Hydrogenations of Butadiene Rubber and Natural Rubber by Reactive Processing

K. Suchiva[†] and K. Boonkerd

National Metal and Materials Technology Center, Bangkok 10400, Thailand and

Department of Chemistry, Faculty of Science, Mahidol Universtiy, Bangkok 10400, Thailand

ABSTRACT : Hydrogenations of BR and NR performed by a noncatalytic method using p-toluenesulphonylhydrazide were carried out by reactive processing. The experimental procedures for carrying out the reaction were established. Two steps comprising premixing of the rubber with TSH followed by hydrogenation in compression mould were proved to be suitable. The percentages of hydrogenation attained by reactive processing were higher than those of the reaction carried out in solution at the same [TSH]/[C=C] ratio, reaction temperature and time. Increasing the reaction temperature and reaction time resulted in increases of the percentage of hydrogenation. For BR, the maximum percentage of hydrogenation obtained was 36% at [TSH] /[C=C]=1/1.5. For NR, the highest percentage of hydrogenation was 34% at [TSH]/[C=C] =1/1.5. Cis-trans isomerisation was also observed to occur during hydrogenation of both BR and NR. Thermal stabilities of the hydrogenated BR and NR were shown to improve over those of the unhydrogenated counterparts.

I. Introduction

Chemical modifications of polymers are conventionally carried out in solution or in latex. The obvious disadvantages are the high cost involved with the use of solvent and recovery of the modified product. Use of solvent also provides potential hazard in connection with fire and toxicity. Modification of polymer by reactive processing whereby the reaction is carried out in processing equipment such as mixer or extruder offers an attractive alternative mean since the method is solventless, consumes less energy and requires less plant investment compared with the wet chemistry process. In the case where an extruder is used, chemical modification becomes a continuous process and high production output is possible. Chemical modifications of polymers by reactive processing, in the past, have largely been applied to plastics.[1] Application of this technology to rubber, however, has

---

[†]To whom all correspondence should be addressed

been slower to develop.

For chemical modification of diene rubber, hydrogenation has been found to be a useful mean for improvement of its resistance to thermal oxidative degradation. Furthermore, hydrogenation can also provide a method for generating new products that may be difficult to prepare by other means. For example, hydrogenation of 1,4-polyisoprene will give an alternating copolymer of ethylene and propylene which is difficult to access by conventional polymerisation method.

The conversion of unsaturated polymers to saturated ones can be effected by both catalytic and non-catalytic hydrogenations.[2] In the case of noncatalytic hydrogenation, diimide (N_2H_2) is widely used as hydrogen donating agent. Hydrogenation using diimide has been found to be relatively simple since it can be carried out at atmospheric pressure under moderate temperatures ($100 \sim 250 \,^{\circ}C$). As a consequence, noncatalytic hydrogenation has been widely used to prepare hydrogenated species in laboratory.

Diimide can be obtained by a number of ways such as oxidation of hydrazine (NH_2NH_2), usually in the presence of a small amount of copper(II) ions, the decarboxylation of potassium azodicarboxylate in the presence of a proton source and the thermolysis of arylsulphonylhydrazide.[3,4] The thermolysis of arylsulphonylhydrazide is the most widely used method to hydrogenate polymers and p-toluenesulphonylhydrazide (TSH) has been used extensively. TSH can decompose at moderate temperature (about $105\,^{\circ}C$) to give a transitory species diimide and a by-product, p-toluenesulphinic acid, as shown below.

$$H_3C - \bigcirc - SO_2 - NH - NH_2 \xrightarrow{\ 105\,^{\circ}C\ } H_3C - \bigcirc - SO_2H + NH = NH$$
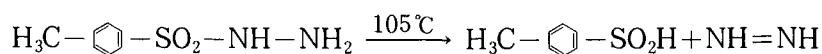
Studies of the use of TSH to hydrogenate diene based polymers and copolymers were published by Harwood and Lenz.[5,6] In addition to the reduction of degree of unsaturation, it has been found that the use of TSH to hydrogenate unsaturated polymer gives rise to a side reaction which is the attack of olefinic sites by p-tolulenesulphinic acid, a by-product from the decomposition of TSH. Protonation of olefinic functionality by p-toluenesulphinic acid is likely to lead to a variety of ionic reactions on the polymer backbone, including chain cleavage, coupling/cyclisation reactions, and addition of the p-toluenesulphinate anion.[7-9] To avoid the protonation of unsaturated polymers during hydrogenation using TSH, Hahn[10] found that the addition of tri-n-propyl amine could eliminate the side reaction on butadiene containing polymers and copolymers. This is because of preferred protonation of the amine instead of the olefin. Thus, the propensity of the p-tolylsulphinate anion to attack at the polymer backbone should greatly decrease. Besides incorporation of the by-product, it was also reported that cis-trans isomerisation occurs in partial hydrogenation using TSH.[5,6] In hydrogenation of cis-butadiene rubber, the change of some of the cis units in the backbone to the trans configuration was revealed by Raman spectroscopy.[11]

The present work reports a study of non-catalytic hydrogenation of two diene rubbers, butadiene rub-

ber (BR) and natural rubber (NR), by reactive processing, employing TSH as a hydrogenating agent.

II. Experimental

1. Materials and Instruments

Two diene rubbers used in this study were 98% cis-1,4-butadiene rubber and the Standard Thai Rubber, STR5L. p-toluenesulphonylhydrazide (TSH), practical grade reagent, was purchased from Fluka. Xylene used as solvent was purchased from JT Baker.

Molar masses and molar mass distributions of BR and its hydrogenated products were determined by using a Waters 150-CV gel permeation chromatography (GPC). The viscosity average molecular weights of NR and its hydrogenated products were determined by viscometric method. The K and a values in the Mark-Houwink equation used were 33.1×10^{-5}ml/g and 0.71 (at 30℃ in toluene), respectively. Perkin Elmer System 2000 FT-Raman spectrometer, Bruker DPX-300 NMR spectrometer were used for characterisation of the chemical structures. Thermal stabilities of the hydrogenated rubbers of different percentages of hydrogenation were determined by DSC. Perkin Elmer DSC7 was used for this study. The samples were heated from 200℃ to 450℃ at a heating rate of 20℃/min under nitrogen atmosphere.

2. Method of Hydrogenation

2.1 Reactive Processing Method

Mixing of the rubber with TSH was carried out in a 79cm³ capacity mixer (Haake Rheocord System 90). For room temperature mixing, the temperature of the mixer was set at 30℃. The rotor speed used was 20rpm and the mixing times were 25 minutes and 15 minutes for BR and NR, respectively.

In the case where hydrogenation reaction was effected by compression moulding, the rubber/ TSH mix was heated in a flat mould of $20 \times 20 \times 0.2$cm in dimension using electric hot press.

2.2 Solution Method

Hydrogenation by solution method was carried out by refluxing the solution of rubber and TSH in xylene (1g of rubber in 150ml of xylene) at required temperature and reaction time. The hydrogenated product was recovered by precipitating in distilled methanol.

2.3 Purification of Hydrogenated Rubbers

The hydrogenated rubbers were purified by dissolving in distilled hexane and precipitating in distilled methanol. Purification process was repeated three times.

3. Determination of the Percentage of Hydrogenation

The % hydrogenations were calculated from ¹H-NMR spectra by the following formulations,

For BR % Hydrogenation

$$= \frac{A_{\delta 1.25}}{A_{\delta 1.25} + 4A_{\delta 5.41}} \times 100$$

For NR % Hydrogenation

$$= \frac{A_{\delta 0.84}}{A_{\delta 0.84} + 4A_{\delta 5.12}} \times 100$$

(where $A_{\delta x}$ is area of the resonance peak at x ppm.)

III. Results and Discussion

1. Method of Hydrogenation

The hydrogenation reaction was first carried out in the mixer. Thus, BR and TSH were mixed at room temperature and the temperature of the mixer was increased to 105℃. Under this condition it was found that TSH decomposed violently, giving out intense fume. The hydrogenation method was then modified.

TSH was gradually added to the rubber (BR) in the mixer at 105℃. After the addition of TSH was completed, mixing was continued for 60 minutes to allow for hydrogenation reaction to take place. However, it was found by ^{1}H-NMR spectroscopy that only 1% hydrogenation resulted when the [TSH]/[C=C] of 1/2 was used. It was thought that, by gradual addition, the small portion of TSH added would melt on the surface of the rubber mass, therefore TSH could not be effectively incorporated into the rubber. Thus only very low percentage of hydrogenation was obtained. The method of hydrogenation was modified again.

The mixer was now used only to mix the rubber and TSH. The hydrogenation reaction was effected separately in a compression mould without problem. The reaction temperature could also be raised from 105℃ up to 115℃. At 120℃ severe fuming again occurred. This method was adopted for carrying out hydrogenation of both BR and NR throughout the present study.

In the mixing step, it took about 15 minutes to add the reagent completely. After that the compound was further mixed for about 10 minutes to make sure that the reagent dispersed homog-eneously. Although a longer mixing time would

Table 1. $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ of BR Before and after Mixing at Various Ratios With TSH for 25 minutes

Sample	[TSH]/[C=C]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
BR	0	237,000	529,000	2.23
A	1/3.5	211,000	595,000	2.82
B	1/2.5	211,000	631,000	2.98
C	1/1.5	229,000	632,000	2.76

Table 2. $\overline{M}_v$ of NR before and after Mixing With TSH for 15 and 25 minutes

Sample	[TSH]/[C=C]	Mixing time (minutes)	$\overline{M}_v$
NR	0	–	610,000
D	1 : 2	15	285,000
E	1 : 2	25	98,000

result in higher homogeneity of the mixture, breakdown of the rubber could also occur. In order to check whether BR degraded under the mixing conditions, the MW and MWD of BR were determined. The results are shown in Table 1.

From Table1, it can be seen that MW of BR after mixing at above condition reduced slightly. It was thought, therefore, that the the mixing condition used (total mixing time 25 minutes and rotor speed 20rpm) was suitable for preparing compound for hydrogenation.

For NR, degradation occurred at a much greater extent than in BR during mixing with TSH. This can be seen from the measurement of MW ($\overline{M}_v$) shown in Table 2.

From Table 2, it can be seen that mixing of NR with TSH for 25 minutes caused a reduction of $\overline{M}_v$ from the initial value of 610,000 to 98,000, indicating serious degradation occurring. The mixing time of NR with TSH was then decreased to 15 minutes (10 minutes for addition of TSH and 5

minutes for further homogenisation). The $\overline{M}_v$ (sample D in Table 2) measured after mixing was shown to be 285,000. Although the 15 minutes mixing time still resulted in a significant extent of degradation of NR, this mixing time was used for solid-state hydrogenation of NR, as it was difficult to reduce the mixing time further without sacrificing homogeneity of the rubber/TSH mixture.

2. Hydrogenation of Butadiene Rubber

The mole ratio of TSH to the double bond ([TSH]/[C=C]) was varied as shown in Table 3. Hydrogenation reaction was carried out at two reaction temperatures, 105℃ and 115℃. The reaction time was varied between 60 and 180 minutes. The hydrogenation products were character - ised by ¹H-NMR spectroscopy, and typical spectrum is shown in Figure 1.

From the ¹H-NMR spectrum, % hydrogenations was calculated. The results are given in Table 3.

From Table 3, it will be seen that the [TSH]/[C =C] ratio had the greatest effect on the % hydrogenation of BR. Increasing the [TSH]/[C= C] ratio from 1/3.5 to 1/2.5 and 1/1.5 resulted in increases of the % hydrogenation from 17% to 23%
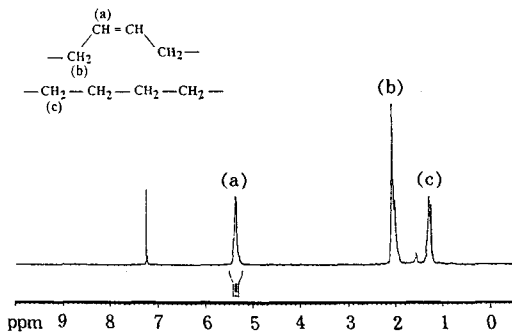
Table 3. Percentage of Hydrogenation of BR

[TSH]/[C=C]	Reaction time (minute)	% Hydrogenation	
		105℃	115℃
1/3.5	0	0	0
	60	15	17
	80	16	17
	100	17	18
	120	16	17
	180	16	17
1/2.5	0	0	0
	60	16	22
	80	19	22
	100	21	21
	120	21	25
	180	22	23
1/1.5	0	0	0
	60	16	29
	80	22	34
	100	26	39
	120	28	31
	180	36	36

Table 4. Comparison Between the Degree of Hydrogenation of BR by Solution Method and by Solid State Method

[TSH]/[C=C]	% Hydrogenation	
	Solution	Solid state
1/3.5	3	17
1/2.5	5	23
1/1.5	10	36

Fig. 1. ¹H-NMR spectrum of partially hydrogenated BR.

and 36%, respectively. The reaction temperature and reaction time had relatively small effects on the % hydrogenation attained in the manner depending on the [TSH]/[C=C] ratio.

Hydrogenation of BR was also carried out in solution for comparison. The results obtained shown in Table 4 revealed that hydrogenation of BR by reactive processing (solid state) gave higher % hydrogenation than hydrogenation carried out in

Table 5. The Percentages of Hydrogenation of NR
Carried out at 115℃

[TSH]/[C=C]	Reaction time (minute)	% Hydrogenation	
		Solid state method	Solution method
1/2	0	0	-
	10	6	-
	20	12	-
	30	16	-
	40	19	-
	50	20	-
	60	20	2
	80	21	3
	100	20	-
	120	20	4
1/1.5	0	0	-
	60	24	-
	80	29	-
	100	34	-
	120	32	-
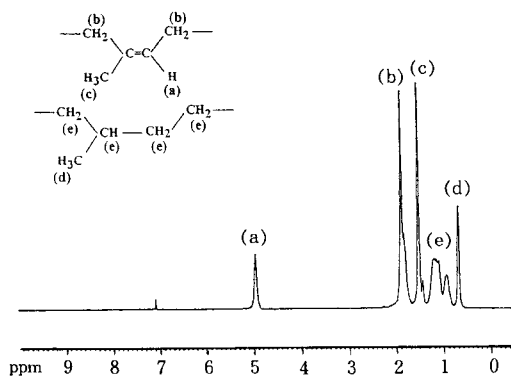
Fig. 2. ^{1}H-NMR spectrum of partially hydrogenated NR.

solution at all [TSH]/[C=C] ratios.

3. Hyrogenation of Natural Rubber

Hydrogenation of NR was carried out at 115℃ with the [TSH]/[C=C] ratio and the reaction time varied as shown in Table 5. The ^{1}H-NMR

spectrum of hydrogenated NR is shown in Figure 2. It can be seen from Table 5 that the % hydrogenation of NR was dependent on the [TSH]/[C=C] ratio. For the [TSH]/[C=C] ratio of 1/2, the maximum % hydrogenation (ca. 20%) was obtained within 40~50 minutes reaction time. When the [TSH]/[C=C] ratio was increased to 1/1.5, the % hydrogenation increased to 24~34%, depending on the reaction time.

Hydrogenation of NR by solution method was also studied for comparison. The results given in Table 5 showed that the % hydrogenation that could be obtained by using the same [TSH]/[C=C] ratio and the same reaction times were 5~10 times lower than those prepared by solid state reactive processing method.

4. Secondary Reaction

It was well-known that hydrogenation by diimide generated from TSH not only saturates the double bonds but also causes cis-trans isomerisation of the 1,4-units.[11] The change of the cis units to the trans configurations in the backbone was determined by Raman spectroscopy and NMR spectroscopy. For the present study, cis-trans isomerisation of polydienes was also found to occur.

In the case of BR, cis-trans isomerisation could obviously be seen from Raman spectrum shown in Figure 3. The Raman bands of cis and trans units appeared at 1650 and 1664cm^{-1}. The peak at 1664cm^{-1} associated with the trans configuration was not observed for BR before hydrogenation.

For cis-trans isomerisation of NR, the shift between ν(C=C) in Raman spectra of cis-trans isomers could not be resolved, therefore, this tech-
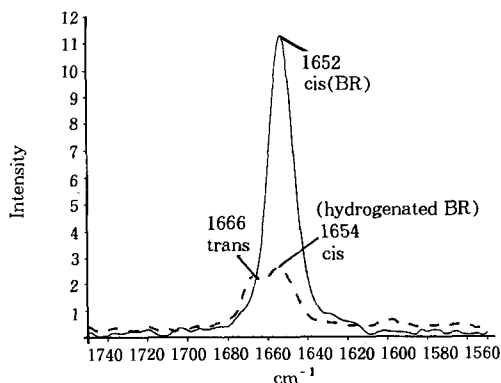
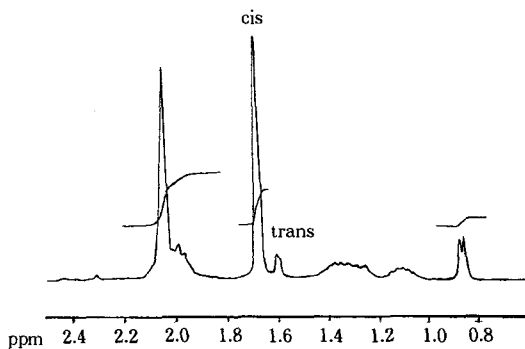Fig. 3. Raman spectra of C=C bonds of BR before and after hydrogenation.

Fig. 4. ¹H-NMR spectrum of the hydrogenated NR.

nique could not be used. On the other hand, in ¹H-NMR, cis and trans isomers of NR appear at 1.7 and 1.6ppm, respectively. Therefore, cis-trans isomerisation of NR could be observed by ¹H-NMR. Figure 4 shows evidence of cis-trans isomerisation of NR during solid-state hydrogenation.

Besides cis-trans isomerisation, it has been reported that use of TSH to hydrogenate unsaturated polymers also gives rise to the other side reaction which is the attack at olefinic sites by p-toluenesulphinic acid, a by-product from the decomposition of TSH. The incorporation of this by-

product can be observed by ¹H-NMR spectroscopy. If addition of p-toluenesulphinic acid to the double bonds occurs, resonance peaks will be observed at 2.4ppm for the paramethyl and at 7.7ppm for the aryl ring protons ortho to the sulphur substituted ring carbon. It can be seen from Figures 1 and 2 that no signal was observed at above positions. Therefore, it may be concluded that no addition of p-toluenesulphinic acid to residual double bonds of BR and NR occurs.

5. Thermal Stability of Hydrogenated BR and NR

One of the major objectives for hydrogenating polydienes is to improve their thermal and oxidative stabilities by reducing the amount of unsaturation in the molecules. Therefore, the thermal stabilities of hydrogenated BR and NR obtained were assessed using DSC.

Figure 5 shows DSC thermograms of BR and its hydrogenated products. The thermal stability was assessed by the onset temperature, the peak temperature and the size of the decomposition peak. Table 6 gives a summary of the onset and maximum temperatures of the decomposition peak.

It can be seen from Table 6 that as the percentage of hydrogenation of the sample increased, the onset temperature and the peak temperature increased slightly. The results obtained, thus, confirmed that hydrogenation of BR did occur which resulted in a decrease in the unsaturation level and hence improvements in the thermal stability of the hydrogenated products.

The thermal stabilities of NR hydrogenated to different levels can be seen from their DSC thermograms shown in Figure 6. The relevant pa-
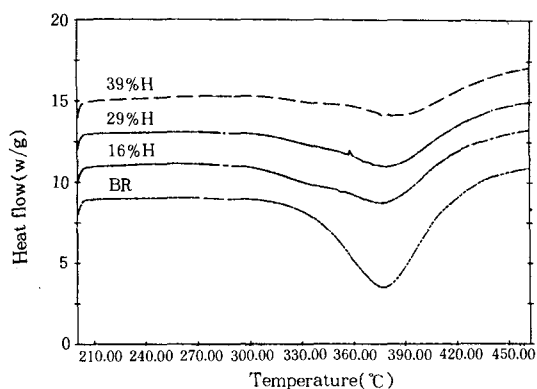
Fig. 5. DSC thermograms of BR and its hydrogenated products at various percentages of hydrogenation under N_2 atmosphere.

Fig. 6. DSC thermograms of NR and its hydrogenated product at various percentages of hydrogenation under N_2 atmosphere.

Table 6. Onset and Maximum Decomposition Temperatures of the Hydrogenated BR at Various Percentages of Hydrogenation Compared With Those of the Original Material

% Hydrogenation	Onset(℃)	T_{max}(℃)
0(BR)	331	377
16	320	376
29	337	379
39	349	383

Table 7. Onset and Maximum Decomposition Temperatures of the Hydrogenated NR of Various Percentages of Hydrogenation Compared With Those of the Original Material (NR)

% Hydrogenation	Onset(℃)	T_{max}(℃)
0(BR)	335	368
6	337	379
19	341	384
29	345	385
32	350	390

rameters measured are displayed in Table 7.

It can be seen from the results of Table 7 that the onset temperatures of decomposition and the corresponding maximum temperatures of hydroge-
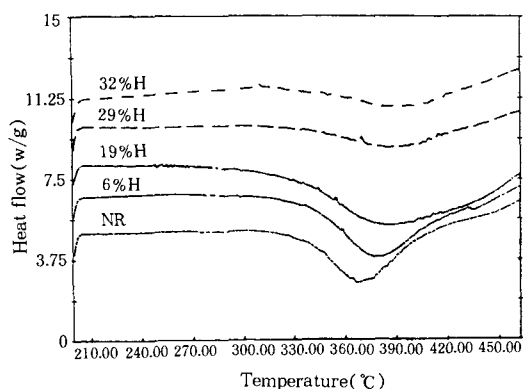
nated NR were higher than those of the unhydrogenated NR. Comparison among the hydrogenated NR shows that both the onset and the peak temperatures of decomposition shift to higher temperature as the % hydrogenation of the sample increases.

Results of the DSC study, thus, suggest that the thermal stability of NR could be improved by hydrogenation, and the extents of improvement increased with increasing level of hydrogenation.

IV. Conclusion

Hydrogenations of BR and NR using p-toluenesulphonylhydrazide as hydrogenating agent were possible by reactive processing. The % hydrogenations attained with both BR and NR depend principally on the [TSH]/[C=C] ratio. The reaction temperatures and reaction times studied had lesser effects. The highest % hydrogenation obtained in the present study were 36% and 32% for BR and NR, respectively. Hydrogenations in solid state were found to yield higher %

hydrogenation than those carried out in solution under comparable conditions. Cis-trans isomerisation was also observed to during hydrogenation of BR and NR by reactive processing. Finally, the thermal stabilities of both hydrogenated products studied were shown to improve over those of the unhydrogenated counterparts, with the degrees of improvement increase with increasing % hydrogenation.

References

1. D. J. Burlett and J. T. Lindt, *Rubber Chem. Technol.,* **66**, 411 (1993).

2. N. K. Singha, S. Bhattacharjee and S. Sivaram, *Rubber Chem. Technol.,* **70**, 309 (1996).

3. H. O. House, "Modern synthetic reactions", ed. by H. O. House, 2 nd ed., p. 228, Benjamin INC., 1972.

4. N. J. Cusack, C. B. Reese, A. C. Risius and B. Roozpeikar, *Tetrahedron Lett.,* **32**, 2159 (1976).

5. H. J. Harwood, D. B. Russell, J. A. Verthe and J. Zymonas, *Makromolekulare Chemie,* **163**, 1 (1973).

6. L. A. Mango and R. W. Lenz, *Makromolekulare Chemie,* **163**, 13 (1973).

7. H. G. M. Edwards, *Macromolecule,* **25**, 525 (1992).

8. J. Podesva, P. Spacek and C. Konak, *J. Appl. Polym. Sci.,* **44**, 527 (1992).

9. H. G. M. Edwards, A. F. Johnson, I. R. Lewis and M. A. Macleod, *Polymer,* **34**, 3184 (1993).

10. S. F. Hahn, *J. Polym. Sci.: Part A.,* **30**, 397 (1992).

11. S. Poshyachinda and V. Kanitthanon, *Spectrochimica Acta,* **50A**(11), 2011 (1994).