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SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF HYDROGENATED LIQUID NATURAL RUBBER

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ABSTRACT

Liquid natural rubber (LNR) is a low-molecular-weight polymer resulting from degradation of natural rubber (NR) with a similar monomer along the backbone chain. Hydrogenated LNR (HLNR) was synthesized from LNR, in which diimide generated through the thermolysis of *p*-toluenesulfonyl hydrazide (TSH) served as the source of hydrogen. The products' structure was confirmed on the basis of changes in main peaks featuring carbon–carbon unsaturated bonds in Fourier-transform infrared and nuclear magnetic resonance spectra after hydrogenation. Gel-permeation chromatography showed that HLNR had a lower molecular weight ($M_w < 10^4$) than LNR ($M_w < 10^5$) and NR ($M_w > 10^6$) because of chain degradation during hydrogenation. The targeted conversion percentage ($>90\%$) was attained by manipulating the reaction parameters. A ratio of 3:1 TSH/LNR was optimum for achieving a high percentage of hydrogenation at 130 °C in a 6 h reaction period. Thermogravimetric analysis indicated that the hydrogenation process increased the degradation temperature of LNR. HLNR also can act as a compatibilizer to improve the miscibility of natural rubber/polystyrene blends based from an optical microscope. [doi:10.5254/rct.15.84869]

INTRODUCTION

Current plastic and rubber industries mainly use various synthetic rubbers produced from petroleum instead of natural rubber (NR) because of the relative ease of processing and resulting high throughput offered by synthetic rubbers in manufacturing. For example, the monomer of isoprene is isolated from the C5 hydrocarbon obtained from petroleum cracking. The isoprene monomer is then dimerized to form dipentene or used as a monomer to produce synthetic *cis*-1,4-polyisoprene.¹ C5 hydrocarbon can be isolated from synthetic rubber only because of the complex chemistry of the latter. However, the costs of using synthetic rubbers are higher than those for NR. Therefore, sustainable development initiatives have recently promoted the use of the natural products such as NR in industrial manufacturing. NR is a natural organic compound that consists of *cis*-1,4-polyisoprene as the main component, which exhibits excellent elasticity, resistance to tearing, and desirable dynamic properties. NR also contains nonrubber components such as phospholipids and proteins, which have a strong influence on the material properties.² However, the application of NR is limited because it can be easily degraded by ozonolysis, exposure to light, and oxidation owing to the presence of double bonds in its chain. Therefore, researchers have focused on chemical modification of NR to improve these properties.

Liquid natural rubber (LNR) is a form of NR with a microstructure similar to NR but with shorter polymeric chains, and the molecular weight is lower than 100 000 u. Because its viscosity is lower than 1500 P at temperatures below 100 °C, LNR is also defined as an NR precursor or modified NR that can be pumped or poured without assistance from an external medium such as a solvent.³ Nor and Ebdon⁴ reported that LNR can flow at room temperature, which makes it much easier to mix and cheaper to process than NR. Several techniques are used to synthesize LNR from NR such as redox, thermal oxidation, ozonolysis, and photo-oxidation. Phinyocheep and Duangthong⁵ prepared LNR by oxidative degradation (redox) of natural rubber latex (NRL), using

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a system consisting of phenylhydrazine (reducing agent) and O_2 . A more advanced method uses the pyrolysis of *cis*-1,4-polyisoprene by controlled thermal depolymerization (thermal oxidation) at 300–380 °C, and the product formed is liquid polyisoprene, which has a lower molecular weight compared with the starting material.⁶ Solanky and Singh⁷ stated that oxidative degradation can be carried out with the ozone controlling to produce LNR. Ozonolysis reaction toward polymer usually was followed by curing with an oxidative agent such as O_2 , H_2O_2 , or potassium iodide in acetic acid or a reducing agent such as triphenylphosphine, Zn, $NaBH_4$, or $LiAlH_4$. Ibrahim and Dahlan⁸ also reported that LNR can be produced via photo-oxidative degradation of NR using UV light.

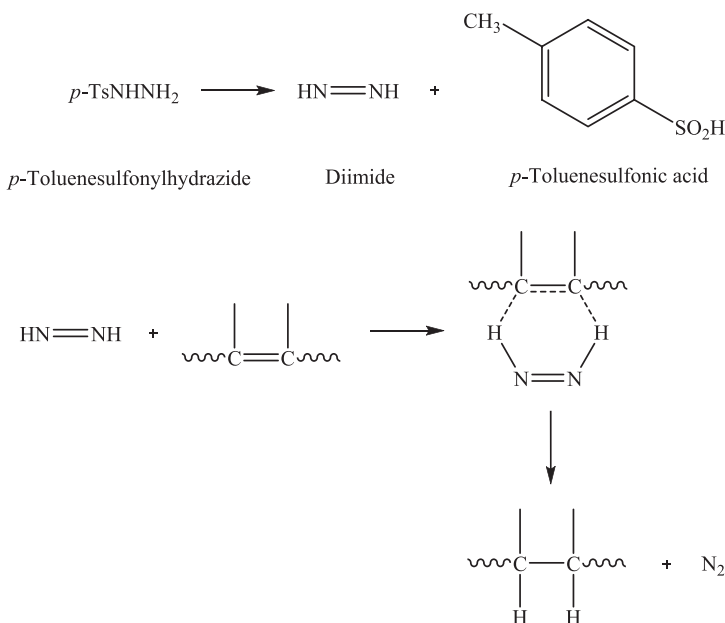
Hydrogenation is one of the promising techniques for countering the drawbacks of NR by changing its unsaturated structure completely to a polypropylene–polyethylene (PP–PE) copolymer or partially to saturated LNR. This type of modification can also be an alternative way to obtain the synthetic terpolymer, ethylene–propylene–diene-monomer (EPDM), which has a higher decomposition temperature than NR. Therefore, hydrogenated natural rubber (HNR) has a high potential to serve as a new “green polymer” to replace synthetic EPDM in the polymer industry. The hydrogenated structure of the newly synthesized HNR can also enhance the properties of NR, such as increased resistance to oxidation and increased degradation temperature, which make it more thermally stable. In this work, LNR was used instead of NR because its short polymeric chains form a cleaner structure that is free of nonrubber and complex ions, making it is easier to control the hydrogenation process.

Researchers have recently developed both catalytic and noncatalytic hydrogenation toward diene elastomers.⁹ Most of the hydrogenations were carried out through the catalytic method, which requires a specific reactor such as a glass reactor, an autoclave reactor, or a Parr reactor. Joó¹⁰ hydrogenated olefins using water-soluble tertiary phosphine complexes of rhodium and ruthenium; Kongparakul et al.¹¹ hydrogenated NRL using a second-generation Grubbs catalyst; Wang et al.¹² hydrogenated the copolymer acrylonitrile–butadiene (NBR) latex in the absence of an organic solvent using Wilkinson’s catalyst. Singha and Sivaram¹³ also produced hydrogenated NBR latex under mild conditions by using water-soluble analog of Wilkinson’s catalyst. Gan et al.¹⁴ also reported hydrogenation using a co-catalyst, in which the nickel 2-ethylhexanoate catalyst was used together with triisobutylaluminum.

However, catalytic hydrogenation is usually very expensive because the reaction uses transition metal-activated hydrogen, which is a rare material. Meanwhile, noncatalytic hydrogenation can be carried out by using a much cheaper reagent. For example, Mahittikul et al.¹⁵ reported that the diimide generated in situ can be used to hydrogenate NRL by thermolyzing *p*-toluenesulfonyl hydrazide (TSH). TSH is a commonly used reagent for hydrogenation as it can release a diimide (N_2H_2) intermediate when degraded at about 100 °C, which subsequently acts as a source of hydrogen, as shown in Scheme 1. Recent work on hydrogenation of LNR via diimide sources (TSH and 2,4,6-trimethylbenzenesulfonyl hydrazide) also has been carried out by Azhar et al.¹⁶

The isoprene–styrene diblock copolymer is hydrogenated by the diimide that is generated in situ via thermolysis of TSH.¹⁷ TSH has also been widely used for the hydrogenation of various types of polymers. A diimide derivative of TSH was used in the hydrogenation of cyclopentene resulting from metathesis polymerization.¹⁸ Samran et al.¹⁹ also hydrogenated NR and various epoxidized natural rubbers using diimide generated in situ in the thermal decomposition of TSH. The major advantages of diimide are its ability to reduce $C=C$ double bonds and its nonreactivity toward the functional group that interferes with the catalyst of hydrogenation. Therefore, owing to its selectivity, diimide offers a suitable alternative to catalytic hydrogenation.²⁰

The main objective of this work is to study the reaction conditions that can induce efficient hydrogenation of LNR, using TSH as a source of hydrogen. LNR was used in this research instead of



SCHEME 1. — Thermolysis of TSH and hydrogenation of unsaturated polymer by diimide.

NR because of its cleaner structure after depolymerization process that remove unwanted molecules inside NR such as agglomerated, coagulated, back-biting, and cyclized polyisoprene that blocked the certain area inside NR. By removing these unwanted species, the blocked area inside NR can be accessed to perform other reactions, such as hydrogenation. The effects of TSH concentration, reaction time, and reaction temperature on the percentage of hydrogenation were examined. The targeted conversion percentage (>90%) of HLNR was achieved by manipulating these three parameters. The effectiveness of the hydrogenation product as a filler in blending between NR and polystyrene (PS) also was studied. Tensile strength of the NR/PS blend was slightly improved after HLNR was added as a filler. From the morphology study using an optical microscope, the homogeneity of the NR/PS/HLNR blend was better compared with without any filler.

EXPERIMENTAL

MATERIALS

Natural rubber grade SMR L was supplied by the Malaysia Rubber Board. Reagent grade toluene (>99%), methanol (>99.8%), and ethanol (95%) were purchased from RM Chemical (Himachal Pradesh, India) and used as received. Reagent grade methylene blue ($\geq 95\%$), rose bengal (95%), and TSH (97%) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received. Polystyrene grade Idemitsu PS was supplied by Petrochemicals (Malaysia) SDN BHD.

PREPARATION OF LNR

NR was soaked in toluene until it was completely swollen. A catalytic amount of methanol (10 mL), rose bengal (0.100 g), and methylene blue (0.066 g) was added to the swollen NR. The mixture of NR was stirred for 10 d using a mechanical stirrer with 10–30 rpm under visible light at room temperature. NR slowly degraded to LNR with time; the product was then centrifuged at 6000 rpm to separate the gel formed during photodegradation. Preparation of LNR in these

studies referred to the photo-oxidative degradation method developed by Ibrahim and Dahalan in 1998.⁸ The method of Ibrahim and Dahalan manipulated light for the degradation of NR, and several functional groups such as hydroxyl and carbonyl were formed during the process. These active groups play the main role for improving blending miscibility between two or more polymers that are immiscible because the only interaction is expected to come from the active sites of LNR.⁸

HYDROGENATION OF LNR

A solution of LNR with 10% dried rubber content was prepared. Different amounts of TSH were added to a fixed volume of LNR solution at TSH/LNR weight ratios of 1:1 to 4:1 to examine the effect of TSH concentration on the percentage of hydrogenation. Each mixture was heated to a temperature between 110 and 150 °C and stirred (500–750 rpm) for 1–7 h. The products were filtered and coagulated with ethanol to remove the residual TSH. Finally, it was dried in a vacuum oven to remove any remaining solvent.

BLENDED OF NR/PS

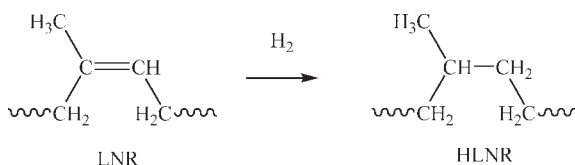
First, NR and PS of several compositions were inserted into a Thermo Haake Rheomix machine for 15 min at 50 rpm and 160 °C. After that, the products of blending were pressed until 50 kgf/cm² at 150 °C to form a molding for the tensile (ASTM D412-68 type B) test. These steps were repeated for the blending of NR/PS/LNR and NR/PS/HLNR.

INSTRUMENTATIONS AND CHARACTERIZATIONS

The structure of the products was determined by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. FTIR spectroscopy was used to determine different transformations in the functional group after hydrogenation, while NMR spectroscopy was used to examine the microstructure of the product. In addition, integration of signals from proton NMR (¹H-NMR) was used to estimate the percentage of conversion from LNR to HLNR. FTIR samples were prepared by brushing them on a NaCl glass plate, and their spectra were obtained using an FTIR spectrometer (Spectrum BX, PerkinElmer, Waltham, MA, USA). Samples were dissolved in CDCl₃ for measurements with the NMR spectrometer (JNM-ECP 400, JEOL, Japan). Gel-permeation chromatography (GPC) was used to obtain the average molecular weights (M_w) and associated dispersity (*D*) of the samples. Tetrahydrofuran was used as the eluent to dissolve the samples before scanning with an isocratic high-performance liquid-chromatography pump (1515 Isocratic HPLC Pump, Waters Corporation, Milford, MA, USA) and a refractive-index detector (2414 RI detector, Waters Corporation). The thermal stability of the samples was determined using thermogravimetric analysis (TGA) and its derivatives (TGA/SDTA 851°, Mettler Toledo, Switzerland). The tensile properties of the blend samples were calculated by using a Universal Testing Machine (Instron/5566, Singapore) at 5 mm/min with a 50 N load. For the morphology study, an optical microscope (Axiotech 100 HD, Carl Zeiss, Oberkochen, Germany) was used to observe the surface of the solid blend products. Resolution magnification at 50× was used to observe the surface of the NR/PS blends.

METHOD OF CALCULATION

The percentage of conversion from LNR to HLNR was calculated from the ¹H-NMR spectra of HLNR. The number of H atoms in each isoprene monomer unit and in HLNR provides important information for the calculation. Theoretically, there are seven paraffin H atoms in each isoprene



SCHEME 2. — Hydrogenation of LNR to form HLNR.

monomer unit, and the number increases to 10 after hydrogenation, as shown in Scheme 2. Equation 1 was derived based on Kongparakul et al.¹¹ to calculate the percentage of hydrogenation,

$$\text{Degree of olefin conversion}(\%) = \frac{100(A - 7B)}{A + 3B} \quad (1)$$

where A is the peak area of paraffin proton ($-\text{CH}_2-$ and $-\text{CH}_3$; 0.6–2.1 ppm) and B is the olefinic protons ($=\text{CH}$; 5.1 ppm).

RESULTS AND DISCUSSION

STRUCTURE OF LNR AND HLNR

The microstructures of LNR and 94.4% HLNR were characterized by FTIR, and the spectra are shown in Figure 1. The main peaks are located at 1664 and 834 cm^{-1} , and they correspond to $\text{C}=\text{C}$ stretching and olefinic $\text{C}-\text{H}$ bending, respectively.²¹ The intensity of both peaks decreases as a result of the hydrogenation of LNR, which reduced the amount of $\text{C}=\text{C}$ and olefinic $\text{C}-\text{H}$. The signal at 1590 cm^{-1} in the 94.4% HLNR spectrum corresponds to the aromatic $\text{C}=\text{C}$ peak from *p*-toluenesulfonic acid (TSA), which was the side product of thermolysis of TSH. Several peaks between 1500 and 900 cm^{-1} are more intense than they appear in the LNR spectrum (before hydrogenation), and the stronger signals in that range originated from the paraffin $\text{C}-\text{H}$ bending vibrations owing to the increasing number of alkane groups after hydrogenation.

The NMR spectra of LNR and HLNR are shown in Figure 2 (^1H -NMR) and Figure 3 (^{13}C -NMR). The ^1H -NMR spectrum of LNR shows signals at 1.71, 2.09, and 5.16 ppm, which are attributed to the group of unsaturated methyl, unsaturated methylene, and olefinic proton, respectively. After hydrogenation, these signals were reduced and new signals appeared in the range of 0.60–1.50 ppm, corresponding to the methane group, methylene, and the methyl group.²¹

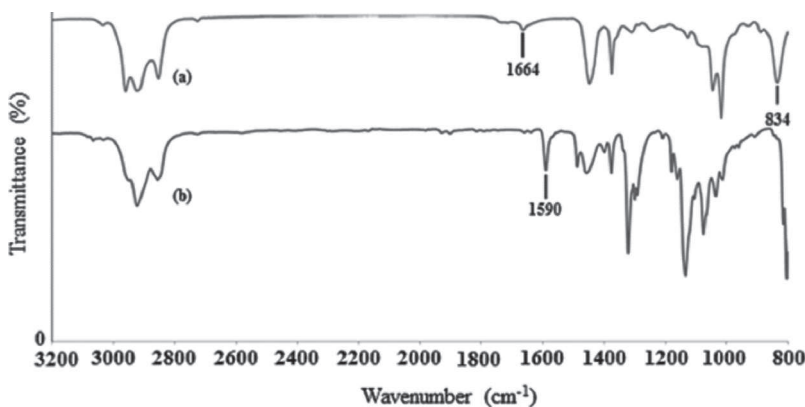


FIG. 1. — FTIR spectra of (a) LNR and (b) HLNR.

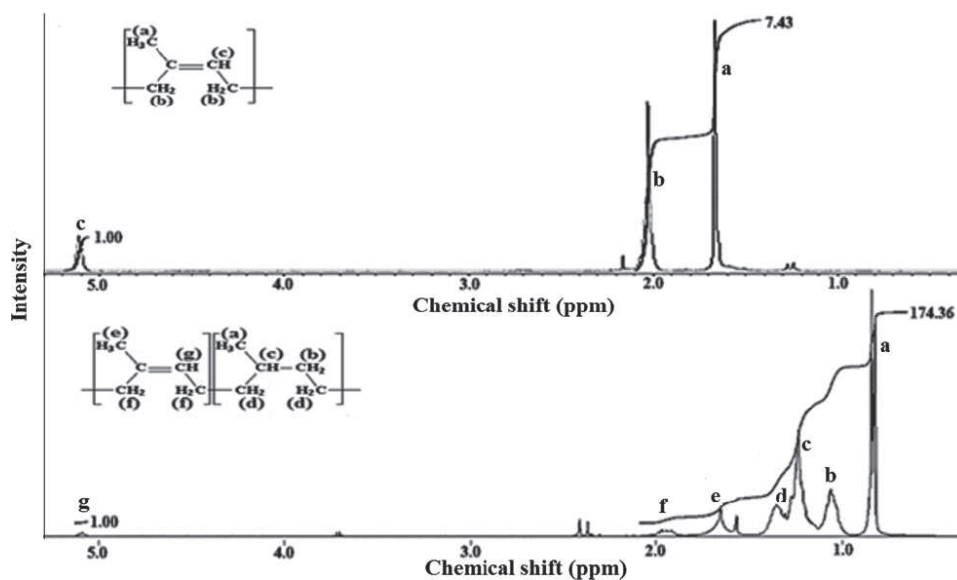


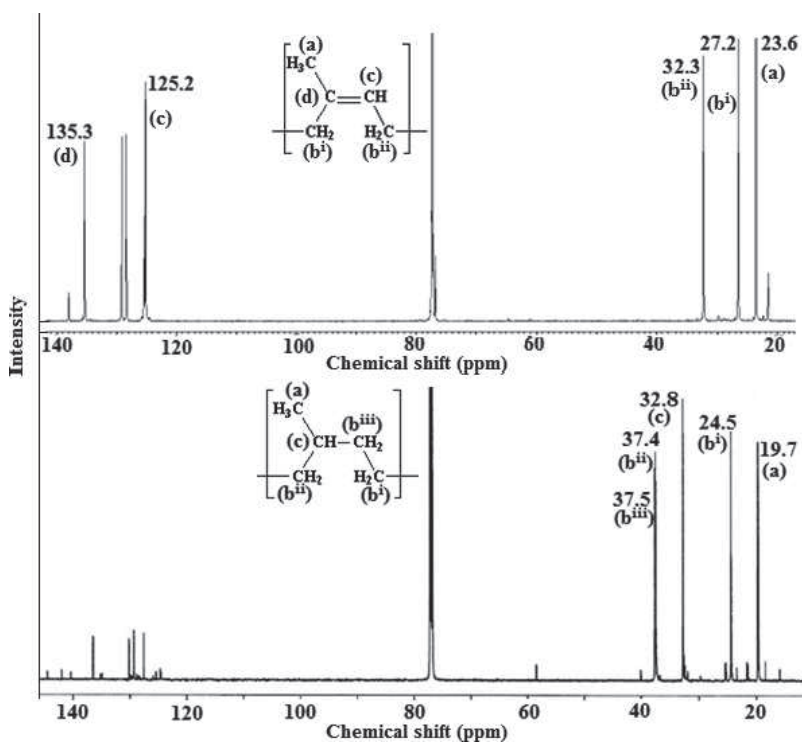
FIG. 2. — ^1H -NMR spectra of (a) LNR and (b) HLNR.

The 94.4% HLNR signals were broader than the LNR signals because the rate of spin-lattice relaxation increased with the increasing number of alkane groups after hydrogenation. The percentage of hydrogenation was calculated from the ratio between the integration of the olefinic proton signal and integration of the signals in the range of 0.60–2.10 ppm. The signals around 2.30–2.50 ppm correspond to TSA. The data of ^1H -NMR are summarized in Table I.

In the ^{13}C -NMR analysis, the spectrum of LNR shows signals at 24.8, 26.2, and 33.1 ppm, which are attributed to the methyl and methylene groups in the product. Meanwhile, the signals at 124.9 and 135.1 ppm correspond to the alkene group. After hydrogenation, several signals increased in the range of 19.0–38.0 ppm because of the increase in alkane groups. The signals at 19.7, 24.5, 32.8, 37.4, and 37.5 ppm correspond to the methane group, methyleneⁱ, methyleneⁱⁱ, methyleneⁱⁱⁱ, and the methyl group.²¹ Owing to the presence of TSA, signals at 19.8, 127.6, 129.4, 130.2, and 136.5 ppm were recorded. The alkene signal cannot be seen in Figure 3b because the hydrogenation was almost completed at that stage. Table II shows the data of ^{13}C -NMR. In conclusion, the FTIR and NMR spectra show the microstructural changes that occurred during hydrogenation.

WEIGHT AVERAGE MOLECULAR WEIGHT OF NR, LNR, AND HLNR

The GPC data of LNR used in the study showed that its M_w was 88 401 u, with a \bar{D} of 8.08. Previously, the M_w and \bar{D} of NR were 1 434 277 and 3.93, respectively. Degradation of NR to LNR removed unwanted species such as agglomeration, coagulation, back-biting, and cyclization of NR. Meanwhile, the GPC data of 94.4% HLNR showed that the M_w of the compound decreased drastically. The M_w of LNR after hydrogenation was 4650 u, with \bar{D} of 1.43 (Table III). From the analysis, we can conclude that the M_w was reduced by almost 95% and \bar{D} by about 82%, which can be justified as the result of the degradation of polyisoprene chains during the addition of hydrogen. Mango and Lenz²² reported that the side product of TSA (Scheme 1) could cause the protonation of olefinic functionality and lead to a variety of ionic reactions on the polymer backbone, including chain cleavage, coupling or cyclization reactions, and addition of *p*-toluenesulfonate anions. If

FIG. 3. — ^{13}C -NMR spectra of (a) LNR and (b) HLNR.TABLE I
 ^1H -NMR DATA FOR LNR AND 94.4% HLNR

Rubber	Chemical shift, ppm	Spectral signal assignment (inference and observations)
LNR	1.71	Unsaturated methyl group ($\text{R}-\text{CH}_3$)
	2.09	Unsaturated methylene group ($\text{R}-\text{CH}_2-\text{R}$)
	5.16	Olefinic proton ($\text{R}-\text{CH}=\text{C}-\text{R}_2$)
HLNR	0.60–1.50	Methane, methylene, methyl (new peaks)
	1.50–2.10	Unsaturated methyl, methylene (decreased and broadened signals)
	5.10	Olefinic proton (decreased signal)

TABLE II
 ^{13}C -NMR DATA OF LNR AND 94.4% HLNR

Rubber	Chemical shift, ppm	Spectral signal assignment (inference and observations)
LNR	24.8, 26.2, 33.1	Methyl, methylene ($\text{R}-\text{CH}_3$ and $\text{R}-\text{CH}_2-\text{R}$)
	124.9, 135.1	Alkene ($\text{R}-\text{CH}=\text{C}-\text{R}_2$)
HLNR	19.7, 24.5, 32.8, 37.4, 37.5	Methane, methylene ⁱ , methylene ⁱⁱ , methylene ⁱⁱⁱ , methyl (increased signals)

TABLE III
WEIGHT AVERAGE MOLECULAR WEIGHTS (M_w), DISPERSITY (\bar{D}), AND
RETENTION TIME OF LNR AND 94.4% HLNR

Rubber	M_w , u	\bar{D}	Retention time, min
NR	1 434 277	3.93	17.0
LNR	88 401	8.08	19.1
HLNR	4650	1.43	23.2

complete hydrogenation can be performed without protonation of olefinic sites, by-products of addition and chain degradation can be minimized or avoided.

EFFECT OF TSH CONCENTRATION

TSH released a diimide (N_2H_2) intermediate during thermal decomposition and served as the source of hydrogen for hydrogenation of LNR. As the reaction proceeded, the color of the reaction mixture changed from milky white (color of TSH) to deep yellow (color of diimide), indicating the dissolution of TSH in toluene to yield diimide. To investigate the effect of TSH concentration on the degree of hydrogenation, the weight ratio of TSH to LNR was varied from 1:1 through 4:1. The NMR analysis suggested that the optimum weight ratio was 3:1 because the hydrogenation level exceeded 90% at 130 °C in a reaction period of 6 h. Experiments of a shorter reaction duration (4 h) showed that only about 70% conversion was obtained when the weight ratio was between 5:2 and 4:1 owing to limited reaction time or incomplete reaction. Figure 4 shows the percentage of hydrogenation based on the TSH/LNR weight ratio for 4 and 6 h of reaction time. For the 6 h reaction period, an increment of 0.5 ratio of TSH compared with LNR gave an increase of about 15% hydrogenation. With a 3:1 ratio, hydrogenation patterns began to flatten, indicating the hydrogenation of LNR almost reaches a maximum degree of hydrogenation. To summarize, the degree of hydrogenation is directly proportional to the TSH concentration due to the higher concentration of hydrogen provided by diimide generated from thermolysis of TSH.

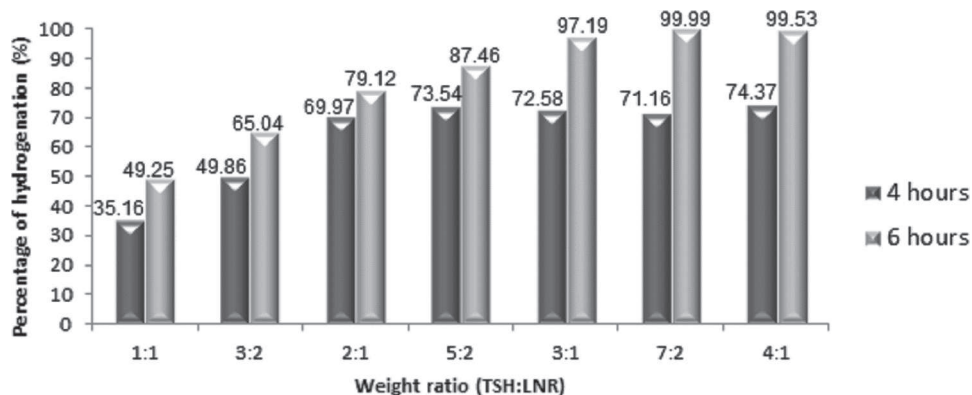


FIG. 4. — Percentage of conversion after 4 h (left bar) and 6 h (right bar) of hydrogenation.

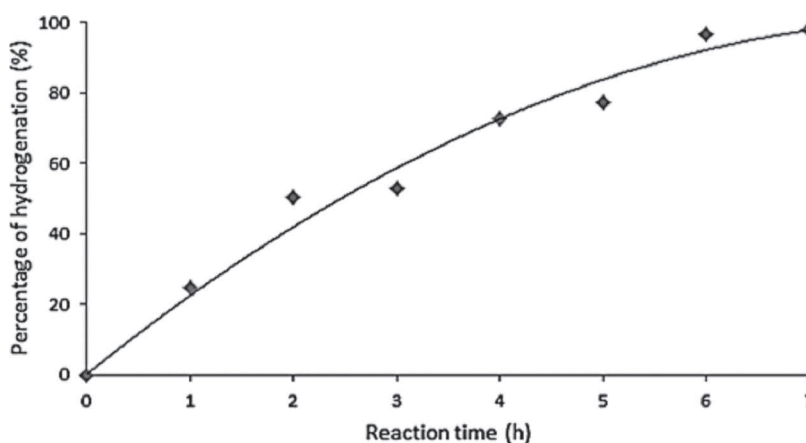


FIG. 5. — Effect of reaction times on percentage of conversion.

EFFECT OF REACTION TIME

The effect of reaction time on LNR hydrogenation was investigated by varying the reaction time from 1 to 7 h. The TSH and LNR mixing ratio, temperature, amount of toluene used, and dry rubber content were kept constant at 3:1, 130 °C, 15 mL, and 10%, respectively, for all experiments. The results suggest that the conversion of C=C increased exponentially with increasing reaction time, as shown in Figure 5. Interesting patterns were observed in these studies, starting with the drastic increment from 0% to 50.6% for the first 2 h, 50.6% to 72.6% for the second 2 h, and 72.6% to 96.6% for the third 2 h. Drastic improvement was obtained for every 2 h reaction period. For these studies, the hydrogenation involved the radical group (inside LNR), which makes the reaction process uncontrollable.

EFFECT OF TEMPERATURE

The effect of reaction temperature on HLNR conversion was studied at reaction temperatures of 110, 130, and 150 °C. Other parameters were kept constant, with a TSH/LNR weight ratio of 3:1, 15 mL of toluene as the solvent, a dry rubber content of 10%, and a reaction time of 6 h. The estimation of conversion percentage from the NMR data showed that the hydrogenation of LNR was directly proportional to the reaction temperature, as shown in Table IV. Table IV shows the influence of reaction temperatures on HLNR conversion. Improvement by 11.4% hydrogenation from 83.4% after using 130 °C showed that the targeted degree of hydrogenation can be achieved. By increasing the temperature, the kinetic energy also was increased, hence accelerating the hydrogenation process. Temperature below 100 °C are not relevant to this study because the

TABLE IV
EFFECT OF REACTION TEMPERATURE ON PERCENTAGE OF CONVERSION

Temperature, °C	Percentage of conversion, % ^a
110	83.4
130	94.8
150	99.4

^a Calculated from NMR integration.

TABLE V
DECOMPOSITION TEMPERATURE OF RUBBER SAMPLES

Rubber	Hydrogenation, %	$T_{\text{decomposition}}$, °C
LNR	—	259–377
HLNR	75.9	343–447
HLNR	94.3	360–458
EPDM ^a	—	470

^a The EPDM sample consisted of ethylene and propylene in the ratio of 70/30 and 11.5 wt% of diene.¹⁵

decomposition temperature of TSH is about 100 °C. Hydrogenation cannot be carried out if the diimide is not generated by thermolysis of TSH. The hydrogenation of LNR was almost complete at 150 °C, with the conversion of HLNR at 99.4%.

THERMAL PROPERTIES OF LNR AND HLNR

TGA of LNR and HNLR was carried out to study the effect of hydrogenation on the thermal stabilities of the rubbers. The decomposition pattern of rubber consists of two stages: minor initial decomposition followed by major decomposition. Both of these sublevels indicate the range of decomposition temperatures of the products. Table V shows a comparison of the decomposition temperatures of LNR, HLNR, and standard EPDM.¹⁵ The TGA thermograms and their derivatives are shown in Figure 6. The thermogram of LNR shows a single step of decomposition, whereas the thermograms of both HLNR (75.9% and 94.3% hydrogenation) show two steps of decomposition. The first stage of decomposition of HLNR was due to the side products of TSH thermolysis at about 245 °C. Meanwhile, the second stage was due to HLNR decomposition. The results indicated that hydrogenation improved the thermal stability of LNR, and a higher percentage of hydrogenation also enhanced the decomposition temperature. As the decomposition temperatures of both LNR

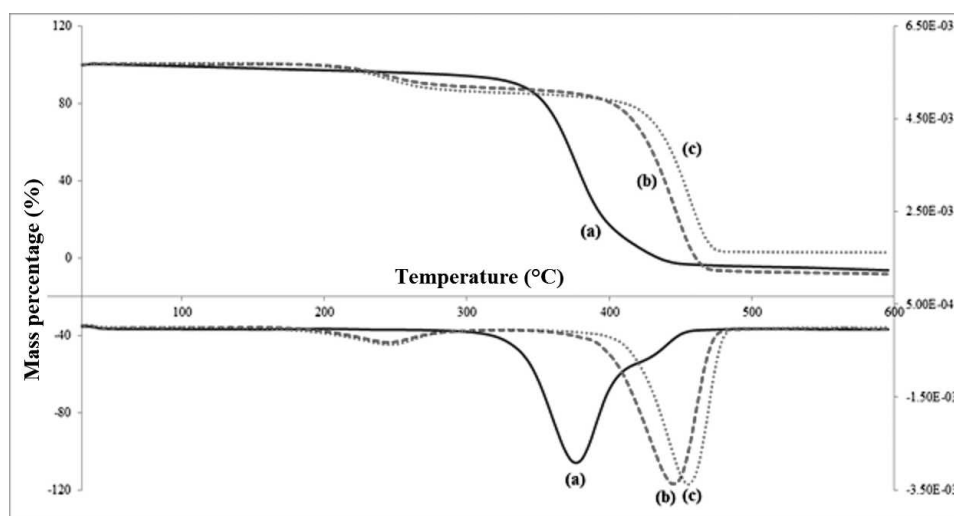


FIG. 6. — TGA thermograms of (a) LNR, (b) HLNR at 75.9% hydrogenation, and (c) HLNR at 94.3% hydrogenation and its derivatives.

TABLE VI
TENSILE STRENGTH OF NR/PS SOLID BLENDS (WITHOUT/WITH FILLER)

Blends	Average tensile strength, MPa	Standard deviation
NR/PS 80:20	0.87	±0.10
NR/PS 60:40	2.04	±0.26
NR/PS 40:60	4.01	±1.55
NR/PS/LNR 40:60:4	4.37	±1.44
NR/PS/HLNR 40:60:4	4.98	±0.46

and HLNR are close to that of standard EPDM,¹⁵ the physical properties of HLNR are projected to be similar to EPDM's.¹⁵

MECHANICAL PROPERTIES OF NR/PS BLENDS

Mechanical testing was carried out to support the effectiveness of HLNR as a compatibilizing agent for NR/PS blends. Several compositions of NR/PS blends were tested, and composition at 40:60 was used for the compatibilizer study. Table VI shows a comparison of tensile strength of the solid blends. Composition of NR/PS of 40:60 was used for mechanical and miscibility studies. Without any compatibilizer, the tensile strength of the NR/PS 40:60 was the lowest compared with the addition of LNR and HLNR. After the addition of LNR (NR/PS/LNR 40:60:4), the average tensile strength was increased from 4.01 MPa to 4.37 MPa. This is due to the LNR structure with active functional groups such as OH and C=O that made a stronger intermolecular force inside the blend.⁸ Meanwhile, the composition of the NR/PS/HLNR 40:60:4 blend had even higher average tensile strength of 4.98 MPa because of the rigidity of the HLNR structure and the good dispersion of the NR particle into the PS matrix. This conclusion was supported from the thermal properties; the degradation temperature of NR or LNR was increased after the hydrogenation process, indicating a stronger intramolecular force.

MORPHOLOGY STUDY

Using an optical microscope, a morphology study was carried out to observe the surface of the blends and their homogeneity. Figure 7 illustrates the surfaces of NR/PS 40:60, NR/PS/LNR 40:60:4, and NR/PS/HLNR 40:60:4 at 50× magnification. The surface of NR/PS 40:60 showed the aggregation of NR because the blending is not well mixed. After LNR was added as compatibilizer, the surface of the blend started to flow into a direction as the homogeneity increased. With the addition of HLNR, the dispersion of the NR particles was even better as the particles dispersed uniformly into the PS matrix. The surface of the blend shows that HLNR can be a compatibilizing agent for NR/PS blending. As mentioned in the earlier subtopic, tensile strength is related to the surface of the samples. The average tensile strength of NR/PS/HLNR is the highest because of the good dispersion of NR particles into the PS matrix.

CONCLUSIONS

The diimide derived from the thermolysis of TSH was found to be a suitable source of hydrogen for the hydrogenation of LNR. A TSH/LNR weight ratio of 3:1 yielded a

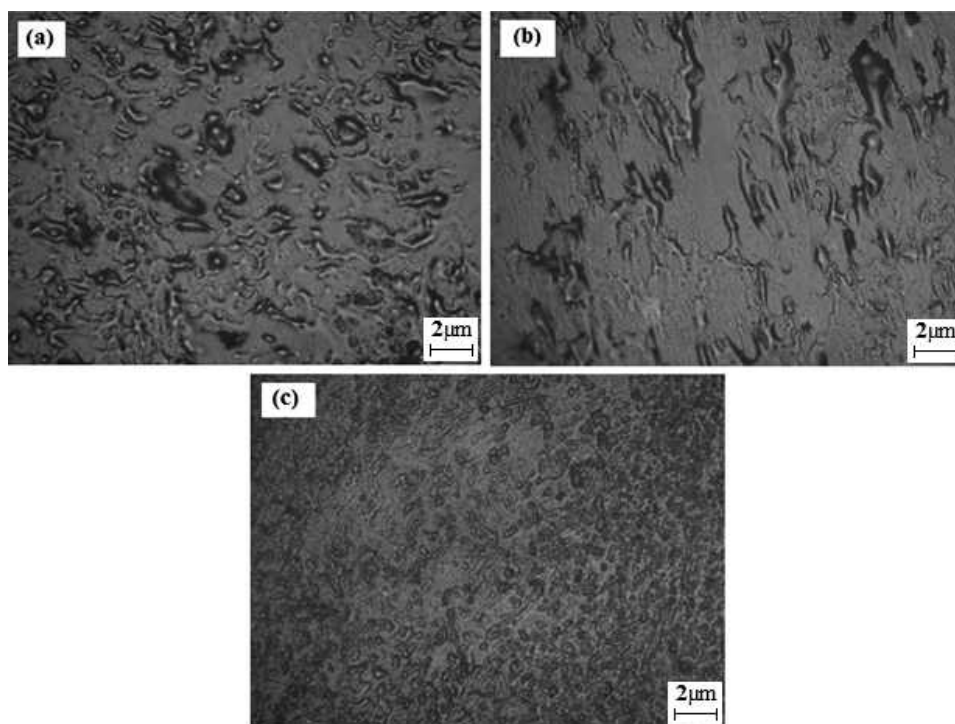


FIG. 7. — Surface of (a) NR/PS 40:60, (b) NR/PS/LNR 40:60:4, and (c) NR/PS/HLNR 40:60:4 at 50 \times magnification using optical microscope.

hydrogenation percentage of more than 90% after 6 h of reaction at 130 °C. Hydrogenation was found to improve LNR's thermal stability proportionately with the percentage of conversion. Therefore, compared with the existing method of synthesizing EPDM, noncatalytic hydrogenation of LNR can potentially serve as an alternate, more eco-friendly, and less costly pathway to obtain EPDM rubber. Other than that, HLNR also can act as an effective compatibilizer to enhance the tensile strength of the NR/PS blend, and the homogeneity of the blend also was improved after HLNR was added to prove that HLNR can be a wise choice of compatibilizing agent for NR/PS blend. Therefore, blending of NR/PS with HLNR as a compatibilizer can be used instead of the existing synthetic rubber–PS blending to reduce costs and provide more sustainable resources.

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