

## Swelling behaviour in n-pentane and mechanical properties of epoxidized natural rubber with different epoxide content

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**Abstract.** Epoxidized natural rubber (ENR) with different level of epoxidation (i.e. 10, 20, 30, 40 and 50 mol% indicated as ENR10, ENR20, ENR30, ENR40 and ENR50, respectively) were prepared. They were then vulcanized by using efficient system vulcanization. The effect of epoxide content on curing characteristic, swelling and mechanical properties in N-pentane was investigated. The Attenuated Resonance Fourier Transform Infrared (ATR-FTIR) and H-Nuclear Magnetic Resonance (H-NMR) were used to determine the epoxidation level. Glass transition (T<sub>g</sub>) of ENR samples was determined by using Direct Scanning Calorimetry (DSC). The result revealed that the resistance of ENR in N-pentane increased with increasing epoxidation level, which indicated by decreasing equilibrium mol uptake and diffusion coefficient. The compression set of ENR and aging resistance increased with increasing epoxide content, except ENR50 was due to ENR 50 have two T<sub>g</sub> value. However, the value of hardness and tensile strength were not effected by epoxidation level.

### 1. Introduction

Epoxidized natural rubber (ENR) is chemical modified rubber from natural rubber (NR), whereby some of the unsaturation double bond are converted into epoxides groups, which are randomly distributed along the polymer chain. The most interesting effects of epoxidation on NR lie in the physical properties of vulcanizates. Increasing of epoxide level in ENR vulcanizate has contributed to shorter scorch time [1], better rubber filler interaction and mechanical properties [2], higher polarity (oil resistance) and glass-transition temperature (T<sub>g</sub>) [3], lower resilience (more damping), air permeability (comparable to butyl rubber and medium-acrylonitrile-content NBR), higher hysteresis, and better wet traction [4]. However, ENR has lower thermal stability, it was degraded along with the increment of heating rate [5].

The application of ENR in rubber compound and rubber blend has increase the oil and non-polar solvent resistant properties. The oil and non-polar solvent resistant properties was reflected on swelling behavior test result. Tanrattanakul *et al.*, (2003) [3] studied the swelling behavior ENR vulcanizate in toluene, ether, engine oil, gear oil, ASTM oil and motor oil. Furthermore, Ismail *et al.*, (2001) [6] investigated the swelling behavior of silica and carbon black filled ENR compound in toluene. However, there is very little information about swelling behavior of ENR vulcanizate with different epoxy content in n-pentane. N-pentane is the appropriate solution to replace LPG, according



to the requirements of Indonesian rubber seal product standard (SNI 7655:2010). The investigation about the swelling of ENR in n-pentane is very important to inform the possibility utilization of ENR in LPG rubber seal.

In this study, effect of epoxy content (10, 20, 30, 40 and 50%) in silica filled ENR was investigated. The epoxide content, Tg and viscosity properties of ENR was investigated. Moreover, the curing characteristic, mechanical properties and swelling behavior of silica filled ENR were studied.

## 2. Experimental Research

### 2.1 Chemicals

Fresh natural rubber latex was collected from local plantation, Ciomas-Indonesia. Anionic surfactant (Emulgen) was distributed by KAO Indonesia Chemicals. Silica of Zeosil175Gr was supplied from Solvay. Vulcurent as anti-reversion and rhenofit 1987 were supplied from Rhein Chemi. Protease enzyme (Papain), sulfur, silane-Si69, TiO<sub>2</sub>, pigmen, antilux, DTDM, TMTD, CBS, zinc oxide, stearic acid, and DOP were supplied from local suppliers. n-pentanewas obtained from Merk.

### 2.2 ENR Preparation

ENR was prepared from deproteinized natural rubber latex (DPNR) phase by enzymatic process. Followed by adding 0.3 mol/mol isoprene unit of formic acid to suspend the enzymatic reaction of DPNR. Afterward, ENR was produced by forming the *insitu* performic acid in DPNR stage to produce ENR with epoxide level 10% (ENR10), 20% (ENR20), 30% (ENR30), 40% (ENR40) and 50% (ENR50). The epoxidation reaction condition was tabulated in Table 1.

**Table 1.** Epoxidation reaction condition of ENR

Sample	Temperature (°C)	Time (h)	H <sub>2</sub> O <sub>2</sub> concentration (mol/mol isoprene unit)
ENR10	60	6	0.4
ENR20	60	6	0.5
ENR30	60	6	0.75
ENR40	65	6	0.75
ENR50	65	5.5	1

### 2.3 ENR Characterization

The ENR characterization was done to determine epoxide level, Tg and viscosity of ENR. The epoxy content of ENR was determined by ATR and H-NMR instrument. IR spectra were obtained on Thermo Fisher Scientific, Madison, Wisc within the wave number range from 4000 to 400 cm<sup>-1</sup>. Epoxy content of IR spectra was analyzed by OMNIC software version 8.0 and epoxide level was determined according to Chakraborty *et al.*, (2010) [7]. H-NMR measurement was carried out by a JEOL JNM ECA 500, 500 MHz nuclear magnetic resonance spectrometer using CDCl<sub>3</sub> as solvent. The

determination of epoxide contents of nmr spectra was determined according to Phinyocheep and Boonjarairak (2006) [8].

Transition temperature ( $T_g$ ) was obtained by DSC 8000 Perkin Elemer instrument. The confirmation of epoxide content estimation was done by calculating % epoxide content based on  $T_g$  value, as shown below [9]. Given that  $T_g$  of NR is -62.26, according to experimental  $T_g$  measurement of DPNR. Moreover, the  $T_g$  value increases by 0.92°C/mol % [9].

$$\text{Epoxide content (mol \%)} = \frac{T_g \text{ of ENR} + 62.26}{0.92} \quad (1)$$

Moreover, viscosity of ENR was recorded by mooney viscometer. The rubber were heated at 100°C for 1 min preheating and 5 min heating.

#### 2.4 Compounding and Curing

The formulation of ENR compounds are given in Table 2. Each compounds of ENR were mixed using a two-roll mill (Berstorf), which was maintained at  $65 \pm 5^\circ\text{C}$ . The mastication of ENR was done on 5 min at 55-60°C.

$$\text{CRI} = \frac{100}{t_{90} - t_{52}} \quad (2)$$

**Table 2.** ENR compound formulation

Material	Part per Hundred Rubber (phr)				
	ENR10	ENR20	ENR30	ENR40	ENR50
ENR	100	100	100	100	100
Silica	50	50	50	50	50
Silane	2	2	2	2	2
Rhenofit	2.5	2.5	2.5	2.5	2.5
Pigmen	1	1	1	1	1
Antilux	2	2	2	2	2
MMB	1	1	1	1	1
DOP	5	5	5	5	5
Vulcuren	1	1	1	1	1
ZnO	5	5	5	5	5
Stearic acid	1	1	1	1	1
CBS	1	1	1	1	1
TMTD	2	2	2	2	2
DTDM	1	1	1	1	1
Sulfur	0.3	0.3	0.3	0.3	0.3

Then, curing characteristic of ENR compound was evaluated by moving die rheometer (MDR 2000). The curing characteristic evaluation was included  $t_{90}$  (curing time),  $t_{s2}$  (scorch time), maximum torque ( $S'_{max}$ ), minimum torque ( $S'_{min}$ ), delta torque and curing time index (CRI). The CRI was calculated by equation 2. Afterward, the ENR compound was cured in compression molded under a pressure approximately 100 kg/cm<sup>2</sup> with an optimum cure time of  $t_{90}$ . The ENR vulcanizate was mold as square (15x15 cm) with 2 mm thickness.

### 2.5 Mechanical Properties

Hardness (Shore A) was determined using durometer type A according to ISO 48. The test specimens with 6 mm thick were made up of three layers of rubber from the compression-molded sheets. Tensile strength and elongation at break test was held at room temperature on LyoidTensometer, with crosshead rate 500 mm/min. The test samples were cut from compression-mold sheets using dumbbell shaped type 2 according to ISO 37. Compression set testing was conducted at room temperature (RT) during three days respectively. That test was determined according to ISO 815-2 using the standard test specimen of cylindrical shape of 12 mm in diameter and 6.3 mm thick by compression method.

### 2.6 Thermal Aging

The ENR vulcanizate conditioned at 70°C for 168 h in an oven according to ISO 188 and the mechanical properties changes before and after the thermal aging were then assed.

### 2.7 N-pentane Resistance Properties

N-pentane resistance was obtained by swelling test of NR vulcanizate in n-pentane, conducted at room temperature. The measurement according to the immersion – weight gain method. The samples were removed from the solvent at the specified time, quickly blotted with a filter paper and weighed using electronic balance. The immersing and weighing was continued till equilibrium swelling was attained. The molar percentage uptake ( $Q_t$ ) and sorption coefficient (S) of n-pentane per gram of NBR vulcanized was determined using equation 3 and 4, respectively [10].

$$Q_t = \frac{(M_t - M_0)}{\text{Molecular weighth of n-pentane}/M_0} \times 100 \quad (3)$$

$$S = \frac{M_{\infty}}{M_0} \quad (4)$$

Where  $M_t$  is mass uptake at time  $t$ ,  $M_0$  is the initial mass of ENR vulcanized and  $M_\infty$  is mass of n-pentane absorbed at equilibrium.

### 3. Result and Discussion

#### 3.1 ENR Characterization

The chemical structure of ENR was analyzed by ATR and H-NMR. The IR spectra of DPNR and ENR is shown in Figure 1. Figure 1 shown that the characteristic signal of epoxy ring was shown after epoxidation process, due to IR spectra of DPNR and ENR. The IR spectrum of ENR indicates the appearance of characteristic signals of oxirane group at 1,249 and 870  $\text{cm}^{-1}$ , signals of isoprene NR at 1600 and 835  $\text{cm}^{-1}$ , signals of opening epoxy ring at 3400  $\text{cm}^{-1}$  (asymmetric stretching of O-H), 1727  $\text{cm}^{-1}$  (asymmetric stretching of C=O) and 1064  $\text{cm}^{-1}$  (asymmetric stretching of hydrofuran) [11]. However, the present of O-H in DPNR was indicated  $\text{H}_2\text{O}$  content in DPNR, due to the fresh latex as material based. Furthermore, the epoxy content of ENR was increase with increase absorption of 1,249  $\text{cm}^{-1}$  and 870  $\text{cm}^{-1}$  wave number and decrease absorption of 1600  $\text{cm}^{-1}$  and 835  $\text{cm}^{-1}$  wave number. The opening epoxy ring was shown slightly decrease with increasing of epoxide level.

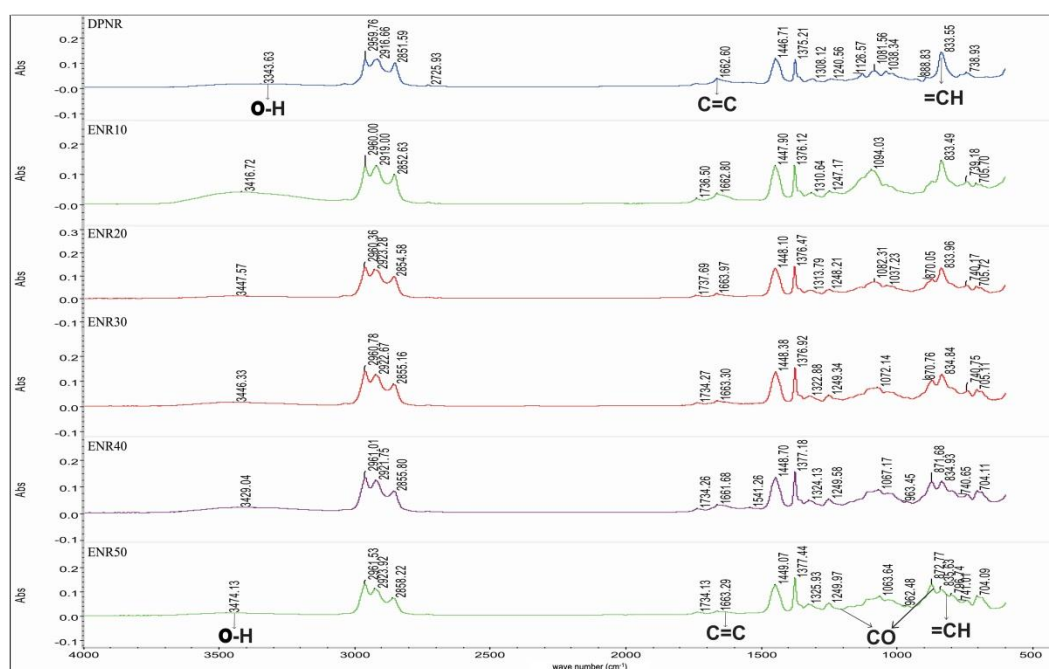
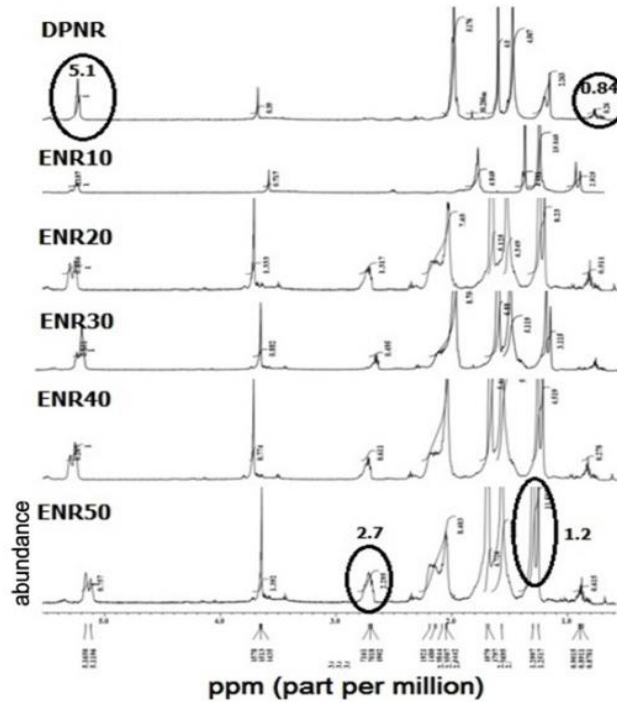


Figure 1. IR spectra of DPNR and ENR

The H-NMR spectrum of ENR in Figure 2 shows the presence of signals at 0.84 ppm and 5.1 ppm assigned to methyl and isoprene units, respectively [8]. After epoxidation of DPNR, other two signals appeared at 2.7 and 1.2 ppm, which were assigned to epoxy group. The increasing epoxide

level was linearly with wide integration at 2.7 ppm. The estimated epoxy group content of the ENR was tabulated in Table 3. The estimate epoxide content was also determined by Tg value of DSC measurement. Based of Table 3, it can be shown that the estimation epoxy group content was relatively same, as an expectation.



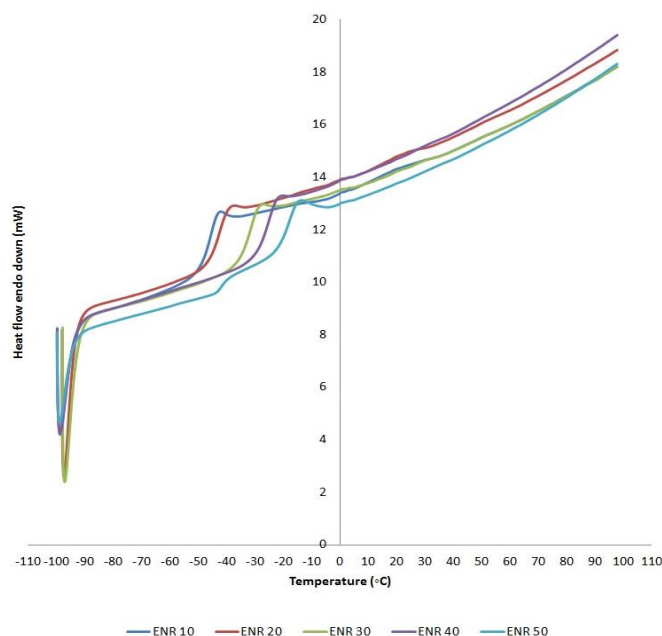
**Figure 2.** NMR spectra of DPNR and ENR

**Table 3.** ENR characteristic

Samples	Tg (°C)	epoxy content (% mol)		
		FTIR	HNMR	DSC
DPNR	-62.26	0	0	0
ENR 10	-46.12	12.52	2.14	17.54
ENR 20	-42.65	20.36	29.19	21.32
ENR 30	-31.88	34.53	31.00	33.02
ENR 40	-25.79	42.56	39.04	39.64
ENR 50	-41.77 & -19.42	52.38	53.91	22.27 & 46.57

The DSC thermograph was shown in Figure 3. As previously reported [4] the Tg of ENR varies linearly with molar epoxy content. Tg value was increased averagely 0.68°C/mol %. Epoxidation process was made natural rubber need more energy for mixing, which due to mooney viscosity value (Table 4). The width range of Tg shown the homogeneity of the samples, which is normally it is somewhat 10°C wide [3,9]. In the present study, ENR samples showed homogeneity in the

epoxidation, indicated by a narrow width ( $<10^{\circ}\text{C}$ ) of the  $T_g$  as shown in Figure 3. However, the thermograph of ENR50 was shown two broad  $T_g$  peaks which has  $>10^{\circ}\text{C}$ . Therefore, in term of ENR50 the result shows the inhomogeneity of epoxidation process.



**Figure 3.** DSC thermograph of ENR

The mooney viscosity of ENR are presented in Table 4. The mooney viscosity of ENR was increased with increasing epoxy content, which fit with Rohadi *et al.* (2014) [2]. This trend was probably due to ENR's themselves possess a relatively high polarity in their structures and possible to form self association via hydrogen bonding or polar interactions between either the same or neighbouring molecules, and even self cross-link due to the opening of the oxirane rings [12]. Moreover, the degradation of ENR mooney viscosity was shown in ENR50. This phenomena probably due to inhomogeneity of epoxidation process, which was shown in DSC thermograph (Figure 3).

### 3.2 Curing Characteristic

The curing characteristic of ENR compound with different epoxy content are given in Table 5. The minimum torque was indicate the viscosity of the compound [13]. The result of minimum torque was increase as epoxide level, which was linier with mooney viscosity result (Table 3). Moreover, maximum and delta torque was increase as increase of epoxide level of the compound. Delta torque is related to crosslink density and stiffness of the rubber vulcanized [14]. Based on Table 2, the crosslink density is expected to increase with increase of epoxide level of the compound. The increasing level of epoxide content was faster the cure time, which due to high cure rate index.

**Table 4.** Mooney Viscosity of ENR

Samples	Mooney viscosity (ML 1+4 at 100°C)
ENR 10	124
ENR 20	103
ENR 30	123
ENR 40	138
ENR 50	128

**Table 5.** Curing characteristic of ENR vulcanizate

Curing Characteristic	ENR10	ENR20	ENR30	ENR40	ENR50
$S_{\max}$ (kg-cm)	11.31	11.3	10.39	11.13	9.92
$S_{\min}$ (kg-cm)	0.2	0.26	0.44	0.51	0.26
$\Delta S$ (kg-cm)	11.11	11.04	9.95	10.62	9.66
$T_{90}$ (min)	4.31	3.29	4.28	4.02	5.05
$T_{s2}$ (min)	1.15	1.18	1.31	1.4	1.55
CRI	31.65	47.39	33.67	38.17	28.57

### 3.3 Mechanical Properties

Table 6 represent the mechanical properties of ENR vulcanizate. The mechanical properties of the rubber was related to the amount of crosslink density [14]. The hardness and tensile strength of the ENR vulcanizate was relatively same, due to the crosslink amount, which was shown on maximum torque (Table 4). The elongation at break and compression set properties indicated the elasticity of the vulcanizate, which reflect on higher elongation at break and lower compression set. ENR50 was reached highest tensile strength. This result was observed that ENR's with a greater degree of polarity has contributed to lead better mechanical properties. Surprisingly that ENR50 have the lowest compression set, normally the compression set increased with increasing the epoxide level [17]. This phenomenon occurred due to inhomogeneity of epoxidation process produced ENR50 that contain two epoxide level 22.27% mol and 46.57 % mol (Table 3).

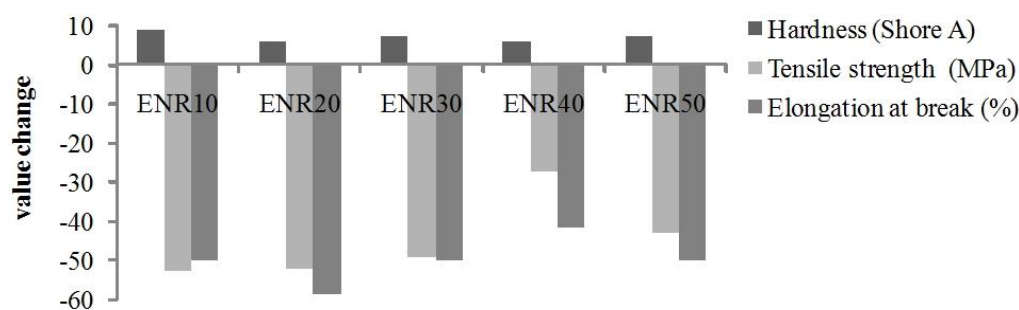
**Table 6.** The mechanical properties of ENR vulcanizate

Mechanical properties	ENR10	ENR20	ENR30	ENR40	ENR50
Hardness (Shore A)	55	59	55	57	55
Tensile strength (MPa)	13.9	12.9	15.2	12.5	16.1
Elongation at break (%)	360	360	420	360	420
Compression set (%)	8.97	9.76	9.62	10.36	7.79



### 3.4 Thermal Resistance Properties

The effect of increasing epoxy content on ENR thermal resistance properties are presented in Figure 4. The thermal resistance properties were observed based on the value change of hardness, tensile strength and elongation at break on before and after thermal degradation. The lower value change indicated increasing vulcanizate resistant to thermal degradation. It clearly observed that increasing of epoxide level was decrease the value change of thermal degradation to the maximum level, which was ENR40. Furthermore, it slightly increased on ENR50 due to the inhomogeneity epoxidation process of ENR 50. This result indicate that ENR40 vulcanizate has optimum resistant to thermal degradation.



**Figure 4.** The thermal resistance properties of ENR vulcanizate

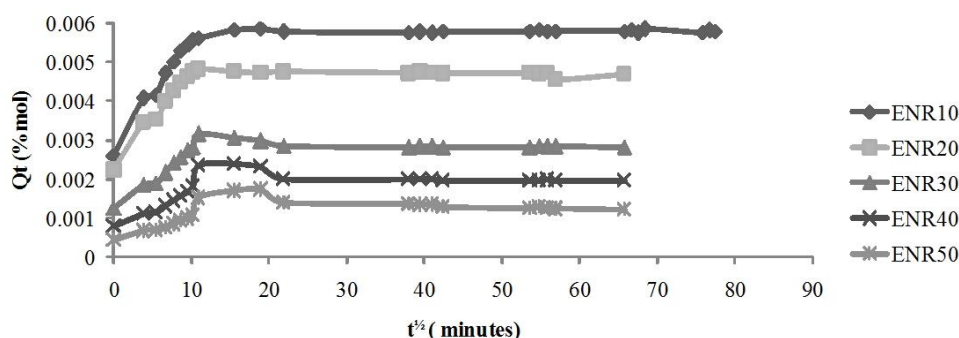
### 3.5 *N*-pentane Resistance Properties

The *n*-pentane resistance properties are clearly manifested in Figure 5 and Table 7. Swelling in *n*-pentane was governed by the competition between the driving force toward “dissolution of the rubber in the low-molecular-weight solvent”, *i.e.* swelling, and the elastic force which increases upon solvent uptake [15]. The figures indicate that the molar percentage uptake increases initially and pass through a maximum and then stable. This trend means that a number of *n*-pentane diffuse into rubber vulcanizates and the distance between the rubber molecules reach equilibrium.

ENR10 has the maximum uptake whereas ENR50 the lowest. Usually, decreased solvent uptake ability was related to increase crosslink. However, the crosslink formed of ENR50, which was shown on maximum torque (Table 2), was lowest. This phenomenon was probably due to high epoxide level can increase the polarity of natural rubber and the solubility parameter of ENR increases with increasing epoxide level [3]. The closer solubility parameter of rubber to solvent, had low driving force to inhibit solvent uptake. The solubility parameter of ENR 0, 26, and 48% was 16.7, 17.4, and 18.2 MPa<sup>1/2</sup> respectively [16]. Whereas, the solubility parameter of *n*-pentane was 14.40 MPa<sup>1/2</sup> [19]. Thus, the epoxide level increases with decreasing the solvent uptake of ENR vulcanizate.

The sorption and equilibrium mol uptake of ENR was linier to molar percentage uptake ( $Q_t$ ) of ENR. Table 6 presented that the sorption and equilibrium mol uptake of ENR was decreased with

increasing epoxide content of the vulcanizate. Increasing of epoxide level in ENR vulcanizate has contributed to higher polarity [3]. ENR's with a greater degree of polarity has contributed to lower sorption and equilibrium mol uptake.



**Figure 5.** Molar percentage uptake ( $Q_t$ ) of ENR with different epoxy level.

**Table 7.** Sorption and equilibrium mol uptake of ENR vulcanized with different epoxy content

Sample	Sorption (S) (%)	Equilibriummol uptake ( $Q_{\infty}$ ) (%)
ENR10	1.4235	0.0058
ENR20	1.3418	0.0048
ENR30	1.2160	0.0029
ENR40	1.1677	0.0020
ENR50	1.1256	0.0014

#### 4. Conclusion

Effect of epoxide level on mechanical properties and n-pentane resistance of ENR vulcanizate has been studied. The chemical structure of ENR through IR spectrum showed that increasing absorption of  $1,249\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  wave number as increase epoxide content of ENR. Moreover, NMR spectrum was signal at 2.7 and 1.2 ppm, which were represented epoxy group, after epoxidation process.  $T_g$  and Mooney viscosity of ENR increase linearly with molar epoxy content. The increasing level of epoxide content was faster the curing time and lead better mechanical properties and thermal resistance of vulcanizate. The increasing thermal resistant was shown in ENR50. In addition, the increasing level of epoxy content was increased the n-pentane resistance of the vulcanizate, which was determined lowest molar uptake, sorption and equilibrium mole uptake on ENR50.

#### Acknowledgment

It is a pleasure to acknowledge the SINAS financial support by State Minister for Research and Technology fund for Indonesian Rubber Research Institute (RT-2015-0207)

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