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Study of Solvent and Catalyst in Diimide Biphasic Hydrogenation System of Natural Rubber

Dody Andi Winarto[1,2], Chandra Liza[2], Mohamad Irfan Fathurrohman[3], Abdulhakim Masa[4], Mochamad Chalid[1,5*]

[1]Green Polymer Technology Laboratory, Department of Metallurgical & Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, West Java, Indonesia
[2]National Research and Innovation Agency, Building #460, Puspiptek Area, South Tangerang 15314, Banten, Indonesia
[3]Indonesian Rubber Research Institute, Jl. Salak no 1., Bogor 16151, West Java, Indonesia
[4]Rubber Engineering & Technology Program, International College, Prince of Songkla University, Hat Yai, Songkhla, 90110, Thailand
[5]Center for Sustainability and Waste Management, Universitas Indonesia, Depok, 16424, Indonesia

Abstract. In Indonesia, solid rubber is the most common form of natural rubber (NR) intermediates because it is easy to store and transport. However, hydrogenation, a process aimed at improving the quality of NR by addressing its vulnerability to environmental factors due to the presence of carbon double bonds, is typically carried out under relatively mild conditions using latex material. This study explores a biphasic hydrogenation approach using solid NR dissolved in a solvent and a hydrogen source (hydrazine hydrate and hydrogen peroxide) mixed in water. The choice of solvents, catalysts, and the water-to-solvent volume ratio were examined for their impact on hydrogenation. Characterization was conducted using Fourier Transform Infrared (FTIR) spectroscopy as a qualitative indicator of hydrogenation. Meanwhile, Nuclear Magnetic Resonance ^{1}H-NMR spectroscopy is used to measure the degree of hydrogenation. The results indicate that partial hydrogenation was successful using toluene as a solvent and ethylene diamine tetra acetic acid diammonium copper (Cu-EDTA) as a catalyst, with variations in water volume influencing the degree of hydrogenation. A degree of hydrogenation of 7.69% was achieved using 15 mL of water. The thermal properties of hydrogenated NR remain comparable to the original material, with improved heat resistance. This biphasic hydrogenation method offers the potential to enhance the properties of NR in various applications.

Keywords: Biphasic hydrogenation; Diimide; FTIR; Natural Rubber; NMR; Thermal analysis

1. Introduction

Natural rubber plays a vital role in various aspects of human life, with applications in fields such as medical equipment and industry (Kim *et al.,* 2020; Saengdee, Phinyocheep, and Daniel, 2020; Inoue and Nishio, 2007). Despite its significance, natural rubber contains carbon double bonds (Cifriadi, Chalid, and Puspitasari, 2017; Piya-areetham, Prasassarakich, and Rempel, 2013) that make it less resistant to oxidation, heat, ozone, and other environmental factors (Ngudsuntear *et al.,* 2022). However, this limitation can be

overcome by chemically modifying it, potentially making it a substitute for the thermally resistant Ethylene Propylene Diene Monomer (EPDM) rubber (Taksapattanakul *et al.,* 2019; Inoue and Nishio, 2007).

Hydrogenation can be employed to enhance the quality of natural rubber (Saengdee, Phinyocheep, and Daniel, 2020; Phinyocheep, 2014; Winters *et al.,* 2002). In this process, solid natural rubber is dissolved in a solvent and then reacted with hydrogen gas, with the help of a catalyst (Ha *et al.,* 2016; Ha *et al.,* 2015; Mahittikul, Prasassarakich, Rempel, 2009; Inoue and Nishio, 2007). Notably, this process demands the use of organic solvents and containers capable of withstanding high pressure, necessitating strict safety precautions. Moreover, these processes involve expensive catalysts and recycling challenges. While hydrogenation can be achieved using aryl-sulfonyl hydrazide thermolysis at temperatures above 100°C, it is accompanied by chain degradation and side reactions.

A milder method to hydrogenate natural rubber is by utilizing latex under conditions of low temperature and atmospheric pressure (Cifriadi, Chalid, and Puspitasari, 2017; Veni and Ma'zam, 2010). This process involves the use of hydrazine hydrate as a hydrogen donor in combination with hydrogen peroxide. Several studies have proven the success of this approach, although some side reactions may cause cross-linking before vulcanization takes place (Cifriadi, Chalid, and Puspitasari, 2017; Hinchiranan, Prasassarakich, and Rempel, 2006).

Although latex offers certain advantages as a raw material, one of its main disadvantages lies in the need for stabilization during transportation to the processing site to avoid coagulation (Winarto *et al.,* 2023). This stabilization process adds complexity and cost to the overall production process. Moreover, transporting latex poses a challenge as it requires a substantial amount of water due to its bulkiness and weight, leading to additional logistical issues and potential environmental concerns. In contrast, solid natural rubber obtained by coagulating latex is the primary intermediate product produced by the Indonesian rubber industry (Yuningtyas, Hakim, and Novianti, 2019), presenting a more manageable and widely used alternative.

The objective of this research is to utilize a biphasic hydrogenation method that involves dissolving solid natural rubber in a solvent. This method also includes the use of a hydrogen source, namely hydrazine hydrate and hydrogen peroxide, which is mixed in water. The goal is to take advantage of the abundance of solid rubber and enhance its quality. The success of the hydrogenation process was evaluated through Fourier Transform Infrared (FTIR) spectral analysis and Nuclear Magnetic Resonance (NMR) spectroscopy. Additionally, the thermal properties of the resulting products were analyzed using Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA).

2.   Experimental Section

2.1. Materials

The natural rubber crepe was obtained from the Research Center for Rubber Technology, Indonesia. Toluene, xylene, and n-hexane were obtained from Mallinckrodt Chemical. Hydrazine hydrate (80% solution in water) for synthesis, ethylene diamine tetraacetic acid diammonium copper (Cu-EDTA) salt solution 0.025 M EDTA-Cu $(NH_4)_2$ CAS-No 67989-88-2 Supelco and copper (II) sulfate p.a. anhydrous were products of Sigma-Aldrich, and hydrogen peroxide 35% was products of Merck. Aquadest was provided by Polymer Laboratory BRIN, which was buffer-added so that its pH was 9.

2.2. Biphasic hydrogenation of natural rubber

Natural rubber crepe (0.5 g) was dissolved in 50 mL of the solvent. In a separate container, hydrazine hydrate and copper sulfate were dissolved in 20 mL of aquadest at pH 9 and then poured into a container where natural rubber dissolved. They were mixed and stirred using a magnetic stirrer for 10 minutes at 500 rpm. Then, 2.914 mL hydrogen peroxide was put into the mixture drop by drop. The reaction was stirred for 2 hours and occurred under biphasic conditions, with a concentration ratio $[C=C]:[N_2H_4/H_2O_2]$ of 1:12. The solution was left for more than 2 hours until the water and solvent were separated. The solution from the solvent side was taken out and put into a 250 mL boiling flask. The solvent was removed by rotary evaporation. The remaining material was characterized later. The scheme of the process is shown in Figure 1 below.
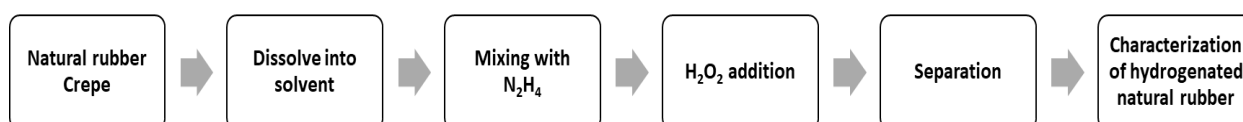
Figure 1 Schematic process of hydrogenation of natural rubber

In this work, the solvent volume used was fixed, at 50 mL. Several solvents, rubber contents, types of catalysts, and acidities of the water used were varied. The experimental conditions are listed in Table 1.

Table 1 Experimental Condition

Variable	Baseline	Range
Types of solvent	Toluene	toluene, xylene, n-hexane
Type of catalyst	Cu-EDTA	$CuSO_4$, Cu-EDTA
The volume of water [mL]	20	15, 20, 25

2.3. Characterization

2.3.1. Fourier Transform Infrared Spectroscopy

An analysis of the IR spectrum was performed using the Agilent Cary 630 FTIR Spectrometer, specifically employing the Attenuated Total Reflectance (ATR) method. The spectral range was from 4000 cm^{-1} to 650 cm^{-1}, with sample scans 32 and a resolution of 4 cm^{-1}.

2.3.2. Nuclear Magnetic Resonance Spectroscopy

^{1}H-NMR and ^{13}C-NMR spectroscopy was analyzed using JNM-ECZ500RlS 1. The sample was diluted in CDCl$_3$. Measurements were performed at 500 MHz. The ^{1}H-NMR was done with a repetition time of 6.75 seconds, 24 scans, and ^{13}C-NMR was done with a repetition time of 2.83 seconds, 1044 scans.

2.3.3. Differential Scanning Calorimetry

Glass transition temperature Tg was performed using Perkin Elmer DSC8000. The sample was put into an aluminum crucible of about 10 milligrams. From RT, the sample was cooled to -100°C and then heated to 20°C at a heating/cooling rate of 10°C/min. Measurement was done in nitrogen condition (50mL/min).

2.3.4. Thermogravimetry Analysis

Thermogravimetry Analysis was performed using Netzsch TG 209 F3 Tarsus. The sample was put into an alumina crucible of about 20 milligrams. The temperature program was conducted from 30°C to 600 °C with a heating rate of 10°C/min. Measurement was done in nitrogen condition (50mL/min).

3.   Results and Discussion

Natural rubber (NR) possesses a predominantly cis-1,4-polyisoprene molecular structure (Widiyati and Poernomo, 2018; Phinyocheep, 2014) as depicted in Figure 2. It contains a tri-substituted C=C bond with two CH_2 substituents and one CH_3 substituent (Smith, 2022). With this structure, NR has FTIR spectra, as shown in Figure 3 (a). It contains both methyl and methylene groups; hence, there are three peaks between 2840 and 3000 cm^{-1}. The unsaturated C–H stretch of natural rubber is at 3022 cm^{-1}, the C=C stretch is at 1664 cm^{-1}, and the C–H wag is seen at 830 cm^{-1}. As a note, through this paper, we use the code PHNR as partially hydrogenated natural rubber, and it is shown the spectral difference between NR and PHNR in Figure 3.
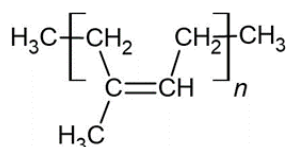
Figure 2 Chemical structure of NR
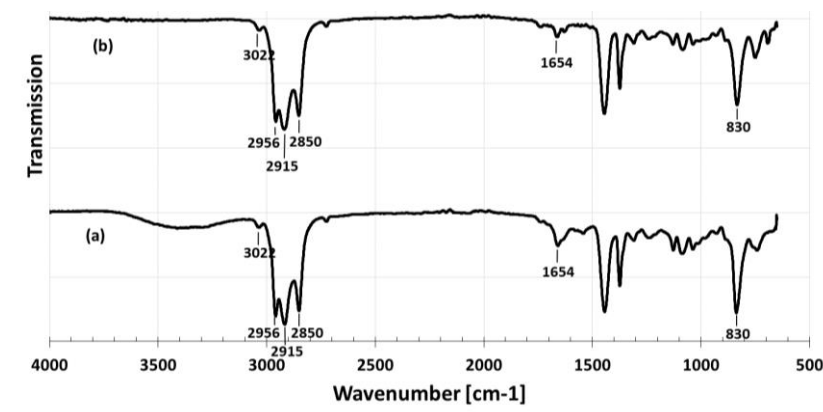
Figure 3 FTIR spectra of NR (a) and PHNR (b)

$$N_2H_4 + H_2O_2 + R_1HC = CHR_2 \rightarrow N_2 + R_1H_2C - CH_2R_2 + 2H_2O \tag{1}$$
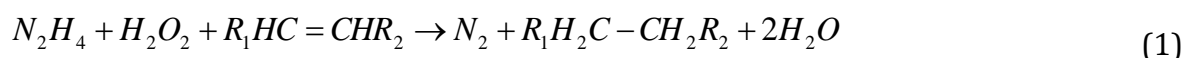
The chemical reactivity exhibited by the carbon-carbon double bond (C=C) within the isoprene repeating unit may be considered as C=C of alkenes. The hydrogenation reaction of natural rubber using diimide as a hydrogen donor occurs according to equation (1), which is a redox type of reaction (Taksapattanakul, 2016; Lin, 2005). $R_1HC=CHR_2$ denotes NR, and $R_1HC–CHR_2$ denotes PHNR. It is expected that the C=C double bond will decrease, and the C–C bonds and CH_2 substituents will increase. This is reflected in the FTIR spectra of PHNR as depicted in Figure 3 (b), where the intensity of transmission of C=C stretch is at 1654 cm^{-1}, and C–H wag is at 834 cm^{-1} increase.

3.1. Solvent screening for hydrogenation NR

In biphasic hydrogenation, NR was dissolved in an organic solvent to increase the surface area of rubber particles. This, in turn, enhances the chances of the reactant encountering and reacting effectively. Therefore, dissolving NR is a crucial step in the process. It is important to mention that using a solvent with high solubility for the solid can significantly improve the reaction rate compared to using a solvent with low solubility for the reagent (Dyson and Jessop, 2016).

The solubility of a material is determined by the interaction between its internal energy. The fundamental theory is based on cohesive energy and solubility parameters. In the context of polymers and solvents, their solubility is influenced by their chemical

structures, with a general understanding that similarity in chemical structure promotes solubility. Additionally, the physical properties of the polymer, particularly for liquids that induce significant swelling, also play a role. For a liquid to be absorbed into a polymer, there must be adequate space or chain flexibility to accommodate it (Arnold, 2003).

On this occasion, we employ the concept of the solubility parameter, denoted as **δ** (Hansen, 2007). According to this approach, a solute is likely to dissolve in a solvent close to its own (Muktaridha, 2021). Based on the data (Hansen, 2007; Arnold, 2003) of dispersion solubility parameter δ**d,** polar solubility parameter δ**p**, and hydrogen solubility parameter δ**h** of the material used in this experiment, the total solubility parameter of each material used in this experiment can be calculated. These are NR (polyisoprene) 17.94, toluene 18.16, hexane 14.90, and xylene 17.90. For comparison, the total solubility parameter of water is 47.91.

NR was found to be soluble in all selected organic solvents. Researchers used xylene, toluene, and hexane to hydrogenate rubbers with a concentration between 1.00% and 2.00% (Samran *et al.,* 2004; Phinyocheep, Pasiri, and Tavichai, 2003). However, based on the calculation of total solubility parameters, toluene and xylene were predicted to be the most suitable solvents for dissolving NR. Toluene has a boiling point of 111°C, and xylene has a boiling point of 138°C. Considering the ease of solvent evaporation for characterization purposes, toluene was selected as the baseline solvent for the experiment.

The hydrogenation of NR was also carried out using these three solvents. The FTIR spectra of the resulting product are depicted in Figure 4. The pattern of the spectra is almost the same. There are several NR's specific peaks. Especially at 3022 cm^{-1}, between 2840 and 3000 cm^{-1}, 1654 cm^{-1}, and 834 cm^{-1} as mentioned in Figure 3 (a). However, there is an increase in the intensity of transmission at wavenumbers 1654 cm^{-1} and 834 cm^{-1} using hexane (b) and toluene (c) as solvents. These indicators suggest that hydrogenation of NR has occurred. This has been confirmed by Cifriadi, Chalid, and Puspitasari (2017), Mahittikul, Prasassarakich, Rempel (2009), Inoue and Nishio (2007), who also observed hydrogenation using FTIR spectra. However, in the case of xylene (d), the transmission intensity at wavenumber 1654 cm^{-1} remains low. This is probably due to the water content in the sample, while the FTIR measurement can be seen in a broad peak at the wavenumber of 3400 cm^{-1} and shifting the baseline of the spectra.
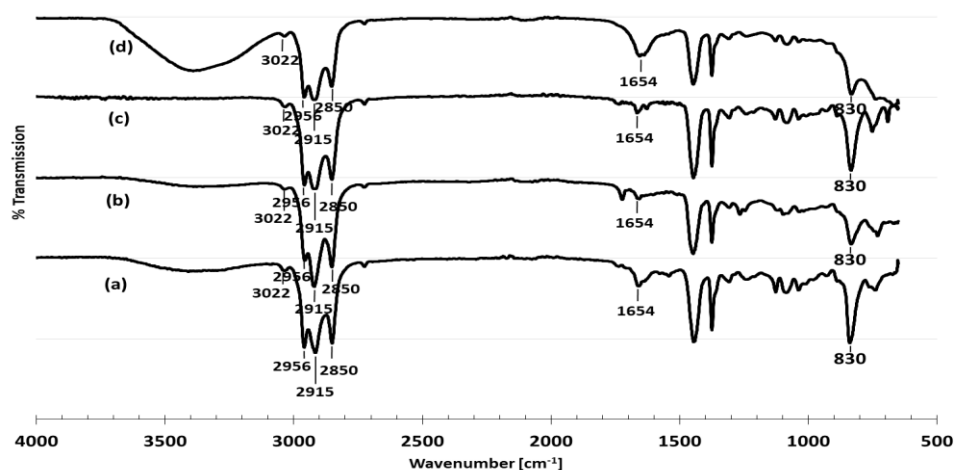

Figure 4 FTIR spectra of NR (a) compared with PHNR using (b) hexane, (c) toluene, and (d) xylene

3.2. Type of catalyst for hydrogenation NR

The possible reactions that occur between hydrazine and hydrogen peroxide are described in the following equation. Diimide (N$_2$H$_2$) is an intermediate product, formed due

to the reaction between hydrazine and hydrogen peroxide, reaction (2). Diimide then reacts with the C=C double bond in natural rubber, reaction (3).

$$NH_2 - NH_2 + H_2O_2 \rightarrow NH = NH + 2H_2O \tag{2}$$

$$NH = NH + CH_2 = CH_2 \rightarrow N_2 + CH_3 - CH_3 \tag{3}$$
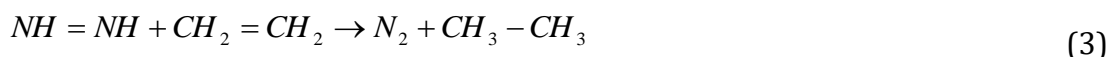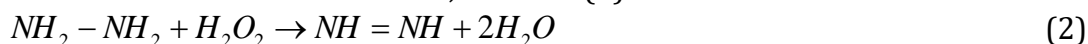
In the case of the presence of a C=C double bond in natural rubber and metal ions as catalysts, reaction (3) predominates. The use of this catalyst will increase the reaction for the formation of diimide, and Cu^{2+} is a suitable ion for use in hydrogenation using diimide (Mahittikul, Prasassarakich, Rempel, 2007).

Unlike hydrogenation with the latex system where copper ions are in 3 locations (water medium, polymer particle surface, and inside of the particles) (Lin, 2005), copper ions in the biphasic hydrogenation system exist solely within the water medium, and will only interact with the polymer when stirring is initiated. If this copper ion is only in the water medium, there will be no C=C reduction; therefore, stirring is very important. The reaction was run at 500 rpm.

The study compares the use of two catalysts, Cu-EDTA and $CuSO_4$, in the biphasic hydrogenation of NR. A total of 20 mL of water was used in the experiment. Figure 5 displays the FTIR spectra of the hydrogenation product. Notably, an increase in transmission intensity at wavenumbers 1654 cm^{-1} and 834 cm^{-1}, indicating the occurrence of hydrogenation of NR.
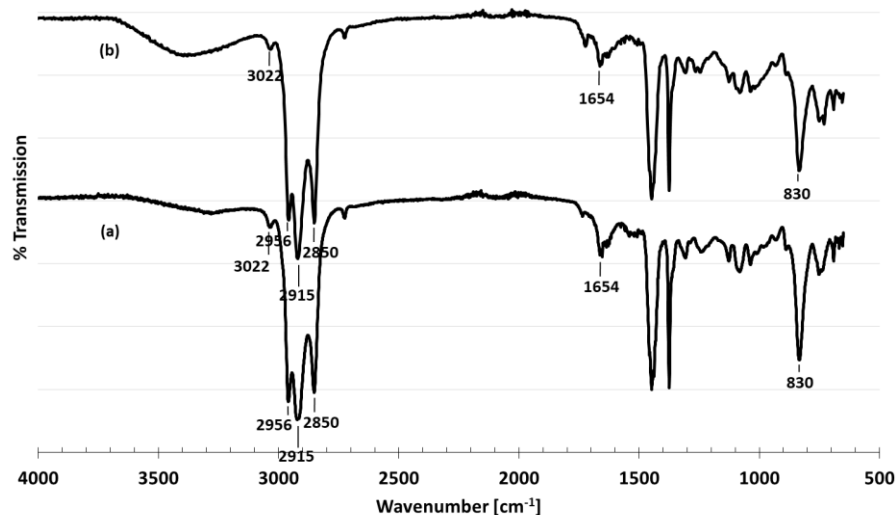
**Figure 5** FTIR spectra of PHNR using (a) EDTA and (b) $CuSO_4$

3.3. Solvent of catalyst used in the hydrogenation of NR

In this experimental work, the catalyst is a substance dissolving in water. Therefore, the amount of water was also considered to be optimized by varying amounts of water in the biphasic hydrogenation system. In this series, EDTA is used as a catalyst. Variations of water amounts of 15, 20, and 25 mL were used for dissolving N_2H_4. The product of hydrogenation was analyzed using FTIR and presented in Figure 6. It is noted that there is an increase in the intensity of transmission of FTIR spectra at wavenumber 1654 cm^{-1} and 834 cm^{-1}. This indicates that partial hydrogenation of NR occurred.

Figure 7. presents the ^{1}H-NMR spectra of natural rubber (NR). The spectra exhibit three main characteristic peaks at 1.67 ppm, 2.03 ppm, and 5.2 ppm, corresponding to the proton signals from methyl and methylene groups in isoprene units and proton signals in proximity to the C=C bond.

After analyzing the ^{1}H-NMR spectra of hydrogenated natural rubber, we observed a decrease in intensity at the peak of 5.2 ppm. At the same time, a new peak appeared at 0.8

ppm, and there was a noticeable increase in signals at 1.1 ppm. These changes can be attributed to the presence of saturated $-CH_2$ and $-CH_3$ groups in the hydrogenated NR . The appearance of $-CH_2$ was expected from the hydrogenation reaction and was also observed in the spectra FTIR in Figure 3 due to the reduction of C=C in NR. Based on these findings, the degree of hydrogenation resulting from the biphasic hydrogenation reaction of NR, with varying amounts of water used, is presented in Table 2. The degree of hydrogenation was calculated following the method presented by Taksapattanakul (Taksapattanakul, 2016).
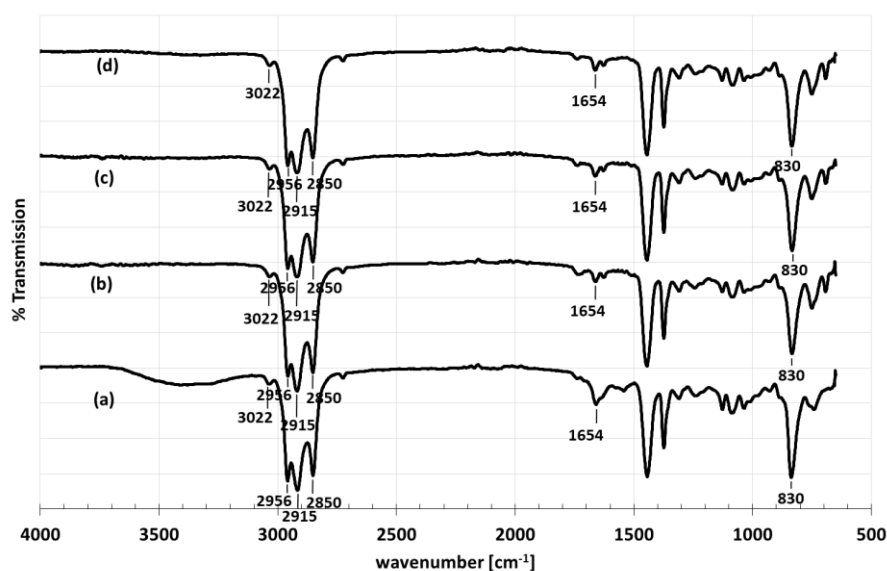
Figure 6 FTIR spectra of NR (a) compared with PHNR using water (b) 15 mL, (c) 20 mL, and (d) 25 mL
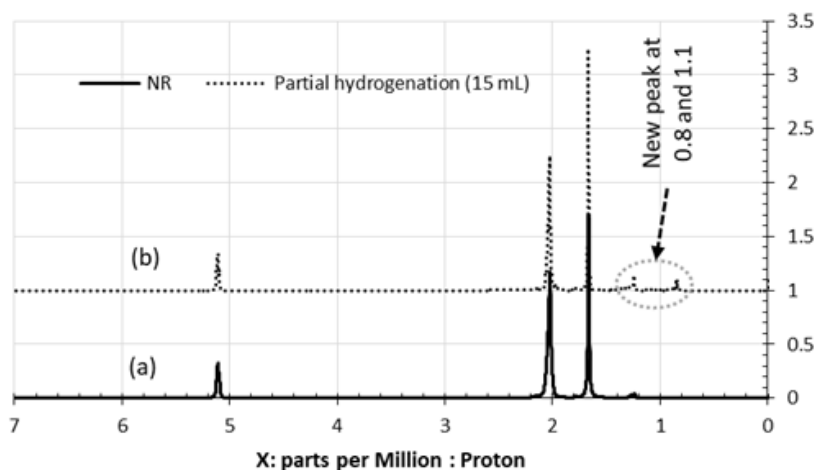
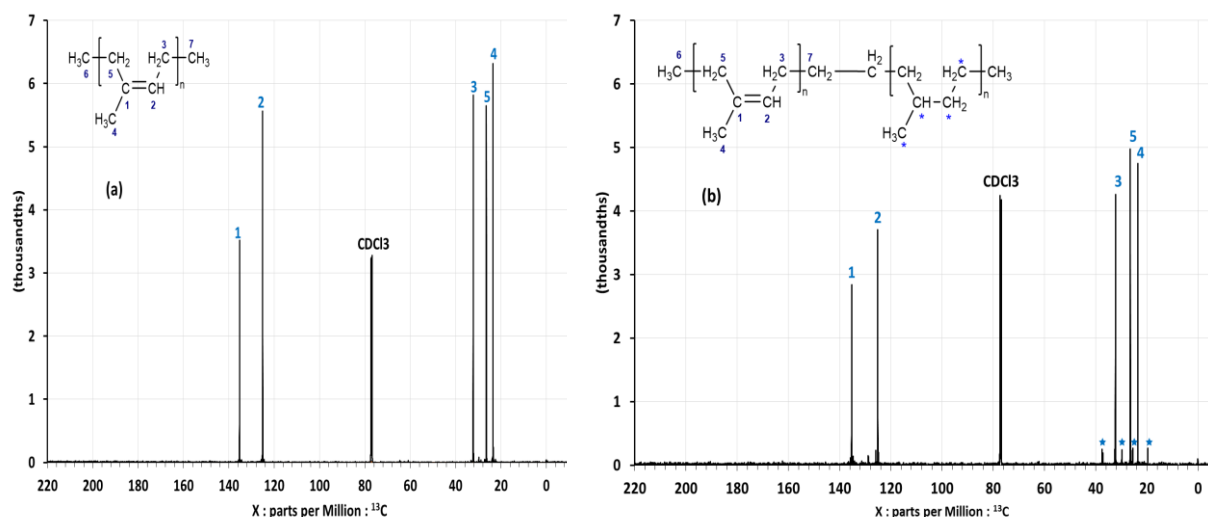**Figure 7** ^{1}H-NMR spectra of NR (a) compared with PHNR using water (b) 15 mL

Table 2 Degree of hydrogenation of PHNR

	Degree of hydrogenation %
NR	0
PHNR using Water 15 mL	7.69
PHNR using Water 20 mL	6.25
PHNR using Water 25 mL	5.96

Figure 8 (a) displays the ^{13}C-NMR spectra of NR, featuring several specific peaks. Notably, the peak at 135.2 ppm correlates with the carbon atom at position 1, while the peak at 125.5 ppm corresponds to the carbon atom at position 2. Additionally, peaks at 23.4

ppm, 26.4 ppm, and 32.2 ppm are associated with the C of methyl and 2-methylene (carbon atoms at positions 4, 5, and 3).

On the other hand, Figure 8 (b) illustrates the ^{13}C-NMR spectra of PHNR, revealing several new peaks (position ★). These peaks are observed at 19.7 ppm, 25.6 ppm, 29.9 ppm, and 37.4 ppm, attributed to $-CH_3$, $-CH_2$, $-CH-$, and $-C(CH_3)-CH_2$ indicating that some reduction in the C=C double bond has occurred and PHNR was produced. This is in line with the results from other literature (Mahittikul, Prasassarakich, Rempel, 2006; Samran, 2005). This evidence provided by ^{13}C-NMR spectra also aligns with FTIR spectra observed in Figure 3 and confirms that partial hydrogenation has occurred.

Figure 8 ^{13}C-NMR spectra of NR (a) compared with PHNR using water (b) 15 mL

3.4. Thermal Properties of PHNR

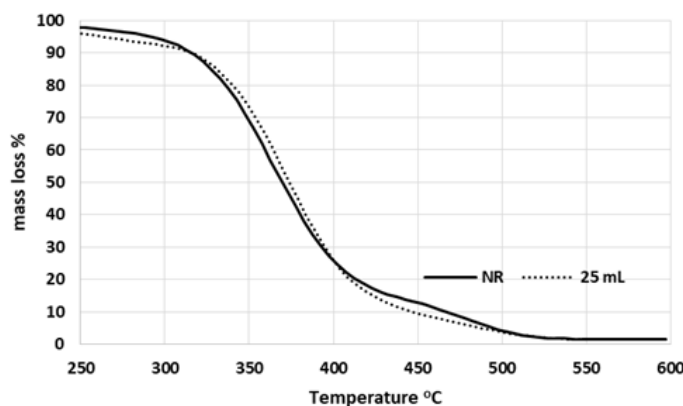Figure 9 illustrates a thermogram of hydrogenated NR within the temperature range of -70°C to -40°C. The figure displays a notable change in heat flow between -70°C and -60°C, indicating the presence of the glass transition temperature (Tg) in the material. Tg represents the temperature at which the polymer's mechanical properties shift from a brittle material to an elastic material, resulting from changes in chain mobility. NR is elastic at room temperature but becomes brittle when the temperature falls below Tg. The Tg of NR is approximately -65°C. Interestingly, PHNR still exhibits a Tg around that temperature. Therefore, the application of hydrogenated NR is expected to remain in the same conditions as the initial NR.
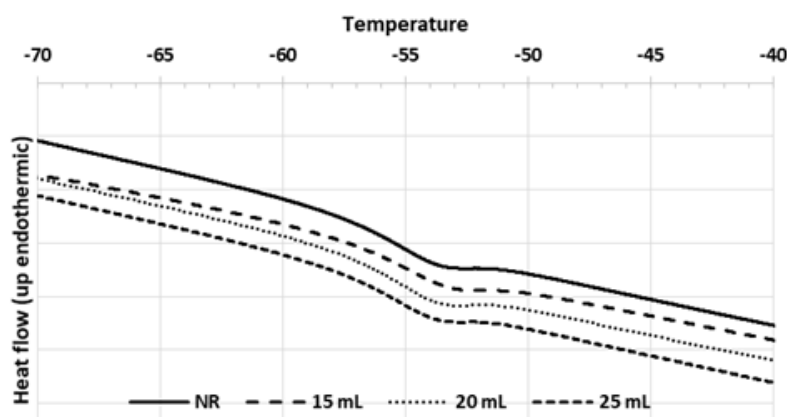

Figure 9 DSC thermogram of NR (a) compared with PHNR using water (b) 15 mL, (c) 20 mL, and (d) 25 mL

Meanwhile, Figure 10 displays the thermogram obtained from TGA analysis, which shows the degradation temperature as the temperature where the thermogram exhibits the minimum derivative. Table 3 summarizes the results, clearly indicating that the degradation temperature of hydrogenated NR increases with the amount of water used.

Figure 10 Thermogram of NR compared with PHNR using water 25 mL
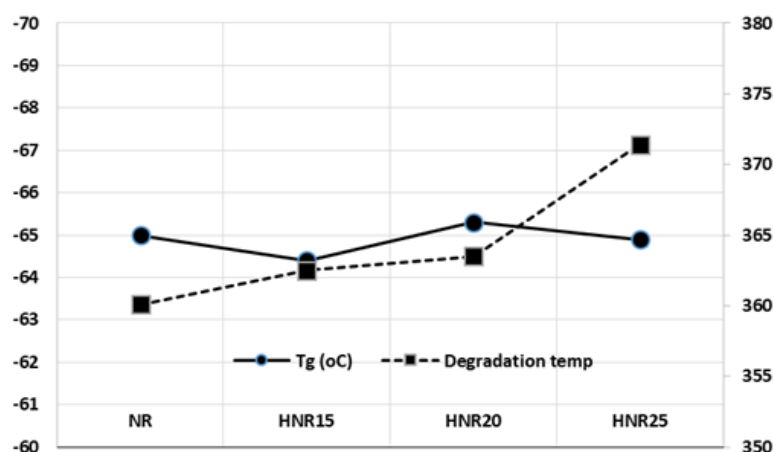
Figure 11 Effect of water used in biphasic hydrogenation and Tg of the PHNR

Figure 11 demonstrates that the glass transition temperature (Tg) of hydrogenated natural rubber remains unchanged compared to that of natural rubber. However, the degradation temperature of hydrogenated natural rubber is observed to be higher than that of natural rubber. Consequently, it is anticipated that the application temperature of hydrogenated NR will remain the same while offering improved heat resistance, given its tendency for increased degradation temperature.

Table 3 Thermal characteristics of hydrogenated NR

	Tg (°C)	Degradation temp (°C)
NR	-65.0	360.1
PHNR using Water 15 mL	-64.4	362.5
PHNR using Water 20 mL	-65.3	363.5
PHNR using Water 25 mL	-64.9	371.4

4. Conclusions

The biphasic hydrogenation of natural rubber using hydrazine hydrate and hydrogen peroxide was successfully conducted. Hydrogenation was confirmed by ^{13}C-NMR, and the degree of hydrogenation was calculated using ^{1}H-NMR. The highest degree of

hydrogenation of the product from the biphasic hydrogenation was 7.69%, achieved using 15 mL of water. The glass transition temperature (Tg) of the product was comparable to that of pre-hydrogenated natural rubber but improves its heat resistance. Nevertheless, the attained highest degree of hydrogenation (7.69%) may be considered relatively modest. Therefore, future research of biphasic hydrogenation should focus on exploring alternative reaction conditions to increase the degree of hydrogenation, as higher levels might be preferable for specific applications.

Acknowledgments

References

Arnold, J.C., 2003. Environmental Effects on Crack Growth in Polymers. In: *Comprehensive Structural Integrity. Oxford: Pergamon*

Cifriadi, A., Chalid, M., Puspitasari, S., 2017. Characterization of Hydrogenated Natural Rubber Synthesized by Diimide Transfer Hydrogenation. *International Journal of Technology,* Volume 8(3), pp. 448–457

Dyson, P.J., Jessop, P.G., 2016. Solvent Effects in Catalysis: Rational Improvements of Catalysts via Manipulation of Solvent Interactions. *Catalysis Science and Technology,* Volume 6(10), pp. 3302–3316

Ha, N.T., Kaneda, K., Naitoh, Y., Fukuhara, L., Kosugi, K., Kawahara, S., 2015. Preparation and Graft-copolymerization of Hydrogenated Natural Rubber in Latex Stage. *Journal of Applied Polymer Science,* Volume 132(34)

Ha, N.T., Kosugi, K., Kawahara, S., Nghia, P., 2016. Mechanism of Heterogeneous Hydrogenation of Natural Rubber in Latex. *KGK Kautschuk Gummi Kunststoffe,* Volume 69, pp. 71–76

Hansen, C.M., 2007. Hansen Solubility Parameters: A User's Handbook, In: *Chemical Rubber Company (CRC)*

Hinchiranan, N., Prasassarakich, P., Rempel, G., 2006. Hydrogenation of Natural Rubber in the Presence of OsHCl (CO)(O$_2$)(PCy$_3$)$_2$: Kinetics and Mechanism. *Journal of Applied Polymer Science,* Volume 100(6), pp. 4499–4514

Inoue, S.I., Nishio, T., 2007. Synthesis and Properties of Hydrogenated Natural Rubber. *Journal of Applied Polymer Science,* Volume 103(6), pp. 3957–3963

Kim, D.Y., Park, J.W., Lee, D.Y., Seo, K.H., 2020. Correlation between the Crosslink Characteristics and Mechanical Properties of Natural Rubber Compound via Accelerators and Reinforcement. *Polymers,* Volume 12(9), p. 2020

Lin, X., 2005. Hydrogenation of unsaturated polymers in latex form. *Ph.D. Ph.D. Thesis, University of Waterloo*

Mahittikul, A., Prasassarakich, P., Rempel, G.L., 2006. Hydrogenation of Natural Rubber Latex in the Presence of OsHCl(CO)(O2)(PCy3)2. *Journal of Applied Polymer Science*, Volume 100(1), pp. 640–655

Mahittikul, A., Prasassarakich, P., Rempel, G.L., 2007. Diimide Hydrogenation of Natural Rubber Latex. *Journal of Applied Polymer Science*, Volume 105(3), pp. 1188–1199

Mahittikul, A., Prasassarakich, P., Rempel, G.L., 2009. Hydrogenation of natural rubber latex in the presence of [Ir (cod)(PCy3)(py)] PF6. *Journal of Molecular Catalysis A: Chemical*, Volume 297(2), pp. 135–141

Muktaridha, O., Adlim, M., Suhendrayatna, S., Ismail, I., Bakar, N.H.H.A., 2021. Photocatalytic Degradation of Skim-Latex-Vapor Odor Using Iron-Doped Zinc Oxide. *International Journal of Technology*, Volume 12(4), pp. 739–748

Ngudsuntear, K., Limtrakul, S., Vatanatham, T., Arayapranee, W., 2022. Mechanical and Aging Properties of Hydrogenated Epoxidized Natural Rubber and Its Lifetime Prediction. *American Chemical Society (ACS) Omega,* Volume 7(41), pp. 36448–36456

Phinyocheep, P., 2014. Chemical Modification of Natural Rubber (NR) for Improved Performance. *Chemistry, Manufacture and Applications of Natural Rubber*, pp. 68–118

Phinyocheep, P., Pasiri, S., Tavichai, O., 2003. Diimide Hydrogenation of Isoprene–Styrene Diblock Copolymers. *Journal of Applied Polymer Science*, Volume 87, pp. 76–82

Piya-Areetham, P., Prasassarakich, P., Rempel, G.L., 2013. Organic Solvent-free Hydrogenation of Natural Rubber Latex and Synthetic Polyisoprene Emulsion Catalyzed by Water-soluble Rhodium Complexes. *Journal of Molecular Catalysis A: Chemical*, Volume 372, pp. 151–159

Saengdee, L., Phinyocheep, P., Daniel, P., 2020. Chemical Modification of Natural Rubber in Latex Stage for Improved Thermal, Oil, Ozone and Mechanical Properties. *Journal of Polymer Research,* Volume 27, pp. 1–13

Samran, J., 2005. A Study of Non-catalytic Hydrogenation of Natural Rubber. Ph.D. Thesis, Universite Du Maine

Samran, J., Phinyocheep, P., Daniel, P., Derouet, D., Buzare, J.Y., 2004. Spectroscopic Study of Di-imide Hydrogenation of Natural Rubber. *Macromolecular Symposia, Wiley Online Library*, Volume 216(1), pp. 131–144

Smith, B., 2022. The Infrared Spectra of Polymers IV: Rubbers. *Spectroscopy*, Volume 37, pp. 8–12

Taksapattanakul, K., 2016. Thermoplastic Vulcanizates Based on Hydrogenated Natural Rubber/Polypropylene Blends. *Ph.D. Thesis, Le Mans*

Taksapattanakul, K., Tulyapitak, T., Phinyocheep, P., Ruamcharoen, P., Ruamcharoen, J., Daniel, P., 2019. Hydrogenated Natural Rubber as an Alternative Replacement to Ethylene-Propylene-Diene-Monomer (EPDM) Rubber in Terms of Thermal-oxidative Degradation Properties. *Polymer Science, Series B*, Volume 61, pp. 567–573

Veni, B., Ma'zam, M., 2010. Hydrogenated Natural Rubber from Different Types of Preserved Latex. *Journal of Rubber Research*, Volume 13, pp. 103–109

Widiyati, C., Poernomo, H., 2018. Design of a Prototype Photoreactor UV-LEDs for Radiation Vulcanization of Natural Rubber Latex. *International Journal of Technology,* Volume 9(1), pp. 291–319

Winarto, D.A., Liza, C., Pemuji, A., Chalid, M., 2023. Feasibility Study of Latex Stability for Free Solvent Hydrogenation to Natural Rubbers. *In:* International Conference on Chemical Science and Engineering, pp. 27–35

Winters, R., Heinen, W., Verbruggen, M.A.L., Lugtenburg, J., Van Duin, M., De-Groot, H.J.M., 2002. Solid-State ^{13}C NMR Study of Accelerated-Sulfur-Vulcanized ^{13}C-Labeled ENB–EPDM. *Macromolecules*, Volume 35, pp. 1958–1966

Yuningtyas, C.V., Hakim, D.B., Novianti, T., 2019. Integration of the Indonesian Natural Rubber Market with the World Market. *Journal of Rubber Research*, Volume 37(2), pp. 139–150