

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Preliminary Study on Hydrogenation of Natural Rubber

Theoretically, homogeneous hydrogenation uses a soluble catalytic complex to activate the reaction between hydrogen molecule and carbon-carbon double bond. Singha, *et al.* [7] had shown that chloro-tris(triphenylphosphine) rhodium(I),  $\text{RhCl}(\text{PPh}_3)_3$ , is highly effective towards the hydrogenation of natural rubber. However, dichloro-tris(triphenylphosphine) ruthenium(II),  $\text{RuCl}_2(\text{PPh}_3)_3$ , is known to be good homogeneous hydrogenation catalyst [14] for mono-olefinic and ketones. In addition, this complex is quite soluble in toluene, which makes it possible for attempting to hydrogenate natural rubber. In this study, the same condition as described by Singha, *et al.* [7] was chosen for the first trial. Therefore, hydrogenation of 0.50 g of natural rubber in 50 ml toluene was carried out using  $\text{RuCl}_2(\text{PPh}_3)_3$  0.09 g as a homogeneous catalyst. Quantitative hydrogenation could be achieved after 22 hrs at 100°C and 40 bar hydrogen pressure. Unlike  $\text{RhCl}(\text{PPh}_3)_3$  catalyst system, which is quite reactive and addition of  $\text{PPh}_3$  is need, the  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst system can catalyze the hydrogenation reaction without adding  $\text{PPh}_3$  [14].

When a catalyst was added into natural rubber solution, a sudden change from clear solution to brown color appeared. At the end of the reaction, the brown solution turned dark. The hydrogenated product was precipitated as colorless solid after adding excess methanol. It was then analyzed by using FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy.

#### 4.1.1 Product Analysis by FT-IR Spectroscopy

The FT-IR spectra of natural rubber and hydrogenated product were shown in Figure 4.1.

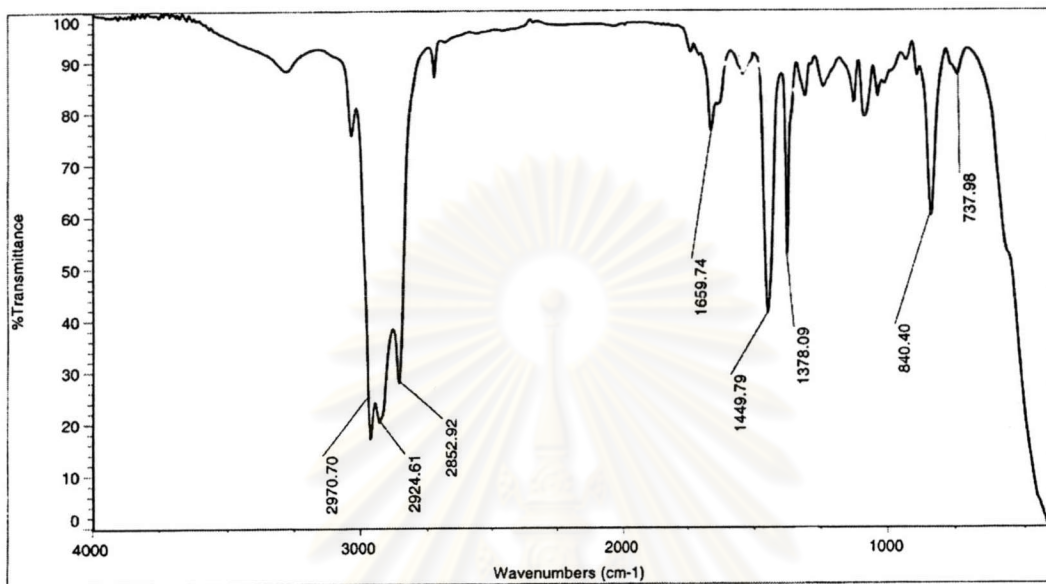


Figure 4.1a FT-IR spectrum of natural rubber (Film on NaCl).

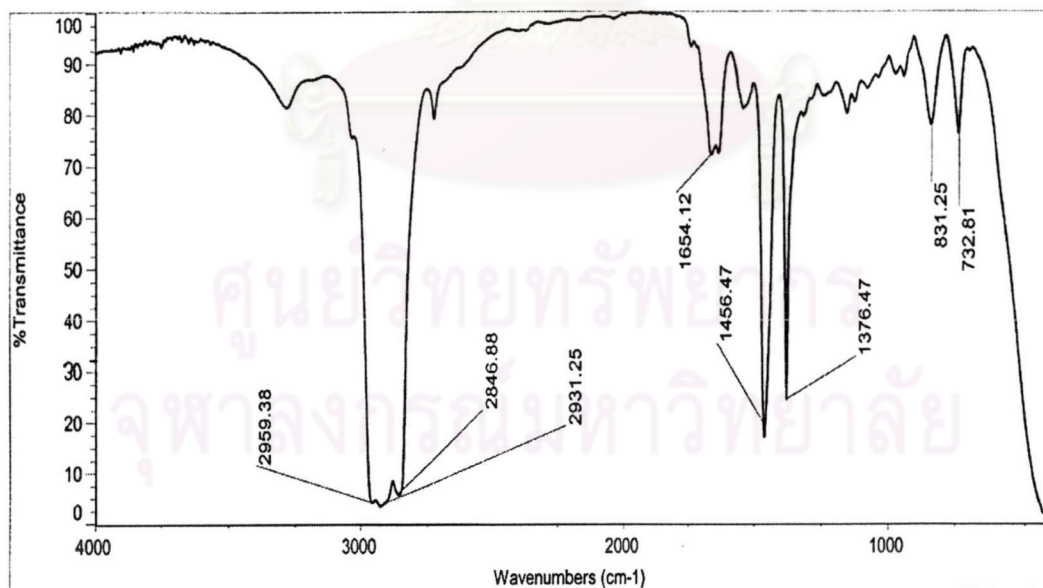


Figure 4.1b FT-IR spectrum of hydrogenated natural rubber (Film on NaCl).

The FT-IR spectrum of natural rubber (Figure 4.1a) exhibited the absorption bands of olefinic (C=C) stretching vibration at  $1659\text{ cm}^{-1}$ , the aliphatic ( $\text{CH}_2$ ,  $\text{CH}_3$ ) bending vibration at  $1449\text{ cm}^{-1}$ , the methyl group ( $\text{CH}_3$ ) bending vibration at  $1378\text{ cm}^{-1}$ , and the olefinic (C=C-H) out of plane bending at  $840\text{ cm}^{-1}$ .

The hydrogenated natural rubber showed a similar spectrum (Figure 4.1b). As expected the intensity of some absorption bands was relatively changed, The intensity of the absorption band at  $840\text{ cm}^{-1}$  due to trisubstituted olefinic C-H bonding, decreased while a very intense absorption peak appeared at  $735\text{ cm}^{-1}$ , which was attributed to the  $-(\text{CH}_2)_3-$  group formed through hydrogenation. This observation confirmed that natural rubber was partially hydrogenated by using  $\text{RuCl}_2(\text{PPh}_3)_3$ .

#### 4.1.2 Product Analysis by NMR Spectroscopy

The formation of hydrogenated natural rubber could also be identified by  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopic techniques. The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of natural rubber and hydrogenated product were shown in Figures 4.2 and 4.3 respectively.

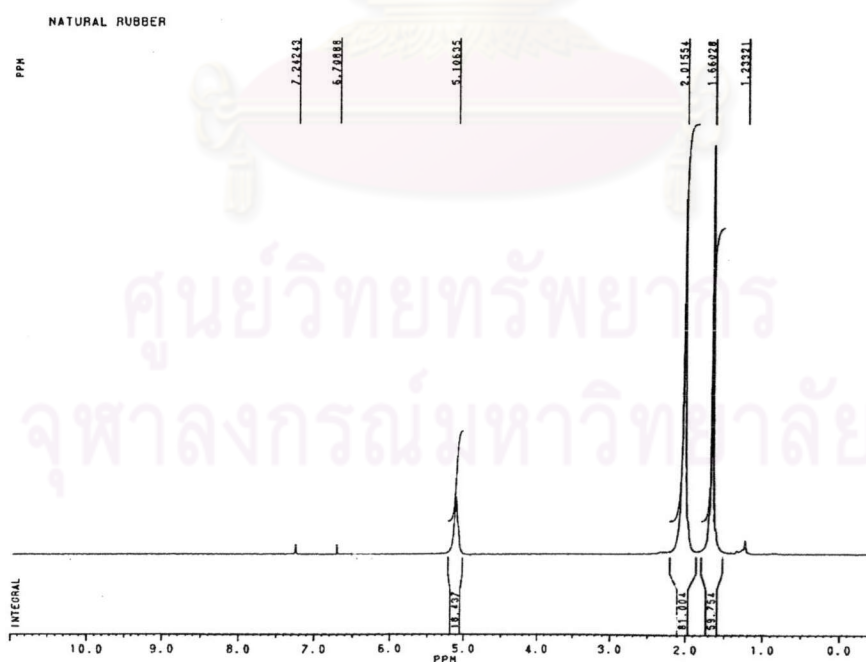


Figure 4.2a  $^1\text{H}$ -NMR spectrum of natural rubber ( $\text{CDCl}_3$ ).

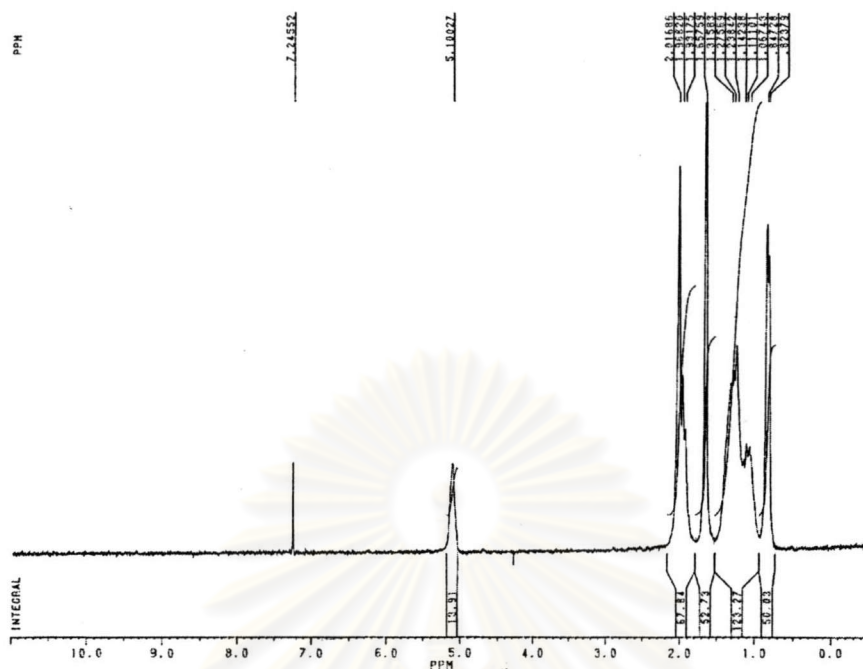


Figure 4.2b  $^1\text{H-NMR}$  spectrum of hydrogenated natural rubber ( $\text{CDCl}_3$ ).

In Figure 4.2a, the signals in  $^1\text{H-NMR}$  spectrum of natural rubber can be assigned as follows: the signals at  $\delta_{\text{H}}$  5.10, 2.01, and 1.66 ppm belonged to olefinic protons, methylene ( $-\text{CH}_2-$ ) protons, and methyl ( $-\text{CH}_3$ ) protons, respectively. Two additional signals in at  $\delta_{\text{H}}$  1.2 and 0.8 ppm were observed in  $^1\text{H-NMR}$  spectrum of the hydrogenated product. These are attributed to saturated  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups, respectively. These indicate that the reaction between hydrogen and carbon-carbon double bond occurred during hydrogenation. However, the partially  $\text{C}=\text{C}$  molecule could be added by hydrogen atom, which observed from the peaks for olefinic proton still remain. Besides  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectra could be confirmed the hydrogenation reaction.





Strictly alternating character was established by  $^{13}\text{C}$ -NMR. From Figure 4.3a, the peaks at  $\delta$ 135 and 125 ppm belong to the olefinic carbons. Upon hydrogenation, four new peaks emerged at  $\delta$  38, 33, 26 and 20 ppm, which are assigned for  $\text{C}_{(2)}$ ,  $-\text{CH}_{(4)}$ ,  $\text{C}_{(3)}$  and  $-\text{CH}_3_{(1)}$  carbons, respectively (Figure 4.3b). The peaks at  $\delta$  135 and 125 ppm for olefinic carbons still remained but their intensity decreased. Similar findings were also reported by Gan, *et al.* [19] and Singha, *et al.* [7].

The  $^{13}\text{C}$ -NMR and FT-IR provided only qualitative results. Therefore,  $^1\text{H}$ -NMR was used to calculate the percentage of hydrogenation of natural rubber in this study.

The percentage of hydrogenation of each hydrogenated product was determined from the ratio of the peak area of saturated protons and unsaturated protons appeared in  $^1\text{H}$ -NMR spectrum. The calculation was taken by using Microsoft Excel program [20] described in Appendix A.



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## 4.2 Preparation of Hydrogenated Natural Rubber

The hydrogenated natural rubber was prepared by using ruthenium catalyst as homogeneous system in toluene. Several parameters, such as reaction temperature, hydrogen pressure, reaction time, and the amount of catalyst were varied. The products were monitored by FT-IR spectroscopy and for the percentage of hydrogenation of each product was determined by calculation based on its  $^1\text{H-NMR}$  spectrum. The appropriate condition yielding high percentage of hydrogenation was investigated.

### 4.2.1 Effect of Reaction Temperature on Percentage of Hydrogenation

The hydrogenation reaction was carried out at temperature ranged from 70 to 150°C. Other parameters of hydrogenation were kept constant as follows:

- Natural rubber loading                      0.5 g/50ml toluene (1%w/v)
- Catalyst amount                                0.09 g
- Hydrogen pressure                            30 bar
- Reaction time                                 24 hours

The results from these reactions were shown in Table 4.1.

Table 4.1 The effect of reaction temperature on percentage of hydrogenation.

Entry No.	Catalyst (g)	Rubber (g)	Temperature (°C)	%Hydrogenation
1	0.0907	0.5090	70	28
2	0.0924	0.5017	80	38
3	0.0998	0.5009	90	59
4	0.0901	0.5010	100	63
5	0.0910	0.5141	120	59
6	0.0905	0.5014	130	42
7	0.0904	0.5110	150	35

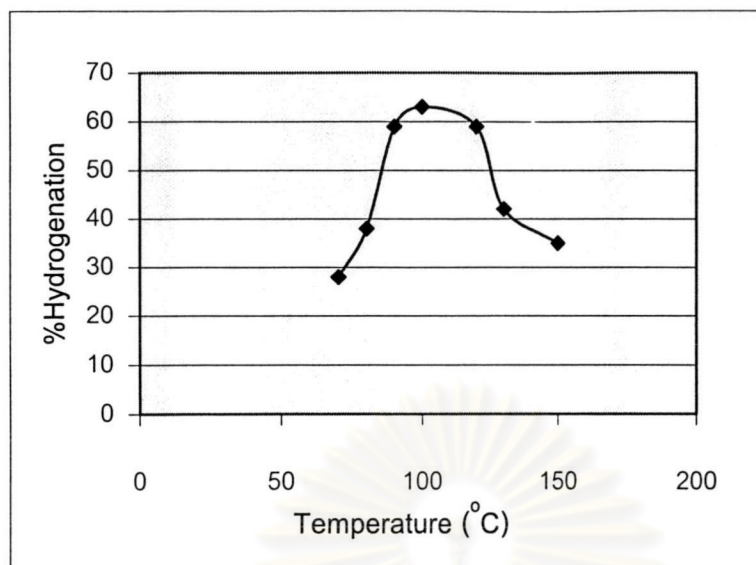


Figure 4.4 Effect of reaction temperature on the percentage of hydrogenation of natural rubber.

In Figure 4.4 higher temperature resulted in the increase of hydrogenation of natural rubber. However at the temperature higher than 100°C, the percentage of hydrogenation decreased. It seems that 100°C is the best temperature for hydrogenation system. At lower reaction temperature, the activity of  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst is rather low, while, at higher temperature, natural rubber can be degraded. A maximum of 63% hydrogenation was achieved at 100°C.

This result agrees well with the observation by Singha, *et al.* [12] for poly(styrene-co-butadiene) and Rao, *et al.* [14] for polybutadiene hydrogenation using  $\text{RuCl}_2(\text{PPh}_3)_3$ . Even though the use of  $\text{RuCl}_2(\text{PPh}_3)_3$  was found to be very active at 130-150°C for the hydrogenation of poly(nitrile-co-butadiene) [13], the hydrogenation of natural rubber was at the highest at a lower temperature (at 100°C).

Therefore, the appropriate reaction temperature which higher percentage hydrogenated natural rubber was chosen at 100°C.



#### 4.2.2 Effect of Hydrogen Pressure on Percentage of Hydrogenation

The hydrogenation reaction was carried out at hydrogen pressure ranged from 20 to 40 bars. Other parameters of hydrogenation were kept constant as follows:

- Natural rubber loading                      0.5 g/50ml toluene (1%w/v)
- Catalyst amount                              0.09 g
- Reaction temperature                      100°C
- Reaction time                                24 hours

The results from these reactions were shown in Table 4.2.

Table 4.2 The effect of hydrogen pressure on percentage of hydrogenation.

Entry No.	Catalyst (g)	Rubber (g)	Pressure (bar)	%Hydrogenation
8	0.0909	0.5011	20	31
9	0.0924	0.5049	25	55
4	0.0901	0.5010	30	63
10	0.0913	0.5014	35	65
11	0.0902	0.5012	40	66

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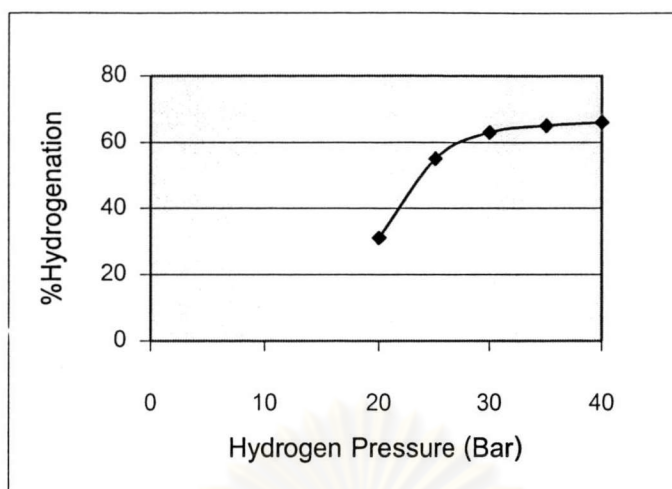


Figure 4.5 Effect of hydrogen pressure on the percentage of hydrogenation of natural rubber.

Figure 4.5 showed that the percentage of hydrogenation increased with the increase of hydrogen pressure from 20 bar and it became almost constant when the pressure approached 40 bar. It has been known that hydrogen pressure has effected on the initiation of the reaction [10]. Initially, the hydrogen gas was dissolved in the solution. Then, it reacted with the catalyst to form reactive species, which then reacted with the double bond of polyisoprene. At a low hydrogen pressure, the reaction occurred slowly since less hydrogen could dissolve in the solution. At a pressure higher than 30 bar, it seemed that the amount of hydrogen dissolved in the solution almost reached a maximum. That would be the reason why after hydrogen pressure was 30 bar, the percentage of hydrogen became constant.

The results of these experiments are much lower than the hydrogen pressure of the homogeneous  $\text{RhCl}(\text{PPh}_3)_3$  catalyst, which 40 bar for the hydrogenation of natural rubber in toluene was reported by Singha, *et al.* [7], and 50 bar for the hydrogenation of polybutadiene reported by Rao, *et al.* [14].

It could be concluded that an optimum hydrogen pressure for hydrogenation natural rubber using  $\text{RuCl}_2(\text{PPh}_3)_3$  was 30 bar.

#### 4.2.3 Effect of Reaction Time on Percentage of Hydrogenation

The hydrogenation reaction was carried out at reaction time ranged from 0-30 hours. Other parameters of hydrogenation were kept constant as follows:

- Natural rubber loading                      0.5 g/50ml toluene (1%w/v)
- Catalyst amount                                0.09 g
- Reaction temperature                        100°C
- Hydrogen pressure                            30 bar

The results from these reactions were shown in Table 4.3.

Table 4.3 The effect of reaction time on percentage of hydrogenation.

Entry No.	Reaction time (hrs)	%Hydrogenation
12	2	22
13	4	34
14	6	43
15	8	49
16	10	53
17	12	57
18	16	59
19	20	61
4	24	63
20	28	64
21	30	64

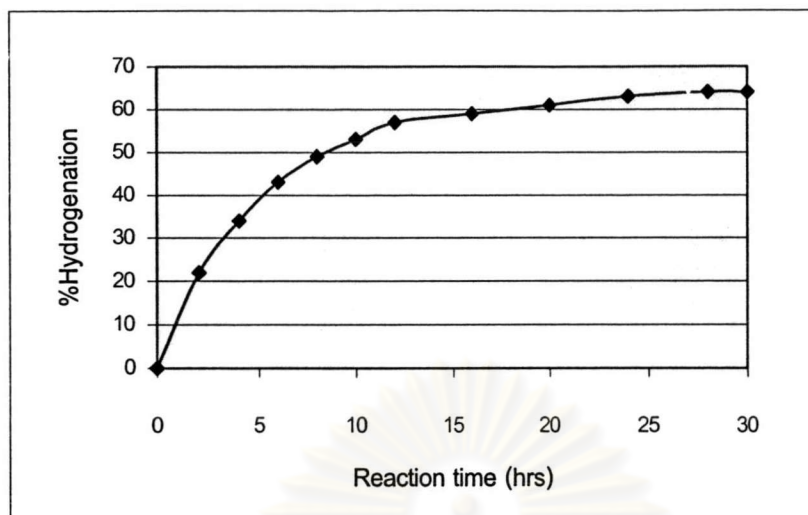


Figure 4.6 Effect of reaction time on the percentage of hydrogenation of natural rubber.

In Figure 4.6 it is shown that the percentage of hydrogenation increases with the increase in reaction time. After 24 hours, it becomes almost constant. The maximum hydrogenation was 63 % at 24 hours of reaction.

The reaction time for natural rubber is longer than the hydrogenation of other polymer reported earlier using the same catalyst. Guo, *et al.* [13] have shown that greater than 95% hydrogenation (NBR) could be achieved in 11 hours. Rao, *et al.* [14] indicated that a maximum 99% of conversion (polybutadiene) is obtained at 6 hours reaction time. This suggested that the hydrogenation of C=C in polyisoprene in this condition was far slower than for NBR and polybutadiene. This indicated the strong effect caused by steric hindrance related to the extra methyl group on the polymer chain, which presumably impedes C=C complexation at the catalyst center [23,27]. Nevertheless, there is no report about the degradation during hydrogenation by other catalyst.



#### 4.2.4 Effect of Catalyst Amount on Percentage of Hydrogenation

The hydrogenation reaction was carried out at various amounts of catalyst ranged from 0.05-0.15 g. Other parameters of hydrogenation were kept constant as follows:

- Natural rubber loading                      0.50 g/50ml toluene
- Reaction temperature                      100 °C
- Hydrogen pressure                      30 bar
- Reaction time                      24 hours

The results from these reactions were shown in Table 4.4.

Table 4.4 The effect of catalyst amount on percentage of hydrogenation.

Entry No.	Catalyst		Rubber (g)	%Hydrogenation
	(mmol)	(g)		
22	1.043	0.0502	0.5012	37
23	1.460	0.0704	0.5011	50
24	1.669	0.0824	0.5049	60
4	1.877	0.0901	0.5010	63
25	2.086	0.1001	0.5010	70
26	2.295	0.1102	0.5015	75
27	2.503	0.1201	0.5011	83
28	2.712	0.1304	0.5021	84
29	3.129	0.1502	0.5035	91

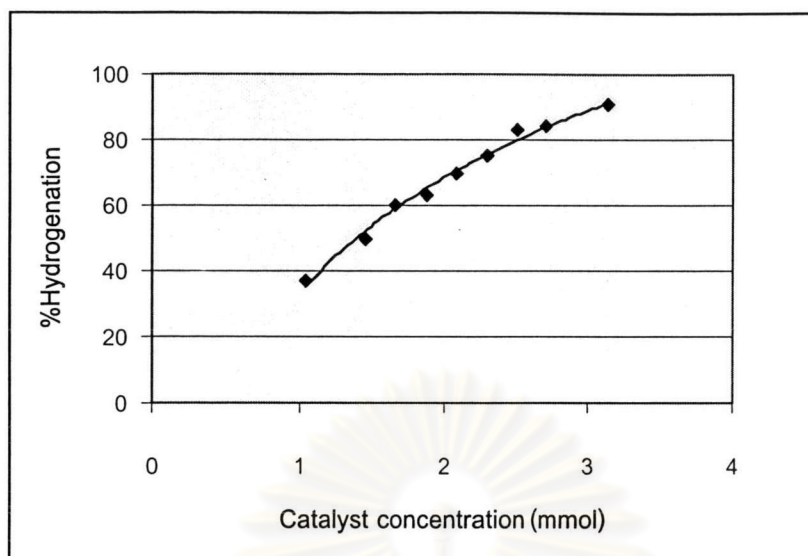


Figure 4.7 Effect of catalyst amount on the percentage of hydrogenation of natural rubber.

Figure 4.7 exhibited that the catalyst amounts played an important role in the extent of hydrogenation of natural rubber. The reduction of double bonds increased with the catalyst amount. At 0.15 g (3.129 mmol) of  $\text{RuCl}_2(\text{PPh}_3)_3$ , hydrogenation as high as 90% was achieved. However, the catalyst amount of 0.09 g (1.877 mmol) are preferable because of its significantly lower cost and its capability to hydrogenate 63% of the C=C in natural rubber. A higher catalyst amount is needed to obtain a reasonable reaction speed and to achieve high hydrogenation, but its cost is more expensive.

The hydrogenation of natural rubber proceeds *via* the metal hydride pathway as reported for synthetic rubber using  $\text{RuCl}_2(\text{PPh}_3)_3$  as shown in Figure 4.8.

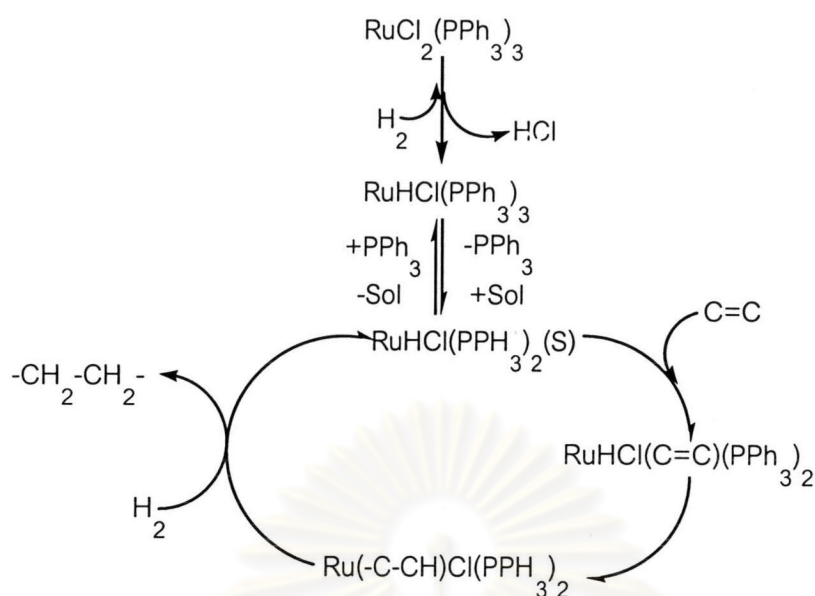


Figure 4.8 The cycle of hydrogenation of natural rubber using  $\text{RuCl}_2(\text{PPh}_3)_3$ .

These observation can be explained by involving the hydride pathway mechanism for hydrogenation [12]. Hydrogen first reacts with  $\text{RuCl}_2(\text{PPh}_3)_3$  to form hydrido-tris(triphenylphosphine) ruthenium(II) chloride,  $\text{RuHCl}(\text{PPh}_3)_3$ . This is the reactive species in the hydrogenation of natural rubber.  $\text{RuHCl}(\text{PPh}_3)_3$  undergoes ligand exchange with solvent to form  $\text{RuHCl}(\text{PPh}_3)_2(\text{S})$ . This active species reacts with the double bond to form a metal alkyl complex. The metal alkyl complex undergoes dissociation, resulting in the formation of saturated polymer.

In comparison, the hydrogenation of butadiene using  $\text{RuCl}_2(\text{PPh}_3)_3$  needs less amount of catalyst than that required by natural rubber. The rate of hydrogenation of natural rubber is slower than that of polybutadiene, presumably, because of the trisubstitution at the carbon-carbon double bond in natural rubber [7]. Moreover, the presence of proteins that adsorbed on the rubber particle can obstruct the hydrogenation of natural rubber to some extent.

From all experiments, It can be concluded that the optimum conditions for the hydrogenating of 0.5 g natural rubber in toluene 50 ml was at temperature of  $100^\circ\text{C}$ , hydrogen pressure of 30 bar for 24 hours by using 0.09 g (1.88 mmol)  $\text{RuCl}_2(\text{PPh}_3)_3$ . This condition resulted in 63% hydrogenated natural rubber.

### 4.3 Molecular Weight and Molecular Weight Distribution of Hydrogenated Natural Rubber.

During hydrogenation, it is possible that degradation of natural rubber can occur. In order to investigate the presence of side reactions, such as degradation molecular weight and molecular weight distribution of natural rubber and hydrogenated products were determined by GPC. The effect of temperature, hydrogen pressure, and catalyst amount on the degradation of hydrogenated products were investigated.

#### 4.3.1 Effect of Reaction Temperature on MW and MWD

The effect of temperature on average molecular weights and molecular weight distribution (MWD) are shown in Table 4.5 and Figure 4.9.

Table 4.5 The effect of reaction temperature on MW and MWD.

Entry No.	Temperature	%Hydrogenation	$M_w \times 10^4$	$M_n \times 10^4$	MWD
4	100°C	63	11.5	6.52	1.76
5	120°C	59	8.86	4.75	1.86
6	130°C	42	4.68	2.47	1.89
7	150°C	35	3.52	1.74	2.02

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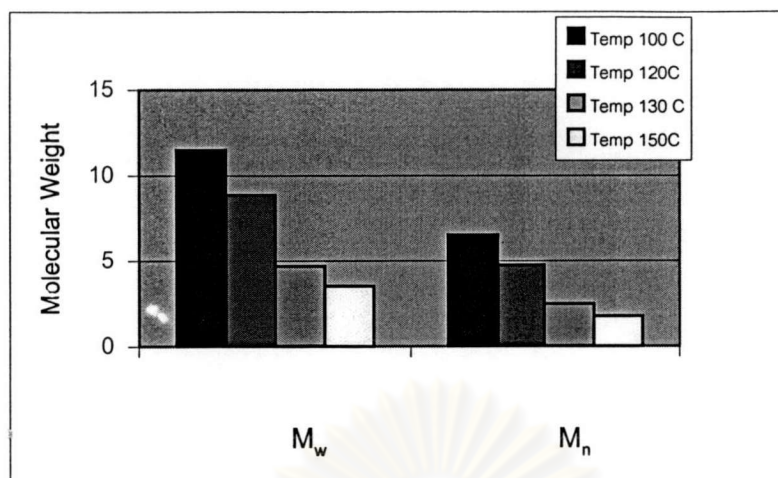
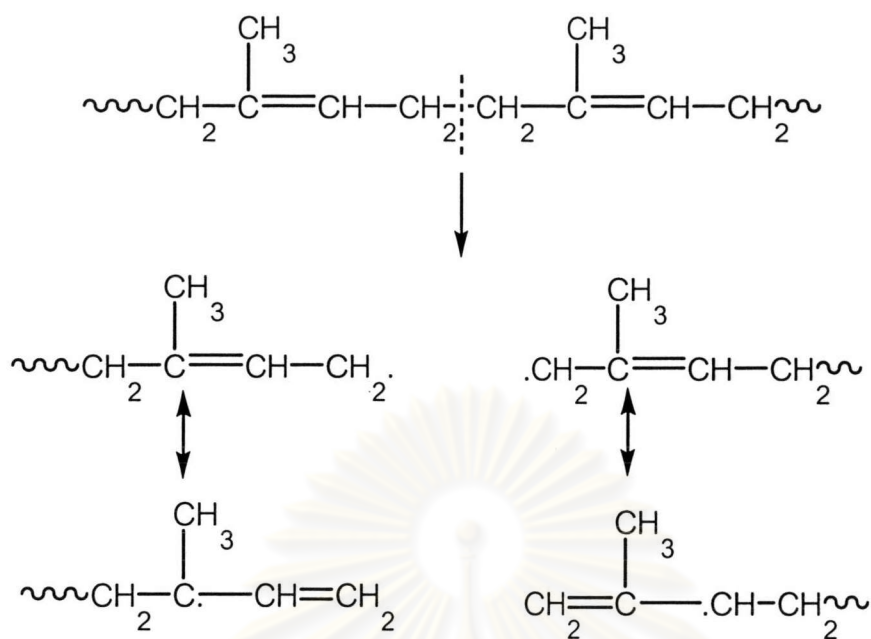


Figure 4.9 Effect of reaction temperature on molecular weight.

Figure 4.9, revealed that when the temperature increased, MW of the products decreased while the MWD increased. It can be explained that the degradation of the hydrogenated natural rubber might occur after its formation. The cleavage along polymer main chain could occur more readily at higher temperature. Furthermore, when hydrogenation reaction of natural rubber was carried out at high temperature, it was believed that some side reaction probably occurred such as degradation and cyclisation [30]. Generally, chain cleavage is believed to cause the change of MW rather than cyclisation as the reaction was investigated at rather high temperature. The degradation leads to form radical at the allylic position of the double bond [30].

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It was believed that the hydrogenation is the reaction that reduces the amount of double bond and causes chain cleavage more difficult to occur. It is possible that hydrogenation took place before chain scission.

#### 4.3.2 Effect of Hydrogen Pressure on MW and MWD

The effect of hydrogen pressure on average molecular weight (MW) and molecular weight distribution (MWD) is shown in Table 4.6 and Figure 4.10.

Table 4.6 The effect of hydrogen pressure on MW and MWD.

Entry No.	Pressure	%Hydrogenation	$M_w \times 10^4$	$M_n \times 10^4$	MWD
4	30 bar	63	11.5	6.52	1.76
10	35 bar	65	20.6	9.76	2.07
11	40 bar	68	22.8	10.9	2.17

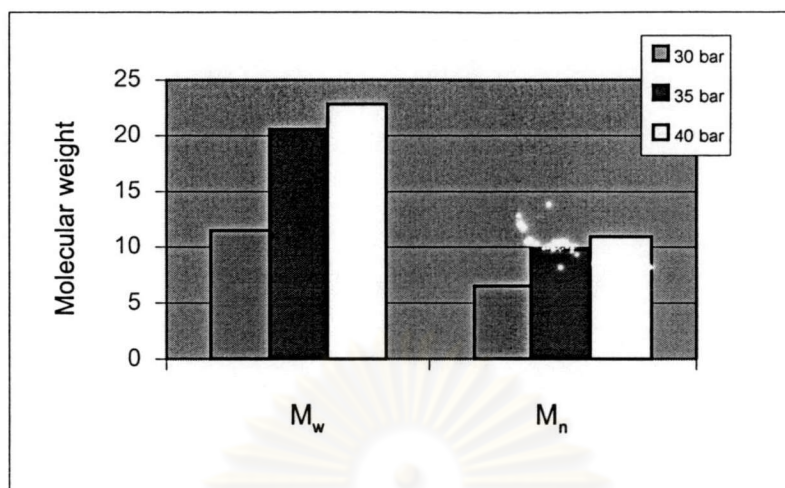


Figure 4.10 Effect of hydrogen pressure on molecular weight.

Figure 4.10, showed that when hydrogen pressure increased, molecular weight and MWD of hydrogenated natural rubber increased. These molecular weight are, however, lower than that of untreated natural rubber. It can be explained that at high pressure, hydrogen molecule that dissolved in the solution increased, the formation of catalyst reactive species was increased. Then, the hydrogenation increased with the increase in hydrogen pressure. The amount of double bonds was reduced.

#### 4.3.3 Effect of Catalyst Amount on MW and MWD

The effect of catalyst amount on average molecular weight (MW) and molecular weight distribution (MWD) is shown in Table 4.7 and Figure 4.11.

Table 4.7 The effect of catalyst amount on MW and MWD.

Entry No.	Catalyst	%Hydrogenation	$M_w \times 10^4$	$M_n \times 10^4$	MWD
4	0.09 g	63	11.5	6.52	1.76
28	0.13 g	84	17.1	8.61	1.98
29	0.15 g	91	19.8	9.83	2.01

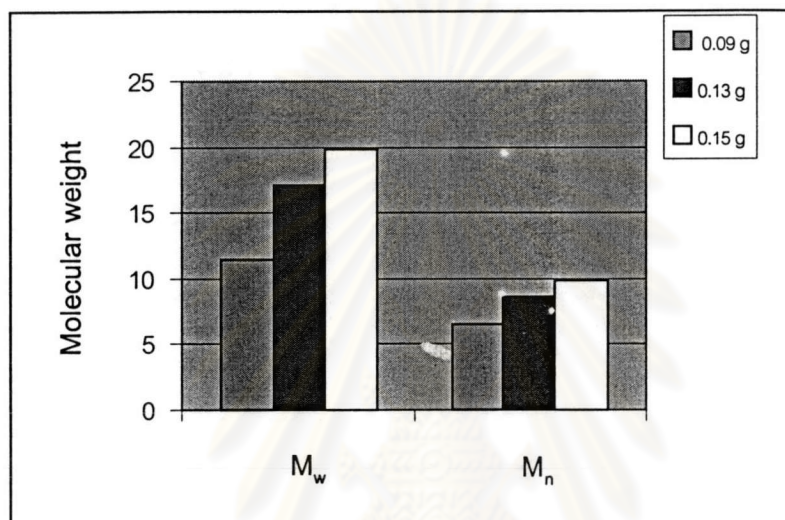


Figure 4.11 Effect of catalyst amount on molecular weight.

Figure 4.11, the obvious result is the influence of catalyst amount on MW and MWD of the hydrogenated products. While increasing catalyst amounts, we found that lower MW and MWD of the hydrogenated products were increased lower than natural rubber. It may be explained that when the catalyst amount were increased, the reactive species of catalyst also were increased, which could interact with more unsaturated molecule. Then, the degradation reaction could occur difficultly. Due to the degradation of hydrogenated products might happen after its formation.

#### 4.3.4 Effect of Catalyst on MW and MWD

The effect of catalyst amount on average molecular weight (MW) and molecular weight distribution (MWD) is shown in Table 4.8 and Figure 4.12.



Table 4.8 The effect of catalyst on MW and MWD.

Entry No.	Sample	%Hydrogenation	$M_w \times 10^4$	$M_n \times 10^4$	MWD
0	NR	0	43.1	16.1	2.68
30	Non-cat.	0	33.9	13.1	2.59
4	Cat. 0.09 g	63	11.5	6.52	1.76

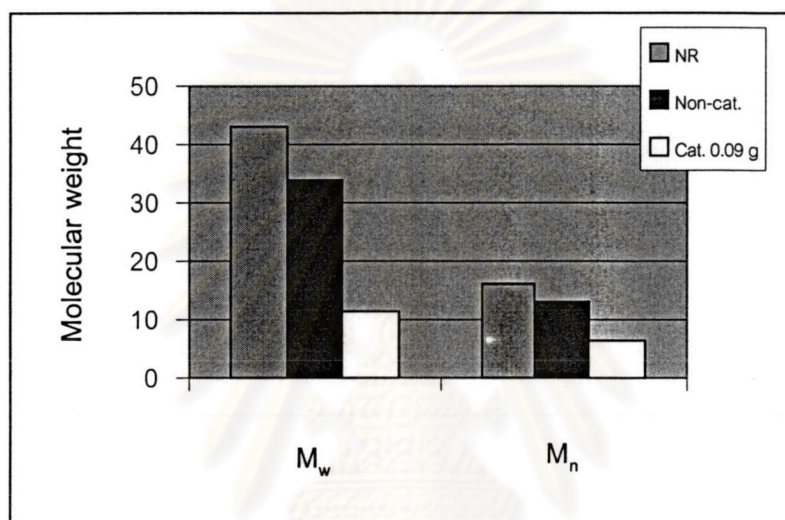


Figure 4.12 Effect of catalyst on molecular weight.

In Figure 4.12, it was found that a catalyst could reduce MW and MWD. The MW and MWD of hydrogenated natural rubber without catalyst, which was performed of the same condition was slightly different from natural rubber. It was observed that this catalyst caused the molecule of natural rubber to degrade. It believed that the catalyst mechanism is the complication system. It is difficult at present to give adequate meaning to these results.

From this investigation, it could be clearly seen that the degradation occurred during the hydrogenation process. However, recent work examining the hydrogenation of styrene-butadiene rubber catalyzed by  $\text{RuCl}_2(\text{PPh}_3)_3$  has not mentioned any problem with the degradation. Rao, *et al.* [14] estimated that no degradation occurred during the catalytic hydrogenation reaction, but he also reported that the hydrogenated product

was found to include the short chain branching and long chain branching. Martin, *et al.* [27] supported that the polymer molecular weight was not altered greatly during hydrogenation by using Ru complex. Charmondusit, *et al.* [20] illustrated that no degradation and no crosslinking occurred during the catalyst as  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{Pcy}_3)_2$  on cis-polyisoprene hydrogenation. There are no reported any problem with crosslinking, which occurred during hydrogenation by using  $\text{RuCl}_2(\text{PPh}_3)_3$ . For the hydrogenation of natural rubber, by using  $\text{RhCl}(\text{PPh}_3)_3$  [7], no degradation was observed during the reaction. In this studies, however, the degradation of natural rubber took place during the hydrogenation process by using  $\text{RuCl}_2(\text{PPh}_3)_3$  as a catalyst. Therefore,  $\text{RuCl}_2(\text{PPh}_3)_3$  in this study also comes into play not only catalyze the hydrogenation reaction, but also effect the degradation of the polymer chain.



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#### 4.4 Thermal Characterization

It has been known that dienic polymers cannot resist high temperature treatment because their unsaturation in the molecular structure could initiate degradation reaction through formation of radical at allylic position of the double bonds. In the case of natural rubber, the modification by hydrogenation reaction should increase the thermal stability of the modified product as the degree of unsaturation decreased. Thermal behavior of hydrogenated natural rubber was analyzed by using DSC and TGA techniques. The measurement of resistance to heat was recorded on TGA. The heat required to give molecular deformation of polymers, i.e.  $T_g$  was recorded by DSC.

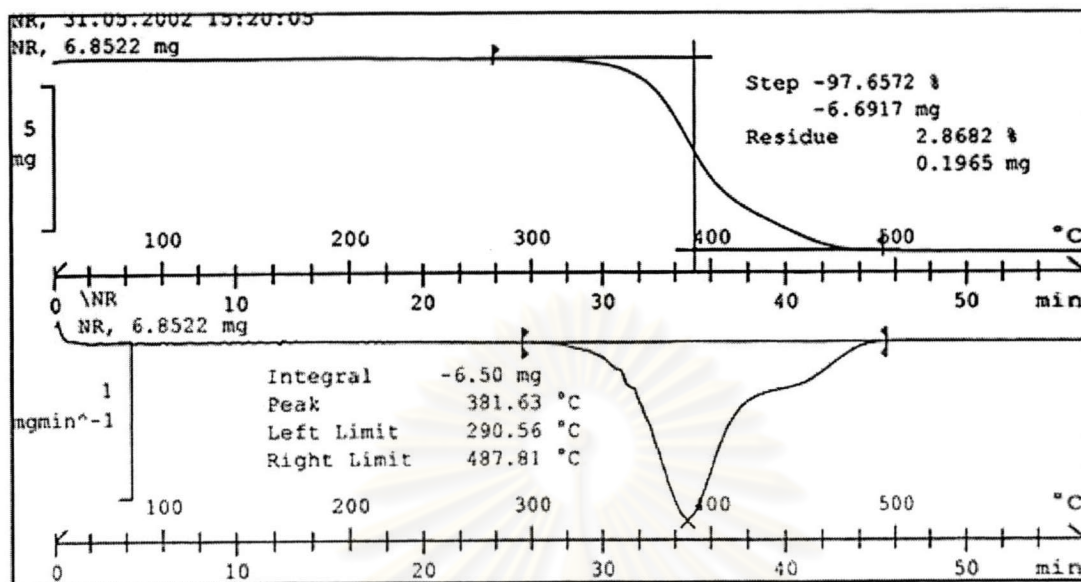
##### 4.4.1 Thermal Stability Study by TGA

TGA of natural rubber and hydrogenated products were measured under nitrogen at a heating rate 10 of  $^{\circ}\text{C}/\text{min}$ . The initial decomposition temperature was determined from the onset of the decomposition temperature. The maximum decomposition temperature ( $T_{\text{max}}$ ) was calculated from the peak maximum of the derivative of TGA curves. Weight loss curves of natural rubber and some hydrogenated products are exhibited in Figure 4.13 including the first derivative curves. Initial decomposition temperature (IDT) and  $T_{\text{max}}$  changes are shown in Table 4.9.

Table 4.9 Initial decomposition temperature (IDT) and Temperature at maximum weight ( $T_{\text{max}}$ ) of natural rubber and hydrogenated natural rubber.

Entry No.	Sample	IDT ( $^{\circ}\text{C}$ )	Temperature: $T_{\text{max}}$ ( $^{\circ}\text{C}$ )
0	Natural rubber	290.56	381.63
4	HNR 63 %	329.55	447.52
28	HNR 84 %	339.55	450.45
29	HNR 91 %	344.50	453.92

## (a) Natural rubber



## (b) Hydrogenated Natural Rubber 63%

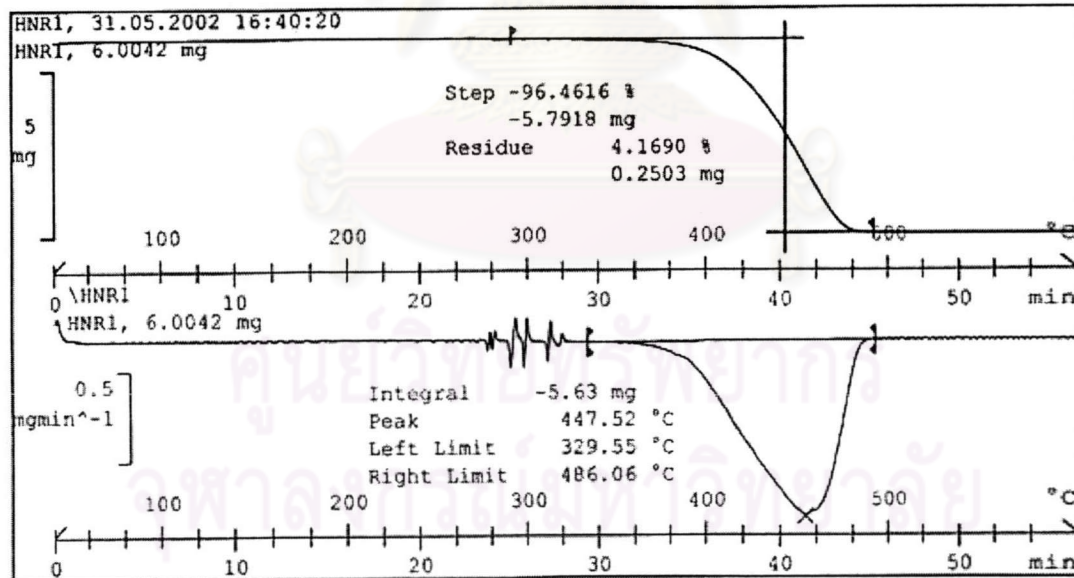
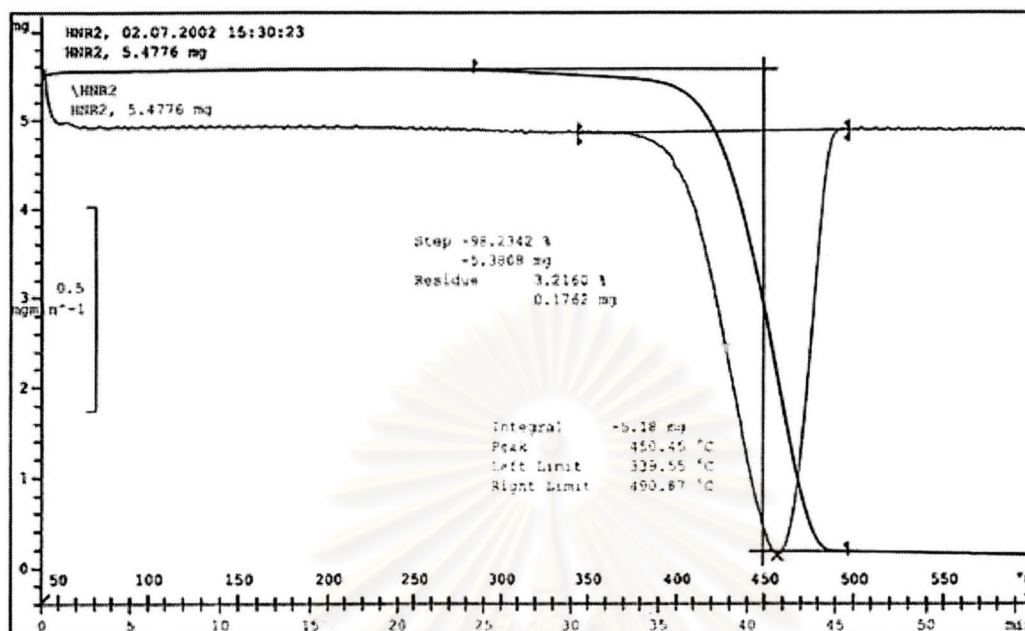


Figure 4.13 TGA curves of Natural rubber (a) and Hydrogenated Natural Rubber 63% (b).



## (c) Hydrogenated Natural Rubber 84%



## (a) Hydrogenated Natural Rubber 91%

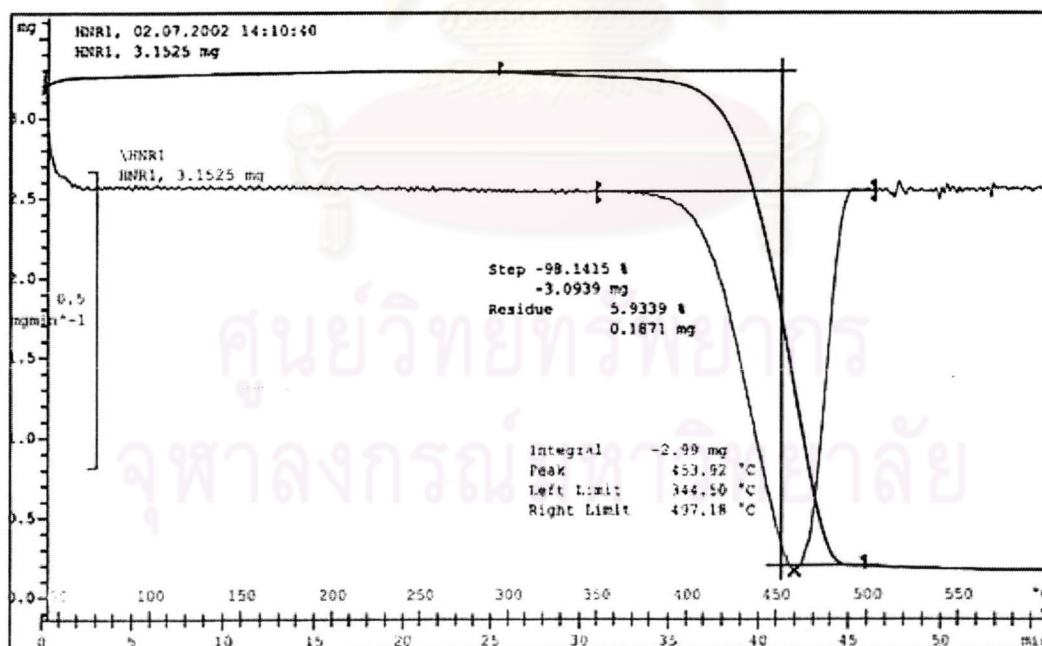


Figure 4.13 (continued) TGA curves of Hydrogenated Natural Rubber 84% (c) and Hydrogenated Natural Rubber 91%(d).

IDT increases with the degree of hydrogenation. The  $T_{max}$  increased with increasing hydrogenation of carbon-carbon double bond (C=C) in the elastomer. The  $T_{max}$  can be raised from about 381.63 °C for natural rubber to 453.92 °C for hydrogenated natural rubber at 91 %hydrogenation. By comparing the temperatures at the maximum weight change (Table 4.9), as expected, hydrogenated products possess better thermal stability than natural rubber although they have lower molecular weight as indicated by GPC. Thermal stability of hydrogenated products increased as %hydrogenation increased. Therefore, the thermal stability of natural rubber was modified by hydrogenation reaction.

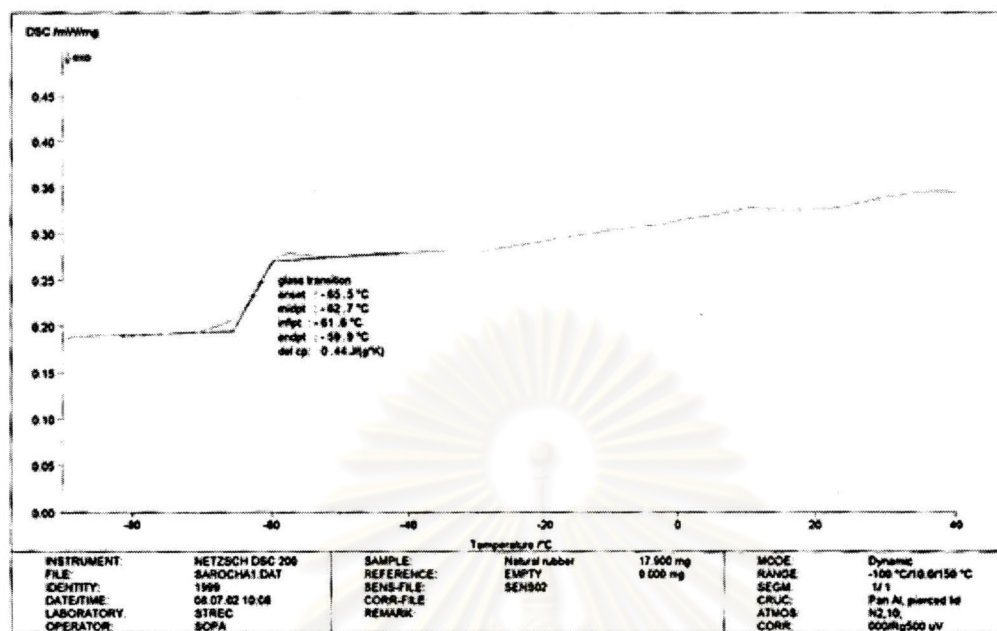
#### 4.5.2 Glass Transition Temperature Determination by DSC

The glass transition temperature ( $T_g$ ) was calculated from DSC thermograms. The DSC curves of natural rubber and some hydrogenated products are exhibited in Figures 4.14. The results of  $T_g$  are shown in Table 4.10.

Table 4.10 Glass transition temperature of natural rubber and hydrogenated products.

Entry No.	Sample	$T_g$ ( °C)
0	Natural rubber	-62.7
4	HNR 63%	-61.2
29	HNR 91%	-60.6

## (a) Natural rubber



## (b) Hydrogenated Natural Rubber 63%

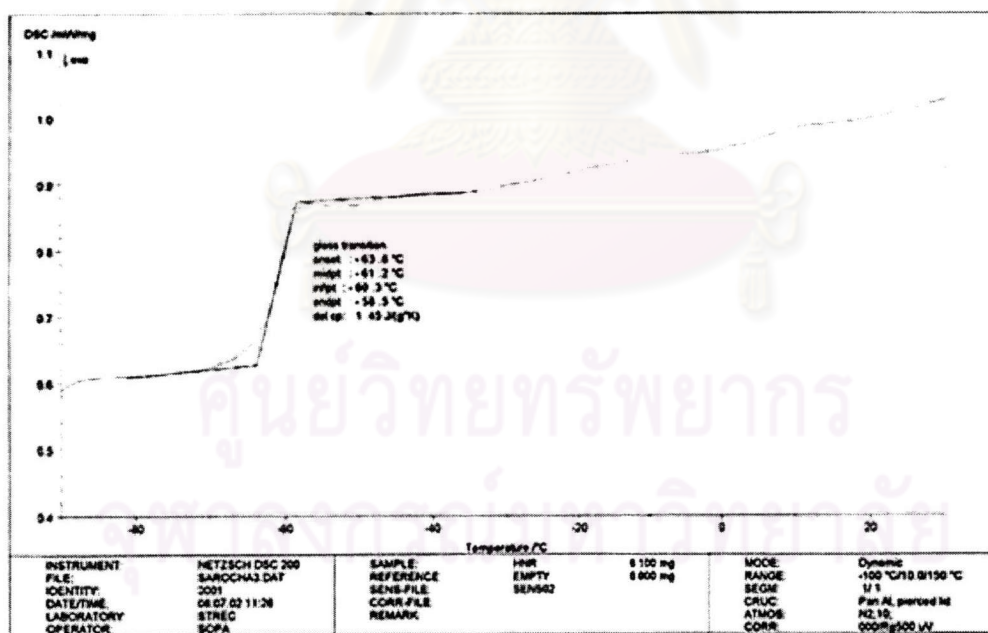


Figure 4.14 DSC curves of Natural rubber (a) and Hydrogenated Natural rubber 63% (b).

## (c) Hydrogenated Natural Rubber 91%

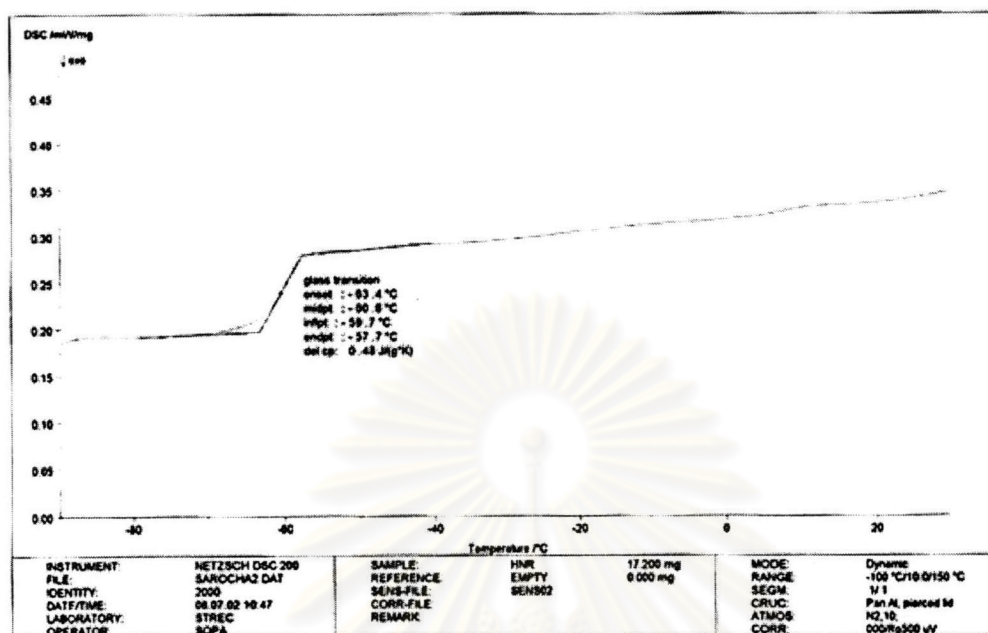


Figure 4.14 (continued) TGA curves of Hydrogenated Natural Rubber 91%(c).

The hydrogenated natural rubber were found to have glass transition temperatures ( $T_g$ ) below ambient, and 1-2°C higher than that of the natural rubber. The increase in  $T_g$  was resulted from the higher amount of saturated chains, which allowed close arrangement of polymer chains. Therefore, more energy was required to move these closely packed chains [30].

TGA and DSC results confirm that thermal stability of hydrogenated natural rubber was improved.