DETERMINATION OF CHEMICAL AND MECHANICAL PROPERTIES OF HYDROGENATED NATURAL RUBBER SYNTHESIZED AT SEMI PILOT SCALE

Santi Puspitasari, Adi Cifriadi, and Asron Ferdian Falaah
Indonesian Rubber Research Institute, West Java Indonesia

Abstract

The use of natural rubber goods for outdoor based applications like elastomeric bearing pads is limited by their low thermal oxidative resistance. This weakness could be improved by chemical modification such as diimide transfer hydrogenation of natural rubber in the latex phase. Diimide is a reactive hydrogen donor substance which is generated in situ by oxidation of hydrazine hydrate with hydrogen peroxide. In this research, the hydrogenated natural rubber was synthesized by diimide transfer hydrogenation at semi pilot scale at a capacity of 2.5 kg latex concentrated/batch. The aim of the research was to determine the chemical and mechanical properties of hydrogenated natural rubber obtained from the semi pilot scale reaction. Unmodified natural rubber was used as a control. The result of the evaluation showed that the diimide substance produced from a higher hydrogen peroxide concentration could effectively convert unsaturated C double bonds into saturated C single bonds in the natural rubber molecular chain. The improvement of the thermal oxidative resistance is illustrated by a higher plasticity retention index and less change in hardness and elasticity for hydrogenated natural rubber prepared from 35 phr hydrogen peroxide. This new type of modified natural rubber could potentially be a substitute for synthetic rubber used in the manufacturing of elastomeric bearing pads.

Keywords: Diimide, hydrogenation, natural rubber, thermal oxidative resistance

INTRODUCTION

Natural rubber derived from Hevea brasiliensis Muell Arg tree, is one of the most commercialized biopolymers in industry. Hevea natural rubber is a white milky sap composed of rubber particles and non rubber compounds such as protein and phospholipid which are dispersed in the serum phase (Rahman et al., 2013; Nawamawat et al., 2010; Sansatsadeekul et al., 2011). The composition of rubber particles in fresh latex reach 94-98% and consists of repeating units of isoprene monomers which are linked together to form cis 1-4 polyisoprene (Kongparakul et al., 2011). Long polyisoprene molecular chains give advantages to the characteristics of Hevea natural rubber such as good mechanical and dynamic properties (Hinchiranan et al., 2006). However, the presence of reactive unsaturated C double bonds within the polyisoprene backbone mean Hevea natural rubber has low thermal oxidative resistance - it will easily deteriorate on contact with oxygen, ozone, and sunlight (Mahittikul
et al., 2006). This weakness limits *Hevea* natural rubber goods for outdoor applications.

Transfer hydrogenation of natural rubber in the latex phase is an alternative recommended procedure that can improve the thermal oxidative resistance of *Hevea* natural rubber. In the transfer hydrogenation process, the reactive C double bonds in the polyisoprene molecular chain will be converted into C single bonds without subsequent molecular chain scissioning (Mahittikul et al., 2009; Piya-areetham et al., 2013). The hydrogenated natural rubber (HNR) has a similar molecular structure to ethylene-propylene alternating copolymer (EPDM) which is known as a high thermal oxidative synthetic rubber (Inoue & Nishi, 2007; Piya-areetham et al., 2013). Thus HNR has the potential as a substitute for EPDM in the manufacturing of outdoor rubber based products (Pruttisirikul et al., 2010).

Transfer hydrogenation of natural rubber latex can be conducted using a diimide compound. Generally, the diimide compound is generated in situ during the transfer hydrogenation by oxidation of hydrazine hydrate with hydrogen peroxide. The mechanism is quite simple compared to conventional hydrogenation since it only needs a homogeneous catalyst and no involvement of diffusion mass transfer as occurs with a heterogeneous catalyst often used in conventional hydrogenation (Mahittikul et al., 2009; Piya-areetham et al., 2013; Wang & Astruc, 2015; Tangthongkul et al., 2005). The method can be carried out at atmospheric pressure. The diimide transfer hydrogenation is a function of proportion of hydrazine hydrate/hydrogen peroxide, type and concentration of homogeneous catalyst, reaction condition and technique. Previous diimide transfer hydrogenation of natural rubber investigations were performed at laboratory scale. Mahittikul et al (2007) stated that cupric acetate was the most reactive catalyst for hydrogenation of high ammoniated natural rubber latex by semi-continuous technique. Furthermore, non-catalytic diimide hydrogenation by seedling technique was conducted by Veni and Ma’zam (2010) and indicated that fresh field latex achieved the highest hydrogenation efficiency compared to another type of the latex. Cifriadi et al (2017) found that the used of deproteinized natural rubber latex on catalytic diimide transfer hydrogenation increased the possibility of side reactions such as depolimerization and crosslink reactions. Thus it was decided to develop the hydrogenation of natural rubber into a semi pilot scale.
The article presents a procedure to synthesize HNR by catalytic
diimide transfer hydrogenation of natural rubber latex at a semi pilot scale
of capacity 2.5 kg latex concentrated/batch. The effect of varying the
hydrazine hydrate/hydrogen peroxide proportion was studied. The
optimum characteristics of HNR were determined based on chemical and
mechanical properties.

MATERIALS AND METHODS

The main materials used in this study included high ammoniated
natural rubber (HANR) latex which was provided by the Indonesian
Rubber Research Institute, hydrazine hydrate 35% was obtained from PT.
Isoclay Acidatama Indonesia, hydrogen peroxide 30% was purchased
from CV. Setia Guna, Bogor. Sodium thiosulfate as neutralizing agent
and calcium chloride as coagulant were also purchased from CV. Setia
Guna, Bogor. Anionic and nonionic surfactants were provided by PT.
KAO Indonesia. Pure analysis grade of boric acid as reaction promoter
was received from Merck Germany.

The diimide transfer hydrogenation of natural rubber was conducted
by using a semi pilot scale stirred tank reactor. The reactor was equipped
with a thermo controller, agitator and jacket heater. Meanwhile for the
chemical analysis a Thermo Scientific Nicolet S5 ATR-FTIR was used to
analyze functional groups and a Wallace Rapid Plastimeter was used to
study the plasticity retention index of HNR. The cure characteristics of
the HNR compound were studied using a Rheometer, while a Lloyd
tensometer was used to determined the elasticity.

The procedure of catalytic diimide transfer hydrogenation of natural
rubber latex concentrated at semi pilot scale was as follows : the HANR
latex concentrate was fed into the reactor and then were added catalyst
boric acid, 0.5 phr anionic surfactant and 0.5 phr nonionic surfactant. The
temperature of reaction rose gradually to reach 40°C. When this
temperature was reached, 45 phr hydrazine hydrate 35% and hydrogen
peroxide 30% at concentrations 30 and 35 phr were added continuously
into the mixture. The reaction was run for 6 hours. For the last 30 minutes
of the reaction, sodium thiosulfate was added to neutralize any unreacted
hydrogen peroxide. The hydrogenated latex was then coagulated using
calcium chloride liquid. The coagulum of hydrogenated natural rubber
(HNR) was milled in a creeper machine. Wet sheet HNR was matured for
24 hours before being dried in the oven at 100°C. Dry sheet HNR was cut
to be analyzed for its chemical properties including degree of
hydrogenation, plasticity retention index, and gel content. Qualitative analyses were also performed as primary indicators of the conversion of the C double bond into C single bond by hydrogenation. Qualitative analyses included physical visualization and FTIR spectroscopy.

The mechanical properties of HNR were determined with reference to SNI 3967:2013, standard quality for elastomeric bridge bearings. The production of HNR vulcanizate began with mastication of the HNR sheet in an open mill. To the soft HNR was added activators, antioxidant, antiozonant, processing aid, accelerators and vulcanizing agent. The HNR compound was then homogenized and matured at room temperature for 24 hours. The HNR compound sample was analyzed for its cure characteristics by Rheometer. Some of the HNR compound was also moulded using a hydraulic press machine at 150°C to prepare samples for mechanical tests. The mechanical tests included parameters such as hardness, tensile strength, elongation at break, compression set, and ozone resistance. The unmodified natural rubber was used as a control.

RESULTS AND DISCUSSION

Physical visualization analysis of HNR is often used as a primary evaluation of the transfer hydrogenation efficiency since it can be used to predict the occurrence of side reactions. Physical visualization parameters consist of color and texture. Figure 1 illustrates the physical visualization of HNR. It can be seen that HNR has a brownish colour, while unmodified natural rubber dried sheet generally has a yellowish colour. HNR also has a solid, hard and non tacky/sticky texture similar to unmodified natural rubber (NR). It means that the diimide transfer hydrogenation of natural rubber latex conditions which were set in the research minimized the possibility of side reactions which increased the hydrogenation efficiency.
Another qualitative analysis to determine the hydrogenation efficiency was by Fourier Transform Infra Red (FTIR) spectroscopy. This procedure can identify changes of functional groups on the natural rubber molecular structure due to diimide transfer hydrogenation. Figure 2 compares the functional groups of unmodified natural rubber (NR) to hydrogenated natural rubber (HNR) synthesized by the addition of 30 and 35 phr of hydrogen peroxide.

The important functional group of unmodified natural rubber is characterized by sharp peaks at wave number 1662 cm\(^{-1}\) (C=C unsaturation, stretching vibration) and 834.18 cm\(^{-1}\) (trisubstituted olefinic =C-H, bending vibration). The peak at 834 cm\(^{-1}\) is known as the fingerprint region of NR (Ibrahim et al., 2014). Other distinct peaks in the unmodified natural rubber FTIR spectra were at 2960.07 cm\(^{-1}\) (CH\(_3\) symmetric, stretching vibration), 1446.89 cm\(^{-1}\) (CH\(_3\) symmetric, bending vibration), 2851.93 cm\(^{-1}\) (CH\(_2\) symmetric, stretching vibration), 1375.32 cm\(^{-1}\) (CH\(_2\) symmetric, bending vibration), and 739.64 cm\(^{-1}\) associated with \(\text{–(CH}_2\text{)}_3\text{–}\) species (Mahittikul et al., 2007; Mahittikul et al., 2009; Arayapranee & Rempel, 2013).

The mechanisms of diimide transfer hydrogenation of natural rubber latex are indicated by three observations. First, the reduction of transmittance intensity at wave numbers around 1662 cm\(^{-1}\) and 833 cm\(^{-1}\) due to the elimination of unsaturated C double bonds and formation of saturated C single bonds on the natural rubber molecular chain by addition mechanism. This mechanism results in an increasing intensity at peak 739 cm\(^{-1}\). The third indicator is the occurrence of a new sharp peak at 3410 cm\(^{-1}\) and 1741 cm\(^{-1}\) attributed to \(-\text{OH}\) and C=O groups, respectively. The new peaks were only observed on HNR FTIR spectra where 35 phr hydrogen peroxide was used in the synthesis. In these
diimide transfer hydrogenation conditions depolimerization has occurred as a side reaction during diimide transfer hydrogenation.

![FTIR spectra](image)

**Figure 2.** FTIR spectra of unmodified natural rubber and hydrogenated natural rubber

Chemical characteristics of raw hydrogenated natural rubber are summarized in Table 1. In this study, the conversion of hydrogenation is measured by the degree of hydrogenation based on the iodine number. Iodine number analysis measures the amount of unsaturation (in the form of C double or triple bonds) in olefin compounds including natural rubber. The iodine number analysis was performed according to the Wijs Method. The degree of hydrogenation is the percentage comparison of the iodine number of hydrogenated natural rubber to unmodified natural rubber. Unmodified natural rubber has the iodine number 434.49 due to the high content of unsaturated C double bonds in its molecular chain. While the hydrogenated natural rubber has iodine number 171.84. The lower iodine number of hydrogenated natural rubber shows the less
unsaturated compound presence in its molecular structure where it has been eliminated by the diimide compound during the transfer hydrogenation. The dramatic reduction of the iodine number of hydrogenated natural rubber was followed with the high value of degree of hydrogenation which reached 60%.

Thermal oxidative resistance of raw rubber is measured based on initial plasticity (Po) and plasticity retention index (PRI) values. High PRI values of raw rubber equal good thermal oxidative resistance (Bonfils et al., 2005). Unmodified natural rubber had Po and PRI values of 49 and 12.5, respectively. The low PRI value of natural rubber is due to the occurrence of a biochemical reaction during the long period of storage by microorganism activity which decomposed the antioxidant including that in the non rubber fraction (Baimark & Niamsa, 2009). Table 1 shows that hydrogenated natural rubber has better thermal oxidative resistance than unmodified natural rubber. The highest thermal oxidative resistance was achieved by hydrogenated natural rubber synthesized by the addition of 35 phr hydrogen peroxide which has a PRI value of 25.5. At a reaction temperature of 40°C, the rise of hydrogen peroxide concentration significantly increases the thermal oxidative resistance of natural rubber due to more reactive hydrogen peroxide reacting with hydrazine hydrate to form diimide compound. This diimide compound will convert the unsaturated C double bonds into saturated C single bonds during transfer hydrogenation. Furthermore, at 40°C less hydrogen peroxide which decomposes becomes hydroxyl radicals. The hydroxyl radicals could attack unsaturated C double bonds which ultimately leads to chain scission. Molecular chain scission should be avoided in hydrogenated natural rubber because it can reduce the thermal oxidative resistance.

The polyisoprene rubber molecular chains were composed of sol and gel fraction (Nimpaiboon et al., 2014). Gel content analysis was used as an indicator of the presence of side reactions. Unmodified natural rubber has a gel content of 60%, while the hydrogenated natural rubber is 58%. The slight decrease of gel content is due to the addition of a small amount of polar substance in the latex system. All reagents involved in the hydrogenation system were polar substances which could decompose the gel fraction caused by intermolecular crosslinking of natural rubber.
Table 1. Chemical properties of hydrogenated natural rubber

<table>
<thead>
<tr>
<th>Concentration, phr</th>
<th>Iodine Number</th>
<th>Degree of hydrogenation %</th>
<th>Gel content, %</th>
<th>Po</th>
<th>PRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2H4 35%</td>
<td>45</td>
<td>171.84</td>
<td>60.45</td>
<td>57.84</td>
<td>48.5</td>
</tr>
<tr>
<td>H2O2 30%</td>
<td>35</td>
<td>171.84</td>
<td>60.45</td>
<td>57.74</td>
<td>49.0</td>
</tr>
</tbody>
</table>

Cure characteristics of hydrogenated natural rubber compound are presented in Table 2. Vulcanizate obtained from curing unmodified natural rubber exhibited a comparatively higher torque modulus than vulcanizate from hydrogenated natural rubber. This characteristic is due to the combination of C-C and polysulfidic crosslinking which possibly produces the high crosslink density in unmodified natural rubber vulcanizate. The crosslink of rubber molecular chains were formed by the addition of C double bonds with sulphur. Whereas, the C double bond on the hydrogenated natural rubber molecular chain has been reduced during hydrogenation showing the lower value according to the limitation of chain orientation that caused the low crosslink density indicated by reduction on rheometeric torque modulus resistance (Hinchiranan et al., 2008). Using the same curing system, hydrogenated natural rubber vulcanizate prepared by addition of 35 phr hydrogen peroxide had the longest optimum cure time and scorch time as predicted as the vulcanizate has a very similar molecular structure to EPDM rubber. Hinchiranan et al (2008) found that the optimum cure time of EPDM/NR blends tended to increase with increasing EPDM content. The shortest optimum cure time of hydrogenated natural rubber from 30 phr hydrogen peroxide might be due to the remaining unsaturated C double bonds on its molecular structure that has a higher reactivity for vulcanization (Hinchiranan et al., 2008).

Table 2. Cure characteristic of hydrogenated natural rubber compound

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unmodified natural rubber</th>
<th>Hydrogenated natural rubber at 30 phr H2O2</th>
<th>Hydrogenated natural rubber at 35 phr H2O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque modulus max, kg-cm</td>
<td>6.21</td>
<td>6.15</td>
<td>5.56</td>
</tr>
<tr>
<td>Torque modulus min, kg-cm</td>
<td>0.54</td>
<td>0.56</td>
<td>0.81</td>
</tr>
<tr>
<td>Torque modulus max-min, kg-cm</td>
<td>5.67</td>
<td>5.59</td>
<td>4.75</td>
</tr>
<tr>
<td>Optimum cure time, minute</td>
<td>04 : 06</td>
<td>03 : 59</td>
<td>05 : 14</td>
</tr>
<tr>
<td>Scorch time, minute</td>
<td>02 : 13</td>
<td>02 : 08</td>
<td>02 : 40</td>
</tr>
</tbody>
</table>
The mechanical properties of hydrogenated natural rubber vulcanizates were compared to elastomeric bearing pad properties since the hydrogenated natural rubber obtained from this study will be developed for use in laminated rubber bearing pads. In Indonesia, the standard requirement of commercial elastomeric bearing pads is set out in Standard Nasional Indonesia (SNI) 3967:2013. The mechanical properties of hydrogenated natural rubber vulcanizates compared to unmodified natural rubber vulcanizates are described in Table 3. In general, it can be shown that the hardness and tensile properties of hydrogenated natural rubber vulcanizates were comparable to those of the unmodified natural rubber vulcanizate. Moreover, hydrogenated natural rubber vulcanized prepared from 35 phr hydrogen peroxide was higher than those synthesized from addition of 30 phr hydrogen peroxide due to the increasing degree of hydrogenation (Ikeda et al., 2008). The hydrogenated natural rubber clearly exhibits longer elongation at breaks due to the low crosslink density (Hinchiranan et al., 2008).

After ageing, the elasticity of hydrogenated natural rubber vulcanizates tended to reduce but the hardness rose. Meanwhile both parameters for unmodified natural rubber increased. Two reaction mechanisms occurred during ageing i.e over vulcanization and scissioning of unreacted C double bonds due to the presence of oxygen. The domination of over vulcanization will increase the crosslink density followed by the rise in hardness and stiffness of rubber vulcanizate (Rattanasom & Prasertsri, 2009). The changes in compression set of both hydrogenated natural rubber vulcanizates tend to decrease with increasing amount of saturation of the elastomers. The less flexible of the hydrogenated natural rubber vulcanizates resulted in lower compression set. All natural rubber vulcanizates showed good ozone resistance due to the presence of antioxidant in the rubber compound formula.
Table 3. Mechanical properties of hydrogenated natural rubber vulcanizates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>SNI 3967-2013 Duro 60</th>
<th>NR</th>
<th>HNR at H$_2$O$_2$ 30 phr</th>
<th>HNR at H$_2$O$_2$ 35 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Shore A</td>
<td>60±5</td>
<td>56</td>
<td>57</td>
<td>55</td>
</tr>
<tr>
<td>Tensile strength (min)</td>
<td>N/mm$^2$</td>
<td>15.5</td>
<td>20.4</td>
<td>20.6</td>
<td>22.5</td>
</tr>
<tr>
<td>Elongation at breaks (min)</td>
<td>%</td>
<td>400</td>
<td>530</td>
<td>610</td>
<td>700</td>
</tr>
<tr>
<td>Compression set change (max)</td>
<td>%</td>
<td>25</td>
<td>24.41</td>
<td>19.11</td>
<td>21.02</td>
</tr>
</tbody>
</table>

Ageing at 70°C, for 168 hours

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Point</th>
<th>+10</th>
<th>4</th>
<th>5</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness change (max)</td>
<td>%</td>
<td>-25</td>
<td>1.60</td>
<td>-14.56</td>
<td>-6.67</td>
</tr>
<tr>
<td>Tensile change (max)</td>
<td>%</td>
<td>-25</td>
<td>1.51</td>
<td>-16.39</td>
<td>-11.43</td>
</tr>
<tr>
<td>Elongation at breaks change (max)</td>
<td>%</td>
<td>-25</td>
<td>1.51</td>
<td>-16.39</td>
<td>-11.43</td>
</tr>
</tbody>
</table>

Ozon resistance test

<table>
<thead>
<tr>
<th>Ozon concentration 25 pphm, at 48 hours, strain 20%, ±37.7°C.</th>
<th>-</th>
<th>No</th>
<th>No</th>
<th>No</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>crack</td>
<td>crack</td>
<td>crack</td>
<td>crack</td>
<td></td>
</tr>
</tbody>
</table>

**SUMMARY**

In this study, the determination of chemical and mechanical properties of hydrogenated natural rubber compared to unmodified natural rubber proved that diimide transfer hydrogenation is an effective chemical modification of natural rubber in the latex phase that improves its thermal oxidative resistance. Plasticity retention index measurements and changes in hardness and elasticity values showed the rise of hydrogen peroxide concentration significantly affected the thermal oxidative resistance of raw natural rubber and its vulcanizates. The hydrogenated natural rubber prepared from the addition of 35 phr hydrogen peroxide appears feasible to be developed as a raw material for the manufacturing of elastomeric bearing pads.

**ACKNOWLEDGEMENT**

The authors gratefully acknowledge the support of the Ministry of Research, Technology, and High Education of Republic Indonesia for the Insentif Sistem Inovasi Nasional (Insinas) research funding in the year 2017. The authors also appreciate the participation of Bimo Ekoyono (Bogor Agricultural University) and Roy Krisna Perdana (Kalimantan Institute of Technology) during the study.
REFERENCES


