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Mechanical Properties and Swelling Behavior of Acrylonitrile Butadiene Rubber with Different Acrylonitrile Contents in N-Pentane

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Abstract: The mechanical properties and swelling behavior of n-pentane through acrylonitrile Butadiene Rubber (NBR) with different acrylonitrile content were studied. In addition to the mechanical and the swelling properties, the curing characteristics and crosslink density were also investigated. The vulcanization kinetic parameters were determined using autocatalytic model. The NBR with 33% acrylonitrile content showed the highest the activation energy. The highest crosslink density was obtained from the NBR with acrylonitrile content 28% and the crosslink density effected to its mechanical properties and swelling behavior. The highest crosslink density exhibited the highest hardness, tensile strength, elongation at break values, the better compression set, the lowest equilibrium n-pentane uptake (Q_∞) and the Sorption coefficient (S). The Diffusion coefficient (D) increased with decreasing the acrylonitrile content.

Key words: Mechanical properties, swelling, n-pentane, acrylonitrile butadiene rubber, contact

INTRODUCTION

Rubber is one of the material that can be used for engineering application such as seal, o-ring and gasket which may contact with organic solvents or oils. Rubber seal in Liquid Petroleum Gas (LPG) valve may contact with LPG that will lead to swelling and causing deterioration of its properties. Therefore, the selection of rubber is important to retain their mechanical properties and dimensional stability on contact with LPG. The swelling testing of rubber seal in LPG is difficult to be applied in the laboratory. According to the requirements of SNI 7655:2010, LPG can be replaced by n-pentane. The mechanical properties that important for rubber seal LPG are compression set, tensile properties and hardness. The lower compression set percentage, the better the material resists the permanent deformation under a given deflection (Mostafa *et al*., 2009).

Acrylo Nitrile Butadiene Rubber (NBR) has excellent oil and non polar solvent resistance which is mainly made by emulsion polymerization. This rubber is one of the most used commercial rubbers for manufacturing technical rubber goods. Many researchers have been extensively studying about the swelling behavior of NBR in different solvent or oil. Wang *et al*. (2014) investigated the swelling properties of NBR in cyclohexane. Choi and Ha (2009) studied the influence of the acrylonitrile content of NBR on the water swelling behaviors of silica-filled NBR composites at room temperature and 90°C. Mostafa *et al*. (2009) investigated the effect of carbon black loading on the swelling behavior of NBR in motor oil. However, there is very little information about the swelling of NBR in n-pentane. The understanding about the swelling of NBR in n-pentane is very important to select the NBR types for LPG rubber seal. The swelling phenomenon is the increase in volume of a rubber due to the absorption of a liquid. The amount of solvents will diffuse into rubber until it reaches the concentration of the liquids is uniform and equilibrium.

In this study, the effect of acrylonitrile content in NBR filled carbon black on mechanical properties and swelling behavior in n-pentane was investigated. The efficient cure system was used by using CBS as primary accelerator and TMTD as secondary accelerator. In addition to the mechanical and the swelling properties, the curing characteristics and crosslink density were also measured.

MATERIALS AND METHODS

Acrylonitrile butadiene rubber of Krynac with acrylonitrile content 26, 33% and NBR of Perbunan with acrylonitrile content 28% were supplied from Lanxess. All NBR have the same value of Mooney viscosity (45 ML (1+4) at 100°C). Zinc oxide, dioctil phatalate (DOP), TMTD, CBS, 2, 2, 4-trimethyl-1, 2-dihydroquinoline (TMQ) and sulfur were purchased from local suppliers. Carbon black 550 was obtained from Cabot. Antilux anti-ozonant from RheinChemie was used in order to increase the ozone resistance. Aktiplast®T from RheinChemie was used as activator agent

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Compounding and curing: The three NBR compounds with different acrylonitrile content were made of NBR (100 phr), carbon black 550 (10 phr), antilux (2 phr), TMQ (1 phr), DOP (5 phr), ZnO (5 phr), aktiplast® T (1 phr), CBS (1.5 phr), TMTD (2.5 phr) and sulfur (0.3 phr). All ingredients were mixed in a two-roll mill with speed of low roll (24 rpm) and friction ratio (1:1.4) maintained at 65±5°C. The rubber compounds were conditioned at room temperature for minimum 16 h. The rubber compounds were compression molded at 150°C under a pressure approximately 100 kg cm^{-2} with the optimum curing time (t_{90}) that was previously determined from Moving Die Rheometer (MDR 2000). The sample thickness of 2 mm sheets was molded.

Determination of crosslink density: The crosslink density of NBR vulcanisates was determined by the Mooney-Rivlin equation based on their stress-strain behavior. The equation based on the theory of rubber elasticity which can be obtained as follows: (Sombatsompop, 1998):

$$F = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \quad (1)$$

$$\frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \quad (2)$$

Where:

F = The force required to stretch the rubber vulcanized
A_0 = The cross-sectional area of the unstretched rubber vulcanized,
σ = Identifiable with F/A_0
λ = The extension ratio (which is $1+\varepsilon$)
ε = Strain
C_1 and C_2 = Constans are characterizing the vulcanized

The constants C_1 and C_2 can be determined by the plot of $\sigma/(\lambda-\lambda^{-2})$ against $1/\lambda$, the intercept of the curve on the $\sigma/(\lambda-\lambda^{-2})$ axis corresponds to the value of C_1 and its slope corresponds to the value of C_2. The value of C_1 can be used to assess the physical crosslink density (η_{phys}) by using Eq. 3 as follows (Sombatsompop, 1998):

$$n_{phys} = \frac{C_1}{RT} \quad (3)$$

Where:

R = The gas constant (8.314 $mol^{-1}.K^{-1}$)
T = The absolute temperature

The test was conducted at 27°C using Zwick tensometer with a crosshead speed 50 mm min^{-1}.

Hardness, tensile and compression set properties: The hardness of NBR vulcanized was determined using durometer type A according to ISO 7619-1. The test pieces 6 mm thick were made up of three layers of rubber from the compression-molded sheets. For the tensile test, dumbbell test pieces type 2 were cut from compression-molded sheets. The tensile properties of the test pieces were determined according to ISO 37 using a Lyoid tensometer with a crosshead speed 500 mm min^{-1}. Compression set test of the NBR vulcanized was determined according to ISO 815 using the standard test specimen of cylindrical shape is 12 mm in diameter and 6.3 mm thick by compression method. The compression set testing was conducted at room temperature.

Swelling behavior: The equilibrium swelling of the NBR vulcanized with different acrylonitrile content in n-pentane were studied using the immersion weight gain method at room temperature. The uniform size cut NBR vulcanized were weighed on an electronic balance with an accuracy of 0.001 g. The cut samples immersed in a glass bottle containing n-pentane. The samples were removed from the solvent at the specified time, quickly wiped 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) of n-pentane per gram of NBR vulcanized was determined using Eq. 4 (Obasi *et al*., 2009):

$$Q_t = \frac{(M_t\text{-}M_0)}{\text{Molecular weight of n-pentane}/M_o} \times 100 \quad (4)$$

Where:

M_t = Mass uptake at time t
M_o = The initial mass of NBR vulcanized

The swelling phenomenon occurs when the solvent adsorbs rapidly to rubber surface followed by diffusion of the solvent into the rubber. The diffusion coefficient of a solvent can be obtained using Fickian's second law of diffusion as follows (Obasi *et al*., 2009):

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \quad (5)$$

Where:

h = The NBR vulcanized thickness
θ = The slope of the initial linear portion of the plot of Qt against $t^{1/2}$
Q_∞ = The equilibrium absorption

The Sorption coefficient (S) was calculated using Eq. 6 (Obasi *et al*., 2009):

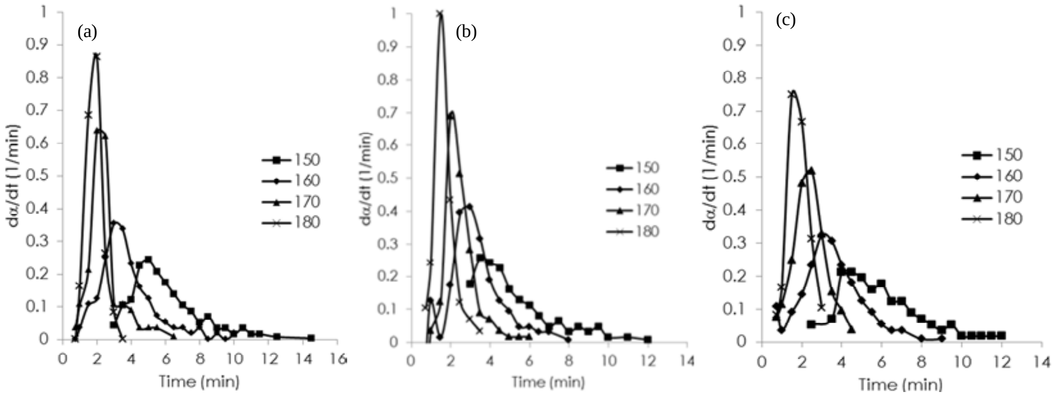

Fig. 1: Vulcanizing rate versus time curves of NBR vulcanizates with different acrylonitrile content: a) 2645; b) 2845 and c) 3345

$$S = \frac{M_\infty}{M_o} \quad (6)$$

where M_∞ is mass of n-pentane sorbed at equilibrium and M_o is the initial mass of NBR vulcanized.

RESULTS AND DISCUSSION

Cure chacteristics and kinetic study: The curing characteristics of NBR compounds a vulcanization temperature 150°C, expressed in terms of the optimum cure time (t_{90}), high (S'_{max}) and low torque (S'_{min}) and delta torque ($\Delta S' = S'_{max}-S'_{min}$) are compiled in Table 1. It can be observed that the optimum cured times slightly decreases with increasing the acrylonitrile content. The decrease in optimum cure time is beneficial in increasing the production rate. The minimum torque of NBR compounds is similar, due to the similarity of Mooney viscosity of NBR. The maximum torque of NBR with low acrylonitrile content (26 and 28%) are higher than NBR with acrylonitrile content 33%. Delta torque of NBR with acrylonitrile content 28% is higher than the other NBR vulcanisates. Delta torque is related to crosslink density and stiffness of the rubber vulcanized (Movahed *et al*., 2015).

The vulcanization kinetic of NBR compounds was analyzed by using rheometer under isothermal condition at 150, 160, 170, 180°C with Moving die rheometer. The vulcanization kinetic parameters were obtained according to vulcanizing curves from rheometer. The degree of conversion (α) in curing reaction is based on the crosslink density that is proportional to the stiffness of the rubber, is defined as follows (Choi *et al*., 2005; Sui *et al*., 2008):

$$\alpha = \frac{S'_t - S'_{min}}{S'_{max} - S'_{min}} \quad (7)$$

where, S'_{min}, S'_t and S'_{max} are the minimum torque value, the torque value at given time of curing and the maximum torque value, respectively.

Figure 1 shows the plot of dα/dt versus time for NBR compounds with different acrylonitrile contents at different temperatures. The maximum of dα/dt of all NBR compounds is reached at time t>0 which is the characteristic of autocatalytic reaction. So, the vulcanization kinetic parameters were determined using autocatalytic model. This model was used by Choi *et al*. (2005) to describe the cure behavior of NBR and its nanocomposites as given:

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1-\alpha)^n \quad (8)$$

Where:

k(T) = The rate constant
m = The reaction order of autocatalytic reaction
n = the reaction order of non-autocatalytic reaction

The rate constant, k, m and n are dependent on temperature. The value of k(T), m and n for all NBR samples was determined using nonlinear regression analysis. The activation energy of NBR samples can be determined using the Arrhenius equation as follows (Choi *et al*., 2005; Sui *et al*., 2008):

$$\ln k(T) = \ln A - \frac{E}{RT} \quad (9)$$

Where:

A = The pre-exponential or frequency factor
E = The activation energy
R = The gas constant
T = The absolute temperature

The activation Energy (Ea) of NBR samples was determined from the slope of the plot of ln k versus 1/T and showed in Fig. 2. All the vulcanization kinetic parameters are listed in Table 2.

The rate constant of all NBR samples increase with increasing the vulcanization temperature. The rate

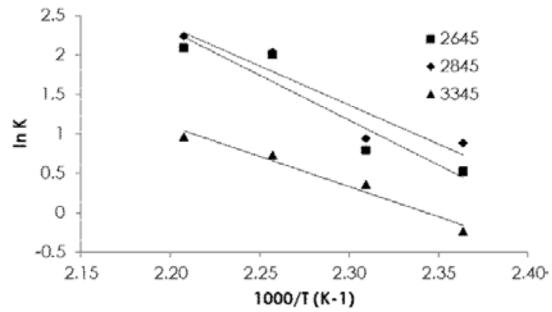

Fig. 2: ln k vs. 1/T of NBR vulcanizates with different acrylonitrile content

Table 2: Vulcanization kinetic parameters of NBR samples

Samples	Vulcanization temperature	Rate constant (min^{-1})	Reaction m	N	Activation ($kJ\ mol^{-1}$)
2645	150	1.68	1.41	1.50	94.680
	160	2.20	1.25	1.42	
	170	7.40	1.77	1.65	
	180	8.05	2.03	1.08	
2845	150	2.40	1.45	1.85	82.270
	160	2.55	1.19	1.41	
	170	7.63	1.85	1.60	
	180	9.36	1.42	1.40	
3345	150	0.79	0.96	1.08	105.63
	160	1.42	1.08	1.12	
	170	2.05	1.08	0.89	
	180	2.61	1.01	0.73	

constant of the 33% of the acrylonitrile content compound is lower than 26 and 28% of acrylonitrile content compounds and the activation energy of NBR with 33% acrylonitrile content is higher than NBR with 26 and 28% acrylonitrile content. It is indicated that the NBR with low acrylonitrile content need lower amount of energy for vulcanization especially for NBR with 28% acyrilonitrile content. Similar results were investigated by Gabriel *et al.* (2014) that studied the vulcanization kinetic of different NBR compounds. Their results showed that the cure rate constant decreased with increasing the acrylonitrile content and the activation energy of a NBR compound with a 33% acrylonitrile content was higher than NBR with 28 and 45% acrylonitrile content.

Crosslink density and mechanical properties: The crosslink density of NBR vulcanisates was determined by the Mooney-Rivlin equation based on their stress-strain behavior. The constants C_1 and C_2 can be determined by the plot of $\sigma/(\lambda-\lambda^{-2})$ against a $1/\lambda$ and showed in Fig. 3. The Mooney-Rivlin curves of NBR with different acrylonitrile content were different. The intercept (2C1) of 28% acrylonitrile content was higher ($0.026\ kg\ cm^{-2}$) than 26% ($0.025\ kg\ cm^{-2}$) and 33% ($0.196\ kg\ cm^{-2}$) acrylonitrile content. Table 3 shows the crosslink densities of NBR with different acrylonitrile content. The crosslink density

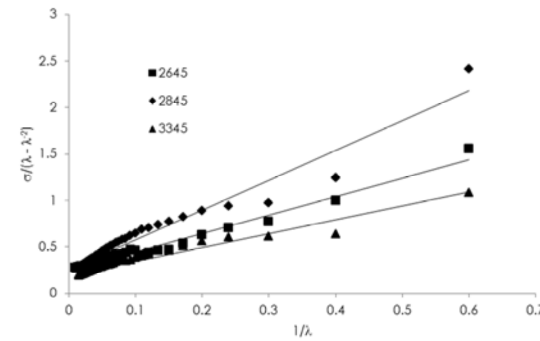

Fig. 3: $1/\lambda$ vs. $\sigma/(\lambda-\lambda^{-2})$ of NBR vulcanized with different acrylonitrile content

Table 3: Crosslink density and mechanical properties of NBR vulcanized with different acrylonitrile content

Samples	Crosslink density ($mol\ cm^{-3}$)	Hardness (Shore A)	Tensile strengt (MPa)	Elongation at break (MPa)	Compression set (%)
2645	5.00×10^{-5}	47	3.6	320	9.69
2845	5.19×10^{-5}	48	5.4	420	8.86
3345	3.96×10^{-5}	45	3.6	410	9.14

of NBR with 26 and 28% acrylonitrile are almost similar. The lowest crosslink density was obtained from the highest acrylonitrile content (33%). The presence of acrylonitrile in NBR slightly increased the crosslink density (Choi and Ha, 2009) whereas the results in current study showed conversely, due to the application of an efficient cure system with low sulfur loading and high accelerator loading. In the case of NBR with 33% acrylonitrile content, the low sulfur level makes the formation of more crosslinks difficult due to the low unsaturation level.

Table 3 shows that the crosslink density affect to mechanical properties of NBR vulcanized depending on the acrylonitrile content of NBR. The hardness and tensile strength of NBR vulcanized were similar trend with crosslink density. The hardness, tensile strength and elongation at break values are comparatively the highest in the case of NBR with 28% acrylonitrile content and the lowest compression set value. The lower compression set, the better the material for used for rubber seal.

Swelling behavior: The swelling behavior of NBR with different acrylonitrile content was investigated using immersion of NBR in n-pentane. Figure 4 shows that NBR with low acrylonitrile content (26 and 28%) have similar curves. The molar percentage uptake increases initially and pass through a maximum and then gradually slows down. The slowing down of swelling curves means that a number of substances pulled out from the rubber vulcanizates and the distance between the rubber

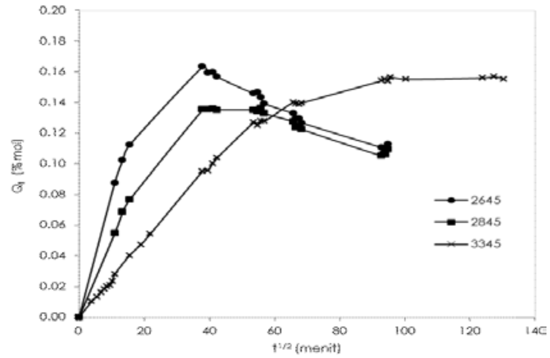

Fig. 4: Molar percentage uptake (Q_t) of NBR with different acrylonitrile content

Table 4: Equilibrium mol uptake, diffusion coefficient and sorption of NBR vulcanized with different acrylonitrile content

Samples	Q_∞ (%)	D (cm^2 min^{-1})	S (%)
2645	0.1634	5.37×10^{-6}	0.1179
2845	0.1363	2.65×10^{-6}	0.0983
3345	0.1565	5.04×10^{-7}	0.1129

molecules decreases. The pulling out of the substances would decrease the properties of rubber (Wang *et al*., 2014).

Table 4 shows equilibrium mol uptake, diffusion coefficient and sorption of NBR vulcanized with different acrylonitrile content. The diffusion coefficient increased with decreasing the acrylonitrile content. However, the equilibrium mol uptake (Q_∞) of NBR with 28% acrylonitrile content was lower than others NBR vulcanized. The values of the sorption coefficient showed the same trend as the equilibrium mol uptake (Q_∞). It was caused by the increased in crosslink density of rubber (Kumnuantip and Sombatsompop, 2003). So, it was concluded that the swelling behavior, not only affected by the acrylonitrile content of NBR but also by the crosslink density of rubber vulcanized.

CONCLUSION

The effect of acrylonitrile content in NBR filled carbon black on mechanical properties and swelling behavior in n-pentane has been studied. The vulcanization kinetic parameters were determined using autocatalytic model and the cure data were obtained from vulcanizing curves. The activation energy of NBR with 33% acrylonitrile content was higher than NBR with 26 and 28% acrylonitrile content. The highest crosslink density was obtained from the NBR with acrylonitrile content 28% and the crosslink density effected to its mechanical properties and swelling behavior. The NBR that contains 28% acrylonitrile content exhibited the highest hardness, tensile strength and elongation at break values and the better compression set than other samples. The Diffusion coefficient (D) increased with decreasing the acrylonitrile content. The NBR with acrylonitrile 28% showed the lowest the equilibrium mol uptake (Q_∞) and the lowest the Sorption coefficient (S). So, it was concluded that the swelling behavior, not only affected by the acrylonitrile content of NBR but also by the crosslink density of rubber vulcanized.

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