BASIC DESIGN OF PROCESS ENGINEERING FOR EPOXIDIZED NATURAL RUBBER PRODUCTION AS RAW MATERIAL FOR OIL RESISTANT PRODUCTS

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Abstract

Natural rubber of Hevea brasiliensis *is a natural polymer which has good damping properties and high elasticity. However, the natural rubber molecule is a nonpolar hydrocarbon polymer which easily swells in oil. Epoxidizing the double bond of the natural rubber molecule is an effort to increase its polarity thereby increasing its resistance to oil. Several of its physical properties will also improve. Epoxidized natural rubber is made from the insitu epoxidation of the rubber molecule in the latex phase using performic acid made from hydrogen peroxide and formic acid. The aim of the experiments in this study was to design the process engineering of the epoxidation reaction from concentrated latex. The reaction was carried out at a temperature of 70 °C for 5 hours with the dose of hydrogen peroxide at 0.75 mol/mol isoprene unit and 0.4 mol/mol isoprene unit of the formic acid dose. The exothermic reaction occurred in a Batch Stirrer Tank Reactor (BSTR) which was equipped with a water cooling system to keep the reaction temperature constant. The reaction product was then neutralized with the addition of ammoniac and sodium thiosulphate in a neutralization tank. The product was then coagulated using a thermal extruder at 80-90 °C to produce Epoxidized Natural Rubber with 40% mol epoxy percent (ENR-40). The ENR was then washed with water to remove the acid residue. At the end, the ENR product was dried at 105 °C. The result showed that this basic design can be used as a reference to produce epoxidized natural rubber from the pilot scale to an industrial scale. Some parameters such as temperature, pressure, time conducted at each stage of the process, process flow diagram, process equipment, production efficiency, and the technoeconomy aspect need consideration in the design.*

Keywords: batch stirrer tank reactor, concentrated latex, epoxidized natural rubber, oil resistance, process design

INTRODUCTION

Natural world rubber consumption is currently dominated by tyre products. There is a need to diversify the use natural rubber downstream, especially in the non-tyre products. Low rubber prices make it even more urgent to diversify. The natural rubber price has seen a decreasing trend in 5 years. The price of SIR 20 which was above 3.32 US$/kg in 2011, moved down to 1.71 US$ at the end of 2014. In August 2017 the price declined further to 1.50 US$. This makes a downstream program to expand natural rubber usage very important. The problem is natural rubber is not resistant to solvents, oxygen, ozone, UV light, and moisture (Vinod et al., 2002), a property very much required in many downstream applications. Therefore, the development technology to modify natural rubber is one important step to improve the weakness of natural rubber in such applications.

In contrast to natural rubber, synthetic rubber has good resistance to solvent, oxidation and ozone. For example NBR has good oil and abrasion resistance, but is low in elasticity, gas permeability, mechanical properties, and has poor resistance to ozone (Yasin et al., 2011). One diversification potential of natural rubber is for use as the rubber component in valves and regulators.

One effort to increase the oil resistance of natural rubber is through chemical modification via the epoxidation reaction. The epoxidation of natural rubber will produce an epoxide ring on the natural rubber polymer chain. The epoxidation reaction can either occur in the latex phase or by using an organic solvent. The epoxidation reaction in latex phase is however more economic than using the organic solvent because the use of organic solvents is too expensive and can also be problematic for the environment (Bradbury & Perera, 1985).

The epoxidation reaction of natural rubber is a reaction between natural rubber and peracid. Peracetic acid and performic acid are widely used as reactants for the epoxidation reaction in the latex phase (Phinyocheep & Boonjairaak, 2006). The epoxidation reaction using performic acid, produced from the insitu reaction between hydrogen peroxide and formic acid, is more easier to use (Phinyocheep & Boonjairaak, 2006), because the epoxidation reaction using performic acid does not require sulfuric acid as catalyst (Figure 1).

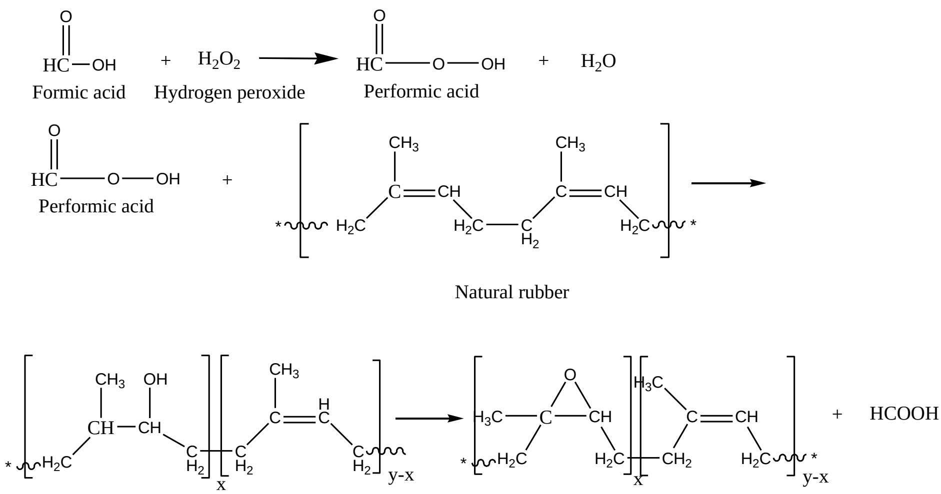


Figure 1. Natural rubber epoxidation reaction (Gelling, 1991)

Epoxidized natural rubber (ENR) has good resistance in the hydrocarbon oil, is more rigid and offers a good possibility for ring opening reaction. ENR is used for products such as oil seals, airtight membranes such as medicine bottles and bicycle tires (Zeng et al., 2008). In future, ENR has the potential to replace synthetic rubber for use in oil resistant products. Therefore, the industrial development ENR should be carried out. Basic data required to design the ENR production process would be useful to develop the ENR industry for a country like Indonesia which has great potential to increase natural rubber production. The aim of this research is to provide information in the form of technical data about the ENR production process at a pilot scale, so it can be used as reference data for application on the industrial scale.

MATERIALS AND METHODS

Material

The material used in this research is fresh natural rubber latex which was obtained from smallholder rubber plantation in Jasinga, Bogor District, concentrated latex with 58,08% dry rubber content was obtained from supplier, formic acid (90%) and hydrogen peroxide (50%). The chemical additives used in this research are emulgen (20%) as anionic surfactant, ammonia, and sodium thiosulphate. The Fourier Transform Infra Red (FTIR) spectrometer used to analyze the epoxy level.

Method

Optimization of Operating Conditions

The optimization was carried out based on the epoxidation reaction in laboratory scale. The epoxidation of natural rubber latex was carried out using two variation of latex (fresh and concentrated latex), two variation of formic acid dose (0.4 mol/mol isoprene unit), and hydrogen peroxide dose as much 0.75 mol/mol isoprene unit at 70 °C for 5 hours. Latex diluted until 20% of dry rubber content, and then 4 phr of emulgen was added to prevent coagulation. Formic acid and hydrogen peroxide was added to the mixture with the determinate dose. Hydrogen peroxide was added with two methods (drops by drops and all at once). The mixture was then stirred and heated at 70 °C for 5 hours. A small portion of latex was pipetted every hour to determined epoxy level using FTIR spectrometer. The expected result is epoxidized natural rubber with 40% of mol epoxidation. The latex formed then neutralized with ammonia and sodium thiosulphate, and then coagulated by heating process. Then, he coagulated then creped and dried. The result from laboratory scale was used as a reference for design of process flow diagram.

Basic Design of Process Flow Diagram

The design of flow diagram process considered of material properties which processed from beginning until the end and production efficiency. The flow diagram was designed based on the optimization of epoxidation reaction on laboratory scale.

Determination of Unit Operation

The unit operation designed to epoxidation reaction at 5 kg/ batch scale. The unit operation was determined based on process flow diagram which designed optimally and efficiently, so it can be used as reference for applied to a great level or industrial scale.

RESULTS AND DISCUSSION

Optimization of Operating Conditions

The result of optimization conditions of epoxidation reaction at laboratory scale are presented in Table 1. Table 1 showed that epoxy level from concentrated latex higher than fresh latex, because fresh latex contains protein which inhibiting epoxidation reaction, so the reaction become slower. At a laboratory scale, the addition of hydrogen peroxide drops by drops produce unstable reaction. Concentrated latex coagulate after 4 hours and 40 minutes reaction, and fresh latex coagulate after 3 hours and 50 minutes reaction. If this result applied for reactor with 5 kg/batch capacity, the reaction will be more unstable and quickly coagulate than laboratory scale, this can be shown by calculation of rate constant which value are presented in Table 1. The rate constant value (k) in the Table 1 showed that reaction with two materials has high k value, but k value from concentrated latex higher than fresh latex.

Table 1. The optimation conditions of epoxidation reaction

Latex	Addition Methode of Hydrogen Peroxide	Time (hours)	Mol Epoxy (%)	Rate constant (k) (dm^3. mol^{-1} s^{-1})
Concentrated latex	Drops by drops	4’40”	46.41	3,6867 x 10^{-5}
	All at once	6	45.08	2,8082 x 10^{-5}
Fresh latex	Drops by drops	3’50”	31.51	2,7142 x 10^{-5}
	All at once	6	36.01	2,0394 x 10^{-5}

As a comparison, the different method of hydrogen peroxide addition was doing. In the previous experiment, hydrogen peroxide was added drops by drop after the temperature reaches 70 °C. In this experiment, hydrogen peroxide was added at once at beginning and then after that the mixture was heated up to 70 °C. The result showed that longer time resulted in higher mol percent of epoxy. The highest rate constant is 2,8082 x 10-5 which was obtained from epoxidation reaction using concentrated latex.

During epoxidation process, the C=C double bond of isoprene unit in natural rubber was converted into epoxy group and various side reaction product, such as carboxyl, carbonyl, hydroxyl, and hydrofuran compounds. The most commonly produced are hydrofuran compounds, not only at concentrated latex but also at fresh latex. This is may occur due to ring-opened reaction of oxyrane group become easier at acidic state resulted hydrofuran compound. The epoxidation reaction using concentrated latex resulted in fewer side reactions than the other reactions. So that, based on reaction kinetics calculation and side reaction product it can be concluded that the optimum epoxidation reaction is using concentrated latex with addition hydrogen peroxide at once. This optimum condition then used as the reference for considerate and calculate for pilot scale reactor manufacturing.

Basic Design of Process Flow Diagram

The first stage for epoxidation process are handling of latex as raw material. Latex is a material which are sensitive from heat and friction. Anionic surfactant (emulgen) was added into latex inside reactor before reaction to prevent coagulation. The addition carried out in stirrer tank before transfered to reactor. The next stage is addition of formic acid and hydrogen peroxide in stirrer reactor to carried out epoxidation reaction. The epoxidation reaction carried out at 70 °C for 6 hours with heating system using circulating hot oil. The circulation process keeps the heat stable, because does not make the hot in one spot. The epoxidation reaction is exothermic reaction, so reactor must be equipped cooling system to keep the reaction temperature constant. The cooling medium used for this process are circulated water.

The epoxidized latex neutralized in netralization tank with addition amonia and sodium thiosulphate. The neutralized latex is then coagulated using heat extruder at 150 °C to produce epoxidized natural rubber. The epoxidized natural rubber is then washed using water to remove acid residue. The next stage is drying process in dryer machine at temperature 105 °C. The dried product is then packaged using balling press machine with the specified size. The process flow diagram are presented in Figure 2.

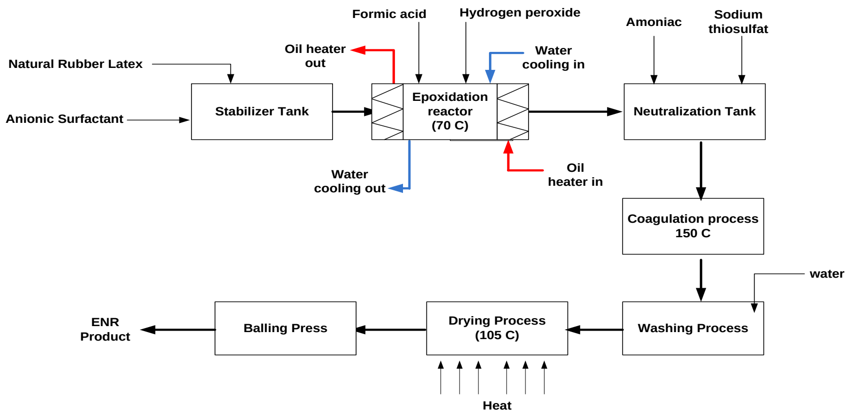


Figure 2. Flow sheet of epoxidized natural rubber production

Determination of Operation Unit

Latex Pumping

The transferring process of latex should using pump for easy in transfer process. There are several types of pump for use in industry such as centrifugal pump, gear pump and screw pump, but this pump not recommended for sensitive liquid such as latex. Latex is a shear–sensitive emulsion, so pump with low shear rate are required. Gear pump are not recommended for shear-sensitive fluids. If used, the inlet pipe must be oversized and operate at low speeds. Centrifugal pump are not recommended for latex because high flow rate operation, so that it can cause high shear, operation at low flow can cause pump failure. Use of screw pump in operation caused high cost in maintenance, and complicated in installation. One of the pump type assessed can be used is diaphragm pump (Figure 3). Diaphragm pump designed to reduces internal friction, can use for sensitive liquid such as latex. The principal of operating diaphragm pump also guarantee that the product flow rate remain constant (Brito, 2012).

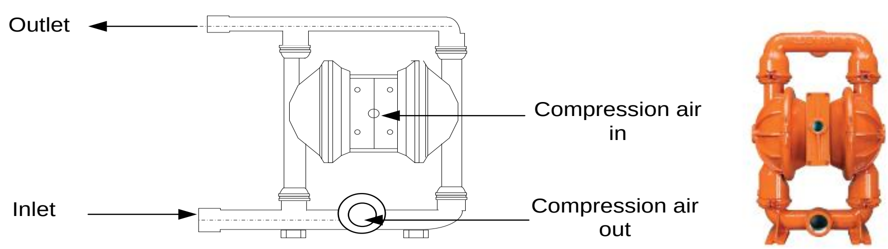
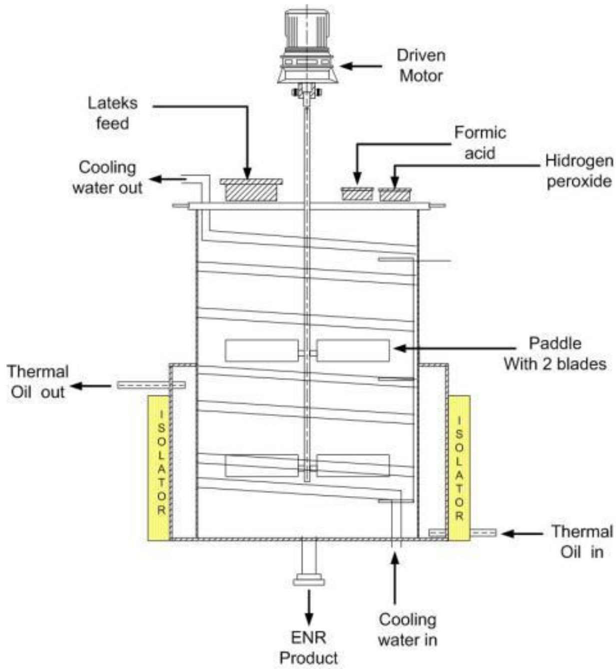


Figure 3. Diapraghm pump

Epoxidized Reactor

The main unit for epoxidized natural rubber production is epoxidation reactor (Figure 4). The appropriated type of reactor for epoxidation reaction is Batch Stirrer Tank Reactor (BSTR), because reaction phase is liquid-liquid and carried out for a long time reaction. The designs of reactor consider volume, agitator type, heating, and cooling system of reactor.



The epoxidation reaction of natural rubber (Figure 1) is pseudo first order reaction, because formic acid (HCOOH) is resulted again, so concentration of formic acid considered constant. In this reaction, only hydrogen peroxide have effect to reaction result. The equation of reaction rate as follows:

$$rx = k \cdot [H_2O_2] \cdot [HCO_3H]$$

Because concentration of formic acid is considered constant, the equation of reaction rate can be formulated as follows :

$$rx = k \cdot [H_2O_2]$$

k value can be obtained from slope of curve relation between ln [1/(1-E)] vs time. The calculation of volume can be used equation as follows :

$$\frac{dN_A}{dt} = rx\ .V$$

$$N_A = N_{AO} - N_{Ao}X$$

$$dN_A = 0 - N_{Ao}dX$$

$$-N_{Ao}\frac{dx}{dt} = rx\ .V$$

$$N_{Ao}\frac{dx}{dt} = -rx\ .V$$

$$t = N_{A0}\int_0^x \frac{dx}{-rx\,.V}$$

$$t = \frac{N_{AX}-N_{A0}}{-rx\ .V}$$

So the equation can be formulated as follows :

$$V = \frac{N_{A0}X}{-rx\,.t}$$

The design of batch reactor should have free space to control the level of liquid to prevent flooding. The free space in batch reactor is assumed as much 30%, so the equation follows:

$$V_T \quad =1.30 \text{ x Reactor Volume (V)}$$

If assumed H/D = 1.5, volume of reactor can be calculated as follows:

$$V_T = \pi \times \frac{1}{4}D^2 \times H$$

$$V_T = \pi \times \frac{1}{4}D^2 \times 1.5\ D$$

$$Vr = \pi \times \frac{1}{4}D^2 \times 1.5\ D$$

Extruder

ENR coagulation process can be carried out using methanol (Gan & Chen Ng, 1985; Roy et al., 1993; Zeng et al., 2008). The use of organic solvents such as methanol is high cost and it’s unprofitable, so its required tools that can coagulation the latex quickly, efficiently and keep the product good. Extruder is appropriate for this coagulation process.

In the market there are available many types of extruder for latex coagulation. Some extruder manufacturers have classified extruders at various scales such as laboratory, pilot, semi works, and commercial scale. For commercial scale is available starting from the smallest capacity of 182 kg/hour to a large capacity of 7250 kg/hour. Power supplies range from the minimum 150 HP to the maximum 4000 HP.

The use of extruder has reduced investment costs because it does not require coagulation tanks and pipeline material. It also reduces production cost because it does not use organic solvent to coagulation process and coagulation time faster. The cleaning process of waste material which left inside the extruder become easier because the screw function on the extruder can sweep away the material quickly. The quality of the epoxidized rubber which resulted from the extruder is good because it does not contain any contaminants.

The extruder temperature for latex coagulation can be adjusted in the range 100-160 °C, but not recommended for temperature settings exceeding 150 °C. The higher the temperature coagulation process will be faster, but if the temperature is too high can decrease the physical properties of ENR product. The single screw extruder type used in this process can be seen in Figure 5.

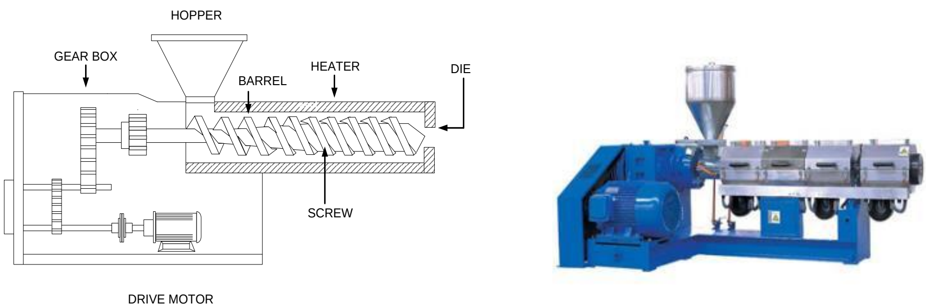


Figure 5. Singgle screw extruder

Washing and Drying Process

The washing process of product from extruder carried out by soaking in water. The washing process carried out in wash tank with equipped of agitator for better washing. Bucket elevator installed to take coagulated epoxidized rubber from wash tank. Bucket elevator was commonly used in crumb rubber industry.

For drying process of ENR can be used several type of dryer such as tray and trolley dryer. Trolley dryer is easier to apply for mass production. The ease of operation and mobility becomes consider to select the appropriate dryer. Trolley dryer is more suitable for drying process of ENR. The drying temperature not exceed the temperature at extruder, so dryer temperature is set 100-110 °C. Crumb rubber industry commonly using temperature 115-130 °C for drying up to 2-4 hours. Adjusting of temperature and time retention in dryer greatly determine the quality of ENR product.

ENR product from dryer should be cooled quickly. The cooling fan should be operated during drying process, so the rubber is not overheating. The cooling system usually carried out to result maximum temperature of rubber at 40 °C. The cooling fan can be installed on the end dryer machine, or installed outside dryer.

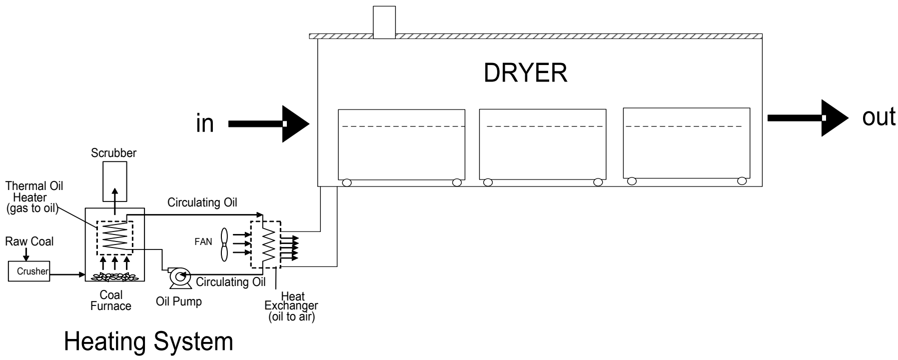
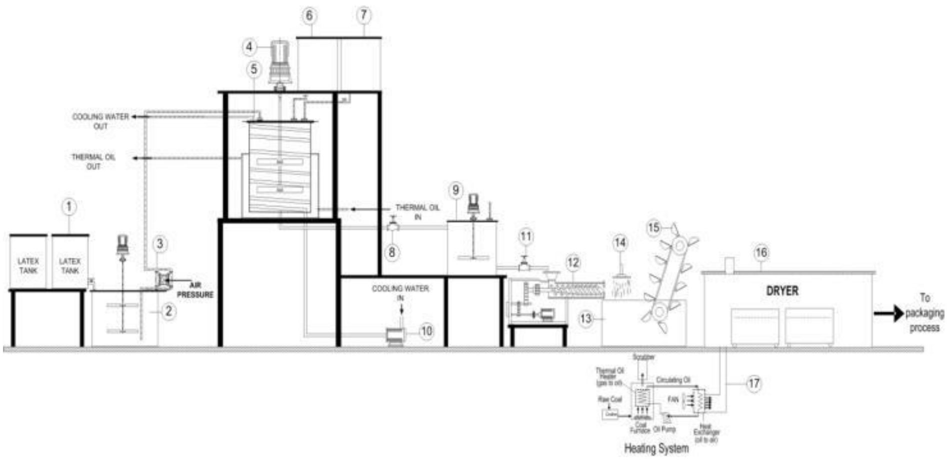


Figure 6. Type of trolley dyer with coal fuel

The purpose of using heat exchanger (HE) with oil as hot media is to change heating system from direct to indirect. The direct heating system from burning coal can produce gas with contain SO_2 and other gas which can cause degrade quality of rubber. Figure 6 presented a burning system with coal and its hot air distribution to dryer. The heated oil in pipe then pumped to HE in rubber dryer. Finally, HE blower used a fan to produce hot air which will be piped into dryer. The indirect system caused usage of coal becomes three times more than using diesel oil, because heat of coal is low than diesel oil.

Layout

In the end of production stage carried out packaging process, but its process optional for the industry. The layout for processing of ENR presented in Figure 7.



No	Component	No	Component
1	Latex Tank	10	Oil transfer pump
2	Stabilizer Tank	11	Outlet valve to extruder
3	Diapraghm pump	12	Extruder
4	Agitator	13	Wash tank
5	Epoxidation Reactor	14	Water sprayer
6	Hydrogen Peroxide Tank	15	Bucket elevator
7	Formic Acid Tank	16	Dryer
8	Outlet valve	17	Heat exchanger
9	Neutralization Tank		

Figure 7. Layout for processing of epoxidized natural rubber

CONCLUSION

Design for processing of epoxidized natural rubber production should consider condition operating parameters such as temperature, time, raw material, and product properties. The specific calculation also required to prevent failures which cause product damage and financial loss. This design is still preliminary design which can use as technical data for production of epoxidized natural rubber and also can be used as reference data for applied to a great level or industrial scale.

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