Effect of urea deproteinization on catalytic hydrogenation of natural rubber latex

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Abstract. Natural rubber is unsaturated biopolymer which has low resistance to heat, oxygen, and ozone. Chemical modification of natural rubber by catalytic hydrogenation can improve its oxidative property. In this study, the catalytic hydrogenation of natural rubber was investigated in latex phase after reduction of protein content with urea. Hydrogenation of deproteinized natural rubber latex was performed by using diimide which generated in situ from hydrazine hydrate/hydrogen peroxide and catalyst (boric acid, cupric sulfate and cupric acetate) at 70°C for 5 h. The hydrogenation system was stabilized with sodium dodecyl sulphate. The hydrogenation of deproteinized natural rubber (HDPNR) was confirmed by FTIR analysis. The result indicated that cupric sulphate was extremely active catalyst which was showed by the elimination of C=C transmittance bands at 1660 cm⁻¹ on HDPNR spectra and highest degree of hydrogenation. Furthermore, urea deproteinization increased possibility of side reactions during catalytic hydrogenation as seen on the reduction of gel content compared to undeproteinized natural rubber.

1. Introduction

The fresh natural rubber latex derived from Hevea brasiliensis (Willd.) Muell.Arg is composed of rubber particles and non-rubbers fraction mainly protein and phospholipid which are dispersed in water phase [1-3]. While on natural rubber particle itself is consist of 94% rubber hydrocarbon molecules of cis-1,4_polyisoprene surrounded by protein-phospholipid layer which maintain the stability of rubber particle [4]. Whereas long polyisoprene chain give advantages such good mechanical and dynamic properties to natural rubber characteristic [5]. The existence of reactive unsaturated C double bond within the polyisoprene backbone cause natural rubber is easily deteriorates when expose to oxygen, ozone, and sunlight [6]. This weakness limits the natural rubber application especially in the manufacture of outdoor rubber based product.

Thermal oxidative degradation of natural rubber can be prevented by physical technique such as blending or coating of natural rubber with another polymer which acts as a thermal oxidative stabilizer [7,8]. Another method is by chemical modification as hydrogenation of natural rubber in latex phase. Reduction of C=C double bond by hydrogenation without being followed by scissioning of the molecular chain will significantly improve the thermal oxidative resistance of natural rubber [9,10]. Catalytic
transfer hydrogenation is preferred than conventional. Transfer hydrogenation require an addition of non-H\textsubscript{2} compound and homogeneous catalys since they provide higher selectivity and simplicity mechanism owing to no involvement of diffusion mass transfer as occur in heterogeneous catalyst [9-12]. Diimide is highly reactive intermediate non-H\textsubscript{2}compound which can be generated in situ during hydrogenation by oxidation of hydrazine hydrate by hydrogen peroxide, the decarboxylation of potassium azodicarboxylate, thermal decomposition of p-toluenesulfonyl hydrazine and the photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione [13-18]. The hydrogenated natural rubber (HNR) has similar molecular structure to ethylene-propylene alternating copolymer (EPDM) rubber [19,20]. Thus HNR is potential to substitute EPDM rubber to achieve better thermal oxidative stability on outdoor rubber based product [21].

The diimide hydrogenation is strongly depends on the ratio concentration of hydrazine hydrate/hydrogen peroxide, type of homogeneous catalysts, reaction condition and technique. Mahittikul et al., (2007) found that cupric acetate was the most reactive catalyst for hydrogenation of high ammoniated natural rubber latex by semi-continuous technique [22]. Furthermore, non-catalytic diimide hydrogenation by seedling technique was done by Veni and Ma’zam (2010) indicated that fresh field latex achieved highest hydrogenation efficiency compared to another type of the latex [23].

The use of hydrogen peroxide as strong oxidizing agent increase the possibility of side reaction such as depolymerization and gel formation by crosslink reaction of non rubber constituent which can compete to the diimide hydrogenation [6,24]. Moreover, the protein contained in natural rubber are also suggested can reduce hydrogenation efficiency due to the protons of the amine group are electron donating species that may react with the diimide via metathesis hydrogenation [25]. This research used urea deproteinized natural rubber latex in order to reach high degree of catalytic diimide hydrogenation. Urea deproteinization offers simplicity on deproteinization method of natural rubber compared to enzymatic deproteinization [26,27]. The aim of the present research was to investigate the effect of urea deproteinization on the properties of hydrogenated rubber (HDPNR) synthesized by catalytic diimide hydrogenation of natural rubber latex by using various homogeneous catalysts.

2. Material and Method
Commercial high ammoniated natural rubber latex concentrated (NRL) (dry rubber content, DRC as 56%) was provided by Indonesian Rubber Research Institute (Bogor, Indonesia). Hydrazine hydrate (purity 80%), 30% aqueous hydrogen peroxide, boric acid, cupric sulfate, cupric acetate, urea, and sodium dodecyl sulfate (SDS) were purchased from Merck, Germany. Technical grade of silicon oil as antifoam agent, acetone and calcium chloride as coagulants were received from local supplier.
The latex deproteinization used Alfa Laval Centrifuge machine to separate the protein bound urea in serum fraction. While the hydrogenation was conducted in a 500 mL three necked round bottomed flask which was equipped with thermometer, reagent droplet vessel, and gaseous N$_2$ inlet tube. Heating and agitation were facilitated by Cimarex Thermolyne hot plate magnetic stirrer. The qualitative analysis used Thermo Scientific Nicolet S5 ATR-FTIR. Thus the oxidative resistance of raw HNR was measured by using Wallace Rapid Plastimeter.

2.1. Urea Deproteinization of Natural Rubber Latex (DPNR)

Urea deproteinization of NRL procedure was referred to previous work [27]. NRL concentrate was added by 0.1% urea and dispersed in a SDS 1% solution until the DRC reached 30%. The NRL was incubated at room temperature for 60 min and low speed of agitation. The NRL incubation was followed by centrifugation at 15000 rpm. The cream fraction of NRL was redispersed in a distilled water to make 30% DRC and recentrifuged to wash residual protein in the NRL. The deproteinized natural rubber (DPNR) latex concentrate obtained was preserved with 0.2% ammonia and 0.2% SDS to ensure the stability before being used in diimide hydrogenation. DPNR was characterized the protein content by Kjeldahl Method.

2.2. Catalytic Diimide Hydrogenation of DPNR Latex (HDPNR)

The diimide hydrogenation of DPNR latex was run at various types of preservative and homogeneous catalyst. Semi-continuous reaction technique was applied to the system. DPNR latex concentrate was fed into the flask, followed by addition of distilled water to make 30% DRC. Gaseous N$_2$ was purged into the DPNR latex under agitation for 15 min to remove dissolved oxygen. The temperature of the DPNR latex was raised gradually up to 70°C. Thus, 2 per hundred rubber (phr) of hydrazine hydrate and 0.05 phr of catalyst were added to the DPNR latex, respectively. 3 phr hydrogen peroxide was added dropwise at particular rate for 2 h in order to maintain an isothermic condition. The diimide hydrogenation was continued for 3 h after the last hydrogen peroxide droplets. At the end of the reaction, the hydrogenated deproteinized natural rubber (HDPNR) latex was coagulated by using the mixture of acetone and CaCl$_2$ 5% solution (1:1). The HDPNR coagulum was milled on creeper machine and dried at 50°C for 24 h before characterized.
2.3. Characterization of HNR

2.3.1. FTIR Spectroscopy Analysis.

The microstructure of HDPNR samples were determined by using Thermo Scientific Nicolet S5 ATR-FTIR spectroscopy. The FTIR spectra of HDPNR were scanned in transmittance mode at wavenumber within the range of 4000 to 500 cm\(^{-1}\). Each HDPNR sample was scanned twice before confirmed.

2.3.2. Iodine Number and Degree of Hydrogenation.

The conversion of unsaturated C double bond onto saturated C single bond on natural rubber molecular chain by diimide hydrogenation was determined by iodine number calculation referred to Wijs Method by following equation (1).

\[
\text{Iodine Number} = N \times 12.69 \times \left( \frac{V_B - V_A}{m} \right)
\]  

Remarks:
- \(N\): normality of sodium thiosulfate solution after standardization (N),
- \(V_B\): volume sodium thiosulfate for blank titration (mL),
- \(V_A\): volume of sodium thiosulfate for HDPNR titration (mL),
- \(m\): mass of HDPNR (g).

Degree of hydrogenation was determined referred to the following equation (2).

\[
\text{Degree of hydrogenation} = \frac{C_0 - C}{C_0} \times 100\%
\]

Remarks:
- \(C_0\): iodine number of DPNR
- \(C\): iodine number of HDPNR

2.3.3. Original Plasticity (Po) and Plasticity Retention Index (PRI) Analysis.

The plasticity tests were designed to provide a rapid assessment of the susceptibility of raw rubber to thermal oxidative resistance. The test procedure for Po and PRI analysis were carried out according to the ASTM D 3194-04 standard. PRI was percentage ratio of Po before and after ageing at specified temperature and time (140°C for 30 min). Equation (3) described the PRI measurement.

\[
PRI = \frac{P_a}{P_o} \times 100\%
\]

Remarks:
- \(P_a\): plasticity after aging,
- \(P_o\): plasticity before aging

2.3.4. Gel Content Analysis.
Gel content of HDPNR was determined referring to following method: 0.125 g finely cut of HDPNR sample was diluted on 25 mL of chloroform and kept for 20 h. The swollen HDPNR then sieve through filter paper. The residue consist of macro gel together with the filter paper was dried at 100°C until definite weight was achieved. The gel content of HDPNR was calculated by equation (4).

$$\text{Gel Content} = \frac{\text{Gel weight}}{\text{HDPNR weight}} \times 100\%$$  \hspace{1cm} (4)

3. Results and Discussion

3.1. Preparation of DPNR Latex

Elimination of protein on NRL by urea deproteinization is confirmed qualitatively by FTIR spectroscopy analysis as describes at Figure 1. NRL spectra shows the presence of protein layer indicated by transmittance bands at 3285 cm\(^{-1}\) and 1544 cm\(^{-1}\) assigned to N-H stretching and N-C=O amide II vibration, respectively [6]. The bands are disappeared at DPNR spectra. The quantitative analysis also indicate that the urea deproteinization cause the protein content of NRL is significantly reduced from 1.37 to 0.44%. It was believed that protein attached on the surface of the natural rubber particle by physical interactions had denatured by urea. Urea formed hydrogen bond to the moieties of the protein which was stronger than covalent binding between protein and rubber particle [28, 29]. Thus, the protein bound urea was dispersed on the serum phase of DPNR latex and being removed by surfactant washing during multistage centrifugation [30]. The function of protein in maintaining the rubber particles stabilization was replaced by ammonia as preservative or SDS surfactant as new stabilizer.

Natural rubber molecules on both NRL and DPNR spectras show distinct bands refer to cis-1,4 polyisoprene for the unsaturated C double bond stretching vibration and =C-H out of plane bending vibration for tri-substituted olefinic at wavenumber around 1660 cm\(^{-1}\) and 833 cm\(^{-1}\), respectively. Another important peaks are showed by transmittance bands at 738 cm\(^{-1}\)correlated to −(CH\(_2\))\(_3\)− species, 2959 and 1447 cm\(^{-1}\) for symmetric C-H\(_3\) bonds stretching and bending vibrations, 2852 cm\(^{-1}\) and 1375 cm\(^{-1}\) for symmetric C-H\(_2\) bonds stretching and bending vibration[10, 22, 31].
3.2. Diimide Hydrogenation of DPNR Latex

FTIR spectra of all of the HDPNR show identical pattern as illustrated at Figure 2. After the hydrogenation process, the transmittance bands at 1660 cm\(^{-1}\) and 833 cm\(^{-1}\) decrease, followed by increasing band at wavenumber around 740 cm\(^{-1}\) assigned to \(-(\text{CH}_2)_3-\) species due to the addition of hydrogen atom from diimide compound to C=C double bond on natural rubber molecular chain. The significant elimination of C=C double bond was occurred on cupric sulphate catalyst addition to hydrogenation of DPNR latex stabilized with SDS. The FTIR spectra also show peaks at wavenumber 3400 cm\(^{-1}\) and 1740 cm\(^{-1}\) representing OH and C=O bonds. Those transmittance bands indicated the occurrence of side reaction such as depolymerisation during hydrogenation [32].

Figure 2. FTIR spectra of HDPNR prepared by various catalyst

Physical visualization of HDPNR as presented at Figure 3 can be used as primary evaluation to the hydrogenation efficiency since it characterizes side reaction. HDPNR prepared with addition of
boric acid has yellowish colour and solid texture, whereas cupric ion catalysts produce brownish colour and soft sticky-paste like texture. The presence of cupric ion in hydrogen peroxide-latex hydrogenation system at certain temperature accelerated the oxidation of natural rubber molecule which caused chain scission or depolymerization. Cupric ion played as prooxidant compound, while hydrogen peroxide formed hydroxyl free radical. By the elimination of protein layer surrounded DPNR particle, the hydroxyl free radical and cupric ion became easier to attack the polyisoprene molecules. Hydroxyl free radical was believed to be more reactive than diimide compound, so at hydrogenation catalysed by cupric ion system, depolymerisation actually dominated. The similar mechanism could be found in the synthesis of liquid natural rubber.

**Figure 3.** Physical visualization of HDPNR

The effect of ammonia and SDS in maintaining DPNR latex stabilization during diimide catalytic hydrogenation to the iodine number and degree of hydrogenation are illustrated at Figure 4 and 5, respectively. The both figures demonstrate that SDS stabilizer produce higher efficiency of hydrogenation compared to ammonia preservative. On catalytic diimide transfer hydrogenation, SDS played dual functions, either as stabilizer of colloidal rubber particles and secondary catalyst due to the presence of sodium atom on the molecular structure. At the same latex stabilization systems, the effectiveness of catalysts in descending order are cupric sulphate > cupric acetate > boric acid. The cation and anion of the catalyst were strongly affected the degree of hydrogenation. Cupric ion was the most suitable metallic cation for catalyzing the diimide transfer hydrogenation of natural rubber. Sarkar et al claimed that the catalytic activity of cupric metal complex depended on the acidity of the ligand and the strength of the metal-ligand interaction [14]. The interaction between metal ion of cupric$^{2+}$ and ligand such SO$_4^{2-}$ was slightly higher than CH$_3$COO$. Boric acid produced lowest degree of hydrogenation since it was more regarded as promoter than an catalyst on hydrogenation [22]. Veni and Ma’zam also purposed that between boric acid and hydrogen peroxide formed hydrogen bond which able to control hydrogen peroxide activity in the reaction medium [23]. The decrease on
hydrogen peroxide activity inhibited the oxidation of hydrazine hydrate in generating diimide at the rubber particle surfaces.

![Figure 4](image1.png)

**Figure 4.** Iodine number of DPNR and HDPNR

![Figure 5](image2.png)

**Figure 5.** Degree of hydrogenation of the HDPNR

Test result of gel content analysis of the HDPNR is described at Figure 6. All of the HDPNR samples have lower gel content compared to unmodified DPNR. The polyisoprene rubber molecular chains were composed of sol and gel fraction [33]. Gel fraction could be used as indicator of the existence of branched or network structures in among rubber molecular chains [30]. Originally, gel fraction contributed by two mechanism such as interlinkage or crosslinking of rubber molecular chains and interaction of protein and phospholipid at the initiating ω-terminal and terminating α-terminal on rubber molecule [23,34,35]. In the study, the gel content formation only affected by the crosslink of rubber molecule since the protein-phospholipid had been eliminated during the deproteinization process. Blackley pointed out that the addition of small amount of polar substance in the latex system can greatly reduce the apparent gel content [36]. All reagents involved in the hydrogenation system were polar substances which could decomposed the gel fraction caused by intermolecular crosslink of natural rubber.
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Figure 6. Gel content of HDPNR

High plasticity indicates better thermal oxidative resistance of natural rubber. Table 1 summarizes the plasticity test result of HDPNR. The undetected PRI value for HDPNR due to the samples were more not resistant to heat and oxygen exposure compared to unhydrogenated DPNR. At temperature of reaction as 70⁰C, hydrogen peroxide either react with hydrazine hydrate to generate diimide but also decomposed to form highly reactive free hydroxyl radical. The hydroxyl radical attacked unsaturated C double bond which ultimately led to chain scission. The dominations of this side reaction was characterized by tacky texture on HDPNR when expose to heat and oxygen.

| Type of rubber         | Po   | PRI (%) |
|------------------------|------|---------|
|                        | Ammonia | SDS | Ammonia | SDS |
| Unhydrogenated DPNR    | 54.5  | 54   | 27.8    | 27  |
| HDPNR-boric acid       | 53    | 36   | NA      | NA  |
| HDPNR- cupric acetate  | NA    | NA   | NA      | NA  |
| HDPNR-cupric sulfate   | NA    | NA   | NA      | NA  |

Remarks: NA : the HDPNR was tacky along the PRI testing

4. Conclusion

The urea deproteinization of natural rubber latex was understood to be an ineffective procedure for preparing diimide hydrogenation of natural rubber. The elimination of protein-phospholipid layer surrounded rubber particle increased the possibility of side reaction such as depolymerisation which also accelerated by the presence of cupric ion catalyst. It was showed by the elimination of C double bond at transmittance band around 1660 cm⁻¹ on FTIR spectra and highest degree of hydrogenation. Furthermore, the reduction of gel content was also indicated the occurance of side reaction such decomposition of intermolecular rubber crosslink.
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