Diimide Hydrogenation of In-situ Epoxidized Natural Rubber Latex

Wanvimon Arayapranee^{1*}, Chanin Ngudsuntear² and Garry L. Rempel³

¹Department of Chemical and Material Engineering, Rangsit University, Pathum Thani, 12000, Thailand ²Department of Chemical Engineering, Kasetsart University, Bangkok, 10900, Thailand ³Department of Chemical Engineering, University of Waterloo, Ontario, N2L 3G1, Canada ^{*}Corresponding author, Email: wanvimon@rsu.ac.th

Abstract

The hydrogenation of epoxidized natural rubber (HENR) via diimide reduction of hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) and boric acid (H_3BO_3) as a promotor was studied. Epoxidized natural rubber (ENR) with 50% mole of epoxide group was carried out by in-situ epoxidation of natural rubber (NR) using performic acid generated from reaction of formic acid/ H_2O_2 in the latex stage and was used as a raw latex material for hydrogenation. Hydrogenation degree of ENR was examined by Fourier transform infrared spectroscopy (FTIR) depending on reaction conditions such as reaction time and temperature and the mole ratio of $H_2O_2/C=C$ and N_2H_4/H_2O_2 . The highest degree of hydrogenation was found to be 80% by using a mole ratio of H_2O_2 to carbon-carbon double bonds (C=C) of 1:1 and N_2H_4 to H_2O_2 of 2:1 at 40°C for 6 h.

Keywords: Epoxidized Natural Rubber, latex, hydrogenation, diimide, epoxidation.

บทคัดย่อ

การสึกษาการไฮโคริจเนชั่นขางธรรมชาติอิพอกไซด์ (HENR) ผ่านไดอิไมด์ที่เกิดจากปฏิกิริขาระหว่างไฮดราซีน (N₂H₄) กับไฮโดรเจนเปอร์ ออกไซด์ (H₂O₂) และกรดบอริก (H₃PO₃) เป็นสารกระตุ้นวิเคราะห์ลักษณะเฉพาะโดยใช้เทคนิคฟูเรียร์ทรานฟอร์มสเปกโตรสโคปี เตรียมขาง ธรรมชาติอิพอกไซด์ (ENR) ที่มีปริมาณหมู่อิพอกไซด์ 50 % โมลจากการอิพอกซิเดชั่นภาขในสภาวะลาเท็กซ์ขางธรรมชาติโดยใช้กรดเปอร์ฟอร์มิกที่ เกิดจากปฏิกิริขาระหว่างกรดฟอร์มิกและไฮโดรเจนเปอร์ออกไซด์ 50 % โมลจากการอิพอกซิเดชั่นภาขในสภาวะลาเท็กซ์ขางธรรมชาติโดยใช้กรดเปอร์ฟอร์มิกที่ เกิดจากปฏิกิริขาระหว่างกรดฟอร์มิกและไฮโดรเจนเปอร์ออกไซด์และใช้เป็นวัตถุดิบสำหรับการไฮโดรจิเนชั่น ตรวจสอบดีกรีไฮโดรจิเนชั่นของ ENR โดยใช้ฟูเรียร์ทรานฟอร์มสเปกโตรสโคปี (FTIR) ซึ่งขึ้นกับสภาวะปฏิกิริขาเช่น เวลาและอุณหภูมิของปฏิกิริขาและอัตราส่วนโมลของ H₂O₂/C=C และ N₂H₄H₂O₂ ดีกรีไฮโดรจิเนชั่นสูงสุดมีค่าเท่ากับ 80% โดยใช้อัตราส่วนโมลของ H₂O₂ ต่อพันธะกู่ (C=C) เท่ากับ 1:1 และ N₂H₄ ต่อ H₂O₂ เท่ากับ 2:1 ที่ อุณหภูมิ 40[°]C เป็นเวลา 6 ชั่วโมง

คำสำคัญ: ยางธรรมชาติอิพอกไซค์ ลาเท็กซ์ ไฮโคริจูเนชั่น ไคอิไมค์ อิพอกซิเคชั่น

1. Introduction

Natural Rubber (NR) obtained from Hevea brasiliensis is a renewable material possessing excellent characteristics such as high tensile strength due to its ability to crystallize upon stretching. However, disadvantages of NR are low in heat, oxygen, and ozone resistance mainly because of its unsaturated chain structure. In addition, it does not perform well when exposed to oils and hydrocarbon solvents, as a result of its non-polar character. Hence, it has limitation in demanding applications. Since there is an increased environmental concern and increased emphasis on the use of renewable resources, many studies have been emphasized on the improvement of the properties of expanding application of natural rubber, which was considered as a sustainable resource, thus enabling it to compete with synthetic rubbers. The chemical modification of NR by hydrogenation, epoxidation, chlorination, and graft copolymerization is a good candidate to improve the properties of natural rubber for an expanding range of applications, while still maintaining its good mechanical properties. Epoxidation, using organic peracid directly (Hong et al., 2005) or produced in situ, takes place readily at the unsaturated groups replacing them by epoxide groups which has turned out to be an attractive material. It has high polarity due to the epoxide group in the chain bringing about an improved resistance towards oils and hydrocarbon solvents (Sharif et al., 2012) while retaining superior strength and fatigue properties due to undergoing strain induced crystallization like that of NR. Two grades of ENR, ENR-25 (25% epoxidation) and ENR-50 (50% epoxidation), have attained commercial importance. ENR-25 can be utilized for tire product because of its good in wet-grip and rolling resistance, whereas, the oil resistance property of ENR-50 was comparable to

that of nitrile rubber (NBR) with 32% of acrylonitrile group. However, ENR has poor heat resistance like NR due to its unsaturated C=C bonds, thus limiting its use in outdoor applications. Hydrogenation is one of the most efficient methods used to reduce the degree of unsaturation in polymers by adding hydrogen atoms to the unsaturated units in the presence of a transition metal catalyst used to speed up the reaction or an inorganic reagent such as diimide (N_2H_2) (Singha et al., 1997) thus enhancing the thermal stability of ENR.

2. Objectives

In this work, an attempt to prepare hydrogenated epoxidized natural rubber (HENR) was performed by epoxidization of natural rubber latex in-situ followed by diimide reduction hydrogenation generated from the reaction of hydrazine/hydrogen peroxide (N_2H_4/H_2O_2) with boric acid as a promotor. The effects of reaction conditions such as reaction time and temperature and the mole ratio of $H_2O_2/C=C$ and N_2H_4/H_2O_2 on the hydrogenation were examined. The chemical structure of the product was characterized by Fourier transform infrared spectroscopy (FTIR).

3. Materials and methods

3.1 Materials

High ammonia natural rubber latex with 60% dry rubber content (DRC) was obtained from the Rubber Research Institute of Thailand (RRIT, Bangkok, Thailand). The latex is composed almost entirely of cis-1,4-polyisoprene. Hydrogen peroxide (50 wt. % in H_2O , stabilized, Sigma) was used as the oxidizer for in-situ epoxidation and hydrogenation with 85% formic acid and 99.9% hydrazine hydrate (Merck Ltd., Bangkok, Thailand). Aromatic polyglycol ether (Lanxess, Singapore) under the trade name Emulvin WA was used as a surfactant. Methanol (commercial grade) was used as coagulant. Antifoaming agents (Dow Corning, silicone oil) were purchased from Facobis Co. Ltd., (Bangkok, Thailand).

3.2 Preparation of in-situ epoxidized natural rubber

500 g of diluted natural rubber latex with 20% DRC was mixed with Emulvin WA surfactant contained to a 1-liter three-necked flask. After stirring 1 h, 85% formic acid and 50% hydrogen peroxide were added into the reactor slowly dropwise, respectively, and stirred under a constant reaction temperature of 40°C for 12 h. To characterize the chemical structure by FTIR, ENR latex was coagulated with methanol and dried at 60°C until constant weight.

3.3 Hydrogenation of epoxidized natural rubber (HENR)

ENR latex (about 15% DRC) was used as the starting reactant for diimide hydrogenation. The ENR latex was hydrogenated by using a hydrazine $(N_2H_4)/hydrogen$ peroxide (H_2O_2) system in a 1-L glass reactor. The hydrazine hydrate was added into the ENR latex. Then, dissolved boric acid was dropped into the latex which was heated up to the reaction temperature. Subsequently, the mixture was heated up to the desired temperature and 50% hydrogen peroxide was slowly added dropwise using a peristaltic pump. During reaction, if the bubbles were formed, few drops of silicone oil, an antifoaming agent, were added. The reaction was left to proceed for 6 h after completely H_2O_2 . The latex was coagulated with methanol to form a rubber gum.

3.4 Characterization

The conversion of the carbon double bonds (C=C) of the samples was investigated by FTIR (Frontier, Perkin Elmer, Inc., USA) spectroscopy. FTIR was employed for examining the functional groups by monitoring the vibrational energy level in specific regions for the different molecules. IR spectra were recorded in the transmittance mode by averaging 8 scans at a maximum resolution of 4 cm⁻¹ over the range of 650 to $3,600 \text{ cm}^{-1}$.

Mole percentages of epoxy group =
$$\frac{100k_1A_2}{A_1 + k_2A_2 + k_3A_4}$$
(1.1)

$$A_1 = A_{835}, A_2 = A_{870} - 0.14A_{835}, A_3 = A_{3,460} - 0.019A_{1,375}$$
(1.2)

The constant values of k_1 and k_2 are 0.77 and 0.34, respectively (Yu et al., 2008). The degree of hydrogenation was calculated by using the cis-carbon double bonds at 835 cm-1 and methyl group at 1,375 cm-1 before and after hydrogenation according to eq (2).

Hydrogenation degree =
$$\frac{\left[A_{835}/A_{1,375}\right]_{before} - \left[A_{835}/A_{1,375}\right]_{after} \times 100}{\left[A_{835}/A_{1,375}\right]_{before}}$$
(2)

4. Results and discussion

In this article, the influence of reaction parameters, namely reaction temperature and time, N_2H_4/H_2O_2 and $H_2O_2/C=C$, on the HENR properties by using diimide hydrogenation in the presence of boric acid as a promotor was examined.

4.1 FTIR spectroscopic characterization

The structure of ENR before and after hydrogenation was characterized by FTIR spectroscopy. Mole percentage of the epoxide group and the degree of hydrogenation were calculated according to eq. (1) and (2), respectively, based on corresponding absorbance of the important peaks as shown in Figure 1. The principal absorption bands of the unsaturated isoprene units at 835 cm⁻¹, 1,375 cm⁻¹, and 1,662 cm⁻¹ were assigned to out of plane deformation of cis- double bonds, deformation vibration of the CH₃, and carbon-carbon double bonds stretching, respectively. The new bands of C-O-C of the epoxy group appeared at 870 and 1,250 cm⁻¹ in FTIR spectra for ENR. This provides evidence that a part of carbon-carbon double bonds are converted to epoxide groups. The mole percentage of epoxide groups of the prepared ENR was 49.54% (ENR-50). However, IR spectra of ENR also shows the remaining peaks for the C=C unsaturation, i.e., at 1,662 cm⁻¹ and 835 cm⁻¹ significantly decreases due to the replacement of the C=C with a carbon single bond, thus, it can be concluded that the ENR was hydrogenated with a more saturated structure when compared with the original ENR spectra.



Figure 1 FTIR spectra of NR, ENR, and HENR with varying hydrogenation degree in the range of 700–3,600 cm⁻¹.

4.2 Effect of reaction time on HENR properties

The reaction time usually plays a very important role in a chemical reaction. The reaction was studied over an interval of time from 0 to 10 h. The hydrogenation reaction was achieved at 40°C, with a fixed amount of C=C of ENR (1.2 mole), mole ratio of $H_2O_2/C=C = 1$ and mole ratio of hydrazine (N₂H₄)

to $H_2O_2 = 1$. The effect of reaction time is illustrated in Figure 2. The C=C conversion, was sharply increased with time initially, and then leveled off for a reaction time greater than 6 h. This is possibly a result in that the fast increment in the hydrogenation degree during the first period of the reaction may be due to the high diffusion rate of the diimide species from the outerside into the inside of the rubber particle. Meanwhile, after 6 h of the hydrogenation reaction, the diffusion of the diimide was retarded by the barrier of the thicker saturated segment resulting in that the amount of diimide for hydrogenation reaction is low providing a limited hydrogenation level.



Figure 2 Effect of reaction time on HENR properties. Condition: mole ratio of $H_2O_2/C=C = 1$, $N_2H_4/H_2O_2 = 1$ and reaction temperature = 40°C.

4.3 Effect of reaction temperature on HENR properties

The reaction temperature usually plays a very important role in hydrogenation according to Arrhenius equation. A series of experiments were carried out from 30-70°C. Form the results of the reaction temperature on the hydrogenation of ENR as shown in Figure 3, it can be seen that the degree of hydrogenation increased initially with an increase in temperature up to 60°C and then slightly decrease with a further increase in temperature. It can be explained that the reactant was low active substance at a low temperature due to a low level collisions between particles and other particles. As the reaction temperature elevated, both the activity of the reactant molecules and probability of particles collision increased, resulting in enrichment of the hydrogenation yield.



Figure 3 Effect of reaction temperature on HENR properties. Condition: mole ratio of $H_2O_2/C=C = 1$, $N_2H_4/H_2O_2 = 1$ and reaction time = 6 h.

4.4 Effect of hydrazine hydrate on HENR properties

Hydrazine was used as the source for diimide production. The influence of hydrazine (N_2H_4) on the hydrogenation of ENR was studied over the range of 0.67-2.00 N_2H_4/H_2O_2 mole ratio is shown in Figure 4. The degree of hydrogenation slightly increased as the N_2H_4/H_2O_2 ratio increases. The main reactions are the N_2H_4/H_2O_2 reaction to produce the diimide attaching to the unsaturated of ENR chains resulting in an increase in hydrogenation degree. Thus, with a higher amount of N_2H_4 , more diimide was generated which is caused of an increase in the degree of hydrogenation.



Figure 4 Effect of N_2H_4/H_2O_2 ratio on HENR properties. Condition: mole ratio of $H_2O_2/C=C=1$, reaction time = 6 h and reaction temperature = 40°C.

4.5 Effect of hydrogen peroxide on HENR properties

In order to investigate the effect of hydrogen peroxide on hydrogenation degree, a series of experiments were carried out over the mole ratio of H_2O_2 to C=C from 0.5 to 1.5 with a fixed amount of C=C of ENR (1.2 mole) and a mole ratio of the other parameters; hydrazine to $H_2O_2 = 1$ under a reaction temperature of 40°C for 6 h. From Figure 5, it can be seen the hydrogenation degree slightly increases as the mole ratio of $H_2O_2/C=C$ increases. The amount of H_2O_2 is an important factor in the diimide generation. Therefore, the increased level of hydrogenation at higher amount of H_2O_2 may be due to the high amount of diimide generation



Figure 5 Effect of $H_2O_2/C=C$ ration on HENR properties. Condition: mole ratio of $N_2H_4/H_2O_2 = 1$, reaction time = 6 h and reaction temperature = 40°C.

5. Conclusion

The hydrogenation of ENR latex was carried out by using a redox system consisting of hydrazine and hydrogen peroxide with boric acid as a promotor. Overall the results showed that an increment in the mole ratios of N_2H_4/H_2O_2 , $H_2O_2/C=C$ and reaction time and temperature directly affect the increase in the degree of hydrogenation.

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7. References

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