Diimide Hydrogenation of Natural Rubber Latex

A. Mahittikul,[1] P. Prasassarakich,[1] G. L. Rempel[2]

[1]Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[2]Department of Chemical Engineering, University of Waterloo, Ontario, Canada N2L3G1

ABSTRACT: Hydrogenation is one important method of chemical modification, which improves the physical, chemical and thermal properties of diene-based elastomers. Natural rubber latex (NRL) could be hydrogenated to a strictly alternating ethylene-propylene copolymer using a diimide reduction system. The diimide reduction technique of NRL was accomplished by using hydrazine hydrate/hydrogen peroxide and Cu^{2+} as catalyst. The hydrogenated products are characterized by FTIR and NMR spectroscopy. It has been found that cupric acetate is a highly active catalyst for the reaction and the addition of a controlled amount of gelatin demonstrated a beneficial effect on the degree of hydrogenation, whereas, sodium dodecyl sulfate (SDS) acted as a stabilizer of the latex particle in the reaction system and reduced the degree of hydrogenation. In the presence of SDS, a longer reaction time and a higher amount of hydrazine hydrate was required for hydrogenation of NRL. Gel formation during hydrogenation does not significantly affect the degree of hydrogenation. Gel inhibitors such as hydroquinone also decrease the degree of hydrogenation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1188–1199, 2007

Key words: hydrazine; hydrogen peroxide; diimide production; cupric ion hydrogenation; natural rubber latex

INTRODUCTION

Hydrogenation of diene-based rubbers helps to improve the thermal and oxidative stability of these polymers when the radical-susceptive C=C are replaced by saturated hydrocarbon bonds. Natural rubber latex (NRL) containing 93–95 wt % of *cis*-1,4-polyisoprene could be hydrogenated to a strictly alternating ethylene–propylene copolymer (EPDM) using a diimide reduction system in latex form. The oxidation of hydrazine provides the active hydrogen species in the form of diimide (NH=NH), which is capable of reducing C=C double bonds.[1] As a potential alternative of the conventional hydrogenation technology, the diimide hydrogenation method, in which gaseous hydrogen, organic solvents, and expensive transition-metal catalysts are not necessary, has received increasing attention in the area of the hydrogenation of polybutadiene-based rubbers in latex form. The reaction between hydrogen peroxide and hydrazine may be used 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.[2] Boric acid tends to be better for promoting the hydrogenation efficiency than do other additives.[3]

Wideman[4] discovered that an elastomer in latex form can be directly converted into its saturated latex form when it was treated with hydrazine hydrate, an oxidant, and a metal ion catalyst (i.e., called the diimide reduction technique) without using a high pressure vessel, organic solvent, or hydrogen gas. Parker et al.[5] proposed a diimide reduction mechanism for hydrogenation of the latex. The diimide hydrogenating agent was generated from the hydrazine/hydrogen peroxide system at the surface of the particles. Carboxylated surfactants adsorbed at the latex particle surface play an important role by forming hydrazinium carboxylates with hydrazine and copper ions. Parker et al.[6] also patented the process for preparation of hydrogenated rubber in latex form. The generated diimide intermediates are stabilized by Cu^{2+} and effectively reduce the carbon–carbon double bonds. He et al.[7] studied the conditions for the hydrogenation of styrene–butadiene rubber (SBR) latex containing some gel via the diimide reduction process. They pointed out that the particle surface was an important parameter in controlling the degree of hydrogenation. The hydrogenation of carbon–carbon double bonds depended on the latex particle size and the extent of crosslinking in the particles. They also found that the gel fraction of SBR latex increased after the hydrogenation. Sakar et al.[8] reported the effects of various reaction conditions for the hydrogenation of SBR latex such as reaction time and temperature, pH of latex, and concentration of the hydrogen peroxide,

hydrazine, and nature of the catalyst on the hydrogenation degree calculated from NMR spectroscopy and also observed the increase in the glass transition temperature with increasing hydrogenation degree due to development of crystalline segments. Xie et al.[9] studied the effect of reaction conditions on both hydrogenation and crosslinking. The use of inhibitors in both the rubber phase and the aqueous phase reduced crosslinking. By using sodium N,N-dimethyl dithiocarbamate and p-tert-butyl-pyrocatechol as the inhibitors, the gel content in the final rubber product could be reduced. Sarkar and co workers[8,10] also presented similar results. Xie et al.[11] investigated the hydrogenation of acrylonitrile–butadiene rubber (NBR) latex by hydrogen peroxide and hydrazine with copper sulfate as catalyst. A hydrogenation degree of 87% was achieved after 6 h at 40°C for a mole ratio of hydrazine to carbon–carbon double bond of 2.5 : 1. Gel formation was a problem for this reaction, thus p-tert-butyl-pyrocatechol was used as an inhibitor for gel formation, and it reduced the % gel from 94.3% to 21.7%. Zhou et al.[12] also studied hydrogenation of NBR latex by hydrogen peroxide and hydrazine with boric acid as catalyst. A hydrogenation degree of 81.3% was achieved within 6 h at 60°C, and only 3% gel content was found when hydroquinone was used as an inhibitor.

This paper reports on a study of the effects of reaction parameters on the degree of NRL via diimide hydrogenation. The properties of the resulting hydrogenated rubber were also examined.

EXPERIMENTAL

Materials

NRL with 60% dry rubber content (DRC) preserved with high ammonia concentration was obtained from Thai Rubber Latex (Bangkok, Thailand). Hydrazine hydrate (>99%) was purchased from Aldrich Chemical Company (Milwaukee, WI). A 30% aqueous solution of hydrogen peroxide was obtained from VWR (Toronto, ON, Canada). Catalysts (cupric sulfate, cupric acetate, cupric chloride, ferric sulfate, cobalt sulfate, magnesium sulfate, zinc sulfate) were used as received from J. T. Baker Chemical (NJ).

Ammonium hydroxide and hexylamine were purchased from Fischer Scientific (Fair Lawn, NJ). Hexadecylacrylamide was prepared from the reaction of acryloyl chloride and hexadecylamine. Acryloyl chloride, hexadecylamine, and amino acid were purchased from Aldrich Chemical Company (Milwaukee, WI). Gelatin was purchased from J. T. Baker Chemical. Hydroquinone and sodium n-dodecyl sulfate (SDS (99%)) were purchased from Aldrich Chemical Company (Milwaukee, WI).

Hydrogenation of NRL

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

Characterization

The final conversion of double bonds (C=C) to single bonds (C—C) in the hydrogenated rubber latex was determined by FTIR. The latex film was cast onto a Zn–Sn plate at atmospheric pressure and dried at room temperature for a FTIR scan obtained with a BIO-RAD Merlin FTS 3000X spectrometer. The final structure of the hydrogenated latex was determined using proton nuclear magnetic resonance spectroscopy (^{1}H NMR). The latex was dissolved in d-chloroform at atmospheric pressure and room temperature and 1H NMR spectra were obtained using a Bruker 300 MHz spectrometer.

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.

The glass transition temperature was obtained from differential scanning calorimetry (DSC) carried out on a Mettler Toledo DSC 822. The sample was initially cooled down to −100°C and then heated up to 20°C with a constant heating rate of 20°C/min under nitrogen atmosphere. Liquid nitrogen was used to achieve the subambient temperature. The glass transition temperature (T_g) was taken as the midpoint of the step in the scan.

The morphology of the sample was observed on a JEM CX100-II electron transmission microscope. The sample was stained with O_sO_4 vapor for 24 h before observation.

RESULTS AND DISCUSSION

FTIR and NMR spectroscopic characterization

Figure 1 illustrates the IR spectra of both NRL and 67.8% hydrogenated NRL (HNRL). The nonhydrogenated latex spectrum shows distinct peaks for the
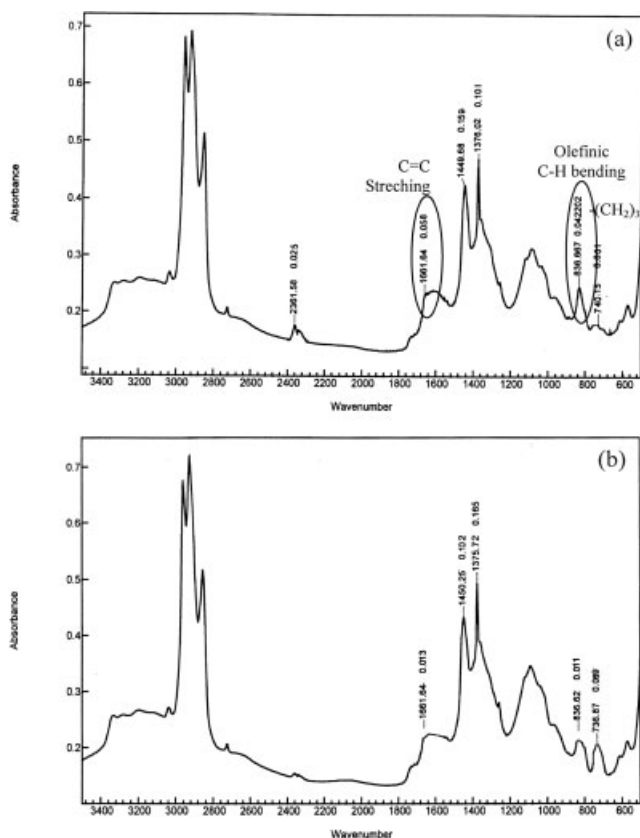
Figure 1 FTIR spectra of (a) NRL and (b) HNRL.

C=C unsaturation, i.e., at 1662 cm^{-1} (C=C stretching) and 836 cm^{-1} (trisubstituted olefinic C—H bending). It can be noted that the absorbance peaks for the C=C unsaturation decrease after the hydrogenation. The augmentation in the band at 737 cm^{-1} attributed to the —(CH$_2$)— species increases as the extent of hydrogenation of C=C increases. 1H NMR spectra for the nonhydrogenated NRL and 67.8% HNRL are provided in Figure 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 —CH$_3$ and saturated —CH$_2$— units. The extent of hydrogenation has been calculated from the 1H NMR spectra by noting the change in the integral of the peaks representing protons for the hydrogenated rubber latex.

Factorial design experiment

To determine the significant reaction factors and the significance of joint factor interactions in the hydrogenation of the latex, a 2^3 factorial experimental design was used.[13] Three principal factors considered to have an effect on the hydrogenation degree of NRL, are concentration of hydrazine [N$_2$H$_4$] concen-

tration of hydrogen peroxide [H$_2$O$_2$], and concentration of rubber as presented in terms of carbon–carbon double bond concentration [C=C]. A two-level factorial design was applied to calculate the effect of the parameters. In this experiment, the level of the factor may be subjectively called '' low (–)'' and ''high (+).'' The ranges of hydrazine concentration, hydrogen peroxide concentration, and rubber concentration were 1.42–3.56M, 1.14–3.56M, and 0.71–2.14M, respectively, as shown in Table I. The reaction temperature was kept constant at 55°C. Cupric sulfate and water concentration were also kept constant at 140.35 μM and 28.49M, respectively. Yate's algorithm was applied to investigate the main effects and interaction effects on the rate constant derived from the experimental data.[14] Table II and III represent 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 III indicate that [N$_2$H$_4$], [H$_2$O$_2$] and [C=C] had a profound influence on the degree of hydrogenation. The [N$_2$H$_4$] and [H$_2$O$_2$] had a positive effect which implied that the degree of hydrogenation increased with an increase in the [N$_2$H$_4$] and [H$_2$O$_2$]. In contrast, [C=C] showed a negative effect on the degree of hydrogenation. The degree of hydrogenation decreased with an increase in [C=C]. Other interactions were moderate for the system. These indicated that the interaction did not give rise to a significant factor effecting the reaction.
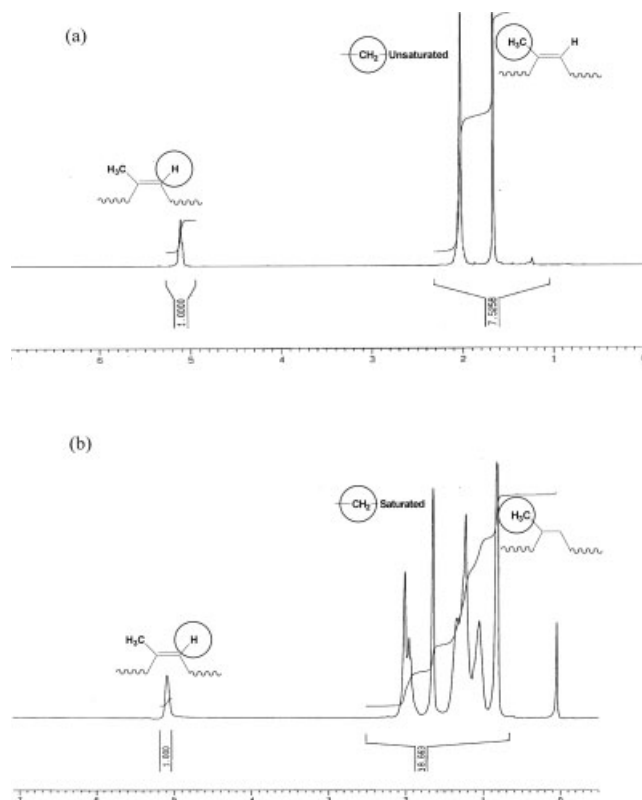

Figure 2 ^{1}H NMR spectra of (a) NRL and (b) HNRL.

TABLE I
Results from 2^3 Factorial Design Experiment for NRL Hydrogenation

Run	[N$_2$H$_4$] (M)	[H$_2$O$_2$] (M)	[C=C] (M)	Degree of hydrogenation (%)
1	1.42	1.14	0.71	38.0
2	3.56	1.14	0.71	51.5
3	1.42	3.56	0.71	46.2
4	3.56	3.56	0.71	69.9
5	1.42	1.14	2.14	24.5
6	3.56	1.14	2.14	31.9
7	1.42	3.56	2.14	27.2
8	3.56	3.56	2.14	42.0
9	1.42	1.14	0.71	37.2
10	3.56	1.14	0.71	50.5
11	1.42	3.56	0.71	47.2
12	3.56	3.56	0.71	70.1
13	1.42	1.14	2.14	23.7
14	3.56	1.14	2.14	32.1
15	1.42	3.56	2.14	26.9
16	3.56	3.56	2.14	42.0

Condition: [H$_2$O] = 28.49M, [CuSO$_4$] = 140.35 µM, T = 55°C, Time = 6 h.

Conversion profile for NRL hydrogenation

The conversion profile for NRL was studied at 55°C in the presence of 1.16M [C=C], 4.67M [N$_2$H$_4$], 4.56M [H$_2$O$_2$], and 23.15M [H$_2$O] (after addition of water, the rubber latex has 14% DRC) using 114 µM cupric sulfate [CuSO4] as a catalyst. The reaction was studied over an interval of time from 0 to 14 h. Figure 3a) shows that the degree 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 increased and then leveled off. The reason for the leveling off of the hydrogenation degree after the first period is possibly a result that diimide was formed as an active species at the surface and then diffused into the outer layer of the latex particles. This concept was also used to explain the degree of hydrogenation after 7 h. At this point, the conversion was quite stable due to the long reaction time that caused the mass transfer limitation of diimide into C=C inside

the latex particle. In addition, the decomposition of diimide during the long reaction time might have occurred. Conversion plots exhibit an apparent first-order dependence for the hydrogenation on C=C concentration. Rate constant (k') has been calculated from the slope of the linear plot of ln(1 – x) versus time [Fig. 3(b)]. The first-order rate equation is shown in eq. (1) where k', a pseudo-first-order rate constant represents the hydrogenation process.

$$\frac{-d[C=C]}{dt} = k'[C=C] \qquad (1)$$

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

Effect of process parameters

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.

Effect of water addition on NRL diimide hydrogenation

The effect of water addition was studied over the range of 0–31M distilled water. The hydrogenation reaction was carried out at 55°C, [H$_2$O$_2$] = 4.55M, [N$_2$H$_4$] = 3.50M, [C=C] = 1.17M and [CuSO$_4$] = 114 µM. The effect of water addition is shown in Figure 4. The result showed that the hydrogenation conversion increased with an increase in the amount of water up until 23.15M water after which hydrogenation conversion decreased. The presence of a small amount of added water in the NRL system reduced the viscous nature of the latex and provided the ease of mixing latex with other substances. It was believed that the cupric ion dispersed in the aqueous phase had higher

TABLE II
Yate's Algorithm Calculation of the 2^3 Factorial Experiment

No.	Design matrix variables			Ave. degree of hydrogenation (%)	Algorithm					Identification
	[N$_2$H$_4$]	[H$_2$O$_2$]	[C=C]		(1)	(2)	(3)	Divisor	Estimate	
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$_2$H$_4$]
3	−1	1	−1	46.8	56.1	36.5	41.2	4	10.3	[H$_2$O$_2$]
4	1	1	−1	70.0	69.0	22.8	16.8	4	4.2	[N$_2$H$_4$]*[H$_2$O$_2$]
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$_2$H$_4$]*[C=C]
7	−1	1	1	27.1	7.9	9.8	−15.3	4	−3.8	[H$_2$O$_2$]*[C=C]
8	1	1	1	42.0	14.9	7.0	−2.8	4	−0.7	[H$_2$O$_2$]*[C=C]*[N$_2$H$_4$]

TABLE III
Calculation of Effects and Standard Errors for 2^3
Factorial Design Experiment

Effect	Estimate	Standard error
Average	41.3	$\pm$1.10 E $-$01
Main effects		
N_2H_4	14.8	$\pm$2.20 E $-$01
H_2O_2	10.4	$\pm$2.20 E $-$01
C=C	$-$20.1	$\pm$2.20 E $-$01
Two-factor interaction		
$N_2H_4*H_2O_2$	4.2	$\pm$2.20 E $-$01
N_2H_4*C=C	$-$3.4	$\pm$2.20 E $-$01
H_2O_2*C=C	$-$3.8	$\pm$2.20 E $-$01
Three-factor interaction		
H_2O_2*C=C$*N_2H_4$	$-$0.7	$\pm$2.20 E $-$01

ability to move around the rubber particles to provide active sites for the occurrence of the hydrogenation reaction. Moreover, water addition 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 23M, it was found that the degree of hydrogenation decreased

Figure 4 Effect of water concentration on NRL hydrogenation. [$CuSO_4$] = 114 μM; [C=C] = 1.17M; [N_2H_4] = 3.50M; [H_2O_2] = 4.55M; T = 55°C for 6 h.

due to the easier dispersion of cupric ion in the aqueous phase than in contact with rubber particles. Thus, the number of active sites for the hydrogenation reaction was reduced. This result was similar to that proposed in Wideman's patent.[4]

Effect of cupric sulfate concentration on NRL diimide hydrogenation

The effect of cupric sulfate concentration on diimide hydrogenation was carried out over the range of 0–684 μM. The hydrogenation reaction was carried out at 55°C, [H_2O_2] = 4.55M, [N_2H_4] = 3.50M, [C=C] = 1.17M and [H_2O] = 23.15M. Figure 5 demonstrates the effect of cupric sulfate concentration and indicates that the copper ion was able to accelerate the formation of diimide from the N_2H_4/H_2O_2 redox system. The copper ion in this system can be present in three locations depending on rubber concentration: (a) in the water medium; (b) at the polymer surface;
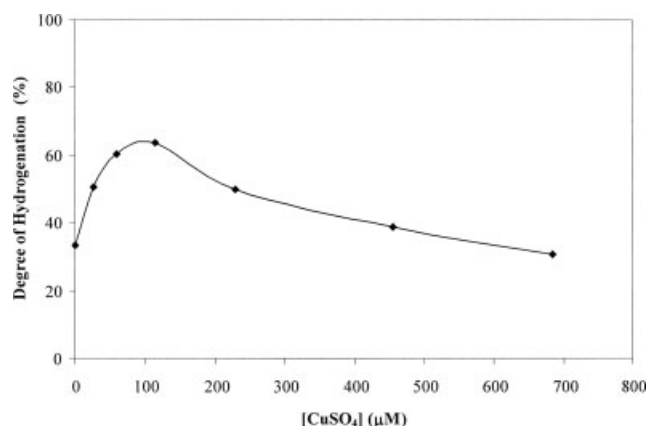

Figure 3 Hydrogenation profile of NRL: (a) conversion profiles and (b) plot of ln(1 $-$ x) as a function of time. [$CuSO_4$] = 114 μM; [C=C] = 1.17M; [N_2H_4] = 4.67M; [H_2O_2] = 4.55M; [H_2O] = 23.15M; T = 55°C.

Figure 5 Effect of cupric sulfate concentration on NRL hydrogenation. [C=C] = 1.17M; [N_2H_4] = 3.50M; [H_2O_2] = 4.55M; [H_2O] = 23.15M; T = 55°C for 6 h.

and (c) inside the latex particle.[7] At high cupric sulfate concentration, copper ion may be present in three locations. On the other hand, copper ion at low cupric sulfate concentration may be present only at 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 eqs. (2) and (3).[9] The disproportionation/decomposition reactions of diimide involve:

$$HN = NH \rightarrow N_2 + H_2 \qquad (2)$$

$$2HN = NH \rightarrow NH_2 - NH_2 + N_2 \qquad (3)$$
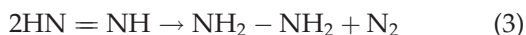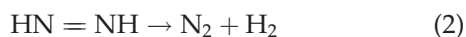
Copper ion added into this system can be distributed over the surface of latex particles by means of a strong complex with the carboxylate soap anions of the surfactant.[5] Thus, the concentration of copper ion at the particle surface is a key factor, which needs to be controlled. To reach a high degree of hydrogenation, the copper ion should reside only at the surface of the latex particle. In this paper, the degree of hydrogenation increased with increasing amount of cupric sulfate concentration up until 114 μM, whereafter the degree of hydrogenation decreased. The rate of diimide formation would be faster at higher concentrations 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 N_2H_4/H_2O_2 reaction (decomposition) to mostly occur in the aqueous phase to result in the reduction of the hydrogenation level of NRL.

Effect of hydrazine concentration on NRL diimide hydrogenation

The hydrazine concentration was varied over the range of 1.2–5.8M. The hydrogenation reaction was carried out at 55°C, [H_2O_2] = 4.55M, [$CuSO_4$] = 114 μM, [$C=C$] = 1.17M and [H_2O] = 23.15M. The effect of [N_2H_4] is shown Figure 6. It was found that the degree of hydrogenation increased with increasing [N_2H_4]. It is possible that the amount of diimide, the active species for hydrogenation process, was increased when the hydrazine was in excess. The rate of the interaction of the diimide species with [$C=C$] was expected to result in an increase in the degree of hydrogenation. Three possible reactions between hydrazine and hydrogen peroxide as shown in eqs. (4)–(6) may confirm this idea.
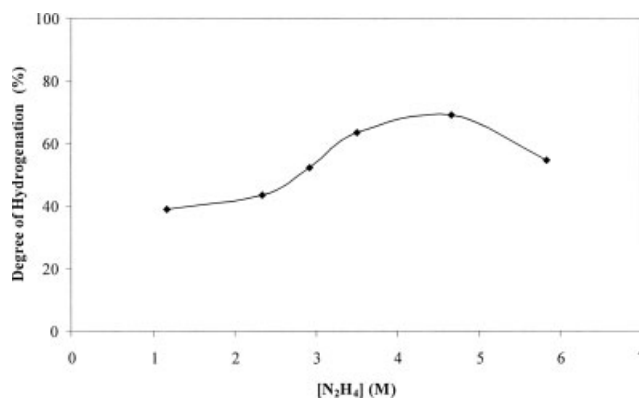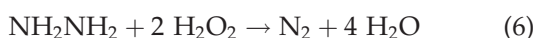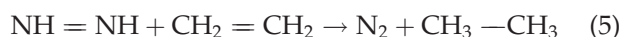
$$NH_2NH_2 + H_2O_2 \rightarrow NH = NH + 2H_2O \qquad (4)$$

$$NH = NH + CH_2 = CH_2 \rightarrow N_2 + CH_3 - CH_3 \qquad (5)$$

$$NH_2NH_2 + 2\,H_2O_2 \rightarrow N_2 + 4\,H_2O \qquad (6)$$

Figure 6 Effect of hydrazine concentration on NRL hydrogenation. [$CuSO_4$] = 114 μM; [$C=C$] = 1.17M; [H_2O_2] = 4.55M; [H_2O] = 23.15M; T = 55°C for 6 h.

In the presence of carbon–carbon double bonds of the isoprene segments in NRL and a metallic ion as a catalyst, reaction (5) was predominant. Diimide species were produced which 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, reaction (6) predominated and a large amount of nitrogen gas was produced. The higher amount of added N_2H_4, the more diimide was produced, and it caused an increase in the degree of hydrogenation. However, the degree of hydrogenation began to slowly decrease when [N_2H_4] was higher than 4.67M. This result can be explained in that the diimide species can self–react at higher concentration of diimide to cause a loss 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.[9] claimed that a higher ratio of rubber and hydrazine was helpful for the decrease in gel formation when a higher degree of hydrogenation of NBRL was attained.

Effect of hydrogen peroxide concentration on NRL diimide hydrogenation

The hydrogenation reaction was carried out by varying hydrogen peroxide concentration over the range of 2.3–11.7M at 55°C, [N_2H_4] = 4.67M, [$CuSO_4$] = 114 μM, [$C=C$] = 1.17M and [H_2O] = 23.15M. Figure 7 shows that the degree of hydrogenation dramatically increased at low [H_2O_2]. Above 6.8M [H_2O_2], the degree of hydrogenation tended to decrease. This occurrence may be attributed from the competitive reaction between hydrazine and H_2O_2 (reactions (5) and (6)). When [H_2O_2] was higher than 6.07M, the degree of hydrogenation decreased due to a possible crosslink reaction, which reduced the number of free carbon–carbon double bonds available for diimide reduction.[8]
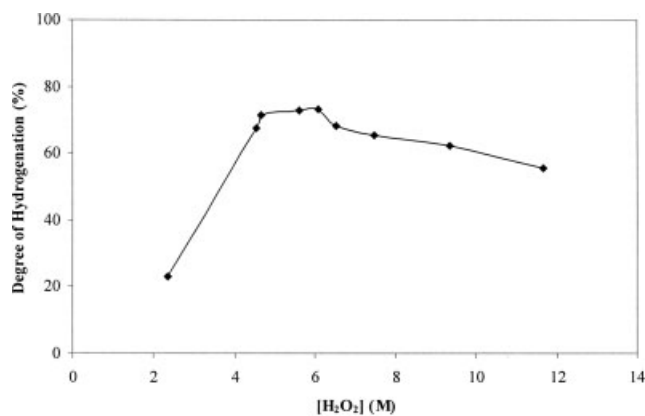
Figure 7 Effect of hydrogen peroxide concentration on NRL hydrogenation. $[CuSO_4] = 114$ μM; $[C=C] = 1.17M$; $[N_2H_4] = 4.67M$; $[H_2O] = 23.15M$; $T = 55°C$ for 6 h.

Moreover, some hydrazine may be consumed by a side reaction (6) at high hydrogen peroxide concentration resulting in a decrease in the degree of hydrogenation. Based on the reaction stoichiometry as shown in eq. (3), the suitable ratio for generation of the diimide species was 1 : 1 of $[N_2H_4]$: $[H_2O_2]$. Parker et al.[2] found the suitable ratio for diimide species in the hydrogenation of NBR latex was 1 : 2, which was the same as the results obtained for hydrogenation of SBR latex reported by He et al.[7] Sakar et al.[10] found the suitable ratio for diimide species to hydrogenate XSBR (carboxylated styrene butadiene rubber latex) was 1 : 2. In this experiment, the optimum ratio of $[N_2H_4]$: $[H_2O_2]$ was b)etween 1 : 0.97 $(4.67M : 4.55M)$ and 1 : 1.29 $(4.67M : 6.07M)$. It was believed that the hydrogen peroxide was easily decomposed, so it was necessary to have an excess of hydrogen peroxide for effective production of diimide under the present reaction conditions used.
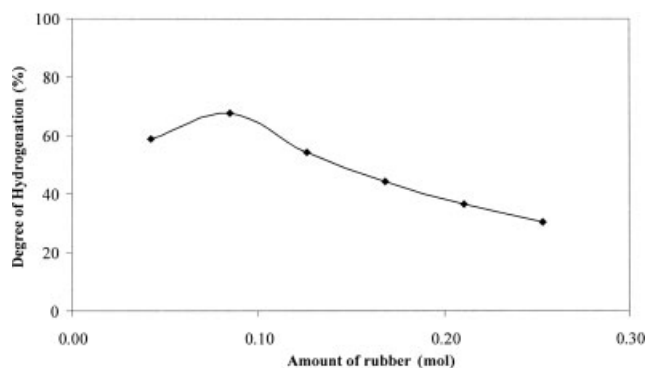
Effect of rubber concentration on NRL diimide hydrogenation

The effect of rubber concentration was studied in terms of rubber volume over the range of 52–153 mL (0.042–0.253 mol) of rubber latex containing 14% DRC in the presence of $H_2O_2 = 0.328$ mol, $N_2H_4 = 0.336$ mol, and $CuSO_4 = 8$ μmol at 55°C for 6 h. The results of these experiments are displayed in Figure 8. These results indicate that the degree of hydrogenation decreased with an increase in rubber volume since it affected the efficiency of diimide species in this system. At high volume of rubber, the diimide species may self-decompose during the hydrogenation process resulting in a low degree of hydrogenation. In contrast, with a small volume of rubber (low rubber concentration), it is possible that diimide hydrogenation reaction occurred in a rubber phase rather than in the aqueous phase. The diimide species was in excess when compared to the rubber species in the system. Therefore, the degree of hydrogenation increased at a low volume of rubber and reached the optimum value at a rubber concentration of 0.08–0.09 mol/L.

Effect of temperature on NRL diimide hydrogenation

The effect of hydrogenation temperature was studied over the range of 45–95°C in the presence of $[H_2O_2] = 4.55M$, $[N_2H_4] = 4.67M$, $[C=C] = 1.17M$, $[CuSO_4] = 114$ μM, and $[H_2O] = 23.15M$. The results of the temperature dependence on the hydrogenation of NRL are shown in Figure 9. The degree of hydrogenation increased initially with increasing temperature. When the temperature was below 55°C, the degree of hydrogenation was quite low. After increasing the reaction temperature above 55°C, the hydrogenation degree increased. These results can be explained on
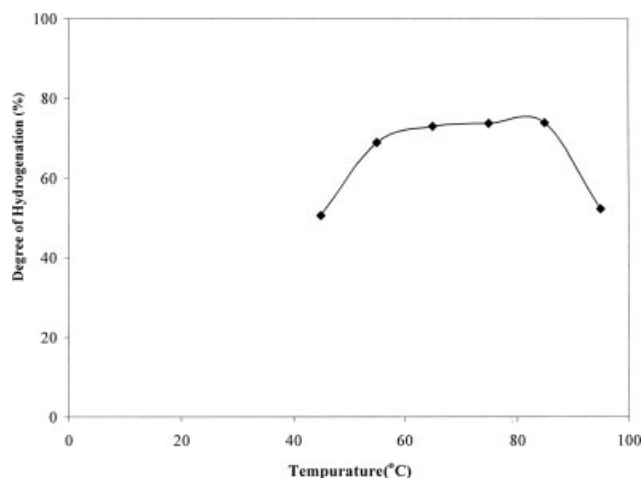

Figure 8 Effect of rubber concentration on NRL hydrogenation: 14.3% DRC of latex; $CuSO_4 = 8$ μmol; $N_2H_4 = 0.336$ mol; $H_2O_2 = 0.328$ mol; $T = 55°C$ for 6 h.

Figure 9 Effect of temperature on NRL hydrogenation $[CuSO_4] = 114$ μM; $[C=C] = 1.17M$; $[N_2H_4] = 4.67M$; $[H_2O_2] = 4.55M$; $[H_2O] = 23.15M$ for 6 h.
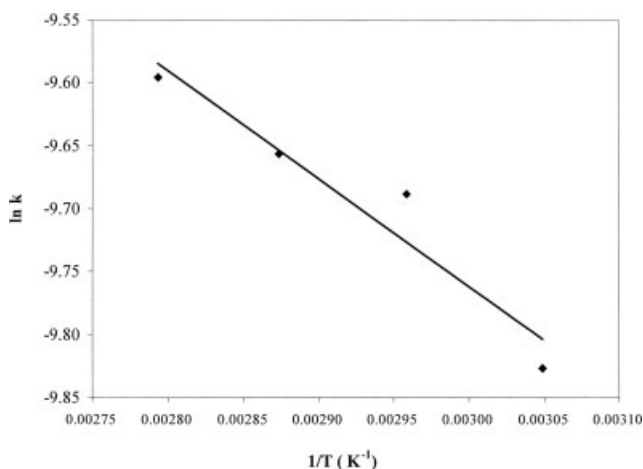
Figure 10 Arrhenius plots for the NR hydrogenation. $[CuSO_4] = 114$ µM; $[C{=}C] = 1.17M$; $[N_2H_4] = 4.67M$; $[H_2O_2] = 4.55M$; $[H_2O] = 23.15M$; $T = 45{-}85°C$ for 6 h.

the basis that the reactant was not effective at low reaction temperature due to collisions of particles. 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_2O_2 tended to decompose more readily and produce free radicals at higher reaction temperature. When the temperature reached 95°C, the degree of hydrogenation was drastically decreased. The suitable temperature for the reaction was in the range of 55–80°C, by which 67.8–80% hydrogenation was achieved within 6 h. The Arrhenius plot is shown in Figure 10. The apparent activation energy calculated from a least square regression analysis of $\ln(k')$ versus $1/T$ was 7.1 kJ/mol providing evidence that the experiments were performed under mass-transfer limitations. The activation energy of NR hydrogenation is lower than that of SBR hydrogenation (9.5 kJ/mol).[8]

Effect of catalyst type

The effect of catalyst type on the degree of hydrogenation was also investigated. Various types of catalysts

TABLE IV
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 µmol, C=C = 84 mmol, N$_2$H$_4$ = 0.336 mol, H$_2$O$_2$ = 0.437 mol, H$_2$O = 1.67 mol, total volume = 90 mL, $T = 55°C$, Time = 6 h.

were examined in the presence of $[C{=}C] = 1.17M$, $[N_2H_4] = 4.67M$, $[H_2O_2] = 4.55M$, $[Catalyst] = 114$ µM, and $[H_2O] = 23.15M$ at 55°C for 6 h. The results are shown in Table IV. These results indicated that the cation and the anion of the catalyst affected the degree of hydrogenation. Table IV shows that the cupric ion and the zinc ion are the most suitable metallic ions for catalyzing the diimide hydrogenation of NRL. The degree of hydrogenation increased with the following order of cations of catalyst: $Mg^{2+} < Fe^{2+} < Cu^{2+}, Zn^{2+}$. For hydrogenation of XSBR latex, Xie et al.[9] claimed that Fe^{2+} was the best catalyst for diimide hydrogenation. The effect of anion has also been studied for given fixed cationic species such as cupric: cupric sulfate, cupric acetate and cupric chloride. From Table IV, the acetate group was found to be the most effective anion for the diimide hydrogenation of NRL. The catalytic activity of the cupric complexes depended upon two properties of the catalyst: the basicity of the ligand, and the strength of the metal ligand interaction.[10] 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 found for diimide hydrogenation of SBR latex.[10]

Effect of impurities

The effect of impurities in the rubber was studied by comparing the degree of hydrogenation between NRL and the deproteinized NRL (DPNRL). The reaction condition was $[H_2O_2] = 4.55M$, $[N_2H_4] = 4.67M$, $[C{=}C] = 1.17M$, $[CuSO_4] = 114$ µM and $[H_2O] = 23.15M$ at 55°C for 6 h. The results shown in Table V indicate that the degree of hydrogenation slightly changed from 67.9% to 69.2% after treating NRL by deproteinization. This implied that impurities such as protein, ammonia, or other nitrogen content in the NRL might not affect the degree of hydrogenation. To confirm this hypothesis, an impurity, such as hexylamine, hexadecylacrylamide, ammonium hydroxide, and amino acid, was added into NRL to increase the impurity level before hydrogenation as shown in Table VI. It shows that such an impurity does not have a significant effect on the degree of hydrogenation.

TABLE V
Effect of Nitrogen Content on Degree of Hydrogenation

Rubber type	Nitrogen content (%)	Degree of hydrogenation (%)
NRL	0.2	67.8
DPNRL	0.02	69.2

Condition: $[N_2H_4] = 4.67M$, $[H_2O_2] = 4.55M$, $[C{=}C] = 1.17M$, $[CuSO_4] = 114$ µM, $[H_2O] = 23.15M$, $T = 55°C$, Time = 6 h. NRL, natural rubber latex; DPNRL, deproteinized natural rubber latex.

TABLE VI
Effect of Nitrogenous Impurities on Degree of Hydrogenation

Substance	Degree of hydrogenation (%)
–	67.9
Hexylamine	66.6
Hexadecylacrylamide	65.8
Ammonium hydroxide	65.4
Amino acid	64.6

Condition: $[N_2H_4] = 4.67M$, $[H_2O_2] = 4.55M$, $[C=C] = 1.17M$, $[CuSO_4] = 114 \mu M$, $[H_2O] = 23.15M$, [Substance] $= 0.5M$, $T = 55°C$, Time = 6 h.

Since H_2O_2 is a strong oxidant, it probably oxidizes the added impurities. In contrast, such impurities have a significant effect on hydrogenation of NRL catalyzed by $OsHCl(CO)(O_2)(PC_{y3})_2$ in the presence of the hydrogen molecule.[15]

Effect of gelatin

The effect of gelatin addition was studied over the range of 0–73 μM in the presence of $[H_2O_2] = 4.55M$, $[N_2H_4] = 4.67M$, $[C=C] = 1.17M$, $[CuSO_4] = 114 \mu M$, and $[H_2O] = 23.15M$ at 55°C for 6 h. Figure 11 shows that the degree of hydrogenation increased when a small amount of gelatin was added into the system. About 74.5% hydrogenation was achieved after adding 7 μM of gelatin. It is possible that the addition of gelatin to 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 increase in the degree of hydrogenation. When gelatin was added in a concentration higher than 7 μM, the degree of hydrogenation was found to decrease. At such a higher level of gelatin, gelatin inhibited the active site of the cupric ion at the surface of the rubber particle.
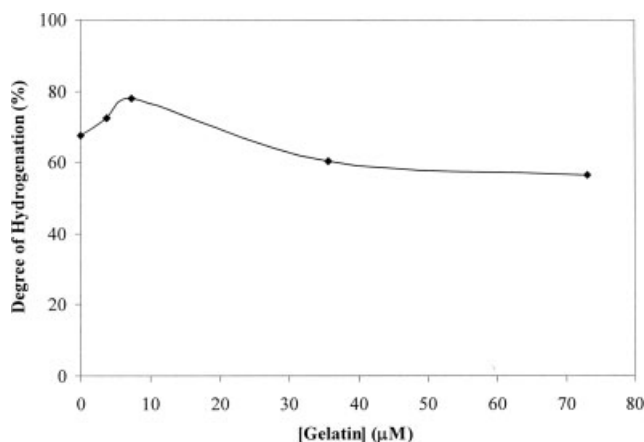
Effect of SDS

The surfactant SDS was used as a stabilizer of the rubber particle and cupric ion in the system. Parker et al.[5] studied the role of surfactant in the diimide hydrogenation process. It was found that the surfactant had a function in stabilizing the cupric ion on the rubber particle. The effect of SDS concentration has been studied from 0 to 1.97 μM in the presence of $[H_2O_2] = 4.55M$, $[N_2H_4] = 4.67M$, $[C=C] = 1.17M$, $[CuSO_4] = 114 \mu M$, and $[H_2O] = 23.16M$ at 55°C for 6 h. It was found that the increase in the SDS concentration decreased the degree of hydrogenation as shown in Figure 12. It was possible that the surfactant formed a micelle trap for cupric sulfate which led to a reduction of the amount of diimide species. This caused a decrease in the degree of hydrogenation. Moreover, the rubber particle had a phospholipid as outer layer. 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.

Effect of hydroquinone

Inhibitor was added to the diimide hydrogenation system in an attempt to capture free radicals, then reduce gel content and increase the degree of hydrogenation.[9] Xie et al.[11] used *p-tert-butyl*-pytocatechol as an inhibitor for gel formation. The results indicated that the gel content was reduced from 94.3% to 21.7% for hydrogenation of NBR latex. Zhou et al.[12] also found that the inhibitor could reduce gel content from 80% to 3% and a high conversion of hydrogenation of NBR latex could be achieved. Hydroquinone was applied in an attempt to improve the hydrogenation of NRL. The amount of hydroquinone was studied over the range of 0–12.61 μM in the presence of
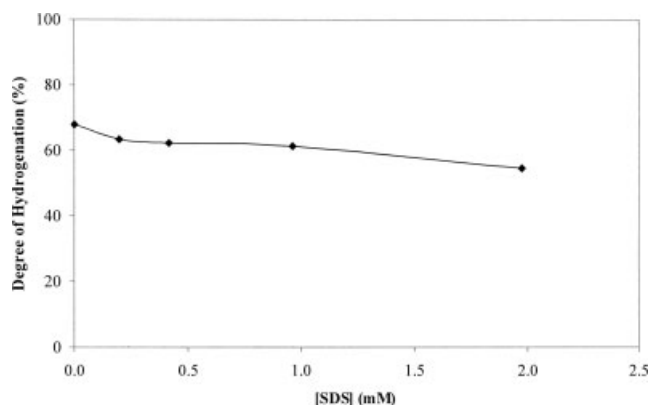

Figure 11 Effect of gelatin concentration on NRL hydrogenation $[CuSO_4] = 114 \mu M$; $[C=C] = 1.17M$; $[N_2H_4] = 4.67M$; $[H_2O_2] = 4.55M$; $[H_2O] = 23.15M$; $T = 55°C$ for 6 h.

Figure 12 Effect of SDS concentration on NRL $[CuSO_4] = 114 \mu M$; $[C=C] = 1.17M$; $[N_2H_4] = 4.67M$; $[H_2O_2] = 4.55M$; $[H_2O] = 23.15M$; $T = 55°C$ for 6 h.
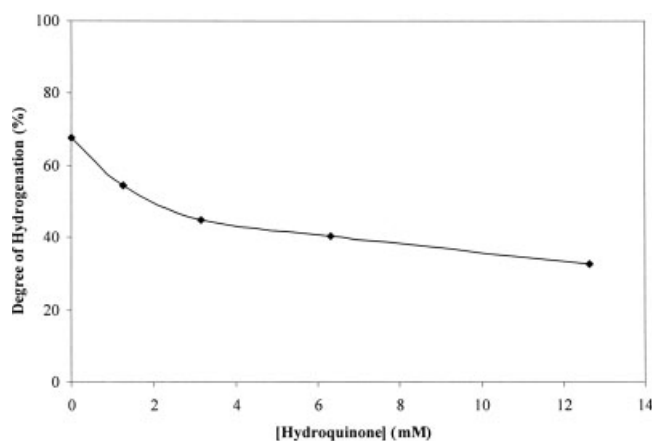
Figure 13 Effect of hydroquinone on NRL hydrogenation [CuSO$_4$] = 114 µM; [C=C] = 1.17M; [N$_2$H$_4$] = 4.67M; [H$_2$O$_2$] = 4.55M; [H$_2$O] = 23.15M; T = 55°C for 6 h.

[H$_2$O$_2$] = 4.55M, [N$_2$H$_4$] = 4.67M, [C=C] = 1.17M, [CuSO$_4$] = 114 µM, and [H$_2$O] = 23.15M at 55°C for 6 h. Figure 13 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 may be possible that hydroquinone captured the diimide species in this system and caused a reduction in the NRL hydrogenation level.

Distribution of carbon–carbon double bonds in hydrogenated NRL particles

The distribution of carbon–carbon double bonds of NRL particles during diimide hydrogenation was studied. The condition in the first treatment was [H$_2$O$_2$] = 4.55M, [N$_2$H$_4$] = 4.67M, [C=C] = 1.17M, [CuSO$_4$] = 114 µM, [H$_2$O] = 23.15M at 55°C for 6 h. The product from the previous treatment was used as the starting material for the next treatment at the same reaction condition (55°C for 6 h) with the amount of H$_2$O$_2$ = 0.328 mol, N$_2$H$_4$ = 0.336 mol, CuSO$_4$ = 8 mmol. Figure 14 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. The increase in the hydrogenation level between treatments was determined as 11.6% (for the first and second treatments), as 4.6% (for the second and third treatments) and as 1.7% (for the third and fourth treatments). The increase 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 a uniform model and a layer model.[7] 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 the forth treatments are very close to the same value. For the layer model, the differences of hydrogenation level between the first and second treatment, the second and the third, and the third and the forth treatments are very different and decrease.

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. After the first treatment, the concentration of the carbon–carbon double bonds in this layer was lower than that of the inner portion of the particle. As a result, the disproportionation reaction among diimide molecules became more competitive in this layer and consequently, resulted in a small increase in hydrogenation level after the second and third treatments. An alternative explanation for this observation may be that the diimide remained copper bonded. The same result was also found in the hydrogenation SBR latex.[7]

Figure 15 shows TEM micrographs of the NRL latex particles before hydrogenation (a), hydrogenation after the first treatment (b), and forth treatment (c). Since O^{s}O$_4$ staining agent can only stain the carbon–carbon double bonds, the lightly colored domain indicates the region of lower carbon–carbon double bond concentration. For the comparison, NRL and HNRL at hydrogenation degree of 67.8% (first treatment) and 85.7% (forth treatment) are shown in this figure. NRL showed relatively sharp particle edges because the concentration of the O^{s}O$_4$ inside the particle was high. On the other hand, 85.7% hydrogenated latex exhibited much lighter color due to the small amount
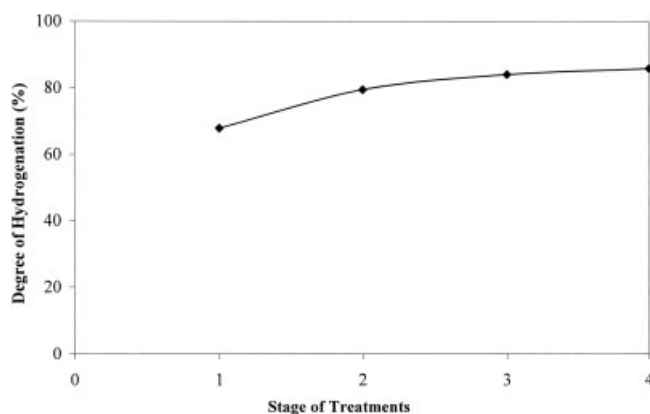

Figure 14 Effect of treatment number on NRL hydrogenation: First treatment [CuSO$_4$] = 114 µM; [C=C] = 1.17M; [N$_2$H$_4$] = 4.67M; [H$_2$O$_2$] = 4.55M; [H$_2$O] = 23.15M; T = 55°C for 6 h; second, third, and forth treatment CuSO$_4$ = 8 µmol; N$_2$H$_4$ = 0.336 mol; H$_2$O$_2$ = 0.328 mol; T = 55°C for 6 h.
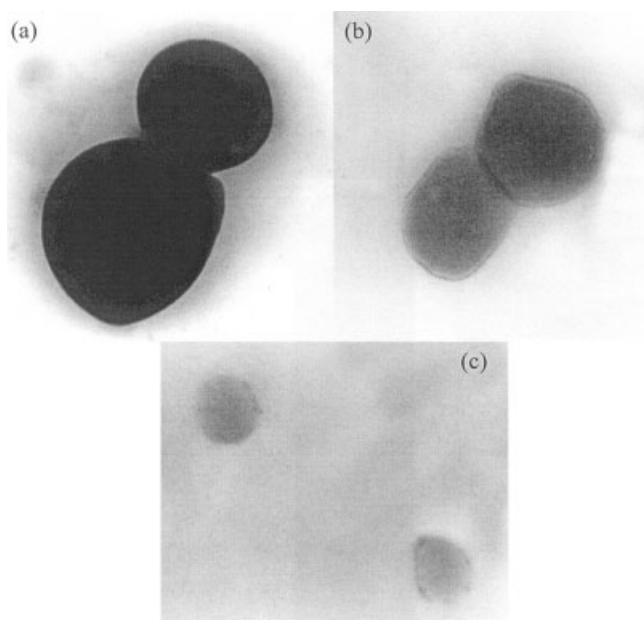
Figure 15 TEM micrographs of (a) NRL, (b) 67.8% HNRL, and (c) 87.5% HNRL (magnification: 2000×).

of carbon–carbon double bond for O^sO_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 seems to be hydrogenated from the outer surface to the center of rubber particle according to the layer model.

Properties of hydrogenated NRL via thermal analysis

Thermal analysis was used to investigate some physical properties of the HNRL. These experiments were carried out using a differential scanning calorimeter (DSC) and thermogravimetric analysis apparatus (TGA) to find the glass transition temperature (T_g) and decomposition temperature, respectively. The
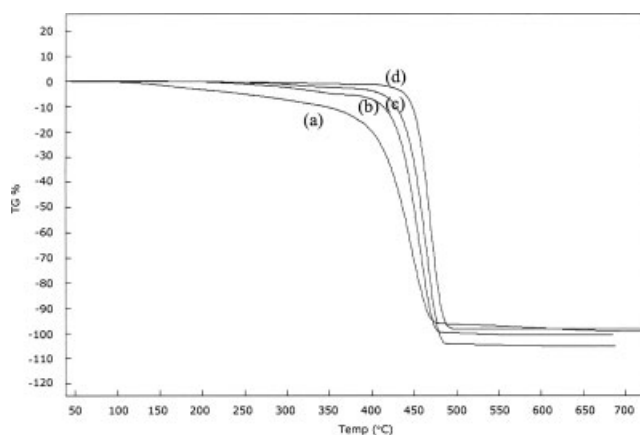

Figure 16 TGA thermograms of NR and HNR at various percentages of hydrogenation: (a) NRL, (b) 37.9% HNRL, (c) 67.8% HNRL, and (d) 87.5% HNRL.
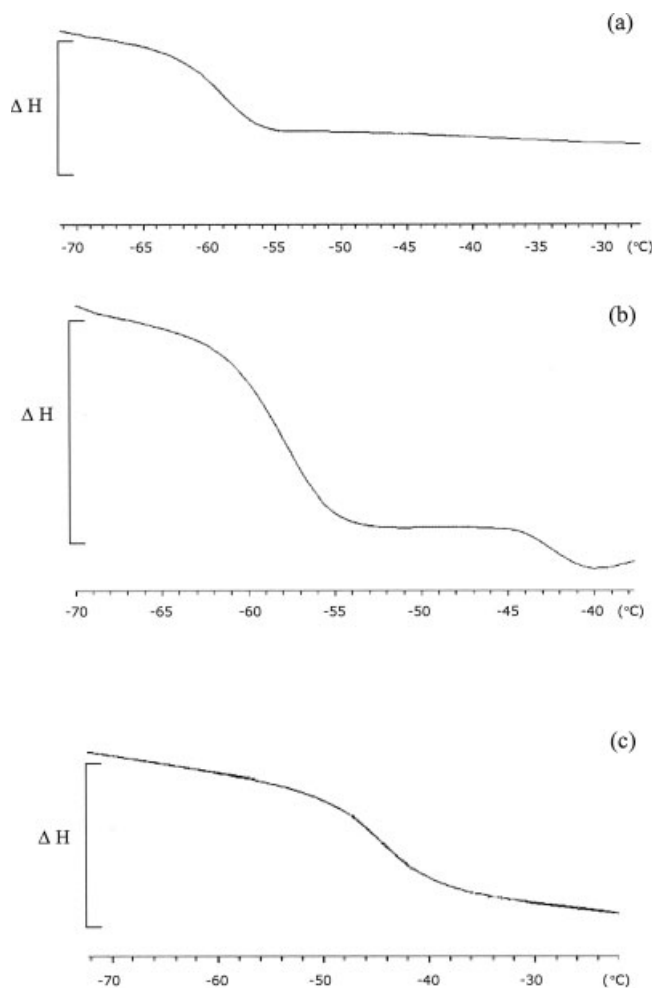
Figure 17 DSC thermograms of (a) NR, (b) HNRL (67.8%), and (c) EPDM.

results of decomposition temperature and T_g of HNRL are shown in Figures 16 and 17 and Table VII.

TGA of NRL, HNRL, and an EPDM was conducted under a nitrogen atmosphere. The TG curves for HNR samples at various % hydrogenations are shown in Figure 16. It can be seen that the polymer degradation occurred via an overall one-step reaction since the TG curve of the samples exhibited one-step and provided smooth weight loss curves. The initial

TABLE VII
Glass Transition Temperature and Decomposition Temperature of Rubber Samples

Rubber	Hydrogenation (%)	T_g (°C)	T_{id} (°C)	T_{max} (°C)
EPDM*	–	−44.6	452.7	470.7
NR	–	−62.3	357.2	380.9
HNR	37.9	−44.7, −64.2	368.6	403.5
	67.8	−44.7, −62.8	390.4	423.3
	87.5	−44.6, −61.9	420.5	451.2

*EPDM has an ethylene/propylene ratio of 50/50 and diene content of 9.5%.

decomposition temperature (T_{id}) was determined from the intersection of the tangent at the onset of the decomposition process. The maximum decomposition temperature (T_{max}) of each sample was obtained from the peak maxima of the derivative of TG curves. The results in Table VII show that both Tid and Tmax of HNR samples increased with an increase in the reduction of carbon–carbon double bonds in NRL. Therefore, the hydrogenation can improve the thermal stability of NRL.

The glass transition temperature, T_g, is one of the most important parameters for characterization of the polymer structure. The T_g is a transition related to the motion in the amorphous section in the polymer. It is determined from the midpoint of the baseline shift of the DSC thermogram. Figure 17b shows the DSC thermogram of the HNRL sample. The DSC thermogram of HNRL sample indicates a two step base-line shift. The first step was at $-60°C$ and the second step was at $-44°C$. This suggested that the HNR sample had two glass transition temperatures. It may be implied that two types of rubber occurred after hydrogenation process. As mentioned above, the rubber was hydrogenated according to a layer model, which therefore has hydrogenated and nonhydrogenated parts. For the hydrogenated part, the glass transition temperature (T_g) of the amorphous rubber phase gradually increased. There was an increase of T_g by $15°C$ which is close to that of EPDM (ethylene/propylene = 50/50, diene = 9.5%), as shown in Figure 17c. It is possible that the amorphous segments were gradually being replaced by the crystalline unit in HNRL. In case of the nonhydrogenated part, the glass transition temperature did not change and it had the same glass transition temperature as NRL at $-60°C$ as shown in Figure 17a.

CONCLUSIONS

Diimide hydrogenation is an alternative route for hydrogenation of NRL in which molecular hydrogen is not required. Around 67.8% of double bond reduction was achieved within 6 h under appropriate reaction conditions. The conversion profile was shown to be first order with respect to C=C concentration. 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 higher when cupric acetate was used as a catalyst. Impurities in the NRL 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 gelatin concentration of 7–9 μM for effective diimide production. The addition of SDS was found to decrease the degree of hydrogenation. The diimide hydrogenation of NRL provides a method to improve the thermal stability of natural rubber. From the TEM micrograph of the HNRL particles, a nonhydrogenated rubber core and a hydrogenated outer layer were observed according to the layer model which also represents the hydrogenation of large SBR lattices.

References

1. Hunig, S.; Muller, H. R.; Thier, W. Angew Chem Int Ed Eng 1965, 4, 271.
2. Parker, D. K; Purdon, J. R. (to The Goodyear Tire & Rubber Co.) U.S. Pat. 5,039,737 (1991).
3. Belt, J. W.; Vermeulen, J. A. A.; Koestermann, M. K. WO 00/09576 (2000).
4. Wideman, L. G. (to The Goodyear Tire & Rubber Co.) U.S. Pat. 4,452,950 (1984).
5. Parker, D. K.; Robert, R. F. Rubber Chem Technol 1992, 65, 245.
6. Parker, D. K.; Ruthenvurg, D. M. (to The Goodyear Tire & Rubber Co./Olin Corp.) U.S. Pat. 5,424,356 (1995).
7. He, Y.; Daniels, E. S.; Klein, A.; El-Asser, M. S. J Appl Polym Sci 1997, 64, 2047.
8. Sarkar, M. D.; De, P. P.; Bhowmick, A. K. J Appl Polym Sci 1997, 66, 1151.
9. Xie, H.Q.; Li, X.; Guo, J. J Appl Polym Sci 2002, 83, 1375.
10. Sarkar, M.D.; De, P.; Bhowmick, A. Polymer 2000, 41, 907.
11. Xie, H.Q.; Li, X. D.; Guo, J. S. J Appl Polym Sci 2003, 90, 1026.
12. Zhou, S.; Bai, H.; Wang, J. J Appl Polym Sci 2072 2004, 91.
13. Montgomery, D. C. Design and Analysis of Experiments; Wiley: New York, 2001.
14. Mason, R. L.; Gunst, R. F.; Hess, L. H. Statistics Design and Analysis of Experiments; Wiley: New York, 1989.
15. Mahittikul, A.; Prasasarakich, P.; Rempel, G. L. J Appl Polym Sci 2006, 100, 640.