>5</sup>	63.5	-43.4, -60.4	390.6	422.3
EPDM <sup>6</sup>	-	-44.6	452.7	470.7

1 HNRL from hydrogenation using OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>.

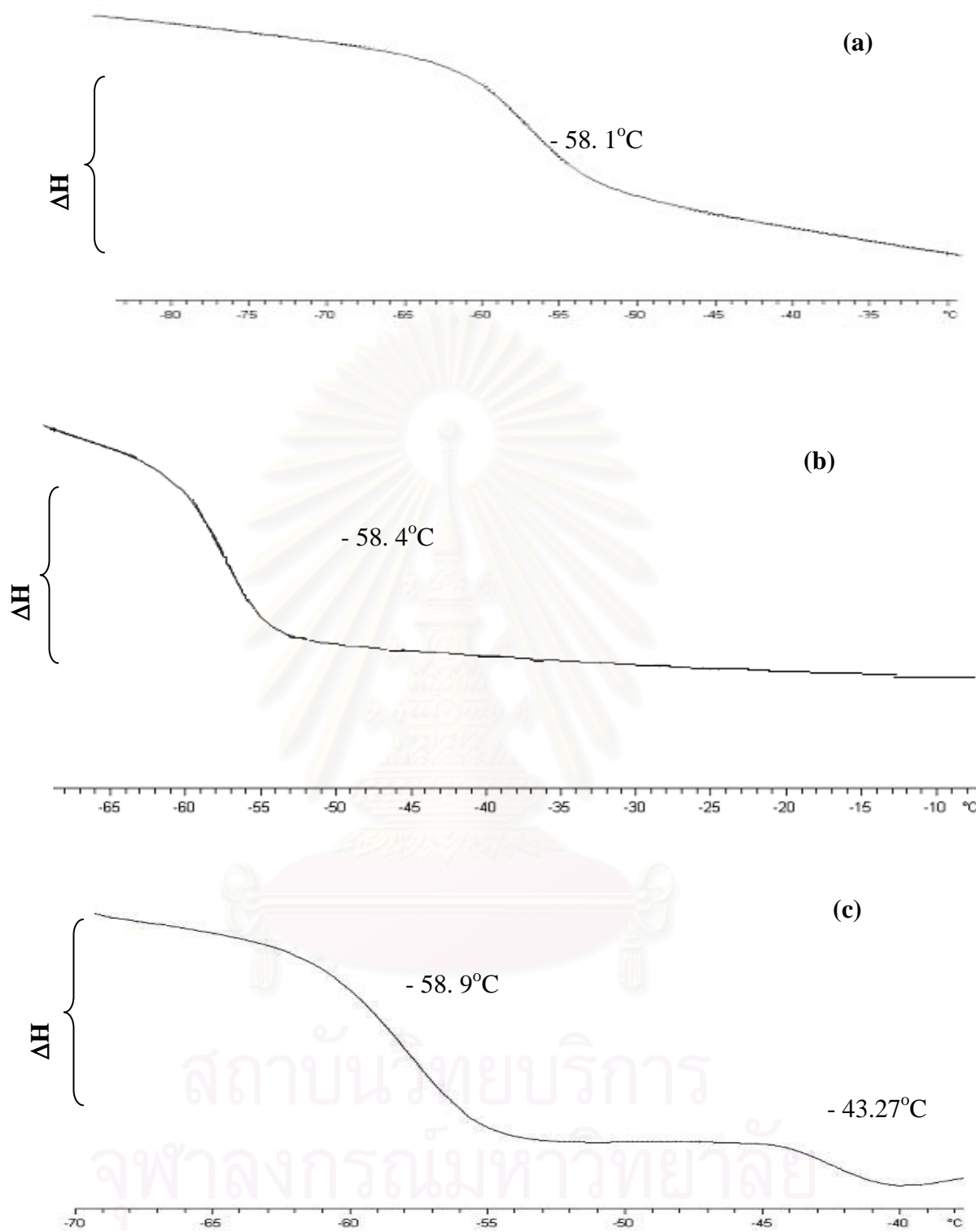
2 HNRL from hydrogenation using [Ir(cod)(PCy<sub>3</sub>)(py)]PF<sub>6</sub>.

3 HNRL from noncatalytic hydrogenation using *p*-toluenesulfonyl hydrazide

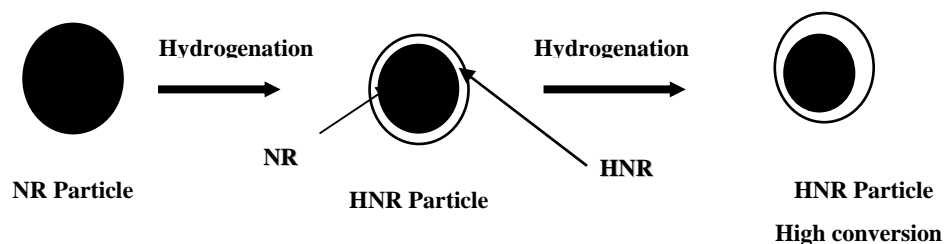
4 HNRL from diimide hydrogenation in presence of cupric ion.

5 HNRL from diimide hydrogenation in presence of boric acid.

6 Ethylene-propylene copolymer (EPDM) (the ratio of ethylene/propylene = 50/50 and 9.5% of diene content).



**Figure 8.3** DSC thermograms of rubber samples: a) HNROs (99.5% hydrogenation) b) HNRTSH (95.7 % hydrogenation) c) HNRDii (85.7%hydrogenation).

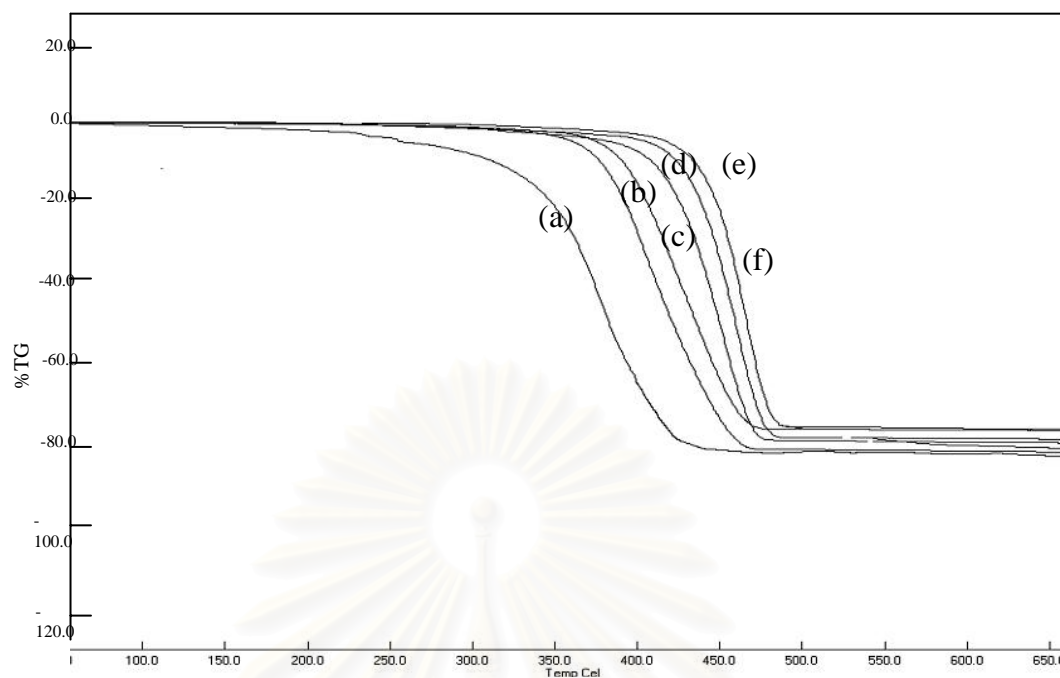


**Figure 8.4** Hydrogenated rubber latex particle model for diimide hydrogenation in presence of cupric ion.

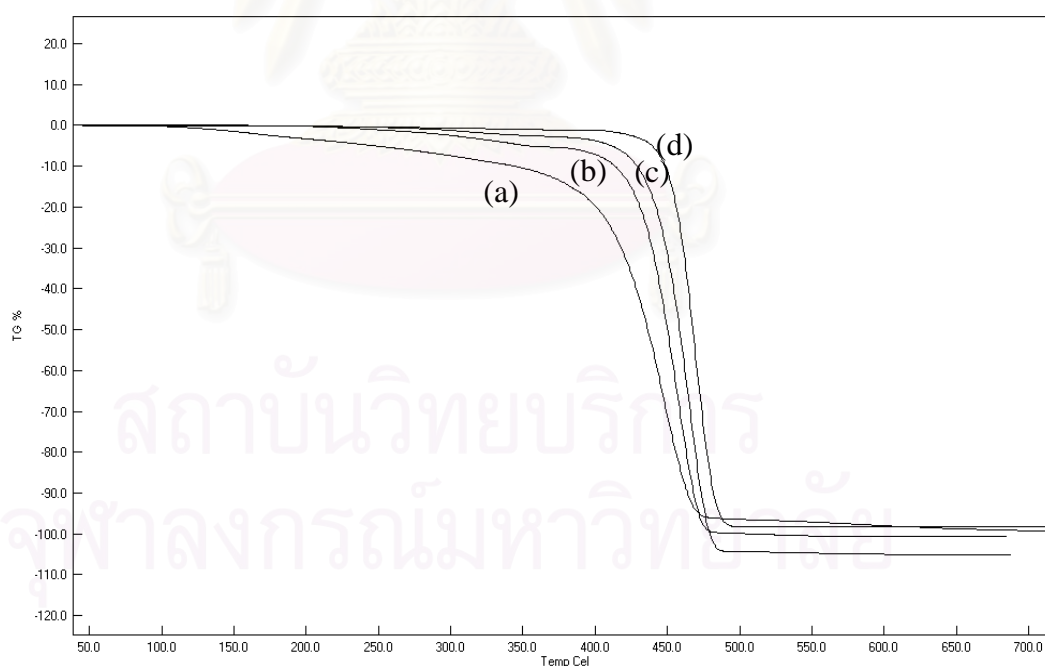
### 8.3.2 Decomposition Temperature

Thermogravimetric analysis (TGA) is a technique which monitors weight losses as the temperature is increased. TGA can directly record the mass change of a polymer with time and a given temperature. Weight losses occur as the result of driving off volatile components and degradation of the polymer at high temperature. Thus, this technique can be used both to examine the state of the material and the process of degradation (Campbell and White, 1989).

Thermogravimetric analysis is used as a method to assess the thermal stability of the polymer samples by monitoring the change in the mass of the sample, which occurs as the temperature is increased at a constant rate. During heating under a nitrogen atmosphere, polymers are degraded by breaking down to smaller fragments, which subsequently volatilize. The degradation behavior of NR after modification via hydrogenation was studied. The results of decomposition temperature of NR, NRL, EPDM and HNR obtained using four different hydrogenation methods (HNROs, HNRIr, HNRDii and HNRTSH) are presented in Tables 8.3. In the presence of nitrogen, there was no weight loss up to 300°C indicating the stability of the material over this temperature range. The weight loss occurred between 300 – 450°C, due to the loss of volatile matter contained within the polymer. Figure 8.5 and 8.6 show the TGA thermograms of the rubber sample obtained from homogenous catalytic hydrogenation of NRL (osmium catalyst) and diimide hydrogenation of NRL in the presence of CuSO<sub>4</sub>. Both figures indicate that polymer degradation is an overall one-step reaction because the TGA curve of the samples is one-step and provides a smooth weight loss curve. The initial decomposition temperature ( $T_{id}$ ) was determined from the intersection of two tangents at the onset of the decomposition temperature.



**Figure 8.5** TGA thermograms of HNROs from hydrogenation using  $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$  at various % hydrogenation: (a) 0%; (b) 39.9%; (c) 50.4%; (d) 79.1%; (e) 99.5%; f (EPDM).



**Figure 8.6** TGA thermograms of HNRDii from diimide reduction in presence of cupric ion at various % hydrogenation: (a) 0%; (b) 37.9%; (c) 67.8% and (d) 87.5%.

The maximum decomposition temperature ( $T_{\max}$ ) of each sample was obtained from the peak maxima of the derivative of the TG curves. The results are provided in Table 8.3. This table shows that both  $T_{\text{id}}$  and  $T_{\max}$  of HNR samples increase with an increase in the hydrogenation of carbon-carbon double bonds in the NRL. Therefore, the hydrogenation could improve the thermal stability of NRL. On comparison with standard EPDM, it was found that  $T_{\text{id}}$  and  $T_{\max}$  of the completely hydrogenated NR were close to those of EPDM. It can be concluded that the structure of HNR provides a facile entry and alternative method to alternating ethylene-propylene copolymers.

These results are similar to the thermal properties behavior of hydrogenated products, reported by Singha (1998) and Charmondusit (2002) for NR and PIP hydrogenation, respectively. Hinchiranan (2004) also reported that the  $T_{\text{id}}$  and  $T_{\max}$  of standard EPDM was little higher (only 5°C) than those of completely hydrogenated NR. From the thermal analysis of NBR and HNBR,  $T_{\text{id}}$  as well as  $T_{\max}$  increased with decreasing carbon - carbon double bond content (Bhattacharjee, 1991). Therefore, the thermal stabilities of all unsaturated elastomers can be improved by hydrogenation. Table 8.3 does not present the different thermal resistance level for the various hydrogenation methods. The thermal degradation resistance was found to depend on the level of hydrogenation. The hydrogenation method did not show any significant effect on thermal degradation resistance.

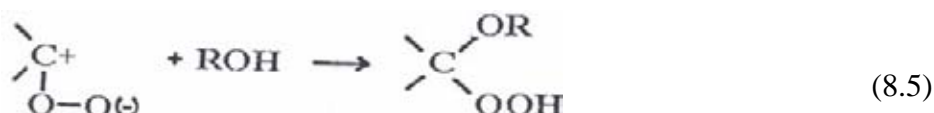
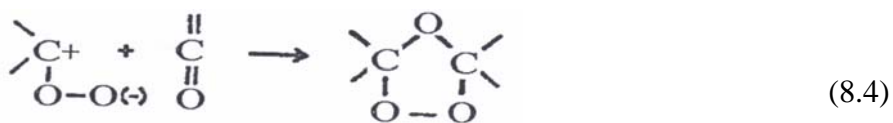
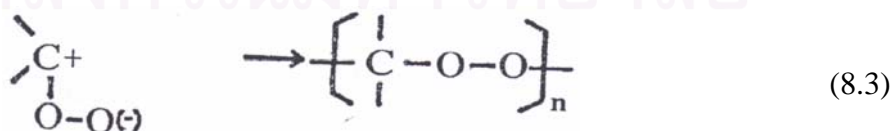
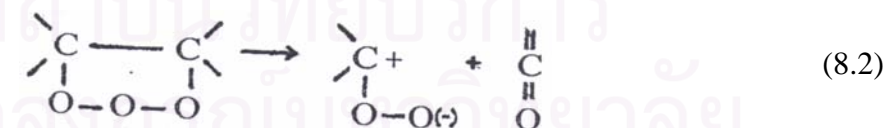
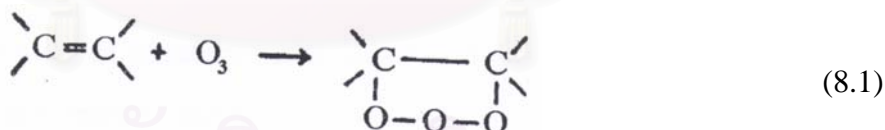
#### **8.4 Ozone resistance of Vulcanized Hydrogenated Natural Rubber**

Many unsaturated rubbers are susceptible to degradation by heat, humidity, light, ozone, radiation etc. (Vinod et al., 2002). The unsaturated structure of the diene hydrocarbon rubber makes them susceptible to attack by ozone. Ozone present in the atmosphere at a concentration in the range of 0 – 7 parts per hundred million (pphm) can severely attack non – resistant rubbers. The series of cracks on the rubber surface develop, over time, which are perpendicular to the applied stress (Findik et al., 2004). The greater level of double bonds within unsaturated rubber, the higher the susceptibility to ozonation. This can often be noted in natural rubber, but in contrast chloroprene rubber (CR) and ethylene propylene diene rubber (EPDM) are less reactive to ozone. Ethylene-propylene rubbers (EPM and EPDM) have a



completely saturated hydrocarbon main chain, so they have excellent ozone resistance and very good resistance to heat and oxidation. Although the incorporation of EPDM into a diene rubber such as NR results in a significant improvement in heat and ozone resistance, it has been found that the polymer blends generally exhibit poor mechanical properties due to imbalance incompatibility and phase separation which occur from dissimilarity in polarity of elastomers (Ghosh et al., 2001). To improve the ozone resistance of unsaturated polymers, an attempt has been made to reduce the C=C unsaturation of some elastomers such as acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) via a hydrogenation reaction. For the case of NR, the structure of NR after the hydrogenation process results is an alternating ethylene-propylene copolymer which is believed to have better ozone resistance

The ozone attack on unsaturated rubber is basically ozone attack on olefin. The mechanism is summarized in Equations 8.1 - 8.5 (Barlow, 1988). The resulting product in the initial step provides a bridging of one side of the double bond with the bond ends of the ozone molecule to form a cyclic ozonide, called an molozonide (eq. 8.1). The molozonide is unstable and breaks down into zwitterions and a carbonyl group (eq 8.2). By recombination of the latter two and in the presence of active hydrogens, three products are possible: a relative stable ozonide (eq. 8.3), a polymeric peroxide formed from the carbonyl oxide (eq. 8.4) or a hydroperoxide (eq. 8.5).



The thermal properties of HNR obtained from homogeneous catalytic hydrogenation, noncatalytic hydrogenation and diimide reduction were studied in the previous section. Therefore, the vulcanized rubbers were also investigated for ozone resistance. In this work, 15 g of hydrogenated product was blended with curing agents at 100°C by using a, Brabender Plasticorder. It was found that the addition of some plasticizers such as paraffinic oil was required to be incorporated in the HNR before adding the vulcanizing agents. The NR and EPDM with 100 parts paraffinic extender oil (Keltan 509x100) were blended with curing agents using the same method as that of HNR. Then, the two batches of rubber obtained from a Brabender Plasticorder were compounded by using a two-roll mill at 70°C. The compounding formulations of the blends are presented in Table 8.4. The details of the blending step and time are given in Table E-1, Appendix E.

The vulcanization characteristics of rubber are usually measured using a rheometer such as oscillating disk rheometer (ODR) to obtain a saving in time and complete information of vulcanization at a desired cure temperature. The rubber mixed with additives was held under pressure between heated plates surrounding a biconical rotor (Morton, ed., 1999). The small rotor oscillates through a small angle. The oscillating resistance of the mixed rubber, which is a measure of the modulus, is recorded as a function of time to give a characteristic cure curve. The hydrogenated product was compressed at a cure time which was derived from the cure curve, and then was prepared for the ozone test.

The cure characteristics of the mixes are summarized in Appendix E. The cure characteristics of EPDM and HNR were obtained at higher cure temperature than that of NR. The results show that the HNR and EPDM required higher values of both scorch time ( $t_2$ ) and optimum cure time ( $t_{95}$ ). EPDM exhibited a longer optimum cure time than HNROs, HNRDii and HNRTSH. It can be noted that the higher oil content present in EPDM obstructed the access of additives to the rubber structure. Hinchiranan (2004) reported that the vulcanization rate decreased with increasing the degree of hydrogenation. Thus, the vulcanization rate of HNROs was lower than that of HNRTSH and HNRDii.

**Table 8.4** Formulation of Mixes for Vulcanization

Components	Mix					
	1	2	3	4	5	6
	NRL	EPDM	HNROs	HNRDii	HNRTSH	NR/HNRDii (60/40)
NR	100	-	-	-	-	60
EPDM <sup>a</sup>	-	200	-	-	-	-
HNROs (94±1%)*	-	-	100	-	-	-
HNRDii (68±2%)*	-	-	-	100	-	40
HNRTSH (93±2%)*	-	-	-	-	100	-
MBT <sup>b</sup>	0.5	0.5	0.5	0.5	0.5	0.5
TMTD <sup>c</sup>	1	1	1	1	1	1
Paraffinic oil <sup>d</sup>	-	-	44	54	70	43
Ultrablend 4000 <sup>e</sup>	-	-	7	7	7	7

ZnO = 5.0 phr; Stearic acid = 2.0 phr and Sulfur = 2.0 phr.

Mixing temperature = 70°C for Mix1, Mix 6 and 100°C for Mix 2 – 5.

<sup>a</sup> Keltan 509x100 (8.7% diene content with 64% ethylene content and 100 parts paraffinic extender oil); <sup>b</sup> 2-Mercaptobenzothiazole; <sup>c</sup> Tetramethyl thiuram disulphide; <sup>d</sup> DN process PA 32T and <sup>e</sup> Tackifier.

\* % Hydrogenation.

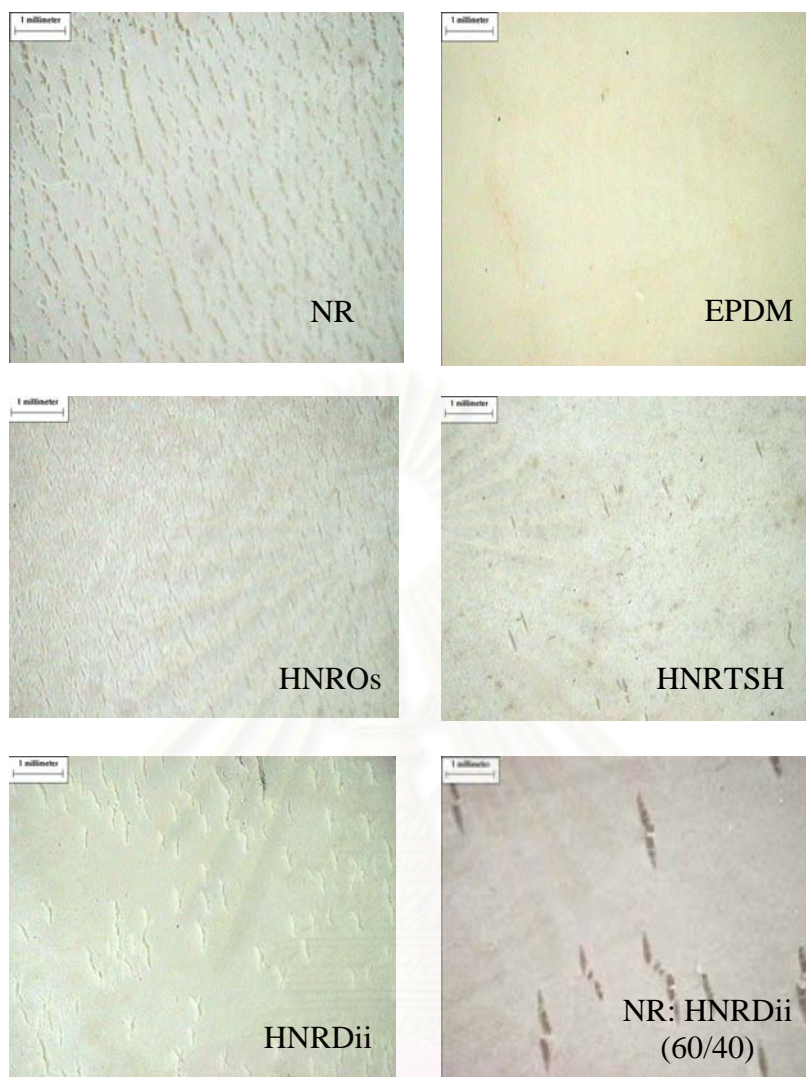
The vulcanizate of HNRL were exposed in a HAMPDEN ozone cabinet at 40°C in an atmosphere of 50 ppm by volume of ozone concentration for 3, 6, 24, 27 and 48 h. Before exposure to the ozone atmosphere, the specimens were stretched by 20% in the absence of light for 48 h. The test method follows the ISO 1431 Part 1 and Physical Testing Standards of Rubbers by Nishi and Nagano (1983). A lens of magnification of about 7 times was used to detect the appearance of cracking. A type of ozone cracking on the rubber surface of each specimen was classified according to Table 8.5. After exposure to the ozone atmosphere at the same condition, the cracking of HNRL, NRL and EPDM was compared and the results are shown in Table 8.6 and Figure 8.7.

**Table 8.5** Classification of Cracking on Rubber Surface (Nishi and Nagano, 1983)

Number of Cracking	Size and Depth of Cracking
A: a small number of cracking	1. That which cannot be seen with eyes but can be confirmed with 10 times magnifying glass.
B: a large number of cracking	2. That which can be confirmed with naked eyes.
	3. That which is deep and comparatively long (below 1 mm).
C: numberless cracking	4. That which is deep and long (above 1 mm and below 3 mm).
	5. That which is about to crack more than 3 mm or about to sever.

**Table 8.6** Ozone Cracking of Vulcanized HNR Compared with NR and EPDM

Rubber	Type of Curing Agents	Type of Cracking				
		3 h	6 h	24 h	27 h	48 h
NR	MBT/TMTD	nc	C-3	C-3	C-3	C-3
EPDM	MBT/TMTD	nc	nc	nc	nc	nc
HNROs	MBT/TMTD	nc	nc	C-3	C-3	C-5
HNRDii	MBT/TMTD	nc	nc	nc	C-3	C-4
HNRTSH	MBT/TMTD	nc	nc	nc	nc	C-3
NR/HNRDii (60/40)	MBT/TMTD	nc	nc	nc	nc	A-3



**Figure 8.7** Surface of rubbers vulcanized by MBT/TMTD curing system after exposure to ozone for 48 h (captured by CCD camera).

Figure 8.7 indicated that significant cracking (C-3) appeared on the surface of the NR specimen at 6 h. For HNROs, significant cracking appeared on the surface of HNR specimens at 24 h. although, the level of hydrogenation achieved was more than 90% because the residual catalyst,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , might catalyze the oxidation of NR. The cracking of HNRDii and HNRTSH was observed on the surface at 27 and 48 h, respectively.



## 8.5 Mechanical Properties

From section 8.2, it was seen that the thermal stability of hydrogenated natural rubber (HNR) was improved. Furthermore, basic mechanical properties of hydrogenated natural rubber (HNR) are required to understand its performance for commercial utilization. The measurement of any technological properties of HNR in the earlier research work was precluded due to the limited scale of its preparation (Bhowmick and Stephens, ed., 1988). In order to measure such properties in this study, scale up NRL hydrogenation was performed to produce a sufficient quantity of HNR for the determination of mechanical properties.

### 8.5.1 Scale Up Hydrogenation of Natural Rubber Latex

For homogenous catalytic hydrogenation of rubber latex, the reaction was carried out in Parr reactor (2 liter reactor) and the hydrogenated rubber (HNROs) yield was about 30 g/batch. In the case of noncatalytic hydrogenation, this reaction was carried out in 2- liter glass reactor and the hydrogenated product (HNRTSH) was about 45 g/batch. Diimide reduction was also carried out in a 2- liter glass reactor and the hydrogenated product (HNRDii) was about 60 g/batch. The results for the scale up of the NRL hydrogenation are summarized in Table 8.7.

Based on the experimental results in Chapter 3 and Chapter 4, both catalysts,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$ , were effective for NR hydrogenation. The addition of acid in the NRL hydrogenation process has shown that 3-chloropropionic acid (3-CPA) and *p*-toluenesulfonic acid (*p*-TSA) enhanced the hydrogenation rate by preventing the poisoning of the catalysts due to impurities present in NRL. Hichiranan (2004) reported that NR hydrogenation catalyzed by Os/3-CPA system yielded higher than 90% conversion within 4 h and the rubber product obtained was white. In contrast, the results of the scale up hydrogenation shown in Table 8.8 indicated that for the Os/*p*-TSA hydrogenation in THF, a high degree of hydrogenation was achieved in short period of time. For the NRL hydrogenation catalyzed by the Ir/*p*-TSA system, the hydrogenation rate was low and only 40% conversion was achieved in 4 h.



**Table 8.7** Comparison of Hydrogenation in Scale Up Reactor

Hydrogenation Type	Acid <sup>1</sup>	Solvent <sup>2</sup>	NRL		Condition	Product form	Time (h)	Product Weight (g)	Degree of Hydrogenation (%)
			(g)	(g)					
<b>Homogenous catalytic</b>									
OsHCl(CO)(O <sub>2</sub> )(PCy <sub>3</sub> ) <sub>2</sub> (140 μM)	p- TSA	THF	50	150°C	27.6 bar, (H <sub>2</sub> )	solid	4	~ 30	98.9
	3- CPA	THF	50	150°C	27.6 bar, (H <sub>2</sub> )	solid	4	~ 30	97.0
	p- TSA	MCB	50	150°C	27.6 bar, (H <sub>2</sub> )	solid	4	~ 30	93.5
	3-CPA	MCB	50	150°C	27.6 bar, (H <sub>2</sub> )	solid	4	~ 30	88.5
	3- CPA	Toluene	50	150°C	27.6 bar, (H <sub>2</sub> )	solid	4	~ 30	80.3
	p- TSA	Toluene	50	150°C	27.6 bar, (H <sub>2</sub> )	solid	4	~ 30	85.4
[Ir(cod)(PCy <sub>3</sub> )(py)]PF <sub>6</sub> (120 μM)	p- TSA*	MCB	50	150°C	41.4 bar, (H <sub>2</sub> )	solid	4	~ 30	64.5
	3- CPA*	MCB	50	150°C	41.4 bar, (H <sub>2</sub> )	solid	4	~ 30	55.5
<b>Noncatalytic</b>									
p-TSH (882 mM) as reducing agent	-	o-xylene	75	135°C	1 bar, (N <sub>2</sub> )	solid	6	~ 45	85.9
<b>Diimide reduction</b>									
CuSO <sub>4</sub> (80 μmol) as a catalyst	-	-	100	55°C	1 bar, (Air)	liquid	27	~ 60	71.6
N <sub>2</sub> H <sub>4</sub> :H <sub>2</sub> O <sub>2</sub> (170 ml:250 ml)									
Boric acid( 100 mmol) as a promoter	-	-	100	55°C	1 bar, (Air)	liquid	27	~ 60	77.5
N <sub>2</sub> H <sub>4</sub> :H <sub>2</sub> O <sub>2</sub> (170 ml:250 ml)									

Acid<sup>1</sup> = 180 mM, Acid<sup>1\*</sup> = 200 mM, Solvent<sup>2</sup> = 1500 ml

It is possible that  $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$  is more sensitive to being deactivated by the amine functional groups in the protein structure present in NR than in the case for  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ . For noncatalytic hydrogenation in 2-liter reactor, 85.9 % hydrogenation was achieved. For the diimide hydrogenation, boric acid system seems to have higher efficiency than cupric sulfate system (metal ion system). This might be due to the poor dispersion of metal ion in the natural rubber latex at high rubber loading. The degree of hydrogenation of HNR prepared in the scale up reactor (2 liter) was not much different from that obtained in the small scale reactor (250 ml).

### 8.5.2 Blend and Vulcanization of Hydrogenated Natural Rubber

Vulcanization is a process to change rubber from essentially a plastic material to either an elastic or a hard material. Vulcanized rubber is highly elastic and resistant to plastic deformation. Normally, rubber mixed with vulcanizing agents and other chemicals such as an activator or fillers is vulcanized by heating at a temperature between 120 and 200°C in a mold of a desired shape and size (Stephens, ed., 1993). Typically, vulcanization can be classified into four systems: sulfur vulcanization, sulfurless vulcanization, peroxide vulcanization and other systems, which make use of certain nonsulfur bifunctional compounds. The most common system used in general rubber industries is a sulfur vulcanization because of the low cost of chemicals and ease of operation. During vulcanization, the long chains of rubber molecules become crosslinked by reactions with the vulcanizing agent to form a three – dimensional structure. The vulcanized rubber loses its tackiness and it has more resistance to deterioration normally caused by heat, light and aging (Morton, ed., 1999).

In this work, 100 g of HNRL was blended with curing agents at 70°C by using a two-roll mill. The NR and EPDM with 100 parts paraffinic extender oil (Keltan 509x100) were blended with curing agents using the same method as that of HNR. The compounding formulations of the blends are presented in Table 8.8. The details of the blending step and time are given in Appendix D. The cure temperature and time was chosen based on the rubber cure characteristic using ODR (Table E-2).

### **8.5.3 Mechanical Properties of Vulcanized Hydrogenated Natural Rubber**

Mechanical properties of vulcanized NR, HNR and EPDM using MBT/TMTD as accelerators were measured in terms of tensile strength, ultimate elongation and hardness. The thin rubber sheets from the two – roll mill were pressed under pressure by compression molding. The thickness of vulcanized sheets was ca. 2 mm. Then, the sheet was cut into standard specimens according to the ASTM test method. The results of mechanical properties are summarized in Table 8.9 and Figure 8.8. The mechanical properties of vulcanizates obtained from NR/HNR and NR/EPDM blends were retained after heat aging. This indicated that vulcanized NR/HNR and NR/EPDM blends are more resistant to heat due to the low unsaturation level in the rubber structures (Ghosh et al., 2001). However, the low content of carbon – carbon double bonds caused the poor mechanical properties of both HNR and EPDM.

It can be noticed that the mechanical properties of vulcanized rubber are quite low; especially, in the case of vulcanized NR. It was possible that the vulcanized rubber sheets for the mechanical properties test might have some defects due to air bubbles remaining inside the rubber after it was pressed in the compression mold. The same result was obtained in previous study (Chapter 6, Hinchiranan, 2004) which reported the low tensile strength of vulcanized NR. Another reason for low tensile strength was due to the formulation of mixes for vulcanization. The formulation was selected for the EPDM vulcanization system and it might not be suitable for NR vulcanization. NR after heat aging exhibited a decrease in tensile strength and increase in hardness. It can be implied that natural rubber degraded after aging. As mention above, the tensile strength of EPDM and NR/HNR (50/50) blends (mix 8-12) before and after aging was not different. It can be noted that that EPDM and NR/HNR blends had resistance to the degradation, and the aging properties was improve due to the addition of HNR in the blends. To improve the tensile properties, carbon black would be used as a reinforcing filler in rubber blends.

**Table 8.8** Formulation of Mixes for Vulcanization

Components	Mix					
	7	8	9	10	11	12
	NRL	EPDM	NR/EPDM (50/50)	NR/HNROs 70 (50/50)	NR/HNRDii70 (50/50)	NR/HNRTSH70 (50/50)
NR	100	-	50	50	50	50
EPDM <sup>a</sup>	-	200	100	-	-	-
HNROs (70±3%)	-	-	-	50	-	-
HNRDii (70±4%)	-	-	-	-	50	-
HNRTSH (70±2%)	-	-	-	-	-	50
MBT <sup>b</sup>	0.5	0.5	0.5	0.5	0.5	0.5
TMTD <sup>c</sup>	1	1	1	1	1	1
Paraffinic oil <sup>d</sup>	-	-	12	12	12	12

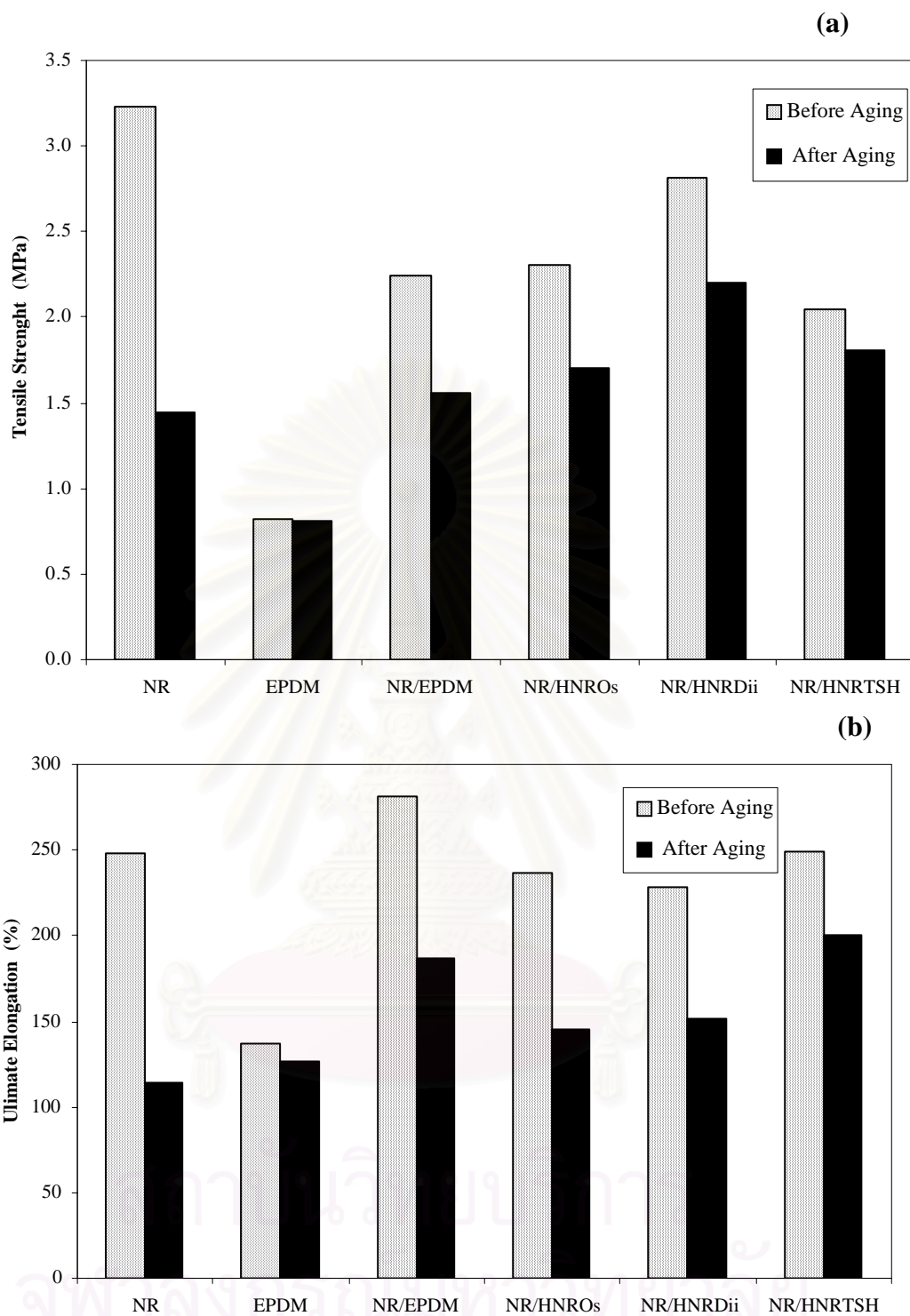
ZnO = 5.0 phr; stearic acid = 2.0 phr and sulfur = 2.0 phr. Mixing temperature = 70°C

<sup>a</sup> Keltan 509x100 (8.7% diene content with 64% ethylene content and 100 parts paraffinic extender oil); <sup>b</sup> 2-Mercaptobenzothiazole; <sup>c</sup> Tetramethyl thiuram disulphide; <sup>d</sup> DN process PA 32T

**Table 8.9** Mechanical Properties of Vulcanized Rubber Samples

Mix	Tensile Strength		Ultimate Elongation		Hardness	
	(MPa)		(%)		(Shore A)	
	Un-aged	Aged	Un-aged	Aged	Un-aged	Aged
7 (NR)	3.23	1.44	248.3	113.9	44.0	52.8
8 (EPDM)	0.82	0.81	137.5	126.7	36.8	37.2
9 (NR/ EPDM) 50/50	2.24	1.55	281.5	186.5	40.6	48.8
10 (NR/HNROs) 50/50	2.31	1.70	236.5	145.6	41.2	42.2
11 (NR/HNRDii) 50/50	2.81	2.21	228.8	151.5	42.2	43.8
12 (NR/HNRTSH) 50/50	2.04	1.81	249.6	200.0	40.8	42.8

Heat aging was done at 100°C for 22 h.



**Figure 8.8** Mechanical properties before and after heat aging at 100°C for 22 h of natural rubber, EPDM and NR/HNR (50/50) blends: a) tensile strength; b) elongation.

#### 8.5.4 Improvement of Mechanical Properties of Vulcanized Hydrogenated Natural Rubber

The poor mechanical properties of vulcanized hydrogenated natural rubbers was reported in section 8.5.3. To increase the tensile strength of NR and NR/HNR blends, the formulation for rubber compounding was changed and carbon black was added. Carbon black is one of most important synthetic fillers for rubber modification. The main purpose for rubber reinforcement is to increase tensile strength, modulus, abrasion and tear strength. Pairpisit (2002) reported that carbon black increased the tensile strength of natural rubber and EPDM blends and 10 phr of carbon black was suitable for high insulation iron crossarm application. In this work, the mixed rubber was blended with curing agents at 90°C by using a two-roll mill. The compounding formulations of the blends are presented in Table 8.10. The details for blending step and time are given in Appendix D. The rubber compound from two-roll mill were pressed under pressure by compression molding at 150°C and time interval from the rubber cure characteristic using ODR (Appendix E).

The results of mechanical properties of vulcanized rubbers are summarized in Table 8.11 and Figure 8.9. The mechanical properties of vulcanized NR, NR/EPDM, NR/HNRDii blends were improved after the blending formulation was changed. Thus, the blending formulation has an effect on tensile strength and elongation properties. The tensile strength of vulcanized NR/HRNDii blend (13.7 MPa) was higher than that of vulcanized NR/EPDM (10.2 MPa). It might be due to the compatibility of NR and HNR. Carbon black addition increased the tensile strength and decreased the ultimate elongation of the NR/HNR blend. It was found that tensile strength of blends was increased when 10 phr of carbon black was added and decreased at high carbon black loading (30 phr). The tensile strength of NR before and after aging was dramatically changed. Upon heating, sulfur-sulfur bond or carbon-sulfur bond in rubber sample was destroyed to result in a lower tensile strength. The tensile strength of NR/EPDM was also decreased after aging. It is probably that the major matrix of NR/EPDM blend was NR which had poor resistance to heat aging. However, the decrease in tensile strength of NR/EPDM blend (82%) after aging was less than NR (91%) which might be due to the addition of EPDM in assisting the degradation resistance. For carbon black addition, the decrease in tensile



strength after aging was reduced to 40%. It was believed that carbon black acted as a reinforcing filler for NR/HNR blends.

**Table 8.10** Formulation of Mixes for Vulcanization

Components	Mix						
	13	14	15	16	17	18	19
	NR	NR	NR/EPDM (70/30)	NR/EPDM (70/30)	NR/HNRDii (70/30)	NR/HNRDii (70/30)	NR/HNRDii (70/30)
NR	100	100	70	70	70	70	70
EPDM <sup>a</sup>	-	-	60	60	-	-	-
HNRLDii (70±4%)	-	-	-	-	30	30	30
Untra blend <sup>b</sup> (4000)	-	-	5	5	5	5	5
Carbonblack	-	10	-	10	-	10	30
MBTS <sup>c</sup>	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD <sup>d</sup>	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Paraffinic oil <sup>e</sup>	-	-	-	-	6	6	6

ZnO = 5.0 phr; Stearic acid = 1.5 phr and Sulfur = 2.0 phr.

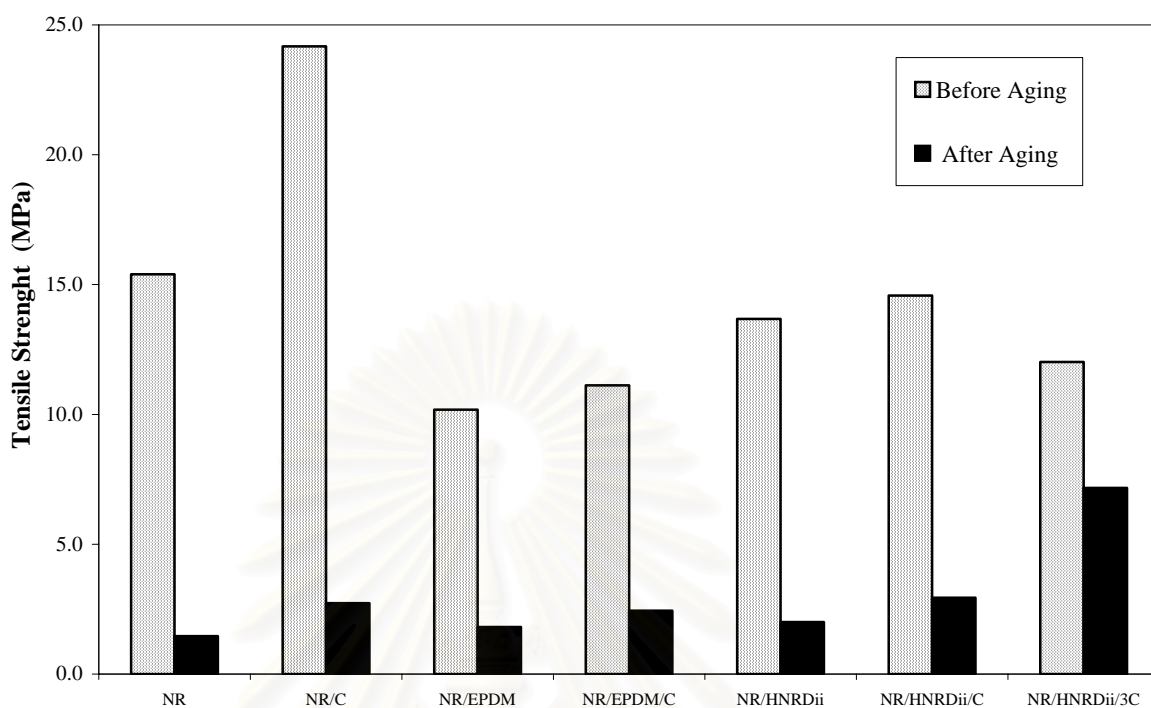
<sup>a</sup> Keltan 509x100 (8.7% diene content with 64% ethylene content and 100 parts paraffinic extender oil); <sup>b</sup>Tackifier; <sup>c</sup> Dibenothiazole disulfide; <sup>d</sup>Tetramethyl thiuram disulphide; and <sup>e</sup> DN process PA 32T.

**Table 8.11** Mechanical Properties of Vulcanized Rubber Samples

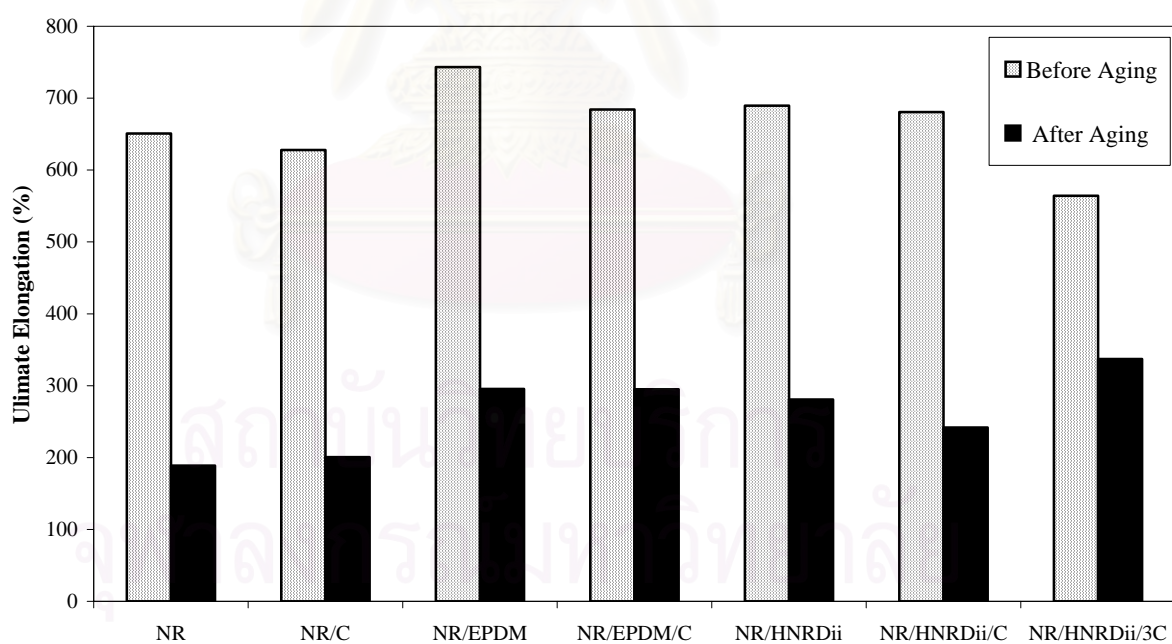
Mix	Tensile Strength		Ultimate Elongation		Hardness	
	(MPa)		(% )		(Shore A)	
	Un-aged	Aged	Un-aged	Aged	Un-aged	Aged
13 (NR)	15.4	1.46 (91%)	650.7	188.8	39.3	46.4
14 (NR/C)	24.2	2.73 (89%)	627.8	200.6	44.7	50
15 (NR/EPDM) 70/30	10.2	1.81 (82%)	743.3	295.5	33.2	38.2
16 (NR/EPDM/C) 70/30/10	11.1	2.44 (78%)	684.3	295.1	33.5	39.3
17 (NR/HNRDii) 70/30	13.7	2.01 (85%)	689.6	280.8	35.5	36.5
18 (NR/HNRDii/C) 70/30/10	14.6	2.94 (80%)	680.6	241.8	42.7	46.8
19 (NR/HNRDii/3C) 70/10/30	12	7.17 (40%)	564.2	337.1	52.1	56.1

Heat aging was done at 100°C for 22 h., ( ) = % Tensile strength reduction.

(a)



(b)



**Figure 8.9** Mechanical properties before and after heat aging at 100°C for 22 h of natural rubber, EPDM and NR/HNR (70/30) blends: a) tensile strength; b) elongation.

## CHAPTER IX

### CONCLUSIONS AND RECOMMENDATIONS

#### 9.1 Conclusions

##### 9.1.1 Hydrogenation of Natural Rubber Latex Catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$

$\text{OsHClCO}(\text{O}_2)(\text{PCy}_3)_2$  functions as an effective catalyst system for hydrogenation of natural rubber latex (NRL) in chlorobenzene. The kinetics of NRL were studied by monitoring hydrogen consumption using a computer gas uptake apparatus. The process showed a first order dependence on concentration of osmium, implying that the active complex is mononuclear. Impurities, which increase with rubber at higher rubber concentration, reduce the catalytic activity. The hydrogenation showed an apparent inverse order dependence on rubber concentration due to impurities. A second-order to zero-order dependence on hydrogen pressure was found as previously observed with PIP. The hydrogenation rate was dependent on reaction temperature and an apparent activation energy for this process was 57.8 kJ/mol. The presence of a sulfonic acid in the hydrogenation process helped to prevent the poisoning of the osmium catalyst by impurities present in the emulsion system

##### 9.1.2 Hydrogenation of Natural Rubber Latex Catalyzed by $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6$

$[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$  was an effective catalyst for the hydrogenation of natural rubber latex in monochlorobenzene. The kinetic results indicated that the hydrogenation was first order on hydrogen pressure and first to zero order with respect to catalyst concentration. The reaction rate implied that the active complex is mononuclear at low catalyst concentration and that a side reaction such as dimerization of the Ir catalyst might be occurring at high catalyst loading. The impurities in natural rubber caused the hydrogenation rate to have an inverse behavior with respect to rubber concentration. The apparent activation energy of the hydrogenation of natural rubber latex was calculated to be 31.8 kJ/mol. The proposed

mechanism and the rate expression for hydrogenation of NRL in the presence of  $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})]\text{PF}_6$  were consistent with the kinetic data. The relative viscosity of the hydrogenated products indicated that there was probably no degradation for the hydrogenated rubber.

### **9.1.3 Noncatalytic Hydrogenation of Natural Rubber Latex in the presence of Diimide Generated in situ**

The noncatalytic hydrogenation of NRL via diimide generated in situ by thermolysis of *p*-toluene sulfonylhydrazide (TSH) is an effective method. The appropriate conditions were at TSH/C=C ratio of 1.8 and a temperature of 135°C, 95 % hydrogenation was achieved. The effective solvent was *o*-xylene. The effect of impurity and water on the degree of hydrogenation were not significant. The conversion profile exhibits an apparent first order dependence for hydrogenation of C=C. The apparent activation energy of the hydrogenation of natural rubber latex was calculated to be 84.2 kJ/mol.

### **9.1.4 Hydrogenation Natural Rubber Latex by Diimide Reduction in the presence of Cupric Ion**

Diimide reduction is an alternative route for the hydrogenation of natural rubber latex. Around 67.8 % double bond reduction was achieved within 6 h under the appropriate reaction conditions. The main factors controlling the hydrogenation of NRL via diimide reduction were concentration of rubber and hydrazine. Low rubber concentration and high hydrazine concentration provided the most favorable conditions. The degree of hydrogenation was highest when cupric acetate was used as catalyst. Impurities in this system did not have a significant effect on the degree of hydrogenation. Gelatin had a positive effect on the degree of hydrogenation as it acted as a stabilizer for the copper ion at an optimum level for effective diimide production. The addition of SDS was found to decrease the degree of hydrogenation. Hydroquinone also showed a negative effect on the degree of hydrogenation. Conversion plots exhibit an apparent first order dependence for hydrogenation with respect to C=C concentration. The apparent activation energy of the hydrogenation of natural rubber latex was calculated to be 7.1 kJ/mol. From the

TEM micrograph, nonhydrogenated rubber core and hydrogenated outer layer were observed according to the layer model.

### **9.1.5 Hydrogenation Natural Rubber by Diimide Reduction in the presence of Boric Acid**

Hydrogenation of natural rubber latex via diimide reduction by using boric acid is also another effective method. The results indicated that the degree of hydrogenation increased with increasing boric acid concentration. The appropriate conditions were at  $N_2H_4/C=C$  ratio and  $H_2O_2/N_2H_4$  ratio of 4 and 1.3, respectively. The kinetic result indicated that the hydrogenation exhibited a first order behavior with respect to carbon-carbon double bond concentration. The apparent activation energy of the hydrogenation of natural rubber latex was calculated as 9.7 kJ/mol.

### **9.1.6 Physical and Mechanical Properties of Hydrogenated Natural Rubber Latex**

Differential scanning calorimetry and thermogravimetric analysis were used to characterize the thermal properties of natural rubber and its hydrogenated products. It was found that the degradation temperature of hydrogenated natural rubber increased with increasing level of hydrogenation. The glass transition temperature of natural rubber after hydrogenation was not different in the case of NRL hydrogenation using the homogeneous catalyst and for the noncatalytic process. For HNRL obtained from diimide reduction in the presence of cupric ion and boric acid, the glass transition changed after hydrogenation and the two glass transition temperatures were found at  $-44^\circ C$  and  $-60^\circ C$  which are representative for EPDM and NR respectively.

The physical properties of vulcanized hydrogenated natural rubber compared with natural rubber and commercial EPDM were investigated. For the ozone resistance test, the vulcanized hydrogenated natural rubber prepared by Os catalytic hydrogenation (90% hydrogenation) exhibited cracking on the surface of the specimens. However, the vulcanized hydrogenated rubber prepared by diimide reduction presented higher ozone resistance than that obtained from hydrogenation using osmium complex. It might be due to the residual carbon double bond, residual osmium catalyst. The mechanical properties of vulcanized HNR blends and EPDM were not

all that different after heat aging at 100°C for 22 hr. This implies that these hydrogenated rubbers are more resistant to heat than natural rubber because of the low saturation level in the backbone chain.

## 9.2 Recommendations

A further study of the hydrogenation of natural rubber should be concerned with the following aspects:

1. Curing behavior for hydrogenated natural rubber

To improve the tensile properties, the vulcanization formulation of hydrogenated rubber should be investigated. For further research work, other chemicals which may improve the tensile properties and curing behavior of hydrogenated rubber should be explored. The peroxide curing system should also be studied.

2. Applications of hydrogenated natural rubber latex

The hydrogenated natural rubber exhibited good resistance to thermal degradation. However the thermal and mechanical properties needs to be improved. Other applications of hydrogenated rubber such as adhesive agent or blending media with other polymers should be further studied.

3. Improvement of diimide hydrogenation process

The addition of thiols to olefinic double bonds has been used for olefin hydrogenation. The thiol addition can be carried out in a solution or in latex form of unsaturated polymers. Diimide hydrogenation process could yield not more than 90% hydrogenation. Therefore, addition of thiol to HNR obtained from diimide reduction should be studied to increase level of hydrogenation over 90%.



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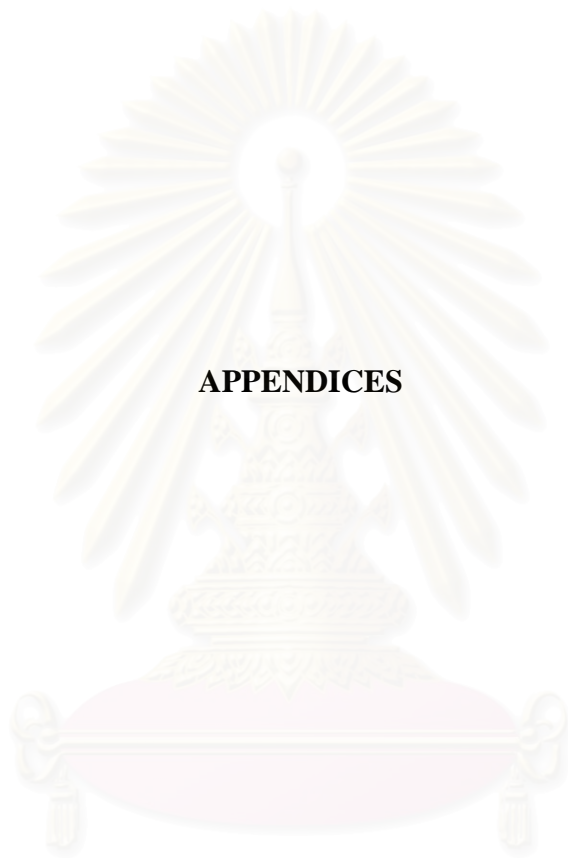
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**APPENDICES**

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## Appendix A

### The Overall Compositions of Rubbers

**Table A-1** Properties of Standard Thai Rubber 5L (STR-5L)

Parameter	Limit
Dirt, retained on 44 $\mu$ aperture (max, % wt.)	0.04
Ash (max, % wt.)	0.40
Nitrogen (max, % wt.)	0.60
Volatile matter (max, % wt.)	0.80
Initial Plasticity, P0	35
Plasticity Retention Index, PRI (min.)	60
Color Lavibond Scale, individual value (max.)	6.0

**Table A-2** Properties of Natural Rubber Latex Concentrated  
(Thai Rubber Latex; 2003)

Properties	Test Result
Total solid Content, %	61.54
Dry rubber Content, %	60.03
Non Rybber Solid, %	1.56
Ammonia Content ( on Total Weight). %	0.70
Ammonia Content ( on Water Phase). %	1.82
pH Value	10.92
KOH Number	0.561
Volatile Fatty Acid Number (VFA)	0.0194
Mechanical Stability Time at 55% TS.,Su.	1,100
Specific Gravity at 25 °C	0.9411
CST.(ml.)	23
Magnesium Content (ppm)	23
Viscosity (60% TS.Spindle no 1.60 rpm.) cps.	64

Remark: Add ammonia laurate 15-0.048%

: Free from pentachlorophenol



**Table A-3** Properties of Ethylene-Propylene-Diene Copolymer

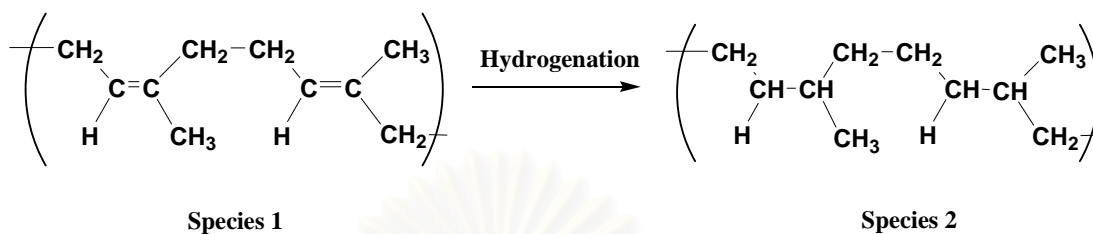
Properties	Typical Values	
	Keltan 509x100	Keltan 314
Type of termonomer	ENB*	ENB
Content of termonomer (% wt.)	8.7	8.0
Ethylene content (% wt.)	64	52
Oil content (% wt.)	50	0
Molecular weight distribution	Medium	Broad
Mooney viscosity	48	33
ML(1+4) 125°C (MU)		

\* Ethylidenenorbonene

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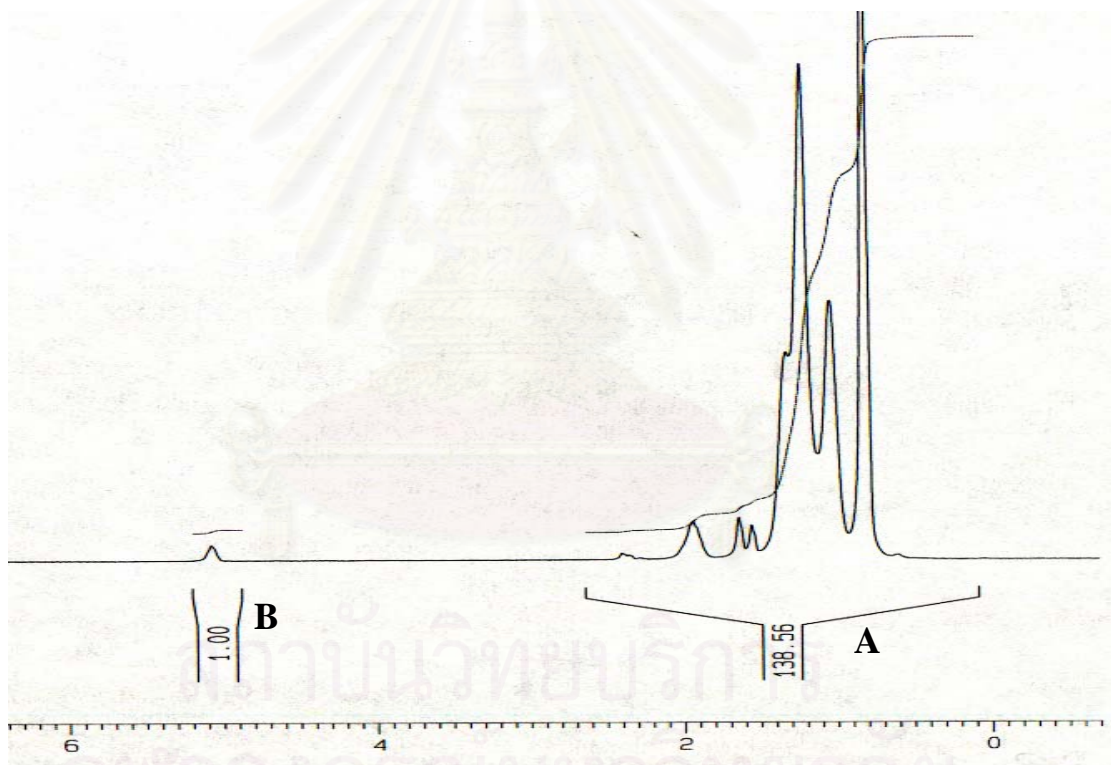
## Appendix B

### Calculation of Level of Hydrogenation



Proton of repeating unit except =CH in Species 1 = 7 protons

Proton of repeating unit in Species 2 = 10 protons



A = Peak area except at 5.2 ppm

B = Peak area at 5.2 ppm

C = Peak area of saturated -CH<sub>2</sub>- and -CH<sub>3</sub>

$$A = 10C + 7B$$

$$C = \frac{A - 7B}{10}$$

Total peak area = Peak area of saturated  $-\text{CH}_2-$  and  $-\text{CH}_3$  + Peak area at 5.2 ppm

$$= \frac{A - 7B}{10} + B$$

$$= \frac{A + 3B}{10}$$

%Hydrogenation = [(Peak area of sat.  $-\text{CH}_2-$  and  $-\text{CH}_3$ )/(Total peak area)] x 100

$$= \left( \frac{A - 7B}{10} \right) \div \left( \frac{A + 3B}{10} \right) \times 100$$

$$= \frac{A - 7B}{A + 3B} \times 100$$

For example: A = 138.56 and B = 1.00

$$\begin{aligned} \% \text{Hydrogenation} &= \frac{138.56 - 7(1.00)}{138.56 + 3(1.00)} \times 100 \\ &= 92.94\% \end{aligned}$$

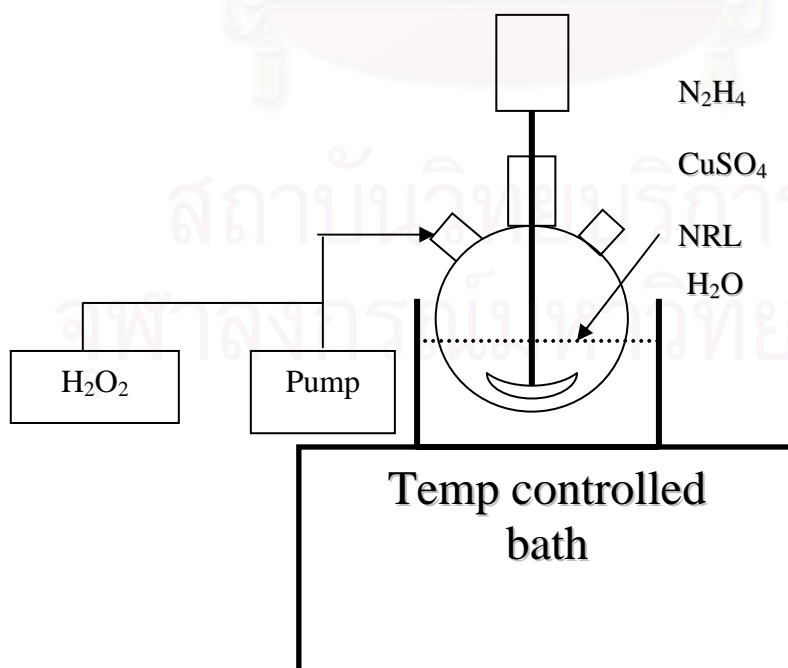
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## Appendix C

### Diimide Hydrogenation Reactor and Recipe



**Figure C-1** Diimide hydrogenation reactor.



**Figure C-2** Diimide hydrogenation diagram.

**Table C-1** Diimide Hydrogenation of Natural Rubber Latex in the Presence of Cupric Sulfate

Substances	Amount
NRL (60% DRC)	10 g
Water	30 ml
Cupric sulfate	0.00205 g
Hydrazine hydrate	17 ml
Hydrogen peroxide	25 ml

For this recipe, 67.8% hydrogenation was achieved at 55°C for 6 h.

**Table C-2** Diimide Hydrogenation of Natural Rubber Latex in the Presence of Boric Acid

Substances	Amount
NRL (60% DRC)	10 g
Water	30 ml
Boric acid	0.62 g
Hydrazine hydrate	17 ml
Hydrogen peroxide	25 ml

For this recipe, 63.5% hydrogenation was achieved at 55°C for 6 h.

**Table C -3** Results of NRL Hydrogenation by Diimide Hydrogenation in the Presence of Cupric ion (Section 6.3.1-6.3.6)

Exp	N <sub>2</sub> H <sub>4</sub> (mol)	H <sub>2</sub> O <sub>2</sub> (mol)	H <sub>2</sub> O (mol)	CuSO <sub>4</sub> ( $\mu$ mol)	C=C (mmol)	Temp (°C)	Total volume (ml)	Degree of Hydrogenation (%)
1	0.252	0.328	1.67	0	84	55	77.5	33.4
2	0.252	0.328	1.67	2	84	55	77.5	50.5
3	0.252	0.328	1.67	4	84	55	77.5	60.2
4	0.252	0.328	1.67	8	84	55	77.5	63.5
5	0.252	0.328	1.67	16	84	55	77.5	49.8
6	0.252	0.328	1.67	33	84	55	77.5	38.9
7	0.252	0.328	1.67	49	84	55	77.5	30.5
8	0.084	0.109	1.67	8	84	55	54.0	30.0
9	0.168	0.218	1.67	8	84	55	67.4	43.4
10	0.210	0.273	1.67	8	84	55	74.2	52.5
11	0.252	0.328	1.67	8	84	55	81.1	63.4
12	0.336	0.437	1.67	8	84	55	90.0	68.8
13	0.420	0.546	1.67	8	84	55	108.0	54.9
14	0.336	0.168	1.67	8	84	55	66.0	23.0
15	0.336	0.336	1.67	8	84	55	81.3	63.8
16	0.336	0.403	1.67	8	84	55	87.2	66.1
17	0.336	0.437	1.67	8	84	55	90.1	69.0
18	0.336	0.470	1.67	8	84	55	93.0	65.2
19	0.336	0.538	1.67	8	84	55	98.9	63.3
20	0.336	0.672	1.67	8	84	55	110.6	59.9
21	0.336	0.840	1.67	8	84	55	129.1	55.4
22	0.336	0.437	0.80	8	42	55	67.1	59.0
23	0.336	0.437	1.67	8	84	55	90.0	67.8
24	0.336	0.437	2.39	8	126	55	103.3	54.1
25	0.336	0.437	3.18	8	168	55	122.4	44.4
26	0.336	0.437	3.98	8	210	55	141.5	36.5
27	0.336	0.437	4.77	8	252	55	167.0	30.6
28	0.252	0.328	0.00	8	84	55	47.5	36.8
29	0.252	0.328	0.28	8	84	55	52.5	40.4
30	0.252	0.328	0.56	8	84	55	57.5	43.2
31	0.252	0.328	0.83	8	84	55	62.5	47.1
32	0.252	0.328	1.11	8	84	55	67.5	51.8
33	0.252	0.328	1.39	8	84	55	72.5	59.5
34	0.252	0.328	1.67	8	84	55	77.5	63.5
35	0.252	0.328	2.22	8	84	55	87.5	51.5
36	0.366	0.437	1.67	8	84	45	90.0	50.7
37	0.366	0.437	1.67	8	84	55	90.0	69.0
38	0.366	0.437	1.67	8	84	65	90.0	72.0
39	0.366	0.437	1.67	8	84	75	90.0	70.6
40	0.366	0.437	1.67	8	84	85	90.0	69.2
41	0.366	0.437	1.67	8	84	95	90.0	52.3



**Table C-4** Results of NRL Hydrogenation by Diimide Hydrogenation in the Presence of Boric Acid (Section 7.2.1-7.2.6)

Exp	N <sub>2</sub> H <sub>4</sub> (mol)	H <sub>2</sub> O <sub>2</sub> (mol)	H <sub>2</sub> O (mol)	H <sub>2</sub> BO <sub>3</sub> (mmol)	C=C (mmol)	Temp (°C)	Total volume (ml)	Degree of Hydrogenation (%)
1	0.336	0.437	1.67	0.0	84	55	90.0	36.4
2	0.336	0.437	1.67	0.5	84	55	90.0	40.0
3	0.336	0.437	1.67	1.0	84	55	90.0	42.9
4	0.336	0.437	1.67	5.0	84	55	90.0	54.1
5	0.336	0.437	1.67	10.0	84	55	90.0	63.5
6	0.336	0.437	1.67	20.0	84	55	90.0	62.5
7	0.336	0.437	1.67	30.0	84	55	90.0	40.2
8	0.042	0.055	1.67	10.0	84	55	47.0	28.0
9	0.084	0.109	1.67	10.0	84	55	54.0	34.0
10	0.168	0.218	1.67	10.0	84	55	67.4	47.0
11	0.252	0.328	1.67	10.0	84	55	74.2	56.3
12	0.336	0.437	1.67	10.0	84	55	81.1	63.6
13	0.420	0.546	1.67	10.0	84	55	90.0	63.1
14	0.504	0.655	1.67	10.0	84	55	108.0	61.2
15	0.336	0.168	1.67	10.0	84	55	66.0	48.5
16	0.336	0.302	1.67	10.0	84	55	78.0	59.0
17	0.336	0.336	1.67	10.0	84	55	81.3	61.4
18	0.336	0.370	1.67	10.0	84	55	84.0	63.7
19	0.336	0.437	1.67	10.0	84	55	90.0	63.7
20	0.336	0.538	1.67	10.0	84	55	98.9	60.2
21	0.336	0.672	1.67	10.0	84	55	110.6	56.5
22	0.336	0.840	1.67	10.0	84	55	129.1	50.2
23	0.336	0.437	0.00	10.0	84	55	47.5	35.4
24	0.336	0.437	0.28	10.0	84	55	52.5	40.1
25	0.336	0.437	0.56	10.0	84	55	57.5	44.6
26	0.336	0.437	0.83	10.0	84	55	62.5	48.6
27	0.336	0.437	1.11	10.0	84	55	67.5	58.8
28	0.336	0.437	1.39	10.0	84	55	72.5	63.1
29	0.336	0.437	1.67	10.0	84	55	77.5	59.8
30	0.336	0.437	2.22	10.0	84	55	87.5	50.3

## Appendix D

### Steps of Rubber Blending

**Table D-1** Steps of Blending for Each Formulation in Barbender Plasticorder (for Table 8.4)

Blending Step	Time of Component Addition (min)					
	Mix1	Mix2	Mix3	Mix4	Mix5	Mix6
	NR	EPDM	HNR	HNRDii	HNRTSHNR/HNR90	
Adding rubber	0	0	0	0	0	0 – 2
Adding paraffinic oil	No**	No	0	0	0	1
Adding ultrablend 4000	No	No	0	0	0	0
Adding ZnO/ Stearic acid	5	1	2	5	6	5
Adding MBT/TMTD	7	3	4	7	8	7
Adding S	9	4	6	9	10	9
Removing rubber	14	7	9	14	15	12

\*\*No = No addition of that component.

**Table D-2** Steps of Blending for Each Formulation in Two-roll Mill (for Table 8.8)

Components	Time of Components Addition into Mixer (min.)					
	Mix7	Mix8	Mix9	Mix10	Mix11	Mix12
	NR	EPDM	NR/EPDM	NR/HNROs	NR/HNRDii	NR/HNRTSH
				70	70	70
			(50/50)	(50/50)	(50/50)	(50/50)
Adding rubber(NR)	0	0	0	0	0	0
Adding rubber (EPDMor HNR)	0	0	3	3	3	3
Adding paraffinic oil	No	No	No	3	3	3
Adding ZnO/Stearic acid	5	1	5	6	6	6
Adding MBT/TMTD	7	3	7	8	8	8
Adding S	9	4	9	10	10	10
Removing rubber	14	7	11	13	13	13

**Table D-3** Steps of Blending for Each Formulation in Two-roll Mill (for Table 8.10)

Components	Time of Components Addition into Mixer (min.)						
	Mix13	Mix14	Mix15	Mix16	Mix17	Mix18	Mix19
	NR	NR	NR/EPDM (70/30)	NR/EPDM (70/30)	NR/HNRDii (70/30)	NR/HNRDii (70/30)	NR/HNRDii (70/30)
Adding rubber (NR)	0	0	0	0	0	0	0
Adding rubber (EPDM or HNRL)	0	0	3	3	3	3	3
Adding paraffinic oil	No	No	No	No	3	3	3
Adding untrablend 4000	No	No	3	3	4	4	4
Adding ZnO/ Stearic acid	5	5	6	6	7	7	7
Adding carbon black	No	7	No	8	No	9	9
Adding MBTS/TMTD	7	10	8	11	9	12	12
Adding S	9	12	10	13	11	14	14
Removing rubber	14	15	12	16	14	17	17

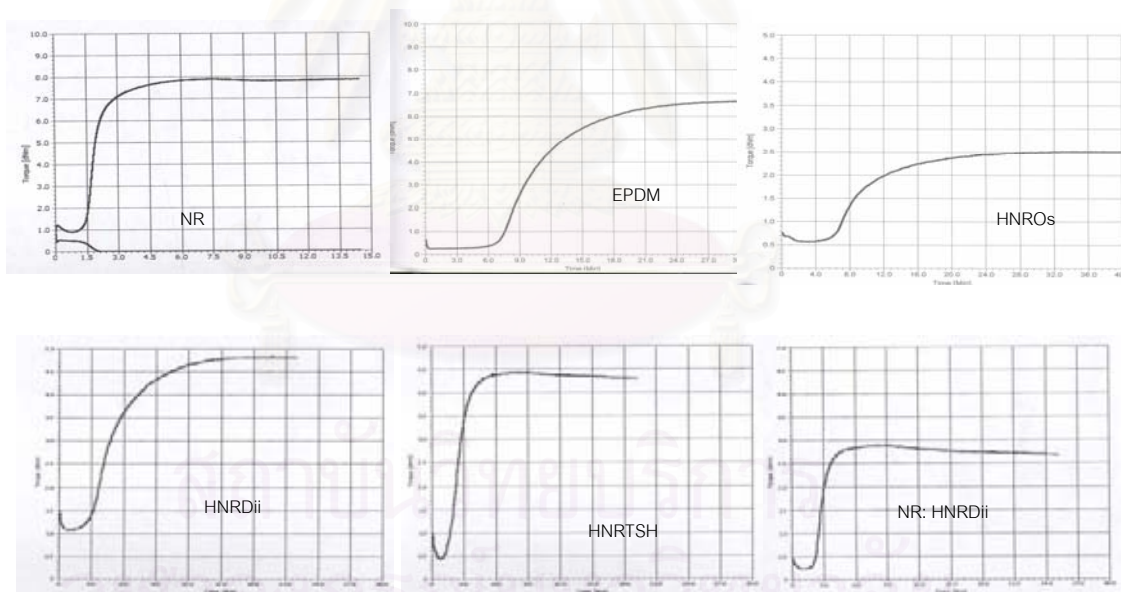
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## Appendix E

### Curing Behavior of Vulcanizates

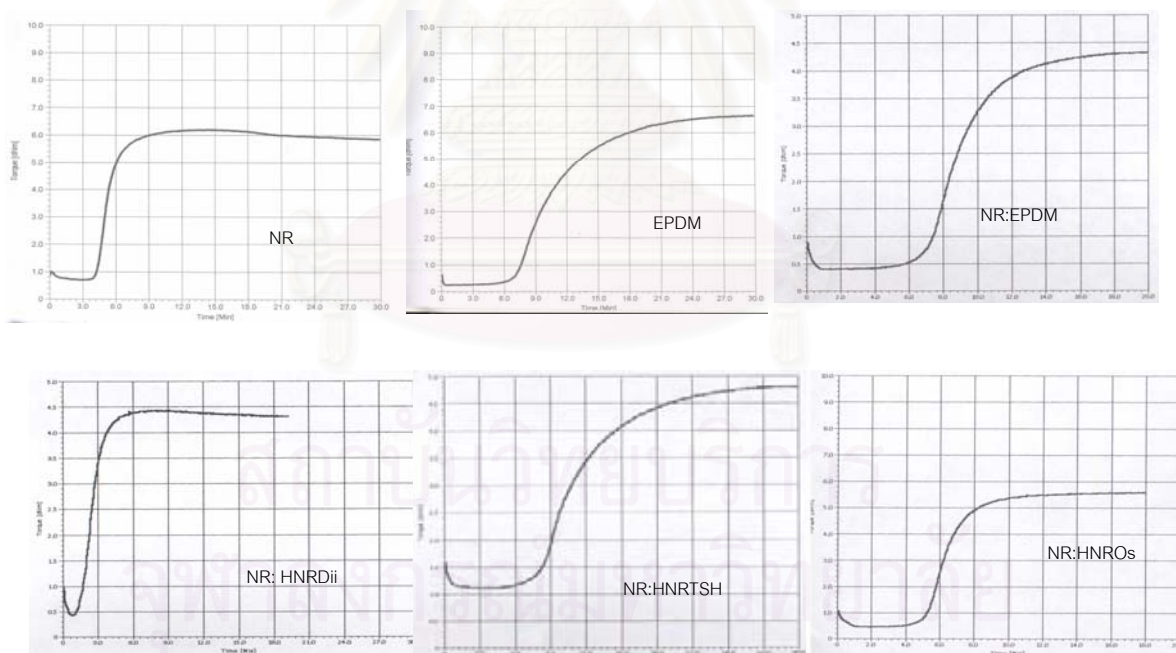
**Table E-1** Cure Characteristics of Vulcanizates Using Oscillating Disk Rheometer  
(For Ozone Test)

Cure Properties	Mix					
	1	2	3	4	5	6
	NR	EPDM	HNROs	HNRDii	HNRTSH	NR/HNRDii (70/30)
Cure temperature (°C)	150	160	160	160	160	160
Scorch time $t_2$ (min)	1.69	7.69	4.85	3.28	4.22	2.45
Optimum cure time $t_{95}$ (min)	4.12	22.01	11.83	4.71	10.86	4.53



**Table E-2** Cure Characteristics of Vulcanizates Using Oscillating Disk Rheometer  
(For Mechanical Test)

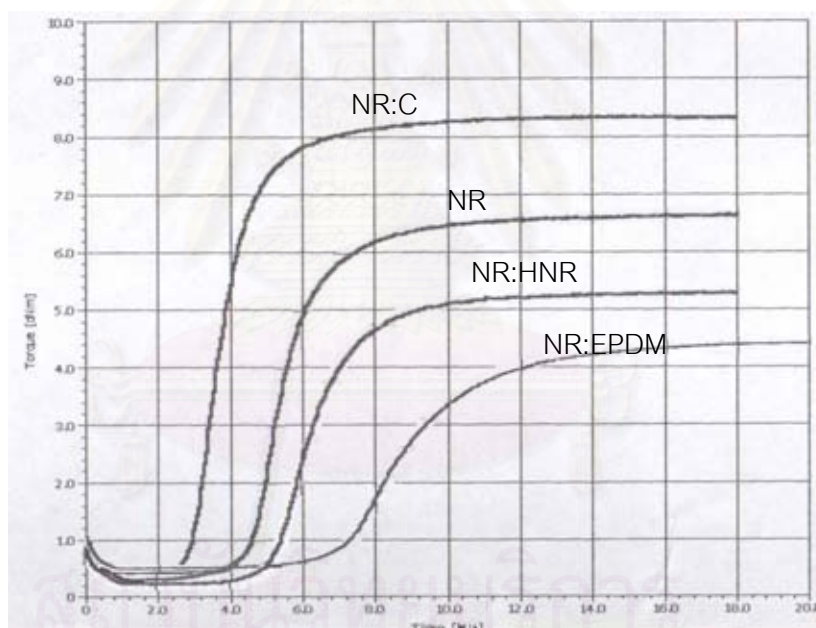
Cure Properties	Mix					
	7	8	9	10	11	12
	NR	EPDM	NR:EPDM (50/50)	NR:HNROs (50/50)	NR:HNRDii (50/50)	NR:HNRTSH (50/50)
Cure temperature (°C)	150	160	160	160	160	160
Scorch time $t_2$ (min)	2.36	11.09	3.42	2.34	2.25	2.71
Optimum cure time $t_{95}$ (min)	5.81	21.30	5.98	4.12	4.43	6.55



**Table E-3** Cure Characteristics of Vulcanizates Using Oscillating Disk Rheometer

(For Carbon Addition Mechanical Test)

Cure Properties	13	14	15	16	17	18	19
	NR	NR:C	NR:EPDM (70/30)	NR:EPDM:C (70/30)	NR:HNROs (70/30)	NR:HNROs:C (70/30)	NR:HNROs:3C (70/30)
Cure temperature (°C)	150	150	150	150	150	150	150
Scorch time $t_2$ (min)	5.12	3.30	7.55	4.95	5.97	3.93	2.67
Optimum cure time $t_{95}$ (min)	8.97	6.53	13.93	15.20	9.71	6.97	6.12



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## Appendix F

### Data of Mechanical Properties of Vulcanizates

**Table F-1** Data of Tensile Strength of Vulcanizates (in Table 8.9)

	NR		EPDM		NR:EPDM		NR:HNROs		NR:HNRDii		NR:HNRTSH	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Tensile	3.24	1.31	0.85	0.82	2.28	1.64	2.29	1.68	2.89	2.27	2.08	1.98
Strength	3.19	1.23	0.79	0.8	2.18	1.52	2.35	1.72	2.74	2.18	1.94	1.61
(MPa)	3.25	1.77	-	0.81	2.27	1.48	2.28	1.69	2.79	2.19	2.09	1.85
Means	3.23	1.44	0.82	0.81	2.24	1.55	2.31	1.70	2.81	2.21	2.04	1.81
S.D.	0.03	0.29	0.04	0.01	0.06	0.08	0.04	0.02	0.08	0.05	0.08	0.19

**Table F-2** Data of Ultimate Elongation of Vulcanizates (in Table 8.9)

	NR		EPDM		NR:EPDM		NR:HNROs		NR:HNRDii		NR:HNRDTS H	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Ultimate	265.4	122.4	148.4	118	284.8	197.3	240.7	150.4	238.9	139.2	264.4	209.4
Elongation	253.4	105.4	126.5	119.5	265.1	187.8	222.1	138.7	211.7	160.8	232.8	180.4
(%)	226.2	124.7	-	142.7	294.5	174.3	246.8	165.4	235.8	154.4	251.5	210.1
Means	248.3	117.5	137.5	126.7	281.5	186.5	236.5	151.5	228.8	151.5	249.6	200.0
S.D.	20.1	10.5	15.5	13.8	15.0	11.6	12.9	13.4	14.9	11.1	15.9	16.9

**Table F-3** Data of Hardness of Vulcanizates (in Table 8.9)

	NR		EPDM		NR:EPDM		NR:HNROs		NR:HNRDii		NR:HNRDTSH	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Hardness	45	53	36	36	43	48	49	40	48	44	45	44
(Shore A)	44	52	35	37	40	49	40	42	40	44	40	44
	44	52	37	36	39	48	39	43	41	43	41	42
	44	54	39	38	41	49	38	44	42	44	38	43
	43	53	37	39	40	48	40	42	40	44	40	41
Means	44.0	52.8	36.8	37.2	40.6	48.4	41.2	42.2	42.2	43.8	40.8	42.8
S.D.	0.71	0.84	1.48	1.30	1.52	0.55	4.44	1.48	3.35	0.45	2.59	1.30

**Table F-4** Data of Tensile Strength of Vulcanizates (in Table 8.11)

	NR		NR:C		NR:EPDM		NR:EPDM:C		NR:HNRDii		NR:HNRDi:C		NR:HNRDii:3C	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Tensile	16.0	1.4	25.2	2.5	9.8	1.9	10.6	2.8	13.39	1.9	14.1	3.0	12.2	6.9
Strength	15.4	1.4	22.0	2.3	11.3	1.8	11.6	2.1	14.68	2.0	14.7	3.0	12.1	6.5
(MPa)	14.8	1.6	25.3	3.3	9.4	1.8	11.1	2.5	12.96	2.1	14.9	2.9	11.7	8.1
Means	15.4	1.5	24.2	2.7	10.2	1.8	11.1	2.4	13.7	2.0	14.6	2.9	12.0	7.2
S.D.	0.6	0.1	1.9	0.5	1.0	0.1	0.5	0.4	0.9	0.1	0.4	0.1	0.3	0.8

**Table F-5** Data of Ultimate Elongation of Vulcanizates (in Table 8.11)

	NR		NR:C		NR:EPDM		NR:EPDM:C		NR:HNRDii		NR:HNRDi:C		NR:HNRDii:3C	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Ultimate	689.7	187.2	641.3	181.1	739.3	309.8	678.2	318.9	694.3	275.1	672.3	236.0	569.3	331.7
Elongation	653.9	182.4	615.4	199.6	775.0	260.9	694.7	265.8	677.2	279.7	674.2	251.2	556.5	333.9
(%)	608.5	196.8	626.8	221.0	715.5	315.7	680.1	300.6	697.3	287.6	695.4	238.2	566.7	345.5
Means	650.7	188.8	627.8	200.6	743.3	295.5	684.3	295.1	689.6	280.8	680.6	241.8	564.2	337.1
S.D.	40.7	7.4	13.0	20.0	29.9	30.1	9.0	26.9	10.8	6.4	12.8	8.2	6.7	7.4

**Table F-6** Data of Hardness of Vulcanizates (in Table 8.11)

	NR		NR:C		NR:EPDM		NR:EPDM:C		NR:HNRDii		NR:HNRDi:C		NR:HNRDii:3 C	
	Unaged		Unaged		Unaged		Unaged		Unaged		Unaged		Unaged	
	d	Aged	d	Aged	d	Aged	d	Aged	d	Aged	Unaged	Aged	Unaged	Aged
Hardness	40.3	45.5	44.4	49.6	32.2	37.5	33.3	39.3	34.8	36.0	40.7	45.7	52.2	56.4
(Shore A)	39.4	48.6	46.0	49.7	33.9	38.9	33.8	39.1	34.8	37.0	43.2	46.7	54.0	58.5
	38.5	46.3	44.0	50.0	32.6	38.0	32.5	39.5	35.3	36.6	43.0	47.4	51.6	55.6
	39.0	46.0	44.5	51.0	36.2	38.3	33.0	39.3	36.1	36.6	45.7	48.5	51.4	54.9
	39.4	45.5	44.6	49.5	32.5	38.4	33.5	39.4	36.4	36.1	41.0	45.6	51.4	55.0
Means	39.3	46.4	44.7	50.0	33.2	38.2	33.5	39.3	35.5	36.5	42.7	46.8	52.1	56.1
S.D.	0.7	1.3	0.8	0.6	0.5	0.5	1.7	0.1	0.7	0.4	2.0	1.2	1.1	1.5

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## VITA

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