

# Chain Scission Reaction of the Indonesian Technically Specified Rubbers in Redox System

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**Abstract**— One of The Indonesian Technically Specified Rubbers is Standard Indonesian Rubber 10, which has a high molecular and viscosity, is difficult for processing to its derivative products. Hence, it needs to be reduced its molecular weight. The Standard Indonesian Rubber 10 molecular weight reducing can be used by chain scission reaction method, which is using hydrogen peroxide and sodium nitrite in redox system. The results of chain scission reaction showed that there was a decrease in molecular weight. The FT-IR spectra of products showed that a carbonyl group.

**Keywords** — Rubber, molecular weight, chain scission reaction, redox

## I. INTRODUCTION

Natural rubber is a compound of cis-1,4 polyisoprene that also a renewable raw material. Natural rubber can be found as latex, gum that is produced from species of plants. Various plants can produce latex but the plant with high commercial and the most developed is *Hevea brasiliensis*. 1-6. Production and consumption of natural rubber is competitive with synthetic rubber. Rubber world situation in 2014, about 58,9% synthetic rubber in total rubber consumption [7]. However, synthetic rubber is developed from petroleum which is unfriendly environmental. It is a big chance to natural rubber to dominate source of world rubber product [8]. Indonesia has many rubber plant farms, which is owned by local society. Latex sometimes is precoagulated before processing in industry. Precoagulated latex was has poor quality. The precoagulated latex is then processed to become Standard Indonesian Rubber (SIR)-10 is classified as The Indonesian Technically Specified Rubbers (The Indonesian TSR). The another raw material can be used for producing SIR 10 is natural latex.

Molecular weight of latex is 100,000 to 1,000,000 [2]. Natural rubber with high molecular weight cause high viscosity will make the treatment process produce rubber product becomes more difficult [4-5,9]. Natural rubber has many C=C double bond, which is reactive to be used in producing other derivative products [10]. Natural rubber degradation can be done by metathesis reaction, chain scission reaction, ozonolysis, photo degradation and degradation with ultrasonic irradiation [9]. Degradation of natural rubber by different process can be made liquid natural rubber (LNR) with lower molecular weight [11]. Natural

rubber degradation in latex solution with by using hydrogen peroxide ( $H_2O_2$ ) and sodium nitrite ( $NaNO_2$ ) reagents produce LNR that has molecular weight less than  $50 \times 10^3$  g/mol that has functional structure at the end of the chain is hydroxyl and carbonyl groups [12]. Oxidative degradation of natural rubber both in an acidic medium and in an alkaline medium has been reported. Natural rubber degradation in an acidic medium has given hydroxyl terminal groups at LNR but in alkaline medium has given LNR with carbonyl terminal groups [13]. Increment of time and temperature reaction degradation cause reduction of molecular weight of natural rubber produced. Degradation of latex produced liquid natural rubber that has both epoxy and hydroxyl groups. The appearance of hydroxyl and epoxy groups was resulted from degradation reaction that use  $H_2O_2$  and  $NaNO_2$  reagent [14]. The method of molecular weight decrement of the natural rubber can be done by using oxidator (air, oxygen or a peroxide) and reductor (metal nitrite and/or metal chloride) [15]. Natural rubber latex degradation by using tert-butyl hydroperoxide an cobalt acetylacetonate will produce liquid natural rubber with molecular weight 30,190 g/mol [16].

This paper investigates the chain scission of SIR-10 in the redox system to produce lower molecular weight.  $H_2O_2$  (30%) and  $NaNO_2$  are used as reagents in chain scission reaction. Characterization of SIR-10 and product is used by viscosimeter and FT-IR spectroscopy.

## II. EXPERIMENTAL SECTION

### A. Materials

Natural rubber that used is SIR-10 that taken from PT IKN (Industri Karet Nusantara) which is under PTPN III Holding company.  $H_2O_2$  (30%) and  $NaNO_2$  were obtained from Merck Germany.

### B. Chain scission reaction of rubber

SIR-10 was soluted in the xylene. Rubber solution was heated until reach temperature of 60 °C. After that,  $H_2O_2$  (30%) of 6 parts per hundred (phr) and  $NaNO_2$  of 6 phr was dissolved in aquadest are added sequently. Chain scission reaction was performed for 2 hours, 4 hours and 6 hours by stirring. Then, rubber product is coagulated by using ethanol. Coagulated rubber was washed and dried.

### C. Characterizations

Intrinsic viscosity and molecular weight of SIR-10 and rubber that produced from chain scission reaction determined based on the result of viscosity testing by using Ostwald viscosimeter. Fourier Transform Infrared (FT-IR) spectrum was recorded on Perkin Elmer Frontier.

## III. RESULTS AND DISCUSSION

### A. Decreasing of Molecular Weight

Solution of SIR-10 in xylene has pale yellow colour. Reaction of SIR-10 and reagents of H<sub>2</sub>O<sub>2</sub> (30%) and NaNO<sub>2</sub> resulted a bright yellow solution.

The characteristic of SIR-10 and product can be seen in table 1.

Table 1. The characterization of Rubber

|                 | Intrinsic Viscosity (g/mL) | Molecular weight (g/mol) |
|-----------------|----------------------------|--------------------------|
| SIR-10          | 216.67                     | 586,080                  |
| Degraded SIR-10 |                            |                          |
| 2 hours         | 117.56                     | 247,745                  |
| 4 hours         | 56.59                      | 88,482                   |
| 6 hours         | 5.45                       | 3,279                    |

The product was resulted from chain scission reaction of SIR-10 has lower molecular weight than SIR-10. Chain scission reaction of SIR-10 caused a decrease of intrinsic viscosity and molecular weight. The decreasing of intrinsic viscosity and molecular weight was performed irregularly for reaction 2 hours, 4 hours and 6 hours. Chain scission of SIR-10 resulted shorter molecular chain with lower polymerization degree so the molecular weight will be lower too.

Clone of rubber trees are determining the molecular weight of natural rubber [17]. Natural rubber in latex phase that used by Ibrahim as raw material at the research of natural rubber degradation has molecular weight 657x10<sup>3</sup> g/mol. Latex that used low ammonia NR latex [12]. Nwanorh researched the degradation of natural rubber by using fresh field natural rubber latex as raw material. Latex that used has viscosity average molecular weight 1,31 x 10<sup>6</sup> [18].

### B. FT-IR Spectra

From Figure 1, it can be seen that FT-IR Spectrum characteristic of SIR-10 is peak at 1664 cm<sup>-1</sup> that shown to –C=C– stretching, peak at 1448 cm<sup>-1</sup> assigned to –CH<sub>2</sub> deformation, and peak at 836 cm<sup>-1</sup> shown to =CH wagging bands [11].

Figure 2. shown FT-IR spectra of chain scission of SIR-10 for 2 hours, 4 hours and 6 hours. It can be seen the wavelength of C=C stretching, –CH<sub>2</sub> deformation, =CH wagging bands and carbonyl group (1698cm<sup>-1</sup>–1739 cm<sup>-1</sup>). The appearance of new band carbonyl group prove that SIR-10 has already cleaved by oxidation reaction.

## IV. RESULTS AND DISCUSSION

Chain scission reaction of SIR 10 in the system of redox produce rubber with lower molecular weight. Molecular weight of SIR-10 has already reduced from 10<sup>6</sup> g/mol to 10<sup>3</sup> g/mol after 6 hours oxidation reaction. Rubber that have

chain scission reaction with H<sub>2</sub>O<sub>2</sub>(30%) and NaNO<sub>2</sub> reagents for 2 hours, 4 hours and 6 hours produce rubber which is the structure consist of carbonyl group that shown of FT-IR Spectra with wave number 1698cm<sup>-1</sup>–1739 cm<sup>-1</sup>. Deformation of carbonyl group band prove the degradation with H<sub>2</sub>O<sub>2</sub>(30%) and NaNO<sub>2</sub> reagents by oxidation of C=C double bands.

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## REFERENCES

- [1] Ichetaonye, S., I., Ichetaonye, D., N., Tenebe, O., G., 2013, *Degradation of Natural Rubber by Xanthomonas SP using Dilute Solution Viscosity Measurement Technique*, American Journal of Polymer Science, 3(3): pp. 52-55.
- [2] Shobha, M. S., Shashidhar, C., Rao, S., H., 2013. Strength Studies of Natural Rubber Latex modified High Performance Concrete, IJERT Volume 2 Issue 5, pp. 1836-1852.
- [3] Sadhan, K. De, White, J.R, 2001. Rubber Technologist's Handbook, Rapra Technology Limited, UK.
- [4] Prasoetsopha, N., 2009. Studies of Modified Natural Rubber/Epoxy Resin Blend, Tesis, Suranaree University of Technology.
- [5] Man, S. H. C, 2008. Styrene-Methyl Metthacrylatedmodified Natural Rubber from Deproteinized Natural Rubber Latex, Thesis, Universiti Sains Malaysia.
- [6] Goutara, Djatmiko, B., Tjiptadi, W., 1976. Dasar Pengolahan Karet, Departeman Teknologi Hasil Pertanian, IPB.
- [7] Rubber Statistical Bulletin, July-September 2014 edition.
- [8] Kunioka, M., Taguchi, K., Ninomiya, F., Nakajima, M., Saito, A., Araki, S., 2014. Biobased Contents of Natural Rubber Model Compound and Its Separated Constituents, Volume 6, pp. 423-442.
- [9] Fainleib, A., Pires R. V., Lucas E. F., Soares B. G., 2013. Degradation of Non-Vulcanized Natural Rubber-Renewable Resources for Fine Chemicals Used in Polymer Synthesis, Polimeros
- [10] Saetung, A., Rungvichaniwat, A., Campistron, I., Klinpituksa, P., Laguerre, A., Phinyocheep, P., Pilard, J-F., 2010. Controlled Degradation of Natural Rubber and Modification of the Obtained Telechelic Oligoisoprenes : Preliminary Study of Their Potentiality as Polyurathane Foam Precursors, Journal of Applied Polymer Science 117:1279-1289.
- [11] Brosse J. C., Campistron I., Derouet D., Hamdaoui A. El., Houdayer S., Reyx D., Gillier R. S., 2000. *Chemical Modifications of Polydiene Elastomers : A Survey and Some Recent Results*, Journal of Applied Polymer Science, 78:1461-1477.
- [12] Ibrahim, S., Mustafa, A., 2014. *Effect of Reagents Concentration and Ratio on Degradation of Natural Rubber Latex in Acidic Medium*, The Malaysian Journal of Analytical Sciences, Vol 18 No. 2:405-414.
- [13] Ibrahim, S., Daik, R., Abdullah, I., 2014. Functionalization of Liquid Natural Rubber via Oxidative Degradation on Natural Rubber, Polymers, 6:2928-2941.
- [14] Isa S. Z., Yahya R., Hassan A., Tahir M., 2007. *The Influence of Temperature and Reaction Time in The Degradation of Natural Rubber Latex*, The Malaysian J of Analytical Sci, Vol. 11(1):42-47.
- [15] Gazeley K. F., Mente P. G., 1996. Metoda Penurunan Berat Molekul Karet di dalam Lateks, Paten Indonesia, ID 0 000 771.
- [16] Klaichim, W., Klinpituksa, P., Waehamad, W., 2009. A novel polymeric herbicide based on phenoxyacetic acid derivatives, Songklanakar J. Sci. Technol, 31(1):57-62.
- [17] Kovuttikulrangsie S., Sakdapipanich J. T., 2005. The Molecular Weight (MW) and Molecular Weight Distribution (MWD) of NR from Different Age and Clone Hevea Trees, Songklanakar J. Sci. Technol, 27(2):337-342.
- [18] Nwanorh, K., O., Enyiebulam, M., E., 1998. *Enhancement of Resistance to Oxidative Degradation of Natural Rubber Through Latex Degradation*, Chinese Journal of Polymer Science Vol 16 No.2:170-175.

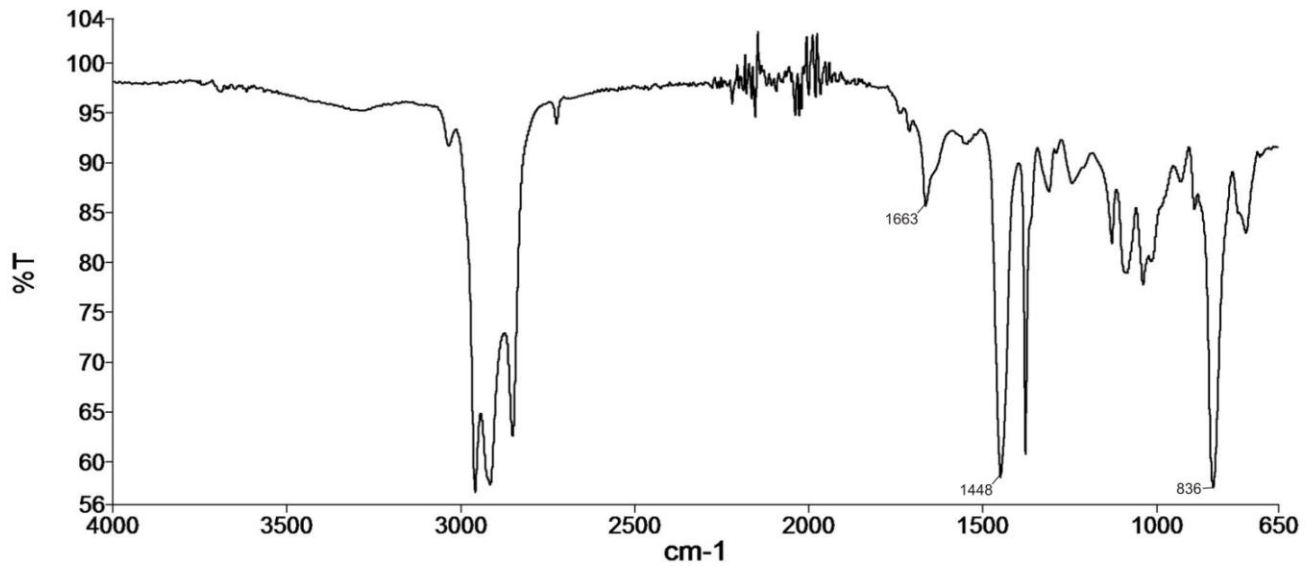


Figure 1. FT-IR Spectrum of SIR-10

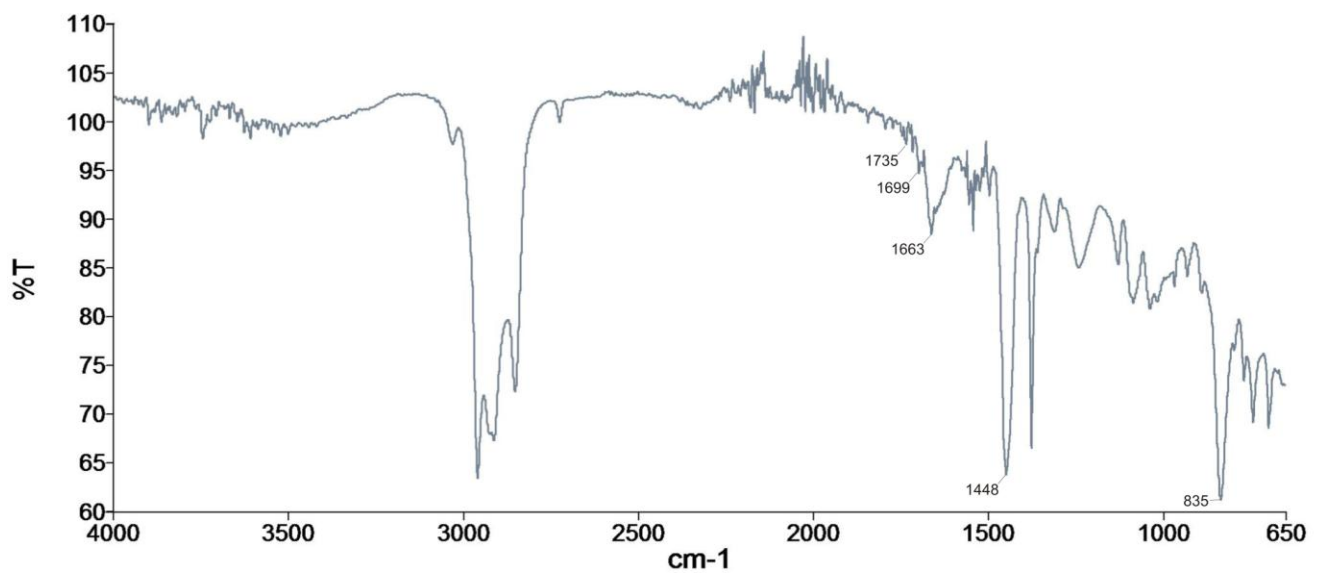


Figure 2. (a) FT-IR Spectrum of Degraded SIR-10 for 2 hours reaction

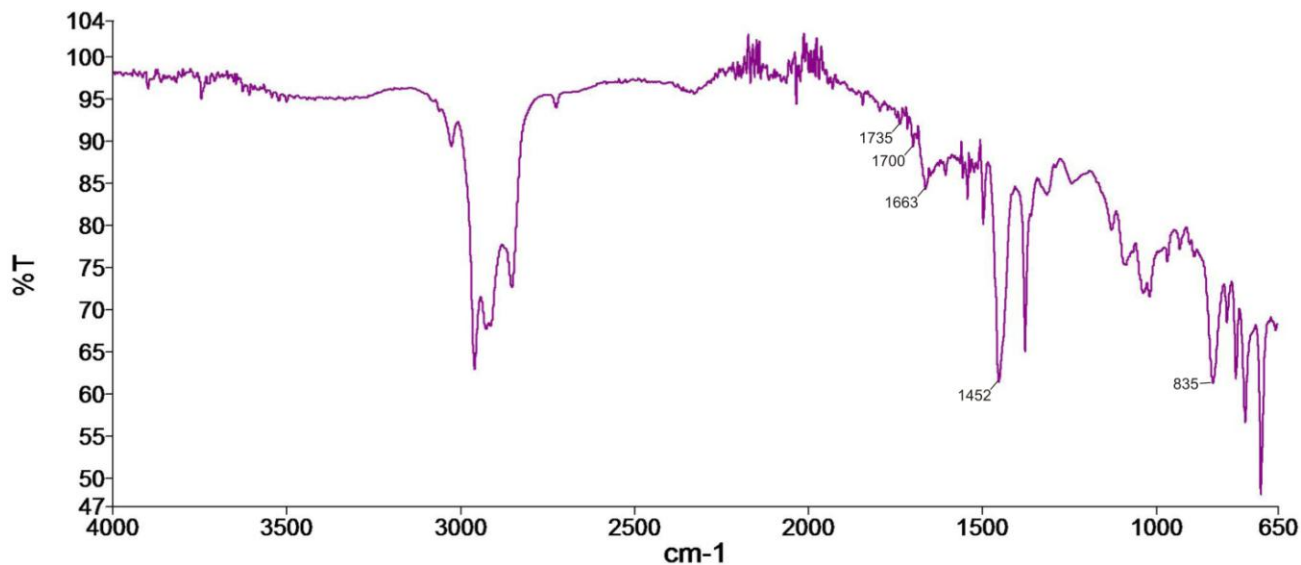


Figure 2. (b) FT-IR Spectrum of Degraded SIR-10 for 4 hours reaction

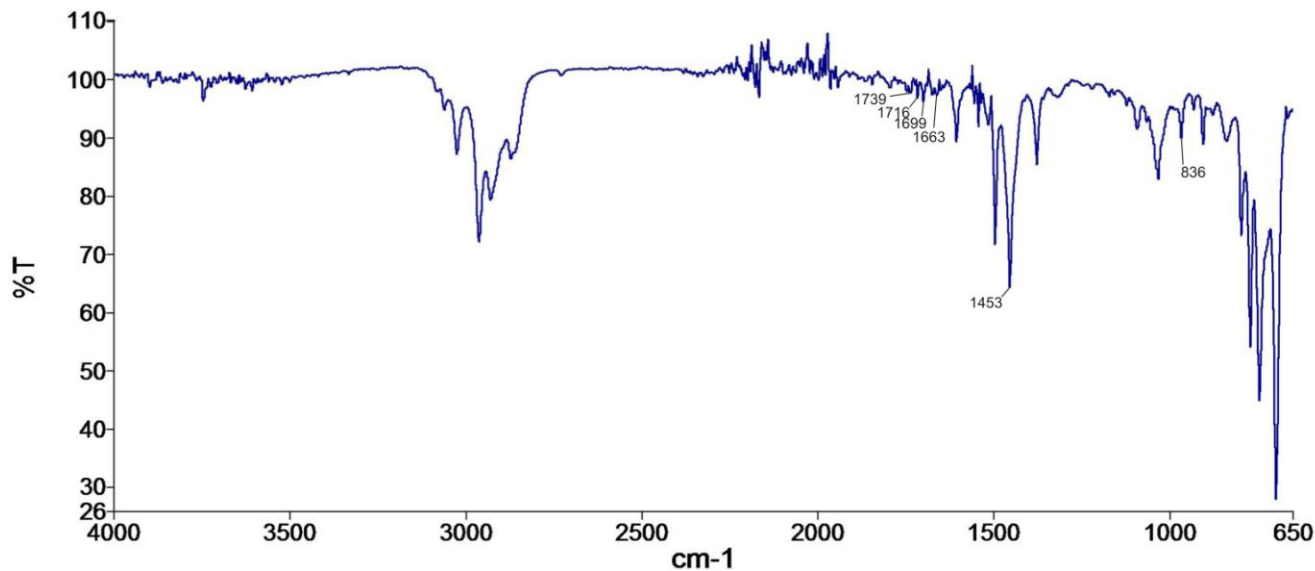


Figure 2. (c) FT-IR Spectrum of Degraded SIR-10 for 6 hours reaction