

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials

1. Smoke sheet rubber : STR 5 L (Rayong Bangkok Rubber, Thailand)
2. Tris(triphenylphosphine)Ruthenium(II)Chloride (Fluka, USA.)
3. Toluene : AR grade (Lab scan, Thailand)
4. Methanol : AR grade (Merck, Germany)
5. CDCl_3 : NMR grade (Aldrich, USA.)
6. THF : HPLC grade (Lab scan, Thailand)

3.2 Instruments

1. Parr reactor 600 ml equipped with mechanical stirrer, temperature controller, and pressure transducer.
2. Fourier-transform infrared spectrophotometer (Perkin-Elmer, model 1760 x) was used for determination of conversion of the reaction.
3. Fourier-transform nuclear magnetic resonance spectrophotometer, $^1\text{H-NMR}$ 500 MHz (JNM.A 500) and $^{13}\text{C-NMR}$ 400 MHz (DPX 400) were used to determine the degree of hydrogenation of natural rubber.
4. Average molecular weight and molecular weight distribution were determined by a Waters 150-C [Millipore] Gel Permeation Chromatography (GPC) equipped with ultrastryragel linear and ultrastryragel $10^3 \mu\text{m}$ columns, using refractometer detector. Polystyrene standards were used for calibration and universal calibration was obtained from a PC base software. Chromatograms of the samples were achieved by using THF as a mobile phase at flow rate of 1.0 ml/min. The data of peak molecular weight (M_p), number averaged molecular weight (M_n), weight averaged molecular weight (M_w) and polydispersity index (M_w/M_n) were reported.

5. Differential scanning calorimeter (DSC) thermograms were obtained from a Netzsch DSC 200). Samples were scanned from -100 to 150 °C at heating rate 10 °C/min.
6. Thermogravimetric analyser (TGA) thermograms were obtained from a Mettler-Toledo/SDTA 851). Samples were scanned from 40 to 600 °C under N_2 atmosphere at heating rate 10 °C/min.

3.3 Hydrogenation Procedure

Hydrogenation was carried out in a 600 ml Parr reactor equipped with mechanical stirrer, temperature controlled, and pressure transducer. Typically, the specified amount of rubber sample was dissolved in 50 ml of toluene in a Schlenk flask under a nitrogen atmosphere by using glove bag, which connected with Schlenk line, overnight. The solution was then transferred into the Parr reactor. The catalyst, 0.09 g was added. The apparatus was partially evacuated and purged several times with hydrogen before filling to the required pressure (usually at 30 bar) and cut off from the gas tank. The autoclave was then heated to the desired reaction temperature. During the course of hydrogenation, the mixture was agitated by stirring at constant speed of 400 rpm overnight. The hydrogenated natural rubber was isolated by precipitation in methanol, filtered, followed by washing with methanol several times, and, finally, the rubber was vacuum dried at room temperature overnight.

Operation and Apparatus

The preparation of solution was done in an inert gas atmosphere (prepurified nitrogen) and used Schlenk line.

Schlenk line

Schlenk line consists of nitrogen and vacuum lines. The vacuum line was equipped with a solvent trap and a vacuum pump, respectively. The nitrogen line was

connected to the moisture trap and the oil bubbler that contained enough oil to provide a seal from the atmosphere. The Schlenk line is shown in Figure 3.1.

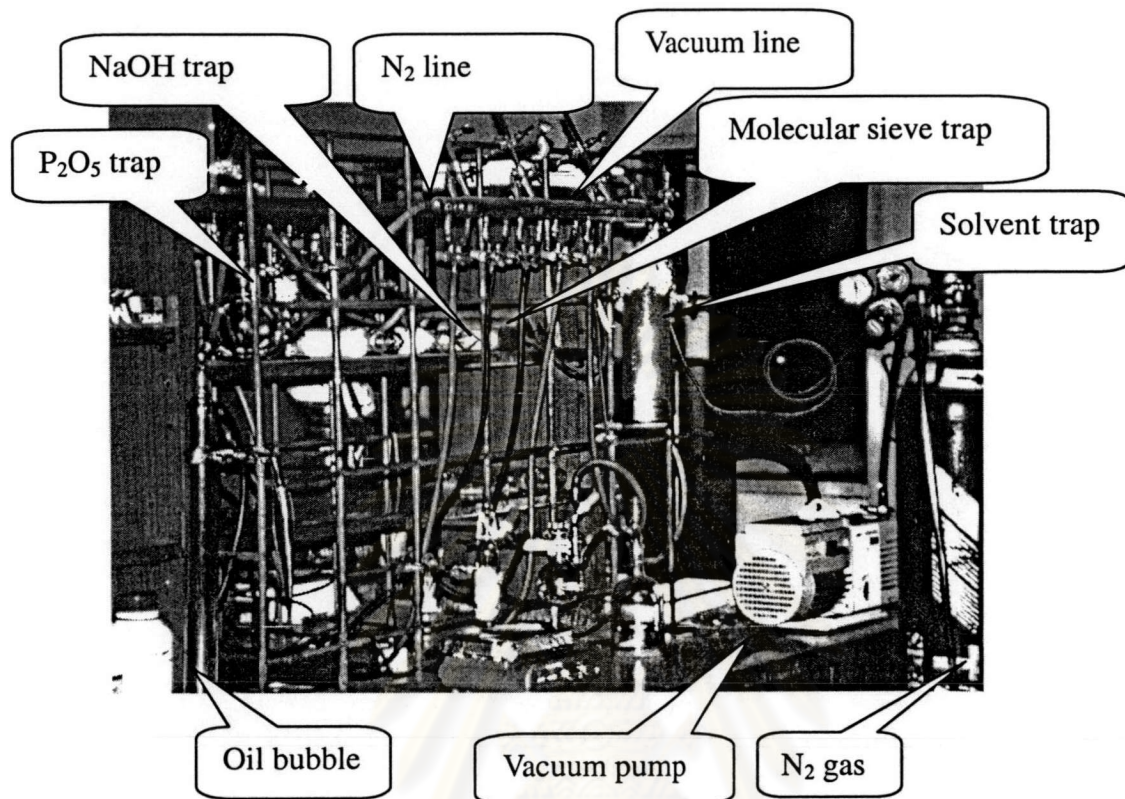


Figure 3.1 Schlenk line.

Schlenk flask

A Schlenk flask has a side-arm to connect to the Schlenk line. Some typical models are shown in Figure 3.2.

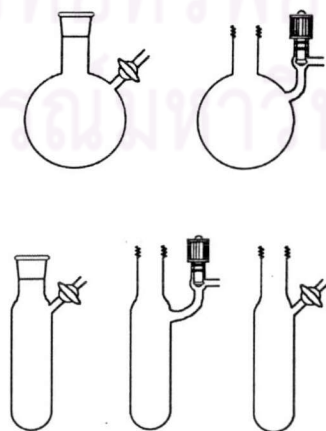


Figure 3.2 Round-bottomed and tube designed for Schlenk flasks.

Glove bag

Glove bag is a moderate-volume gas-tight container, which air or moisture is excluded. The glove bag has a way to connect to Schlenk line, which can be evacuated and filled with nitrogen gas.

Parr Reactor

A Parr 4042, 600 ml of Parr reactor, stainless-steel pressure reactor used for hydrogenation reaction is shown in Figure 3.3. The reactor contained a pressure gauge, safety rupture disc, valves for admitting, valve for releasing gas and valve for removing liquid, a thermocouple and a gas-tight stirrer.

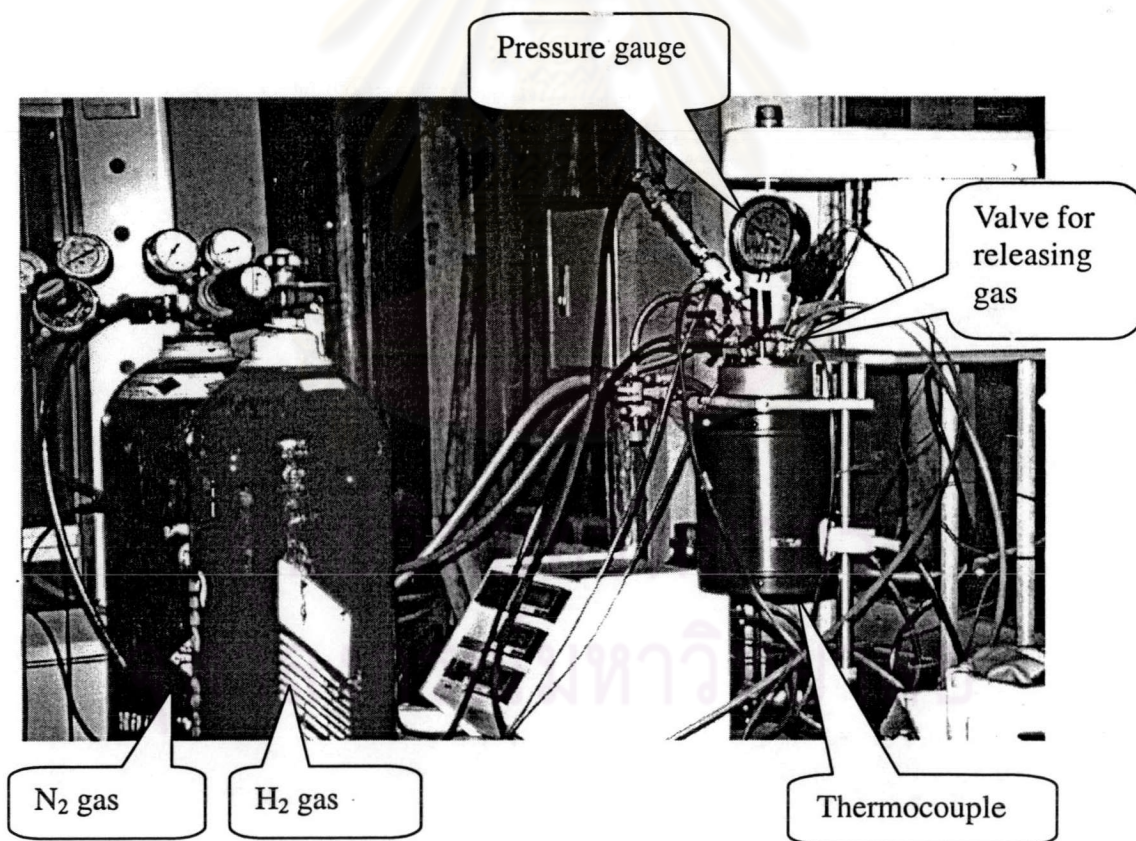


Figure 3.3 Parr reactor.

3.4 Product Analysis by Fourier-Transform Infrared Spectroscopy

Infrared radiation is a form of electromagnetic radiation, which has wave numbers in the range $12,800$ to 10 cm^{-1} . IR spectroscopy measures the absorption of infrared radiation by the vibration or rotation of the molecule. Radiation in the mid infrared region ($4,000$ - 400 cm^{-1}) corresponds to the vibration frequencies of functional groups in the molecules. Therefore, IR spectroscopy can be utilized to study functional group of, especially, organic molecules. The theory of molecular vibration explains the appearance of infrared spectra. The broad wavelength range of infrared radiation, and the few transparent optical materials available, require that infrared instruments be designed with reflective optics; radiation is focused with front-surface aluminize mirrors rather than lenses. Operation takes place in vacuum or the optical path is purged with dry nitrogen because of strong infrared absorption by water vapor and carbon dioxide.

In this study, the functional groups of the hydrogenated natural rubber were investigated using Fourier-transform infrared spectrophotometer (FT-IR: Perkin-Elmer Infrared spectrophotometer, model 1760 x).

Weigh accurate 10 mg of hydrogenated natural rubber sample into a test tube containing 1 ml of toluene. After dissolution was complete, the solution was dropped on NaCl window. The NaCl window was dried by a heat gun, pressed subjected to the FT-IR analysis.

3.5 Product analysis by Fourier-Transform Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is essential for the determination of molecular structure. The majority of atomic nuclei possess a nuclear spin angular momentum. If such a nucleus, i.e., a magnetic dipole, is placed in a magnetic field, it adopts one of a small number of allowed orientations of different energy. For example, the nucleus of the hydrogen atom has just two permitted orientations. The magnetic moment can point in the same directions as the field in the opposite direction. These two states are

separated by an energy ΔE . ΔE may be measured by applying electromagnetic radiation of frequency ν , which causes nuclei to “flip” from the lower energy level to the upper one, provided that resonance condition $\Delta E = h\nu$ (h is Plank’s constant) is satisfied. This is nuclear magnetic resonance spectroscopy.

The resonance frequency of the nucleus depends on the chemical environment of the nucleus in a molecule, an effect known as the chemical shift. For example, the different kinds of H atom have different resonance frequencies and so give rise to separate peaks. For this reason, NMR is an enormously powerful technique for the study of molecules at the atomic level. Details of the techniques are described extensively elsewhere.

In this study, the functional groups of the hydrogenated natural rubber were characterized by nuclear magnetic resonance ($^1\text{H-NMR}$ 500 MHz, JNM.A 500 and $^{13}\text{C-NMR}$ 400 MHz, DPX 400)

Weigh accurate 10 mg of hydrogenated natural rubber sample into an NMR tube containing 0.5 ml of deuterium chloroform (CDCl_3). After dissolution was complete, the solution was analyzed by the FT-NMR.

3.6 Average Molecular Weight and Molecular Weight Distribution

The Gel Permeation Chromatography (GPC) method is a process for the separation of macromolecules according to their sizes. A GPC column is packed with a chromatography material of narrow particle size distribution and controlled pore size. Eluent is pumped through the column at constant flow rate and the solutes to be analyzed are introduced to the column by means of an injection valve. The separation mechanism is based on the ability of the different sized solutes to diffuse in and out of the porous structure and the residence time of the solute molecules within the porous structure. As the dissolved solute passes through the column, the smaller molecules (those with dimensions smaller than pore size of packing materials) will enter the pores thus they will be “delayed” in their elution through the column. On the other hand, the

larger polymer molecules will be unable to penetrate the pores and will be swept along with the solvent front to be eluted before the smaller molecule as shown in Figure 3.4.

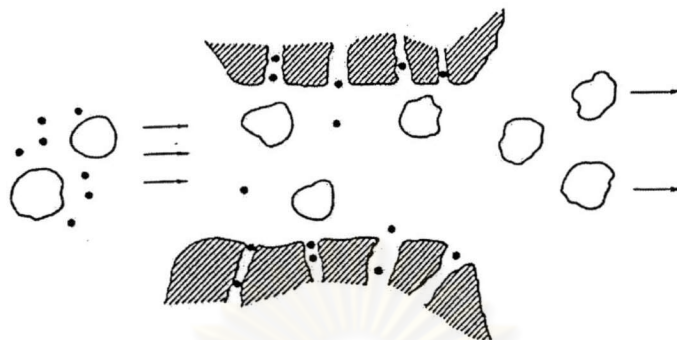


Figure 3.4 Permeation of different sized molecules through porous gel.

Universal Calibration

The calibration of a gel permeation column for a given polymer solvent system requires the establishment of a relationship between the volume of solution eluted (or, equivalently, the elution time for a given flow rate of solution) and the molecular weight of monodisperse fractions of the polymer. The main problem encountered is that monodisperse samples of most polymers are not generally available. However, such samples are available for a few specific polymers. A notable example is polystyrene for which samples having a molecular-weight range of 10^4 of 10^7 .

If a set of monodisperse samples of a single polymer can be obtained, the remaining problem is to establish a relationship for a particular GPC column between the volume of solution eluted and the molecular weight of some chemically different polymer. To solve this problem, a calibration parameter is required which is independent of the chemical nature of the polymer, that is, a universal calibration parameter.

In this study, average molecular weight and molecular weight distribution of natural rubber and its hydrogenated products were determined by a Waters 150-C [Millipore] Gel Permeation Chromatography, using ultrastyrigel linear and ultrastyrigel $10^3 \mu\text{m}$ columns equipped with refractometer detector. Solution of about 0.2-0.3% w/v polymer in tetrahydrofuran (THF) was used with an injection volume of sample being

0.1 ml. THF was used as mobile phase at flow rate 1.0 ml/min. Polystyrene standards were used as calibrants

3.7 Thermal Analysis

Thermal Analysis (TA) is a modern group of analytical techniques, which measure the physical properties of the sample as a function of temperature (dynamic mode) or time at constant temperature (isothermal mode). In this work, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were used to characterize the samples obtained. Some theoretical background regarding DSC and TGA are described here including the analysis methods used in this work.

3.7.1 Thermogravimetric Analysis (TGA)

TGA measures the change in mass of a sample as it is heated, cooled or held isothermally. The change in mass may be caused from degradation of sample, volatile substrate or moisture within sample. TGA can detect percentage of ingredients in sample, degradation temperature, composition difference in blends, etc. In this work, TGA was used to compare thermal stability of natural rubber and hydrogenated products.

The experiment was carried out under nitrogen atmosphere, and the sample weight was approximately 10-20 mg. The sample was heated from 40 to 600 °C at scanning rate 10 °C/min.

3.7.2 Differential Scanning Calorimetry (DSC)

Whenever a material undergoes a change in physical state, such as melting or transition from one crystalline form to another, or whenever it reacts chemically, heat is either absorbed or liberated. Many such processes can initiate simply by raising the temperature of the material.

The schematic representation of DSC systems is in Figure 3.5. The sample and reference are each provided with individual heaters. This makes it possible to use a

“null-balance” principle. It is convenient to think of the system as divided into two control loops, shown in Figure 3.6.

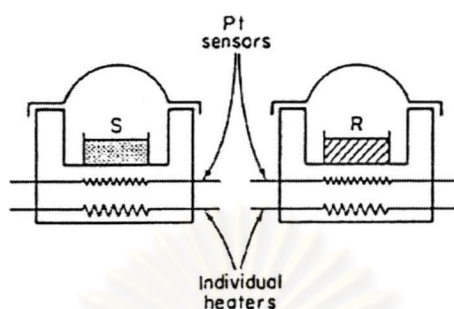


Figure 3.5 Schematic representation of the DSC system.

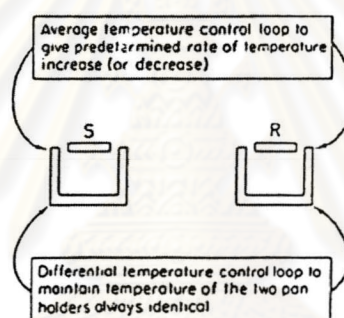


Figure 3.6 Schematic representation of the DSC control loops.

One is for average temperature control, so that the temperature of the sample and reference may be increased at a predetermined rate, which is recorded. The second loop ensures that if a temperature difference develops between the sample and reference (because of exothermic or endothermic reaction in the sample), Thus, the temperature of the sample holder is always kept the same as that of the reference holder by continuous and automatic adjustment of the heater power. A signal, proportional to the difference between the heat input to the sample and that to the reference, dH/dt , is fed into a recorder.

A DSC (a Netzsch DSC 200) was employed in this project to study the Glass transition temperature (T_g) of natural rubber and hydrogenated products.

For T_g determination, about 10-20 mg of each sample was weighted accurately and placed in 50 μ l aluminium pan. The sample was scanned from -100 to 150 $^{\circ}$ C at heating rate 10 $^{\circ}$ C/min under liquid nitrogen was used as coolant.



ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย