Catalyst screening on diimide transfer hydrogenation of natural rubber latex

Mutia Anissa Marsya¹, Bismo Dwi Putranto², Santi Puspitasari³, Adi Cifriadi³, Mochamad Chalid²,*

¹Chemical Engineering, Universitas Bhayangkara Jakarta Raya, Bekasi, West Java, Indonesia
²Department of Metallurgy and Materials Engineering, Universitas Indonesia, Depok, West Java, Indonesia
³Indonesian Rubber Research Institute, Bogor, West Java, Indonesia
*Corresponding author: chalid@metal.ui.ac.id

Abstract. Latex as the precursor of natural rubber has the high elasticity and plasticity superior to synthetic rubber. However, it tends to coagulate easily and makes the latex unstable for thermal treatment such as hydrogenation and compounding, which are required for it to be processed further. Therefore, latex treatment before and during hydrogenation are necessary. In this research, 1% SDS (sodium dodecyl sulphate) as a surfactant, 200 rpm of stirring velocity, 20% of dry rubber content were used as the treatment processing parameter, where the temperature was used as the independent variable, to determine the highest turbidity and the lowest viscosity condition of the latex. After optimum processing temperature, has been obtained, the latex was then hydrogenated with and without the addition of DPNR (Deproteinized Natural Rubber) catalysts which were FeSO₄, boric acid, Zn-Acetate, Cu-Acetate, and CuSO₄. In this case, hydrogenation efficiency measured by means of the degree of hydrogenation that represented by numbers of C double bond. It was found that the interplay between all the variables has different effects towards the colloidal stability of the latex and the effectivity of the hydrogenation itself.

Keywords: DPNR catalysis, latex, hydrogenation, colloidal

1. Introduction
While synthetic rubber is largely produced from petroleum, around one-quarter of the world’s rubber comes from a natural source. Natural rubber (NR) is a renewable hydrocarbon resource produced at a very low cost and is used extensively in the rubber industry [1]. Indonesia is second biggest natural rubber producer in the world after Thailand in the first place and followed by Malaysia and Vietnam respectively. In 2014, Association of Natural Rubber Producing Countries, Indonesian Rubber Association (Gapkindo), and Food and Agriculture Organization of the United Nations, Indonesia produced 3.11 million tons of NR in 2015 and 3.16 million tons in 2015. Natural Rubber (NR) from Hevea brasiliensis has good elasticity and mechanical strength. On the other hand, NR is a polymer with high content of unsaturated carbon double bonds (C=C) which causes of deteriorates resistance of oxidation, ozone and heat [2]. Because of a relatively high reactivity, the unsaturated carbon double bonds are commonly become the main issue in a molecular modification to answer the rubber product challenges [3].
Latex is colloid system where rubber particles covering by protein and phospholipids dispersed in the water [4]. These two compounds as natural stabilizer of latex colloid solution, because rubber particle itself is a non-polar compound and water is a polar one. Not only rubber particles, latex also contains another component such as fat, glycolipids, carbohydrates, proteins, phospholipids and organic materials, etc. Based on the protein content in latex, there are two kinds of latex, they are deproteinized natural rubber (latex DPNR) which produced by using deproteinization process to reduce protein content in latex and non-deproteinized natural rubber without deproteinization process (latex non-DPNR). Fukushima et al. [5] highly suggest to use deproteinized natural rubber in their research, because protein be able to increase gel production in modification process of natural rubber.

Modification of natural rubber which could improves physicals, chemical and thermal properties have been reported using hydrogenation process. The common hydrogenation process uses hydrogen gaseous to conduce the unsaturated hydrocarbon. In this experiment, we use the di-imide compound which could reduce the carbon-carbon double bonds (C=C) in the polymer backbone [6]. Di-imide compound was conducted by oxidation reaction between hydrazine hydrate and hydrogen peroxide. Lin et al. [7] explain the possible reaction between di-imide compound and latex:

\[ \text{N}_2\text{H}_4 + \text{H}_2\text{O}_2 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2\text{O} \]
\[ \text{N}_2\text{H}_2 + \cdot\text{H}\cdot\text{C}=\text{CH} \rightarrow \text{N}_2 + \cdot\text{H}_2\text{C}-\text{CH}_2- \]

Catalyst added to the natural rubber latex hydrogenation reaction is intended to increase the rate of the hydrogenation transfer reaction. Addition of the catalyst is expected to obtain high hydrogenation conversion. A good and suitable catalyst required must be has high selectivity and reactivity for the natural rubber latex hydrogenation reaction, it means that catalyst functions is only to optimizing the hydrogenation transfer reaction without triggering a side reaction [8]. In hydrogenation process with di-imide compound, Parker et al. [9] discovered that the di-imide intermediates are stabilized by Cu\(^{2+}\). Mahittikul et al. [6] have reported study of hydrogenation natural rubber in latex form by di-imide from reaction with cupric sulphate, cupric acetate and cupric chloride as catalyst. The cupric acetate has the best hydrogenation degree for the reaction as catalyst. This paper focus on comparison of the metal ion Zn\(^{2+}\), Cu\(^{2+}\), Fe\(^{3+}\) as catalyst and non-metal catalyst, boric acid, by using deproteinized (DPNR) latex in optimizing of natural rubber hydrogenation. Hydrogenation degree was evaluated by using iodine number method. Temperature effect on colloid stability in latex also evaluated in preparation hydrogenation process.

2. Material and Methods

2.1. Materials
Deproteinized Natural Rubber and Non-Deproteinized Natural Rubber with 0.1% sodium dodecyl sulphate (SDS) as surfactant from Indonesian Rubber Research Institute, Hydrazine Hydrate 98%, Hydrogen Peroxide 30%, catalyst (Cupric Sulphate (CuSO\(_4\)), Cupric Acetate (Cu(CH\(_3\)COO)\(_2\)), Zinc Acetate (C\(_2\)H\(_3\)O\(_2\)Zn), Boric Acid (H\(_3\)BO\(_3\)), Iron (II) Sulphate (FeSO\(_4\)).

2.2. Instrumentation
Optimizing temperature will be analysed by using turbidity meter and viscometer Haake 6 Plus. Hydrogenation degree will be calculated by using Iodine number method and reduction of double bond (C=C) can be investigated by FTIR.

2.3. Procedure
2.3.1. Preparation of Di-imide Hydrogenation. In this study, thermal effect on colloid stability was studied to reduce possibility of flocks forming in hydrogenation process. 300 mL non-deproteinised Natural Rubber with 20% of weight dry rubber content put into hydrogenation reactor and stirred with 200 rpm for 5 hours. The natural rubber solution was heated in the water bath of the reactor with initial
temperature was 25℃. In this stages, the variable of this experiment is temperature, the solution was heated until 25℃ (constant from initial temperature), 35℃, 50℃, 70℃ and 90℃. 10 mL of sample was analysed 3 times for every measurement in every hour (triplo measurements).

2.3.2. Hydrogenation. Deproteinised NR with 25% of weight dry rubber content put into hydrogenation reactor and stirred with 200 rpm for 5 hours. The solution was heated at 50℃ in the water bath of the reactor. The nitrogen gas was bubbled into the solution by using hoses throughout the hydrogenation process to reduce oxygen (O₂) in the solution and inhibit oxidation in hydrogenation process. After stirring for 15 minutes, 24 mL hydrazine hydrate and 0.1% of catalyst was added respectively, and stirred for 30 minutes. Then, the mixture was at 50℃, 6 mL hydrogen peroxide (H₂O₂) was added by dropping it wise for at a rate for 2 hours. Antifoam was added when the froth was formed in the mixture. After 5 hours, hydrogenation process was stopped. 3 samples were made by using acid to make flock of latex. Then the flocks were dried before iodine number test. Experiments was conducted for several times with different catalyst such as Cupric Sulphate (CuSO₄), Cu-Acetate (Cu(CH₃COO)₂), Zn-Acetate (C₄H₆O₄Zn), Boric Acid (H₃BO₃), and Iron (II) Sulphate (FeSO₄).

3. Results and Discussions

3.1. Latex Stability

Colloid stability in latex solution is one of the most important to be considered to inhibit flocculation in chemical modification process of natural rubber. In this study, colloid stability is investigated by using turbidity meter (turbidity) and viscometer (viscosity) in different temperature condition. Viscosity shows how liquid substance flows and turbidity gives information behaviour of colloid latex, whether spread in the mixture or tend to be flocks. These two of characteristics can be related with Browns Motion theory. Temperature has a huge effect on browns motion of latex colloid.

According to the browns motion theory, every particle colloid has a random motion. There are some mechanical treatments has an effect on particle suspended in fluid, for examples are agitation and heated. Fig. 1 shows turbidity value of latex colloid gradually increased at 20℃, 35℃ and reached a pick at 50℃ after that, turbidity line went down at higher temperature. From the line, it can be seen that the optimum temperature for hydrogenation is 50℃ with turbidity value is 19.019 NTU. The turbidity line also gives information that particles can be faster by heating. The higher turbidity indicates that colloid particles spread well in latex solution.

![Figure 1. Viscosity and turbidity value latex colloid in different temperature.](image)

In the last hour of experiment at 70℃, latex solution became more viscous and there was found some flocks stick to beaker glass of hydrogenation reactor. This condition indicated at this temperature, colloid particles did not spread in solution but started to agglomerate. It also happened in experiment at 90℃, where bigger flock was found in the third hours of experiment, stick to turbine agitator of reactor and
solution became more aqueous than initial condition before heating treatment. Flocks can be formed because protein which covering colloid particles as natural surfactant started to damage at 70°C and colloid particles collide each other with faster motion in heating condition.

3.2. Catalyst Screening in Di-imide Hydrogenation

In this experiment, selected catalyst is water-soluble homogeneous catalysts, which were FeSO₄, boric acid, Zn-Acetate, Cu-Acetate, and CuSO₄. The presence of water could help the catalyst to dispersed in the aqueous solution and facilitate the movements of catalyst to the active site of the rubber particles in order to accelerate the hydrogenation process. Referring to the physical observation results of the hydrogenated rubber sheet (HNR) as shown in Fig. 2, can be assessed the effectiveness of the catalyst in the DPNR hydrogenation transfer reaction.

Based on Fig. 2, it appears that wet HNR sheets have different colours and textures with dry HNR sheets. In wet HNR sheet with the addition of transition metal cations catalyst Fe and Cu, (on the top first line of sample) are light brown and soft textured and slightly sticky (tacky). Furthermore, in the same HNR after drying condition, the colour changed into dark brown and soft texture, very sticky like pasta (liquid natural rubber). While in HNR synthesized with the addition of Zn-acetate and boric acid as catalyst has a not significant appearance between wet and dry conditions. The wet HNR is white and hard but not sticky, whereas in dry, the colour of HNR is pale brown; the texture is softer than the dry one and not sticky.

**Figure 2.** Hydrogenated rubber sheet (HNR) wet (left) and dry (right).

Physical changes of HNR between wet and dry condition indicates side reactions occurred and competed with the main reaction of hydrogenation transfer. Significant visible changes of HNR with the addition of Fe and Cu as catalysts is caused by oxidation, because the Cu and Fe is a pro-oxidant which able to bind oxygen and accelerate oxidation reactions in natural rubber molecular chains [10, 11]. In addition, the oxidation reaction is cause of depolymerisation [12].

**Figure 3.** Hydrogenation degree of HNR with different catalyst.
Hydrogenation degree shows the conversion of unsaturated C=C bonds become saturated C-C bonds in the hydrogenated latex form. As shown in Fig. 3, the reaction without catalyst doesn’t show anything and the highest hydrogenation degree was providing by Fe and Cu. This evidence is supported by FTIR result from Fig. 1. in supporting information. In general, the spectral FTIR of HNR is characterized by the elimination or absorption around the 1660 cm⁻¹ wave number for the C=C (vibration stretching) and 830 cm⁻¹ double bonds for the CH bond (bending vibration) followed by increasing of intensity in the number wave 738 cm⁻¹ for bond -(CH2)_3- which caused by breaking of the double bond C=C into the single bond C-C. The FTIR spectra also shown the HNR with the addition of Fe and Cu ion catalysts there is a considerable widespread absorption at wave numbers 3400 cm⁻¹ for OH and 1716 cm⁻¹ bonds for CO bonds which indicates a depolymerisation as side reaction. While in HNR using Zn²⁺ and boric acid did not show absorption at 3400 cm⁻¹ and 1716 cm⁻¹. Depolymerisation in this reaction means the Fe and Cu not only reduce the unsaturated C=C bonds but also reduce the polymer bonds of the rubber latex. It caused the HNR with Fe and Cu form like a pasta which established the colloid rubber system after the reaction hard to agglomerate.

3.3. Catalyst Composition
Composition of catalyst added to mixture in hydrogenation process has an effect on HNR. In this experiment, catalyst was added into the mixture in different composition. Every catalyst was added in 10 and 15 grams in order to see the tendency of increasing catalyst addition.

![Figure 4. Tendency of catalyst addition in NR hydrogenation process.](image)

From Fig. 4, it can be seen that addition of Cu and Fe tend to decrease sharply, because, addition of transition metal in high concentration as catalyst can causes of catalyst distribution in latex as serum phase. Serum of catalyst not only spread on NR particle surface, it also was absorbed into particle and contacted with polyisoprene. While, addition of Zn²⁺ and boric acid as catalyst gradually increase hydrogenation degree. Catalyst serum in particle surface reacted with hydrazine hydrate and hydrogen peroxide to produce di-imide, while catalyst in the inside of particles broke the bond and became cause of depolymerisation. This phenomenon was confirmed by FTIR result.

4. Conclusion
There some considerable factor in hydrogenation process. Colloid stability of latex solution can be affected by temperature. Temperature give an effect on protein and brown motion of colloid particles. Higher temperature makes brown motion of colloid particles become faster and damage protein as natural surfactant. According to the experiment result, optimum temperature for hydrogenation process is 50℃. Catalyst also has big effect on chemical modification natural rubber, deproteinised natural rubber was used in this study to optimize catalyst function. In this study, there are 4 kind of catalyst was used, Ion Cu, Fe, Zn and boric acid. The best catalyst to hydrogenate the rubber latex is Ion Zn catalyst without depolymerisation process as side reaction. The value hydrogenation degree of ion Zn catalyst was 9.57%.
Acknowledgement
We appreciate and thank for the support from DRPM UI through its Program PIT9-2019 Grant Scheme which makes this research possible.

References
[1] Kongparakul S, Ng F T and Rempel G L 2011 Metathesis hydrogenation of natural rubber latex Appl. Catal. A Gen. 405 1-2 129-36
[2] Gumbira-Sa’id E, Rahman N and Febrriyanti L 2005 Pengaruh Hidrogenasi dalam Fasa Lateks pada Karet Alam Hevea Brasiliensis J. Agroindustrial Technol. 14 3 80-6
[3] Chalid M, Putranto B D, Alfiendo M A Y, Desfrandanta J and Agita A 2018 Study on grafting of starch on natural rubber latex via GDEP method AIP Conference Proceedings 2024 1 020066
[4] Goutara B D and Tjiptadi W 1985 Dasar Pengolahan Karet Agroindustri: Jurusan Teknologi Industri Pertanian, Fakultas Teknologi Pertanian, Institut Pertanian Bogor)
[5] Fukushima Y, Kawahara S and Tanaka Y 1998 Synthesis of graft copolymers from highly deproteinised natural rubber J. Rubber Res. 13 154-66
[6] Mahittikul A, Prasassarakich P and Rempel G 2007 Diimide hydrogenation of natural rubber latex J. Appl. Polym. Sci. 105 3 1188-99
[7] Lin X, Pan Q and Rempel G L 2004 Hydrogenation of nitrile-butadiene rubber latex with diimide Applied Catalysis A: General 276 1 123-8
[8] Bhattacharjee S, Bhowmick A K and Avasthi B N 1993 Hydrogenation of epoxidized natural rubber in the presence of palladium acetate catalyst Polym. 34 24 5168-73
[9] Parker D K, Roberts R F and Schiessl H W 1994 The Preparation, Properties and Potential Applications of “Diimide-Hydrogenated” Styrene-Butadiene (HSBR) and Polybutadiene (HBR) Thermoplastic Elastomers Rubber Chemistry and Technology 67 2 288-98
[10] Arnold A and Evans P 1991 Role of fatty acids in autoxidation of deproteinised natural rubber J. Nat. Rubber Res. 6 2 75-86
[11] Lee L h, Stacy C and Engel R 1966 Mechanisms of oxidative degradation. I. Oxidation of synthetic rubbers catalyzed by metallic ions J. Appl. Polym. Sci. 10 11 1699-715
[12] Chaikumpollert O, Sae-Heng K, Wakisaka O, Mase A, Yamamoto Y and Kawahara S 2011 Low temperature degradation and characterization of natural rubber Polym. Degrad. Stab. 96 11 1989-95