Molecular Weight of Liquid Natural Rubber (LNR) Product from the Chemical Depolymerization Process of High Molecular Weight Natural Rubber Latex

Bahruddin, Ivan Fadhillah, Septian, Arya Wiranata, Ida Zahrina
Chemical Engineering Department, Engineering Faculty, Universitas Riau
Jl. HR. Soebrantas, Km. 12.5, Pekanbaru 28293, Indonesia
bahruddin@lecturer.unri.ac.id

Abstract. The molecular weight of natural rubber varies greatly, from only a few hundred thousand to more than one million. Liquid natural rubber (LNR) products generally use natural rubber in the form of latex with a relatively low molecular weight, which ranges from a molecular weight of 600,000 g/mol. This study aims to determine the molecular weight of LNR products made from the chemical depolymerization process of natural rubber latex with a molecular weight of more than one million. The natural rubber used latex with 20% Dry Rubber Content (KKK). The natural rubber depolymerization process used NaNO₂ and H₂O₂ degrading agents with a CoCl₂ catalyst at 80 °C. H₂O₂ levels were kept constant at 1 part per hundred rubber (phr), and NaNO₂ levels vary at 0; 2; 3; and 4 phr. After the reactor temperature reaches 80°C, the CoCl₂ catalyst was added, which level varied at 0; 1; 3; and 5 phr. The reaction time was varied, which 7, 8, and 9 hours. The results of LNR product was purified to form a semi-gel, and molecular weight was analyzed using gel permeable chromatography (GPC). The results showed that the lowest molecular weight of the resulting LNR product was 108,335 g/mol from the initial molecular weight of 1,384,638 g/mol.

Keywords: chemical depolymerization, gel permeable chromatography, liquid natural rubber, molecular weight, natural rubber latex

1. Introduction
Modification of natural rubber is a process to manipulate the structure of natural rubber molecules into natural rubber molecules with characteristic materials or different materials. This modification aims to improve the characteristics of natural rubber to expand the use of natural rubber as a raw material for a product. One of the processes of modification of natural rubber is the degradation of natural rubber or also called natural rubber depolymerization [1]. Depolymerization is the process of breaking the polymer chain by gradually removing the monomer unity in a reaction. Rubber molecular depolymerization aims to obtain low molecular weight rubber materials. Polymer depolymerization can occur mechanically, thermally, chemically, photochemically, and biodegradation. The process can occur by several factors, heat energy, mechanical energy, UV, and chemicals (degradation or oxidizing agents) [2].

The product of the depolymerization process in natural rubber latex is known as Liquid Natural Rubber (LNR) [3]. This product at temperatures less than 100 °C can be poured or pumped without the help of other media. The lower the molecular weight of LNR means that the molecular chain is getting shorter, and the viscosity is also getting lower. Based on molecular weight, LNR consists of two types, LNR with high molecular weight and LNR with low molecular weight (molecular weight LNR <50,000 g/mol). LNR with low viscosity is relatively easy to penetrate the surface pores.
adhesive power is relatively more durable and can be used to make products such as glue, paint, varnish, and printing ink [4]. LNR can be used as plasticizers, additives, and precursors for new materials [5].

LNR products have widely developed in several previous studies. These products generally made by chemical oxidation processes [4], thermolysis, and photodegradation [3] from natural rubber latex. These studies show that the final nature of the LNR is affected by the degradation method, the chemicals added, and the degradation process conditions. LNR with a suitable molecular weight can obtain by developing production technology that can maximize the natural rubber degradation process. This research focused on studying LNR production by chemical methods, specifically related to the effect of CoCl$_2$ catalyst levels and degradation chemicals (NaNO$_2$) on the molecular weight of LNR produced.

2. Methodology

2.1. Materials
The material used in this research was natural rubber latex as the main ingredient obtained from local rubber farmers. The stabilizer used was sodium dodecyl sulfate (SDS) surfactant. The degrading agents used were H$_2$O$_2$ Pa and NaNO$_2$ Pa, with the CoCl$_2$ Pa catalyst. These materials purchased from local distributors.

2.2. Preparation of Natural Rubber Latex
The latex kept in the liquid phase by adding an anticoagulation compound that is 30 ml of ammonia as much as 60 ml per 1 liter of latex. The latex then diluted to obtain natural rubber latex with a dry rubber content (DRC) of 20%.

2.3. LNR Sample Manufacturing and Testing
Natural rubber latex with 20% DRC was then poured into a batch reactor and added H$_2$O$_2$ and NaNO$_2$. H$_2$O$_2$ levels were kept constant at 1 parts per hundred rubber (phr), and NaNO$_2$ levels vary at 0; 2; 3; and 4 phr. After the temperature of the reactor reaches 80ºC, the CoCl$_2$ catalyst added which the level was also varied by 0; 1; 3; and 5 phr. PHR was a measure used by rubber chemists to depict what amount of certain ingredients were needed, generally could be parts per hundred of rubber rarely. The reaction time was varied, which 7, 8, and 9 hours. The LNR product sample was then washed with toluene and coagulated again using methanol, then dried at 85ºC. The LNR sample then tested for its molecular weight using Gel Permeation Chromatography (GPC).

3. Results and Discussion
The graph in Figure 1 shows a decrease in molecular weight Mn (average molecular weight) and Mw (average molecular weight) each time the depolymerization reaction increases. This showed that the increase in depolymerization reaction time causes the polymer chains to degrade more. The more degraded polymer chains, the lower the average molecular weight of the polymer produced. The molecular weight of natural rubber latex samples before the depolymerization process was Mn = 1.385 x 10$^6$ g / mold and Mw = 2.566 x 10$^6$ g / mol. After the depolymerization processed, LNR products with molecular weights that were much lower than the latex material obtained. The lowest molecular weight of LNR product obtained at 9 hours depolymerization time. ie, Mn = 0.144 x 10$^6$ g / mold and Mw = 0.430 x 10$^6$ g / mol.
Figure 1. Effect of Mn and Mw Molecular Weight on Reaction Time

Figure 2. Effect of Mn and Mw Molecular Weight on NaNO$_2$ concentration

Figure 3. Effect of Mn and Mw Molecular Weight on CoCl$_2$ concentration

Figure 2 shows LNR molecular weight's tendency to decrease with increasing concentration of NaNO$_2$ (degradation agent), without using a catalyst. The lowest molecular weight of LNR with Mn =
0.280 x 10^6 g / mol Mw = 0.566 x 10^6 g / mol obtained at a NaNO₂ concentration of 4 phr and the depolymerization processed for 7 hours. Figure 3 shows LNR molecular weight's tendency to decreased with increasing CoCl₂ catalyst concentration. Using CoCl₂ catalyst could reduce the molecular weight of LNR products. Molecular weight produced without using a catalyst is Mn = 0.202 x 10^6 g / mol and Mw = 0.687 x 10^6 g / mol, whereas the use of catalyst was equal to Mn = 0.144 x 10^6 g / mol and Mw = 0.687 x 10^6 g / mol. CoCl₂ catalyst serves to increase the activation energy in the natural rubber latex depolymerization reaction so that the reaction took place faster than without a catalyst. The lowest molecular weight of LNR was obtained at Mn = 0.108 x 10^6 g / mol and Mw = 0.371 x 10^6 g / mol, ie at a CoCl₂ concentration of 5 phr.

The natural rubber depolymerization process can occur chemically through oxidation-reduction (redox) reactions. In the redox reaction system, the compound which generally acts as an oxidizer is hydrogen peroxide, while the reducing agent is nitrite (NO₂⁻). H₂O₂ degrading agent has a cell potential value of +1.77, and NaNO₂ has a cell potential value of +0.96. Compounds with more excellent cell potential value will be more effective as oxidizing compounds. Hydrogen peroxide (H₂O₂) and sodium nitrate (NaNO₂) will react to form peroxynitrite acid [6]. The added hydrogen peroxide will degrade molecular chains through the formation of OH⁻ free radical compounds. Hydrogen peroxide compounds will also undergo a proportional reaction to form water and oxygen, characterized by the appearance of gas bubbles in the mixture. While the sodium nitrite compound added to the latex also undergoes a free radical formation reaction that will attack or break the rubber polymer chain. The formation of free radicals from NaNO₂ compounds is explained through the following reaction equation [6]:

\[
\begin{align*}
\text{NaNO}_2 + \text{H}_2\text{O} & \rightarrow \text{HNO}_2 + \text{NaOH} \quad (3.1) \\
2\text{HNO}_2 & \rightarrow \text{H}_2\text{N}_2\text{O}_4 \quad (3.2) \\
\text{H}_2\text{N}_2\text{O}_4 & \rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} \quad (3.3) \\
\text{N}_2\text{O}_3 & \rightarrow \text{NO}_2^- + \text{NO}^- \text{(Radikal Bebas)} \quad (3.4)
\end{align*}
\]

**Figure 4.** Degradation Mechanism of Natural Rubber Latex Chains to LNR [1].

The mechanism of the reaction of LNR formation was estimated to occur, as shown in Figure 4. On alkaline media, hydrogen peroxide and sodium nitrite react to be oxidizing agents in the degradation process of natural rubber polymer chains. The process that occurs took place in the reactive terminal group, depending on the condition of the system used. Sodium nitrite attack the epoxy ring during degradation and produced NO gas as a result of side reactions. Hydrogen peroxide preferred to oxidize vinylic carbon to form epoxy rings due to it was side reaction, water. Epoxy rings with SP3 hybrids
were very unstable. \( \text{NO}_2^- \) as a nucleophile, will attack substituted carbon chains causing chain termination and produced NO gas due to side reactions [7].

The excessive used of \( \text{NaNO}_2 \) degrading agent causes more NO* free radicals. Excessive free radical NO* compounds created the rubber chain's reactive terminal groups to be increasingly cut off by NO* free radicals. The result was that the rubber chain was getting shorter, and the average molecular weight of the rubber was getting lower. Likewise, excess \( \text{CoCl}_2 \) catalysts, causing reactions to take place more quickly, and excess catalyst compounds did not react with rubber compounds.

4. Conclusion
The molecular weight of liquid natural rubber (LNR) products influenced by the length of reaction time, the concentration of \( \text{NaNO}_2 \) degrading compounds, and the concentration of \( \text{CoCl}_2 \) catalyst. The lowest molecular weight of LNR products produced in this study is 108,354 g / mol from the initial molecular weight of 1,384,638 g / mol, which was the duration of the 8-hour depolymerization reaction, \( \text{NaNO}_2 \) 4 phr, and \( \text{CoCl}_2 \) 5 phr contents.

Acknowledgment
The authors thank the Indonesian Government (especially to DRPM- Deputi Bidang Penguatan Riset dan Pengembangan Kementerian Riset dan Teknologi/Badan Riset dan Inovasi Nasional) that has funded this research.

References
[1] Ibrahim S, Daik R, Abdullah I, Unit M E, Division E and Board M R 2014 Functionalization of Liquid Natural Rubber via Oxidative Degradation of Natural Rubber Polymers 6 12 2928–2941
[2] Ibrahim S, Othman N, Nor Z M and Ismail H 2017 Preliminary Study on Photochemical Degradation of Natural Rubber Latex Macromolecular Symposia. 371 1 22–26
[3] Ibrahim S, Mustafa A and Tan K 2016 Chemical Degradation of Natural Rubber Latex in Acidic Medium Catalysed by \( \text{CoCl}_2 \) and (NH4) Fe-2 (SO4)(2) Journal of Rubber Research/ 18 2 61–71
[4] Phinyocheep P, Phetphaisit C W, Derouet D, Campistron I and Brosse J C 2004 Chemical Degradation of Epoxidized Natural Rubber Using Periodic Acid : Preparation of Epoxidized Liquid Natural Rubber Journal of Applied Polymer Science 95 1 6–15
[5] Dahlan H M, Zaman M D K and Ibrahim A 2000 Liquid Natural Rubber (LNR) as a Compatibilizer in \( \text{NR} / \text{LLDPE} \) Blends Journal of Applied Polymer Science 78 10 1776–1782
[6] Taylor P, Huy H T, Nga N T, Hong L Q, Pham C and Son N 2006 Depolymerization of Natural Rubber Latex Using Phenylhydrazine-FeCl2 System Journal of Macromolecular Science 33 12 37–41
[7] Bae N V, Terlemezyan L and Mihailov M 1993 Epoxidation of natural rubber in latex in the presence of a reducing agent Journal of Applied Polymer Science 50 5 845–849