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

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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 minimalized 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 (2.8082x10^-5 L mol^-1 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 (Venkatarasimhan & 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 hydrofuran), 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 epoxy 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).

\[
A_{370 \text{ corr}} = A_{370} - (0.14x A_{835}) \quad (1)
\]

\[
A_{3460 \text{ corr}} = A_{3460} - (0.019x A_{1375}) \quad (2)
\]

\[
E = \frac{100 x K_1 x A_{370 \text{ corr}}}{A_{355} + K_2 x A_{370 \text{ corr}} + K_3 x A_{3460 \text{ corr}}} \times \text{mol} \% \quad (3)
\]

\[
O = \frac{E x A_{835}}{K_2 x A_{370 \text{ corr}}} \times \text{mol} \% \quad (4)
\]

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

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     | A₉₅₄ and A₈₇₀| 950,734 – 779,101          |

Ring Opening/Side reaction:
- Hydroxyl: A₃₄₆₀ 3702,656 – 3072,047
- Carbonyl: A₁₇₂₂ 1774,189 – 1689,337
- Hydro furan: A₁₀₆₈ 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.

\[
\text{HCOOH} + \text{H}_2\text{O}_2 \xleftrightarrow{k_1} \text{HCOH}_2\text{O}_2 + \text{H}_2\text{O} \quad (6)
\]

\[
\text{NR} + \text{HCO}_2\text{OH} \xrightarrow{k_1} \text{ENR} + \text{HCOOH} \quad (7)
\]

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

Where [NR] and [HCO₂OH] are molar concentrations of double bonds in natural rubber and peroxyformic acid respectively, kᵢ is a rate constant (equation 7), n₁ and nᵢ 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 \( k = k_3 [\text{HCO}_2\text{OH}] \), the rate equation for pseudo first order can be written as equation (9).

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

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
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 peraformic 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

| 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  |
|             | 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  |
|             | 4.5              | 46.41 | 52.34 | 1.25  |
| CL 1        | 0                | 0.00  | 0.00  | 0.00  |
|             | 1                | 9.86  | 89.98 | 0.17  |
|             | 2                | 18.38 | 81.18 | 0.44  |
| FL 2        | 3                | 24.45 | 75.37 | 0.18  |
|             | 4                | 28.29 | 70.73 | 0.98  |
|             | 5                | 32.78 | 66.20 | 1.02  |
|             | 6                | 36.01 | 62.93 | 1.05  |
|             | 0                | 0.00  | 0.00  | 0.00  |
|             | 1                | 10.95 | 89.38 | -0.33 |
|             | 2                | 21.72 | 78.35 | -0.06 |
| CL 2        | 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  |

Table 2. Epoxidation product.

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 x 10^-5               |
| CL 1   | 3.778 x 10^-5               |
| FL 2   | 2.039 x 10^-5               |
| CL 2   | 2.808 x 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 Ruksakulpivat 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 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 2.808x 10⁻⁵ L/mol second.

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