

The investigation of optimum condition of natural rubber epoxidation reaction in latex phase

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Submitted: 26 March 2020

Revised: 1 March 2021

Accepted: 20 April 2021

ABSTRACT

Natural rubber (NR) latex epoxidation is a chemical modification of natural rubber to produce natural rubber with higher polarity (oil resistant) which is commonly called epoxidized natural rubber (ENR). ENR is produced from the reaction of natural rubber latex with performic acid. Performic acid is formed from in situ reaction between formic acid and hydrogen peroxide. During epoxidation process, the carboxyl group of natural rubber is converted into epoxy group and various side reaction products such as carbonyl, hydroxyl, and hydro furan. These side products must be minimized to optimize the epoxy level. The epoxidation reaction was carried out at 70 °C for 6 hours using 2 types of latex: fresh latex (FL) and concentrated latex (CL). The addition of reactant was varied in two ways: dropwise (coded "1") and poured all at once (coded "2"). The epoxy product and rate constant (k) were analyzed to obtain optimum reaction condition. The epoxy and side reaction content were determined by Attenuated Resonance Fourier Transform Infrared (ATR-FTIR). The slope of epoxy-time plotting curve was determined as ENR rate constant (k). The optimum NR epoxidation reaction was achieved in CL2, which exhibited lowest value of side reaction and highest value of k ($2.8082 \times 10^{-5} \text{ L mol}^{-1} \text{ sec}^{-1}$).

Keywords: epoxidation, natural rubber, rate constant, side reaction.

INTRODUCTION

Natural rubber (NR) is a widely applied material because it has an excellent elasticity on high tensile strength, tear strength, and modulus. However, it has low thermal, oxidative, and nonpolar solvent resistance due to high unsaturation (cis-1,4-polyisoprene) structure. This laxity properties limit the utilization of NR in high oil resistance of rubber product. Modification of its chemical structure would alter the properties of NR. Epoxidation is the simplest modification in NR that results in improved thermal, oxidative, and solvent resistance properties. The resulted material is well-known as epoxidized natural rubber (ENR) which has higher polarity (oil resistance), lower resilience, better rubber filler interaction, and mechanical properties (Rohadi *et al.*, 2014; Tanrattanakul *et al.*, 2003). Several articles published the utilization of ENR in high

specified rubber products such as oil spill recovery (Venkatanarasimhan & Raghavachari, 2013), bitumen (Al-Mansob *et al.*, 2014), and tire tread compounds (Kaewsakul *et al.*, 2013).

Epoxidation reaction introduces epoxide groups into NR backbone, which are randomly distributed. Most of epoxidation reactions are performed in latex phase either fresh latex (Roy *et al.*, 1993; Norhanifah *et al.*, 2016), concentrated latex (Chuayjuljit *et al.*, 2015) or deproteinized (Tan *et al.*, 2013; Fathurrohman, 2010), using in situ performic acid which is easily implemented without sulfuric acid as catalyst (Phinyocheep & Boonjairak, 2006). The major problem of natural rubber latex epoxidation reaction is the side reaction formation that produces carbonyl, tetrahydrofuran, and hydroxyl (Roy *et al.*, 1993; Roy *et al.*, 1994; Roy *et al.*, 1991). These substances lead to undesired reaction products

and quality. Many factors affecting the possibility of side reaction in epoxidation process have been investigated including total acid concentration in the reaction mixture (Roy *et al.*, 1993), reaction temperature (Roy *et al.*, 1990; Roy *et al.*, 1991), reaction time (Roy *et al.*, 1991), agitation speed, reagent addition technique, latex concentration, neutralization techniques, and strength of different secondary acids (Roy *et al.*, 1994).

The kinetic study of latex epoxidation reaction has been employed to predict the maximum epoxy level. Roy *et al.* (1991) studied epoxidation reaction following with a pseudo-first order system, which interpreted the epoxidation reaction in a pseudo-first order system with excess hydrogen peroxide. Another study conducted by Roy *et al.* (1990) exhibited that the epoxidation reaction determined second order kinetics wherein excess acid was medium. However, those studies were performed in solid rubber and only few studies that discussed the epoxidation in the latex form with reagent addition technique.

This study investigated the optimum condition of latex epoxidation reaction on pseudo-first order system. Two types of latex were used in this study, i.e. fresh and concentrated latex. They were reacted with excess hydrogen peroxide. The optimum condition reached was based on reaction products and rate constant of this system. The best ENR product was represented on the highest epoxy content, the lowest carboxyl, and side reaction content (hydroxyl, carbonyl, and hydro furan), wherein epoxy content was used in further rate constant (k) calculation. The highest k value was determined as optimum reaction condition.

MATERIALS AND METHODS

Materials

The materials needed in this study were fresh and concentrated latex, anionic surfactant, hydrogen peroxide, formic acid ammonia, and sodium thiosulphate. Fresh latex was supplied by local plantation in Ciomas, Indonesia. Concentrated latex was produced by local smallholder enterprise by centrifugation. Anionic surfactant (emulgent) was distributed by KAO Indonesia Chemicals. Hydrogen peroxide, formic acid, ammonia, and sodium thiosulphate were supplied by local supplier.

Epoxidized Natural Rubber (ENR) Preparation

ENR was prepared from two types of latex, fresh latex (FL) and concentrated latex (CL). First, FL and CL were diluted to 20% of dry rubber content (DRC). Furthermore, FL and CL were stabilized by adding 3 per hundred rubber (phr) of 10% (w/v) anionic surfactant. The epoxidation reaction was conducted by in situ performic acid in both latex stages, followed by adding 0.75 mol/mol isoprene unit of hydrogen peroxide and 0.4 mol/mol isoprene unit of formic acid in laboratory scale reactor. Formic acid is the limiting reactant in epoxidation reaction, hence it was assumed to be constant in the reaction. An excess hydrogen peroxide was needed to enhance epoxy content (Gnecco *et al.*, 1996; Ruksakulpiwat *et al.*, 2008).

The addition of reactant varied in two ways, dropwise and poured all at once, which coded as 1 and 2, respectively. The epoxidation reaction was carried out at 70 °C for 6 hours. Samples were collected every hour to determine ENR profile of product distribution. At the end of the reaction process, an adequate amount of 20% ammonia and 0.2 M sodium thiosulphate were added into the reaction mixture to neutralize the epoxidation process.

ENR Characterization

The ENR profiles such as epoxide level and ENR product distribution were determined by Attenuated Resonance Fourier Transform Infrared (ATR-FTIR), Thermo Fisher Scientific, Madison, Wisc The FTIR were recorded over the wavenumber 4000–400 cm⁻¹ averaging 64 scans at 4 cm⁻¹ resolution. Epoxy content of IR spectra was analyzed with OMNIC software version 8.0 and epoxide level was determined as follows (Chakraborty *et al.*, 2010).

$$A_{870\text{ corr}} = A_{870} - (0,14 \times A_{835}) \quad (1)$$

$$A_{3460\text{ corr}} = A_{3460} - (0,019 \times A_{1375}) \quad (2)$$

$$E = \frac{100 \times K_1 \times A_{870\text{ corr}}}{A_{835} + K_1 \times A_{870\text{ corr}} + K_2 \times A_{3460\text{ corr}}} \times \text{mol \%} \quad (3)$$

$$O = \frac{E \times A_{835}}{K_1 \times A_{870\text{ corr}}} \times \text{mol \%} \quad (4)$$

$$R = \frac{K_1 \times A_{3460\text{ corr}}}{A_{835}} \times \text{mol \%} \quad (5)$$

Where E is epoxy, O is olefin, and R is ring open. K₁ and K₂ are the correction values,

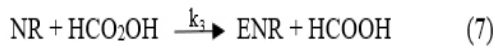
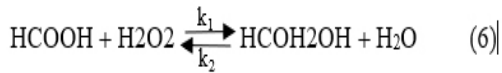
Table 1. Wavelength baseline in ENR reaction product characterization.

Characterization	Absorbance	Baseline wavelength (cm ⁻¹)
Epoxy/Olefin	A ₈₃₅ and A ₈₇₀	950,734 – 779,101
Ring Opening/Side reaction:		
Hydroxyl	A ₃₄₆₀	3702,656 – 3072,047
Carbonyl	A ₁₇₂₂	1774,189 – 1689,337
Hydro furan	A ₁₀₆₈	1097,298 – 1052,943

wherein the correction is due to the interference of the corresponding bonds that determined using H-NMR method. The constants K₁ and K₂ are absolute 0.77 and 0.34 (Chakraborty *et al.*, 2010). The ENR reaction product was determined according to specific wavelength baseline, which was tabulated in Table 1.

Rate Constant of Epoxidation Reaction (k)

An excess hydrogen peroxide on epoxidation reaction was followed by pseudo-first order system (Roy *et al.*, 1993). In situ epoxidation reaction involved two main steps of reaction, (1) formation of peroxyacids and (2) formation of epoxides as exemplified with peroxyformic acid, wherein k₁, k₂, and k₃ are reaction rate constants.



$$-d[\text{NR}]/dt = k_3 [\text{NR}]^{n_1} [\text{HCO}_2\text{OH}]^{n_2} \quad (8)$$

Where [NR] and [HCO₂OH] are molar concentrations of double bonds in natural rubber and peroxyformic acid respectively, k₃ is a rate

constant (equation 7), n₁ and n₂ are the reaction orders with respect to the double bonds and peroxyformic acid. Epoxidation was assumed to be pseudo first order with respect to the double bonds as well as to the peroxyacetic acid and the rate constant was defined as k = k₃ [HCO₂OH], the rate equation for pseudo first order can be written as equation (9).

$$-d[\text{NR}]/dt = k[\text{NR}] \quad (9)$$

The rate data for the epoxidation with peroxyformic acid were fitted in equation (9). Hence, after integration, equation (9) becomes equation (10).

$$\ln([\text{NR}]_0/[\text{NR}]) = kt \quad (10)$$

The rate constant of epoxidation reaction was determined by plotting epoxy (E) to reaction time. The slope of that plotting was described as the rate constant (k) of each reaction condition.

RESULTS AND DISCUSSION

Epoxidation Product

The epoxidation product of the samples is tabulated in Table 2. Values of E, O, and R were determined as the calculation in equation 1 to

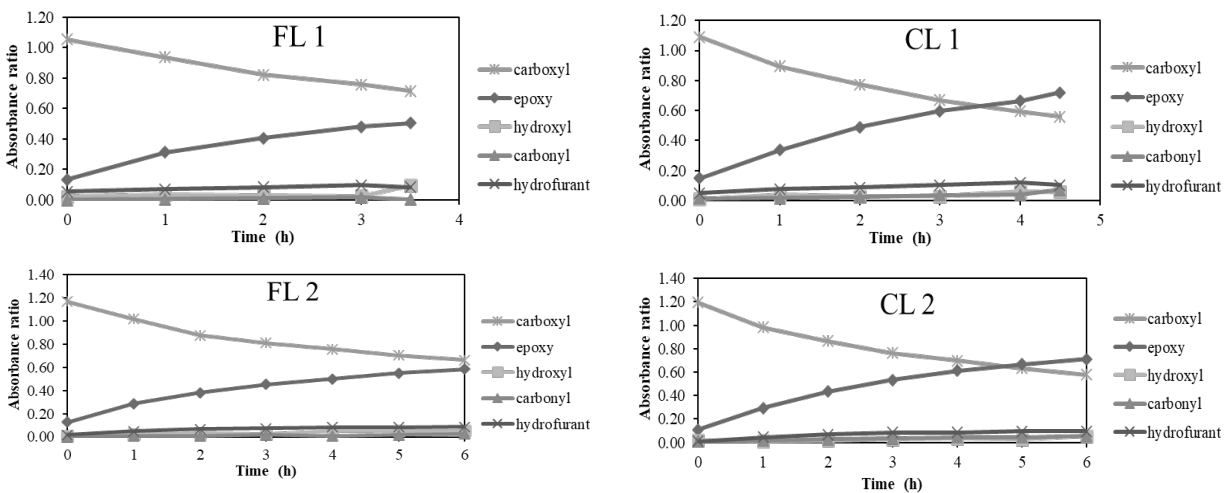


Figure 1. Epoxidation reaction product on various studied parameters.

Table 2. Epoxidation product.

Sample Code	Time Reaction (h)	E (%)	O (%)	R (%)
FL 1	0	0.00	0.00	0.00
	1	12.89	86.59	0.52
	2	21.32	78.28	0.40
	3	27.55	72.29	0.17
	3.5	29.61	67.95	2.44
CL 1	0	0.00	0.00	0.00
	1	15.30	84.08	0.62
	2	27.42	72.25	0.33
	3	36.52	63.21	0.27
	4	42.36	56.33	1.30
FL 2	0	0.00	0.00	0.00
	1	9.86	89.98	0.17
	2	18.38	81.18	0.44
	3	24.45	75.37	0.18
	4	28.29	70.73	0.98
CL 2	0	0.00	0.00	0.00
	1	10.95	89.38	-0.33
	2	21.72	78.35	-0.06
	3	30.07	69.73	0.20
	4	36.02	63.51	0.48
	5	41.22	58.57	0.21
	6	45.08	53.85	1.06

5. The addition of reactant which was poured all at once produced higher epoxy content and side product than dropwise method, which is shown in Table 2 and Figure 1. These results were confirmed by the investigation result of Roy *et al.* (1994), wherein the epoxy product of in situ peracformic acid epoxidation with added reagent dropwise method had lower epoxide

content and tetrahydrofuran than added reagent at once method. This phenomenon is probably because peracid quickly reacted with the nearest isoprene unit of NR to produce an epoxy group; then epoxy group stimulated an acid environment. As a result, acid induced secondary reactions to prevail, resulting in a lower epoxy content and an increasing side reaction (Roy *et al.*, 1994). The

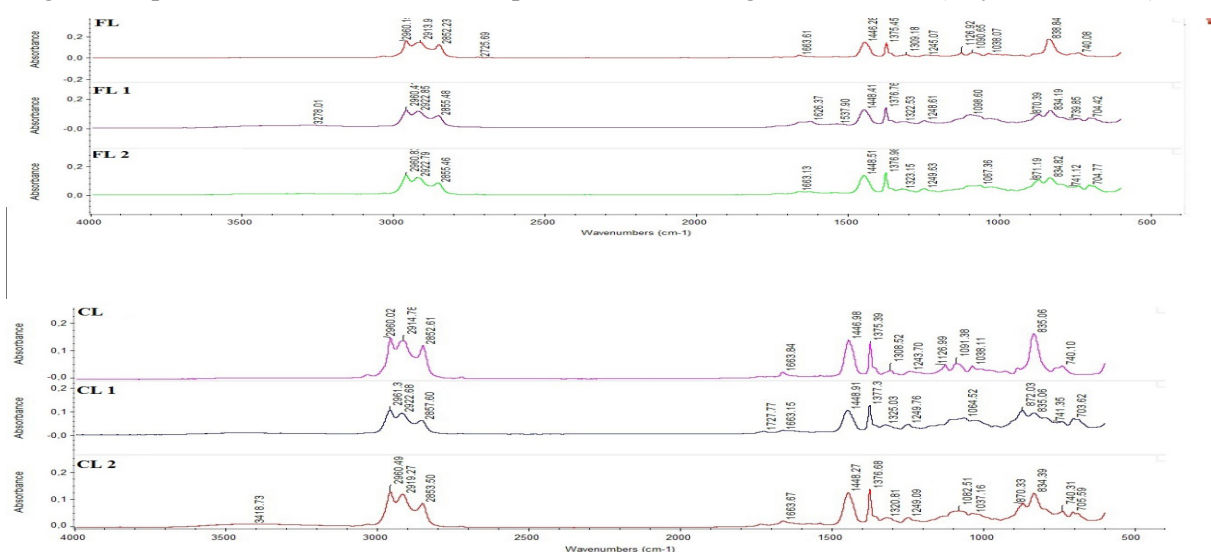


Figure 2. IR spectrum of various samples.

Table 3. The overall rate constant of various samples.

Sample	Rate Constant (L/mol second)
FL 1	2.764×10^{-5}
CL 1	3.778×10^{-5}
FL 2	2.039×10^{-5}
CL 2	2.808×10^{-5}

excess acid environment in epoxidation reaction induced an unstable reaction, which represented a coagulation of ENR in reactor during epoxidation reaction. Table 1 shows that epoxidation reaction of FL1 and CL1 had shorter time reaction than the determined time reaction (6 hour). FL1 and CL 1 samples showed unstable epoxidation reaction, wherein sample was coagulated at 3.5 and 4.5 hours respectively. It was due to excess side reaction formed during reaction. Hence, the optimum reaction time of FL1 was 3.5 h and CL 1 was 4.5.

Table 2 also shows that concentrated latex (in both reactant addition methods) produced higher epoxy content and more stable reaction than the other. This result was consistent as in Ruksakulpiwat *et al.* (2008). This research condition could produce epoxy content around 12-46% (represented as E%) and side reaction less than 3% (represented as O%), with remaining C=C (represented as O%).

The epoxidation reaction product is shown in Figure 1. The epoxy content of ENR increased as the degradation of unsaturation structure (C=C) that acted as simple olefin (O) during longer time reaction. Furthermore, the higher epoxy content, the higher side reaction in all samples would be. This result confirms that the appearance of characteristic signals side reactions such as hydroxyl, carbonyl and hydro furan at 3461.598, 1727.906 and 1064.514 cm^{-1} respectively (Figure 2). The increase of epoxy level leads to increasing gel content (Bac *et al.*, 1991), which is attributed to high side reactions that occurred during epoxidation (Gelling, 1985) and to enhance non-polar solvent resistance (Bac *et al.*, 1991).

Rate Constant of Epoxidation Reaction

Epoxidation reaction with excess hydrogen peroxide is followed by a pseudo-first order system (Roy *et al.*, 1991). The overall rate constant of this system is shown in Figure 3 and Table 3. The slope

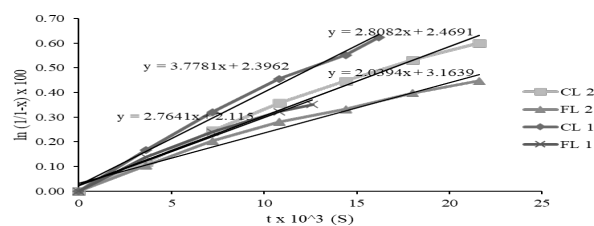


Figure 3. Pseudo-first order kinetic plot for various samples.

value of the plotting data of epoxy content against time reaction exhibits that CL sample has higher rate constant than FL sample. It is probably due to the lower impurity agent in CL. The higher rate constant will enhance the form of epoxy structure, which is confirmed on Table 2.

The addition of reactant in dropwise method has higher rate constant than poured-all-at-once method. It is in line with the formation of epoxy structure (Table 1). The dropwise reactant addition method allowed to produce peracid which quickly reacts with the nearest isoprene unit of NR to produce an epoxy group and further induces excess acid condition in the system then coagulates the latex sample.

CONCLUSION

The optimum condition of epoxidation reaction with pseudo-first order system was conducted on concentrated latex with pour all reactant at once method. The optimum condition reached the highest epoxy level at 45.08% with rate constant of 2.808×10^{-5} L/mol second.

ACKNOWLEDGMENTS

Our gratitude goes to the Ministry of Research, Technology, and Higher Education and the Indonesian Rubber Research Institute as the supporting institution for this research activity.

REFERENCES

- Al-Mansob, R. A., Ismail, A., Alduri, A. N., Azhari, C. H., Karim, M. R., & Yusoff, N. I. M. (2014). Physical and rheological properties of epoxidized natural rubber modified bitumens. *Construction and Building Materials*, 63, 242–248. <https://doi.org/10.1016/j.conbuildmat.2014.04.026>
- Bac, N. V., Terlemezyan, L., & Mihailov, M. (1991). On the stability and in situ epoxidation of natural rubber in latex by performic acid. *Journal of Applied Polymer Science*, 42(11), 2965–2973. <https://doi.org/10.1002/app.1991.070421114>
- Chakraborty, S., Ameta, S. K., Dasgupta, S.,

- Mukhopadhyay, R., & Singhanian, H. S. (2010). Quantitative application of FTIR in rubber. *Rubber World*, 241, 33–39.
- Chuayjuljit, S., Nutchapong, T., Saravari, O., & Boonmahitthisud, A. (2015). Preparation and characterization of epoxidized natural rubber and epoxidized natural rubber/carboxylated styrene butadiene rubber blends. *Journal of Metals, Materials and Minerals*, 25(1), 27–36. <https://doi.org/10.14456/jmmm.2015.4>
- Fathurrohman, M. I. (2010). Studies of oil resistance study of epoxidized natural rubber and deproteinized natural rubber. *Jurnal Penelitian Karet*, 28(2), 82–93.
- Gelling, I. R. (1985). Modification of natural rubber latex with peracetic acid. *Rubber Chemistry and Technology*, 58(1), 86–96. <https://doi.org/10.5254/1.3536060>
- Gneco, S., Pooley, A., & Krause, M. (1996). Epoxidation of low-molecular-weight Euphorbia lactiflora natural rubber with “in situ” formed performic acid. *Polymer Bulletin*, 37, 609–615. <https://doi.org/10.1007/BF00296606>
- Kaewsakul, W., Sahakaro, K., Dierkes, W., & Noordermeer, J. W. (2013). Optimization of epoxidation degree and silane coupling agent content for silica-filled epoxidized natural rubber tire tread compounds. *Advanced Materials Research*, 844, 243–246. <https://doi.org/10.4028/www.scientific.net/AMR.844.243>
- Norhanifah, M., Ruslimie, C., & Rubaizah, M. R. F. (2016). Effect of latex source and neutralisation base for epoxidation on morphology and strength of ENR25 latex. *Proceedings of 13th International Annual Symposium on Sustainability Science and Management*, 42, 775–845.
- Phinyocheep, P., & Boonjairak, K. (2006). Investigation on hydrogenation and epoxidation of natural rubber in latex stage. *International Rubber Conference 2006*, 1–14.
- Rohadi, A. A., Rahmat, A. R., & Kamal, M. M. (2014). Effect of epoxidation level in silica filled epoxidized natural rubber compound on cure, rheological, mechanical and dynamic properties. *Applied Mechanics and Materials*, 554, 71–75. <https://doi.org/10.4028/www.scientific.net/AMM.554.71>
- Roy, S., Gupta, B. R., & Maiti, B. R. (1990). Studies on the epoxidation of natural rubber. *Journal of Elastomers & Plastics*, 22(4), 280–294. <https://doi.org/10.1177/009524439002200407>
- Roy, S., Gupta, B. R., & Maiti, B. R. (1991). Effect of acid concentration and other reaction parameters on epoxidation of natural rubber latex. *Industrial & Engineering Chemistry Research*, 30(12), 2573–2576. <https://doi.org/10.1021/ie00060a010>
- Roy, S., Namboodri, C. S. S., Maiti, B. R., & Gupta, B. R. (1993). Kinetic modeling of the epoxidation of natural rubber with in-situ-formed peracid. *Polymer Engineering & Science*, 33(2), 92–96. <https://doi.org/10.1002/pen.760330206>
- Roy, S., Maiti, B. R., & Gupta, B. R. (1994). Latex stage epoxidation of natural rubber: Effects of agitation, mode of addition of reagents, neutralization technique, and secondary acid. *Polymer Reaction Engineering*, 2(3), 215–240. <https://doi.org/10.1080/10543414.1994.10744452>
- Ruksakulpiwat, C., Nuasaen, S., Poonsawat, C., & Khansawai, P. (2008). Synthesis and modification of epoxidized natural rubber from natural rubber latex. *Advanced Materials Research*, 47-50, 734–737. <https://doi.org/10.4028/www.scientific.net/AMR.47-50.734>
- Tan, S. K., Ahmad, S., Chia, C. H., Mamun, A., & Heim, H. P. (2013). A comparison study of liquid natural rubber (LNR) and liquid epoxidized natural rubber (LENR) as the toughening agent for epoxy. *American Journal of Materials Science*, 3(3), 55–61.
- Tanrattanakul, V., Wattanathai, B., Tiangjunya, A., & Muhamud, P. (2003). In situ epoxidized natural rubber: Improved oil resistance of natural rubber. *Journal of Applied Polymer Science*, 90(1), 261–269. <https://doi.org/10.1002/app.12706>
- Venkatanarasimhan, S., & Raghavachari, D. (2013). Epoxidized natural rubber–magnetite nanocomposites for oil spill recovery. *Journal of Materials Chemistry A*, 1(3), 868–876. <https://doi.org/10.1039/c2ta00445c>