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The use of epoxidized natural rubber for producing rubber seals of LPG tube valves

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ABSTRACT

Rubber seal of Liquified Petroleum Gas (LPG) tube valves should fulfill Indonesian National Standard (SNI 7655:2010), which has high n-pentane resistance properties. This study aimed to design a rubber seal compound based on epoxidized natural rubber which fulfill SNI 7655:2010 requirements. The formulation of compound were designed by using epoxidized natural rubber with varied levels of epoxidation. Epoxidation reaction was occurred in an epoxidation reactor at 70 ºC for 6 hours with 0.75 mole/mole isoprene unit of hydrogen peroxide and 0.4 mole/mole isoprene unit of formic acid. Mechanical properties, ageing properties, and swelling performance in *n*-pentane of the modified natural rubber were tested and the result compared to the minimum requirement of SNI 7655:2010. The result showed that the increasing in epoxidation level made natural rubber becomes more polar so it is more resistant to immersion in n-pentane. Epoxidized natural rubber with levels of 40% and 50% fulfilled specifications for volume change in accordance with the quality requirements in SNI 7655:2010. The use of natural rubber created good elasticity to all level of epoxidized rubber where these properties are needed for rubber seal of LPG tube valve. However, the formulas of compound were less resistant to aging.

Keywords: epoxidized natural rubber, LPG tube valves, oil resistance, rubber seal.

INTRODUCTION

Natural rubber (NR) is often used in many applications that require high mechanical properties. More than 50% of NR is used in tires industry especially for buses, heavy duty truck and aircrafts. In addition, NR also used in some non-tyre products such as rubber hoses, automotive rubber parts, NR foam mattresses and NR gloves. Natural rubber generally has superior mechanical properties than synthetic rubber. However, natural rubber cannot compete with specialty elastomers, especially with regard to properties, such as resistance to UV, sunlight and ozone, gas permeability and oil resistance (Baker & Gelling, 1979).

According to SNI 7655:2010, the material for rubber seal LPG tube valve should resistant to *n*-pentane. Acrylonitrile Butadiene Rubber (NBR), a synthetic rubber, is a polar rubber that has resistance to non-polar solvents and oils (Mostafa *et al*., 2009; Wang *et al*., 2014; Choi & Ha, 2009), however it has low mechanical and dynamical properties. NBR is widely used in many applications which oil resistance is required, such as rubber fuel hoses, rubber gaskets, and roller. Meanwhile, NR has excellent mechanical and dynamical properties (Ismail *et al*., 2014), however NR is easily attacked by oxygen and ozone due to the presence of abundant amount of double bonds in its main chains (Mei *et al*., 2012). Moreover, NR is non-polar rubber that easily deformed by oils and hydrocarbon solvents (Tanrattanakul *et al*., 2003).

The modified products from NR have potential used in manifold rubber products combined with reinforcing fillers, such as carbon black or silica (ten Brinke *et al*., 2003; Choi *et al*., 2005) as well as physical blend with other polymers (Okwu & Okieimen, 2001; Oommen *et al*., 1996), or chemical modification (Roy *et al*., 1993), thus

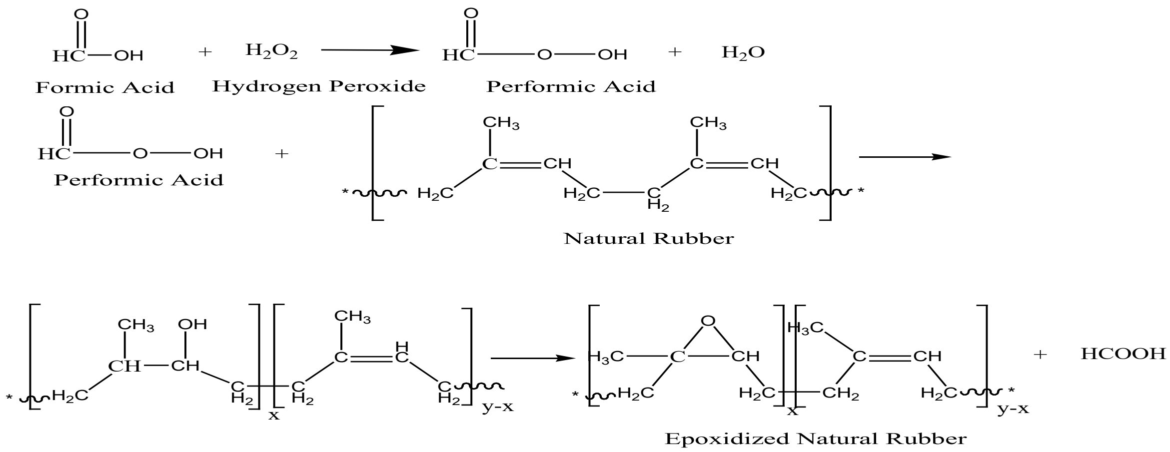

Figure 1. Epoxidation reaction of natural rubber (Baker *et al*., 1985).

modified NR enable to substitute and compete with synthetic rubbers. One of synthetic rubber which can be substituted with modified natural rubber is NBR. To improve the resistance to oil of natural rubber can be done by chemical and physical modification. The chemical modification of NR through an epoxidation reaction using hydrogen peroxide and formic acid in certain dose produces oil-resistant epoxidized natural rubber (Baker *et al*., 1985). The presence of epoxide groups in epoxidized natural rubber (ENR) structure showed higher polarity of ENR than NR (Sengloyluan *et al*., 2012). When natural rubber undergoes an epoxidation reaction, its physical and chemical properties change depends on the degree of epoxidation (Surya *et al*., 2018). The three most common levels of epoxidation that have been commercially produced, were ENR-50, ENR-25, and ENR-10, which referred to 50, 25, and 10 mole percent of epoxidation level, respectively. ENR-25 and ENR-50 can be used in many applications such as oil resistance and low gas permeability rubber products.

Some rubber products such as engine mounts, tires, rubber bearings, and adhesives, can use ENR as raw material. Moreover, ENR-40 has been used as raw material in rubber components manufacturing for tube valve and regulator of LPG (Handayani *et al.* 2017). The present study investigated the different levels of epoxidation to produce rubber seal of LPG tube valve

MATERIALS AND METHODS

Materials

The materials used in this study were technical grade from local suppliers. Materials for epoxidation reaction were natural rubber latex, formic acid, hydrogen peroxide, ammonia, anionic surfactant, acetone, and sodium carbonate. Materials for rubber compounding were vulcanization agent (sulphur), activator (stearic acid and zinc oxide), silane Si-69 (*bis-triethoxysilylpropyl-tetrasulfide*) as coupling agent, color pigment, silica reinforcing filler (Zeosil 175 MP), curing activator (Rhenofit 1987, Lanxess), rubber crosslinker (Vulcuren [*1,6-bis(N,N-dibenzylthiocarbamoyldithio)-hexane*], Lanxess), MMB (*methyl-2-mercaptobenzimidazole*) as antioxidant, DOP (*dioctyl phthalate*) as plasticizer, DTDM (4,4'-*dithiodimorpholine*), TMTD (*tetramethyl thiuram disulfide*) and CBS (N-*cyclohexylbenzothiazole-2-sulphenamide*) as accelerator and also Antilux 654 from Rhein Chemie as antiozonant. The equipments used in this study were epoxidation reactor for ENR synthesized and FT-IR Spectroscopy (Thermo Scientific Nicolet iS5) for epoxidation level analysis. Two roll open mill for mixing of rubber with another materials and also Universal Testing Machine (UTM) for testing of rubber physical properties such as tensile strength and elongation at break.

Methods

Epoxidation reaction

Epoxidized natural rubber (ENR) was used as a raw material in rubber seal manufacturing for LPG tube valve. ENR was made through in-situ reaction between natural rubber, formic acid and hydrogen peroxide at 70 °C with time reaction variation to produce ENR with different levels of epoxidation (Kinasih & Fathurrohman, 2016). Concentrated latex and field latex were used as raw materials to synthesize epoxidized natural rubber in this experiment. Field latex is fresh latex that was obtained from the field after latex being tapped and preserved with ammonia. Concentrated latex was obtained from field latex which was concentrated by centrifugation so that the DRC (Dry Rubber Content) increased from 15-30% to 60%. Both concentrated and field latex were stabilized using anionic surfactant and, then, reacted with formic acid and hydrogen peroxide with the reaction shown in Figure 1.

The excess acid from the latex epoxidation reaction was neutralized with ammonia, then, it was coagulated with acetone to produce white coagulum. The coagulum formed were washed with water and immersed in sodium carbonate solution, then dried at 80 °C. The synthesized of ENR at different levels was occurred in same condition with different reaction time. The epoxidation latex was then tested for each epoxidation level using FTIR at the Indonesian Rubber Research Institute (IRRI). ENR at different levels was then used as raw material in the manufacturing of rubber seal for LPG tube valve.

Rubber seal compounding

ENR was mixed with chemicals in the laboratory two-roll open mill based on the compound formulation. The amount of chemical and filler was fixed in the unit of part hundred rubber (phr) and the degree of epoxidation was varied in range of 10 mole% to 50 mole% as shown in Table 1. The compounds were vulcanized in a laboratory compression machine at 150 °C to form the 2 mm rubber vulcanized sheet. Then, its mechanical as well as physical properties were tested according to the reference standard (SNI 7655:2010).

The other chemicals were the same for all formulas which consisted of 50 phr of Silica 175 MP, 2 phr of Silane Si-69, 2.5 phr of Rhenofit 1987, 1 phr of color pigment, 2 phr of Antilux 654, 1 phr of MMB, 5 phr of DOP, 1 phr of Vulcuren, 1 phr of CBS, 2 phr of TMTD, 1 phr of DTDM, 0.3 phr of sulphur, 5 phr of zinc oxide, and 1 phr of stearic acid.

Table 1. The compound formulation with varied levels of ENR.

Materials	Dosage (phr)				
	A	B	C	D	E
ENR-10	100	-	-	-	-
ENR-20	-	100	-	-	-
ENR-30	-	-	100	-	-
ENR-40	-	-	-	100	-
ENR-50	-	-	-	-	100

Physical and mechanical testing

The physical and mechanical testing of LPG tube valve was conducted according to SNI 7655:2010. The hardness of rubber vulcanized were carried out with Shore A durometer referred to ISO 48-4:2018. In addition, Type 2 dumb-bell test specimens were used for the tensile properties and elongation at break according to SNI ISO 37:2015. Meanwhile, the compression set referred to ISO 815-1:2014 and for swelling volume in *n*-pentane according to ISO 1817:2015. The result of mechanical and physical properties were compared to standard quality of rubber seal for LPG tube valve in SNI 7655:2010 (BSN, 2010).

Level of epoxidation analysis

Levels of epoxidation can be calculated quantitatively by calculating the absorbance in FTIR spectrum. Epoxide rings has characteristics band at wave number 870 cm^{-1}, rings open at wave number 3460 cm^{-1}, the group $-CH_3$ of natural rubber at wave number 1375 cm^{-1} and unmodified olefins at wave number 835 cm^{-1}. Formula for calculating level of epoxidation (E) was showed as equation (1) according to Chakraborty *et al.* (2010).

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

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

$$E = \frac{100\ x\ K1\ x\ A_{870corr}}{A_{835} + K_1 x A_{870corr} + K_2 x A_{3460corr}}\ x\ \text{mol}\ \% \quad (3)$$

Where E is epoxy, K_1 and K_2 is the correction value, wherein the correction is due to the interference of the corresponding bonds and it was estimated to be 14% and 1.9%, respectively (the value was determined from NMR). The constants K_1 and K_2 were absolute 0.77 and 0.34.

RESULTS AND DISCUSSION

Epoxidized Natural Rubber

Two types of latex, concentrated latex with 60% DRC and field latex with 15% DRC, were used as raw materials in order to study the effect of latex types to epoxidation reaction. Synthesis of

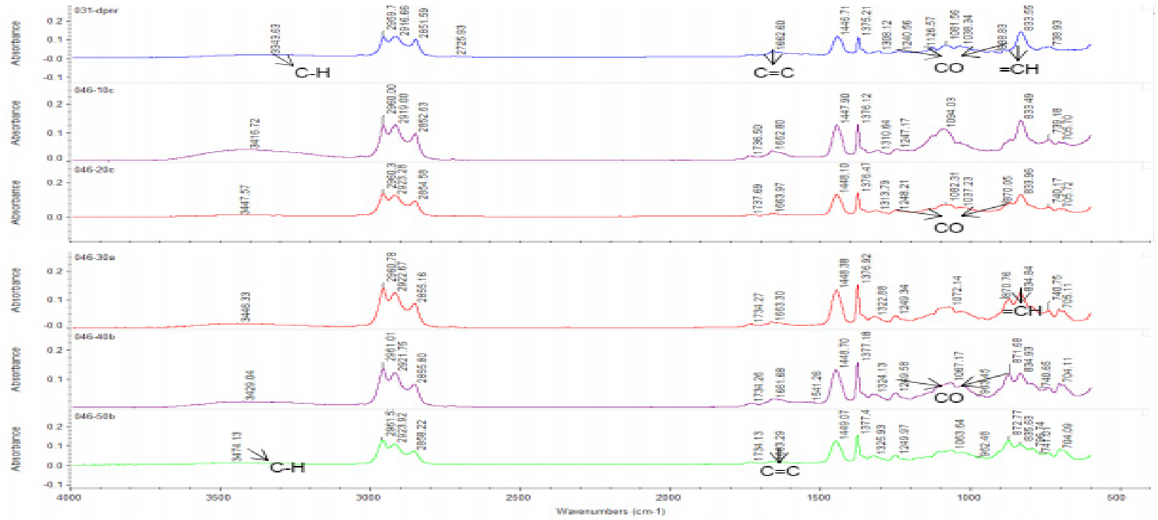

Figure 2. FT-IR spectrum of NR, E-10, E-20, E-30, E-40, and E-50 (from top to bottom).

epoxidized latex was carried out in an epoxidation reactor which was equipped with stirring rod. Epoxidation reaction occurred at 70 °C for 6 h with 0.75 mole/mole isoprene unit of hydrogen peroxide and 0.4 mole/mole isoprene unit of formic acid, the latex was sampling every hour for quantitative analysis of epoxidized level. The reactants, i.e. hydrogen peroxide and formic acid, were added to the latex all at once at the first.

The results of qualitative analysis of E-10, E-20, E-30, E-40, and E-50 are presented in Figure 2. In the figure, it can be seen that when it is compared with FT-IR spectrum of NR, FT-IR spectrum of ENR has absorption characteristics at wave numbers 870 cm^{-1} and 1251 cm^{-1} for absorption of bending and stretching of C-O epoxy groups. In the FT-IR spectrum of ENR, it appeared that there was a decrease in the absorption of the C=C isoprene group of NR at wave number of 1600 cm^{-1} and absorption of stretching C-H alkane groups at wave number 3000 cm^{-1}. The results of qualitative analysis showed that the higher of percent mole epoxy of ENR, the absorption of the C = C isoprene group of NR at wave number of 1600 cm^{-1} became smaller, and absorption of the C-O of the epoxy group at 870 cm^{-1} and 1251 cm^{-1} became greater.

Quantitative analysis to determine levels of epoxidation has been done by calculating the absorbance of FTIR spectrum in Figure 2. The

Table 2. Levels of epoxidation with varied of latex type and reaction time.

Types of Latex	DRC (%)	Time (hours)	Mole percent of epoxy (%)	Type of ENR
Concentrated latex	60	0	0.00	0
		1	10.95	E-10
		2	21.72	E-20
		3	30.07	E-30
		4	36.02	E-35
		5	41.22	E-40
		6	47.08	E-50
Field latex	15	0	0.00	0
		1	9.86	E-10
		2	18.38	E-20
		3	24.45	E-25
		4	28.29	E-30
		5	32.78	-
		6	36.01	E-40

Table 3. Curing characteristics of ENR compounds in variation of epoxidation level.

Curing Characteristics	Units	A	B	C	D	E
S_{max}–S_{min}	Minutes	11.11	11.04	9.95	10.62	9.66
S_{max}	Minutes	11.31	11.30	10.39	11.13	9.92
S_{min}	Minutes	0.20	0.26	0.44	0.51	0.26
T_{90}	Minutes	4.31	3.29	4.28	4.02	5.05
TS_2	Minutes	1.15	1.18	1.31	1.40	1.55

result showed that epoxidation with concentrated latex resulted higher mole percent of epoxy compared to field latex. The longer time of reaction resulted in higher mole percent of epoxy, not only in concentrated latex but also in field latex. As the reaction time increase, the possibility for molecules to collide with each other increase too, so that it increase the conversions of C=C isoprene group of NR to epoxy group.

As in Table 2, epoxidized natural rubber was synthesized from concentrated latex and field latex as raw materials in rubber seal manufacturing for LPG tube valve. Epoxidation reaction from concentrated latex resulted 6 levels of epoxidation i.e. E-10, E- 20, E-30, E-35, E-40 and E-50. In the rubber seal manufacturing for LPG tube valve, we only used 5 type of ENR, i.e., E-10, E-20, E-30, E-40 and E-50. Table 2 shows that type of latex and reaction time affected to the levels of epoxidation. From the data in Table 2, it can be concluded that concentrated latex better to use as raw material for synthesizing epoxidized natural rubber latex than field latex. It was because in concentrated latex, the protein and non-rubber content in latex, which can interfere the epoxidation reaction, has separated and removed by centrifugation so that the epoxidation reaction could run more optimal.

Curing Characteristic

Table 3 shows the curing characteristic of rubber compound. Compound A has the highest torque (S_{max}) and different torque (S_{max}–S_{min}) among other compounds. While compound E-50 was not suitable due to its cross-linking is the lowest which was indicated by the lowest different torque among other compounds. The different torque is related to the crosslink density of rubber (Surya *et al*., 2018), the crosslink density decreased with increasing the level of epoxide due to the increasing level of epoxide decreased the amount of double bond in ENR.

Properties of Rubber Seal Compound

The physical properties of rubber seal compound for LPG tube valve are presented in Table 4. Based on Table 4, the value of hardness, tensile strength, and elongation at break, for all compound, met the requirements in the standard SNI 7655:2010. The presence of natural rubber in the epoxidized natural rubber can improve its elasticity. However, the value of compression set for E-40 compound did not fulfill the requirements in the standard. It could be caused by bad interaction between the filler and E-40 compound.

Table 4. Physical properties of rubber seal compounds with different epoxidation levels.

Physical Properties	Standard Requirement	Vulcanized				
		A	B	C	D	E
Hardness (Shore A)	60 ± 5	55	59	55	57	55
Tensile strength (MPa)	Min. 10	13.9	12.9	15.2	12.5	16.1
Elongation at break (%)	Min. 300	360	360	420	360	420
Compression set, temp. 27±2 °C (%)	Max. 10	8.97	9.76	9.62	10.36	7.79
Ageing at 70 °C, 7 d						
- Hardness, change (Shore A)	± 10	9	6	7	6	7
- Tensile strength, change (%)	± 15	-52.52	-51.94	-49.34	-27.2	-42.86
- Elongation at break, change (%)	+10, -25	-50.00	-58.33	-50.00	-41.67	-50.00
Swelling volume in *n*-pentane at RT, 168 h	Max. +35	55.85	49.81	35.31	29.25	20.38

Compression set value depends on the interaction between filler and elastomer, the best interaction will result the lowest value of compression set. The greater value of compression set indicates that after being compressed, rubber elasticity decreases (Handayani *et al*., 2011). Better interaction between filler-ENR will result better compression set.

On the other hand, the tensile strength and elongation at break, after ageing, for all compounds, did not meet the required standards. It can be concluded that all compounds did not resist to aging. To improve the resistance of the compound to ageing, reformulation should be done with the addition of appropriate chemical. Meanwhile, for the swelling properties in n-pentane, compounds with code E-10, E-20, and E-30 did not fulfill the requirements in the standard, while two other compounds fulfilled the standard requirements. It can be concluded that to fulfill the standard requirement of swelling volume, the compound should use ENR contains mole percent of epoxy more than or equal to 40%.

CONCLUSIONS

From the results of the study, it can be concluded that natural rubber which has been chemically modified by epoxidation reaction can be used as raw material in rubber seal manufacturing for LPG tube valve, with a minimum of 40% epoxy mole content to fulfill one of the requirements in the referenced standard, SNI 7655:2010, i.e., swelling in n-pentane. The use of natural rubber made good elasticity to all level of epoxidized rubber where this property is needed for rubber seal of LPG tube valve. However, the formulas of the compound are less resistant to aging. To improve the resistance of the compound to ageing, research on re-formulation is still in progress with the addition of appropriate chemical.

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