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Research Article

Vulcanization Kinetics and Mechanical Properties of Ethylene Propylene Diene Monomer Thermal Insulation

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Abstract

The vulcanization kinetics of Ethylene-propylene diene monomer (EPDM) rubber thermal insulation was studied by using rheometer under isothermal condition at different temperatures. The rheometry analysis was used to determine the cure kinetic parameters and predicting the optimum curing time of EPDM thermal insulation. The experimental results revealed that the curing curves of EPDM thermal insulation were marching and the optimum curing time decreased with the increasing of temperature. The kinetic parameters were determined from the autocatalytic model that showed a close fitting with the experimental results. It also indicated a suitability of autocatalytic model in characterizing the cure kinetics. The optimum curing time was predicted from autocatalytic model and the kinetic parameters were obtained by using the relationship between degree of conversion, cure temperature, and cure time. The predictions of cure time provided information on the actual curing characteristic of EPDM thermal insulation. The mechanical properties of EPDM thermal insulation with different vulcanization temperatures showed the same hardness, tensile strength and modulus at 300%, except at temperature 70 °C, while the elongation at breaking point decreased with the increasing temperature of vulcanization.

Keywords: Vulcanization kinetics; ethylene-propylene diene monomer; thermal insulation; autocatalytic model

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1. Introduction

Ethylene-propylene diene monomer (EPDM) rubber has advantages properties, such as: low specific gravity, resistance to oxidation, ozonisation and weathering effects. According to those properties, EPDM has emerged as a material for manifold applications including insulation for case-bonded solid rocket motor [1]. Prior to the production of thermal insulation from EPDM rubber, the rubber industry usually performs the curing characterization that will affect to the processing, physical, mechanical and dynamic properties.

Curing characteristic of rubber compound by using rheometer is used to show the vulcanization reaction that revealed by torque-time curve. In addition, the torque-time curve can be used to determine the optimum curing time. However, rheometry testing uses isothermal

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and the thin rubber. Sometimes in the production processes, the curing temperature is different or not constant because it is affected by the thickness of rubber product. So, the reaction condition in laboratory procedures is different with the production processes. Therefore, the method to predict the optimum curing time by using rheometry data is important to be studied.

Several methods to predict the optimum curing time of rubber compounds are available in the literature. Some of well-known methods are numerical methods by using finite element analysis [2], statistical method by using artificial neural network [3] and adaptive neuro-fuzzy inference system [4] and empirical method or cure kinetic [5, 6]. Kinetic model has been studied by several authors to study the rubber cure reaction. Although this technique is empirical model that fail to acknowledge the underlying molecular mechanism [7], but this technique is more practical, because the chemistry of vulcanization is very complex and has not been understood in detail.

Cure kinetics of rubber compound are measured by a variety of techniques. Some of these techniques are swelling methods, measuring tensile modulus, hardness, differential scanning calorimetry (DSC), stress relaxation measurements, chemical identifications which are often based on the determination of the rate of free sulfur disappearance, and measurements of different crosslink types [8]. The most popular method in the rubber industry is based on rheometry because of practical and simple uses. Study of process of cure of EPDM rubbers in moving die rheometer (MDR) was studied by Rosca and Vergnaud [9]. Three EPDM compounds were used, containing 2, 9, and 19% peroxide and having different cure enthalpies. The results showed that it has a good correlation between the results obtained from MDR and the values of the state of cure. The thickness of the sample affected the process of cure.

This paper studied the vulcanization kinetics to predict the curing time using empirical kinetic model by using rheometer and to compare the mechanical properties of EPDM thermal insulation with different vulcanization temperatures.

2. Materials and Methods

2.1. Materials

An ethylene propylene diene rubber, EPDM (Buna 6470, ethylene content: 68 wt%, 5-ethylidene-2-norbornene (ENB): 4.7 and viscosity mooney: 57 ML (1+4) 125° C was provided by Lanxess, Germany. Silica filler (Zeosil 175) was obtained from Rhodia, Korea. Other technical grade chemicals were obtained from local supplier and were used as such.

2.2. Preparation EPDM Compound

Rubber compound was prepared by two-roll mill with slow speed of roll (24 rpm) and friction ratio (1.4) was maintained at temperature of 65±5 °C. The compounding ingredients (antioxidant, 2 phr; silica, 40 phr; carbon black, 1 phr; paraffinic oil, 15 phr; diocthyl phthalate, 5 phr; polyethylene glycol, 2 phr; high styrene resin, 10 phr; Al_2O_3, 5 phr; silane coupling agent, 1.5 phr; zinc oxide, 5 phr; stearic acid, 2 phr; and accelerator: tetramethylthiuram disulfide (TMTD), 0.8 phr; 2-mercaptobenzothiazole (MBT), 1.5 phr; Rhenocure© T/PS, 4 phr and sulfur, 2 phr) were added to the EPDM after incorporation of the silica filler and oil. The accelerator and curing agent were added at the end of mixing. The rubber compound was maturated for 24 hours before molded.

2.3. Cure Characteristic

Cure characteristic of EPDM compound was determined at four different temperatures, i.e. 130, 140, 150, 160 °C using a moving die rheometer (MDR 2000) for 30 minutes according to ISO 6502. Different cure kinetics parameters such as optimum cure time, cure rate index, degree of cross linking or conversion, and apparent activation energy were calculated from the torque-time curves.

2.4. Mechanical Properties

The EPDM compound was compression-molded on electrically heated hydraulic press, at 150 °C and 9.8 MPa with the previously determined the optimum cure time (t_{90}) by MDR 2000. The sample's thickness of 2±0.2 mm sheets was molded. The mechanical testing such as: hardness, tensile strength, modulus 300 and elongation at break of vulcanized rubber, were carried out according to the ISO standards. Five specimens were measured and the median values were calculated.

3. Results and Discussion

3.1. Vulcanization Kinetics Study

Curing characteristic of EPDM compound by using rheometer under isothermal condition gave data on torque versus time, which can be used to evaluate kinetic parameters such as optimum cure time, cure rate index, degree of

cross linking or conversion and activation energy. Figure 1 shows the vulcanization curves of EPDM thermal insulation at various temperatures. Three regions of rubber cure can be seen in the vulcanizing curves for a typical accelerated sulfur vulcanization process. In the first region, there is scorch time or induction period that provided a safe processing time. The second region is the curing reaction period, during which the cross linking network is formed and the stiffness of rubber are increased. The third region is called over cure that may occur as reversion, equilibrium, or marching cure behaviors, according to the compound characteristics [3].

The vulcanization curves in Figure 1 showed that on the third region, the characteristic of the EPDM thermal insulation compound at various temperatures were marching. It means that the stiffness of rubber increase with time. Table 1 shows that the optimum curing time (t_{90}) and scorch time (t_{s2}) decreased with increasing the temperature of vulcanization. The increasing temperature vulcanization also affect to increasing the cure rate index (*CRI*) of EPDM thermal insulation. The increasing of vulcanization temperature causes fast cure rate or decreasing optimum curing time [10]. The characteristic of vulcanization curves is marching, hence, is difficult to obtain the modulus maximum. Modulus maximum (M_{max}) and minimum (M_{min}) were obtained by the MDR 2000 software. Delta torque (DM) of the EPDM thermal insulation compound increased with increasing the temperature of vulcanization, but with a relatively small degree. DM is related to crosslink density and stiffness [11].

Table 1. The curing characterization of EPDM thermal insulation compound

Temperature, °C	ΔM (kg-cm)	t_{s2} (min)	t_{90} (min)	CRI (min^{-1})
130	3.54	8.45	22.03	7.36
140	4.16	5.04	18.39	7.49
150	4.93	3.10	15.06	8.36
160	4.87	2.13	9.36	13.83

The curing kinetics study is used to predict the optimum curing time using empirical kinetic model by using experimental results. The degree of conversion (α) in curing reaction is defined as follows [5,8]:

$$\alpha = \frac{M_t - M_{\min}}{M_{\max} - M_{\min}} \quad (1)$$

where, M_{min} is the minimum torque value, M_t is the torque value at given time of curing, and M_{max} is the maximum torque value.

The isothermal vulcanization kinetics of the rubber compound are usually characterized by two model equations namely, nth-order and autocatalytic model equations [12]. Figure 2 shows the curves of da/dt versus time for EPDM thermal insulation at various temperatures. The reaction rate at any temperature increases initially with conversion and passes through a maximum and then decrease with time. The cure rate increased with increasing

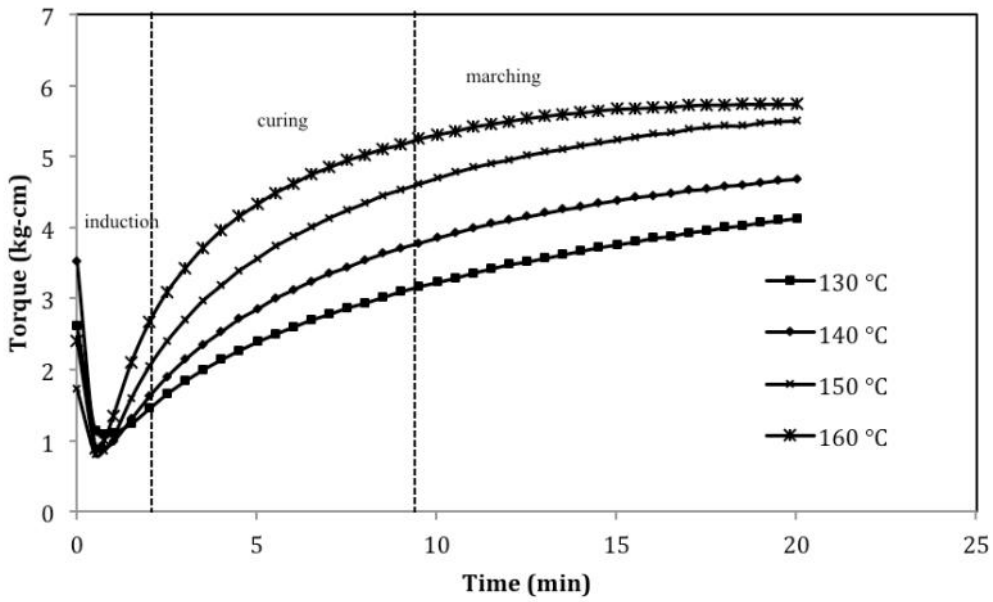

Figure 1. Vulcanizing curves of EPDM thermal insulation at various temperature

the vulcanization temperature. The reaction rate of the system reaches a maximum at a time greater than zero. It indicates that the curing reaction of EPDM compound exhibit autocatalytic reaction. The autocatalytic equation predicts that the maximum reaction rate will occur at any point of time other than the beginning of the reaction. This is because the conversion rate is not only related to the unreacted materials, but also related to the reaction product [12]. The kinetic of autocatalytic reactions can be described as follows [12,13]:

$$\frac{d\alpha}{dt} = k(T)\,\alpha^m (1-\alpha)^n \quad (2)$$

where k is the rate constant and m and n are reaction orders of autocatalytic reaction assumed to be independent of temperature. The value of $k(T)$, m and n was calculated using nonlinear regression fit and listed in Table 2. The temperature dependence of the conversion rate is assumed to reside in the constant (k) through the Arrhenius equation:

$$k = A\exp\left(\frac{E_a}{RT}\right) \quad (3)$$

where, A is pre-exponential factor, E_a is activation energy, R is the gas constant, and T is reaction temperature.

Figure 3 shows that the plot of cure rate versus conversion. In this figure, it shows a comparison between the experimental curves (points) and the model curves (solid lines). The model curves show a close fitting with experimental curves. The maximum value of cure

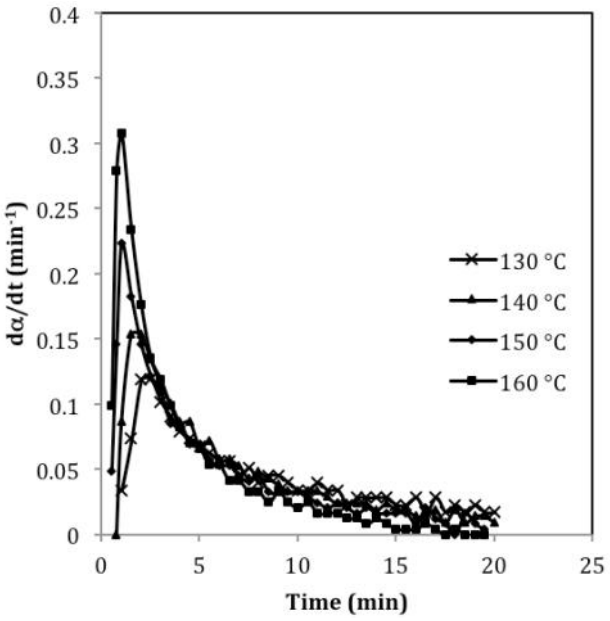

Figure 2. Rate of vulcanization versus time of the EPDM thermal insulation at various temperatures.

Tabel 2. Curing kinetic parameter of EPDM thermal insulation

Curing temperature (°C)	K	M	N	E_a (kJ/mol)
130	0.2202	0.3058	1.6485	46.3661
140	0.2943	0.2662	1.6632	
150	0.3852	0.2458	1.7009	
160	0.5855	0.2261	1.5788	

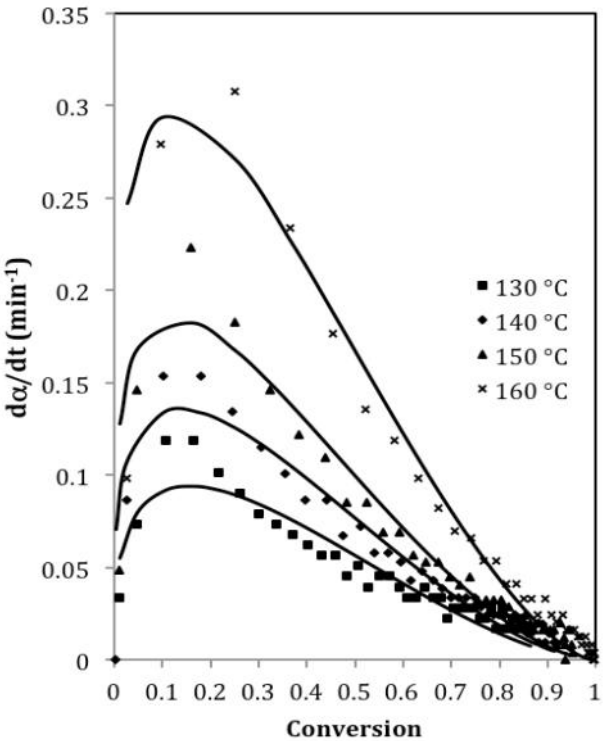

Figure 3. Vulcanization rate versus conversion of the EPDM thermal insulation at various temperatures.

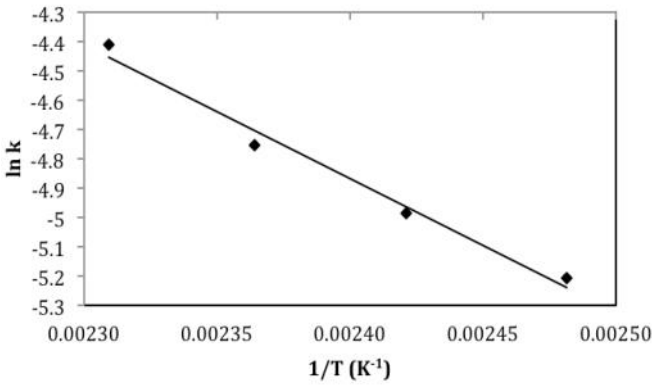

Figure 4. Arrhenius plot of ln k versus 1/T for EPDM thermal insulation

rate appears between conversion 0.1 and 0.2.

Figure 4 shows the Arrhenius plot of ln k versus $1/T$ for EPDM thermal insulation to determine the activation energy of vulcanization (E_a). The activation energy was obtained from the slope of the straight line is given in Table 2.

3.2. Cure time prediction of EPDM thermal insulation

Prediction of cure time of EPDM thermal insulation based on rheometry data is very useful to know the relationship among cure reaction conversion, cure temperature, and cure time. The cure time prediction can be performed by integrating Equation (2) and $k(T)$ substituted from Equation (3):

$$t = \int_0^{\alpha} \frac{1}{k(t)\alpha^m(1-\alpha)^n} d\alpha \quad (4)$$

$$t = \int_0^{\alpha} \frac{1}{k(t)\alpha^m(1-\alpha)^n} \exp\left(\frac{E_a}{RT}\right) d\alpha \quad (5)$$

For the EPDM thermal insulation, the mean reaction orders for autocatalytic reaction were m = 0.26 and n = 1.65. The activation energy was 5577 kJ.mol^{-1}, and the pre-exponential factor was 218600 min^{-1}. Thus, the cure time of

Table 3. The optimum cure time (t_{90}) of EPDM thermal insulation

Temperature, °C	130	140	150	160
Eq. 7, min	28.97	20.72	15.06	11.11
Model (Eq. 6), min	28.24	20.21	14.69	10.84
Experiment, min	22.03	18.39	15.06	9.36

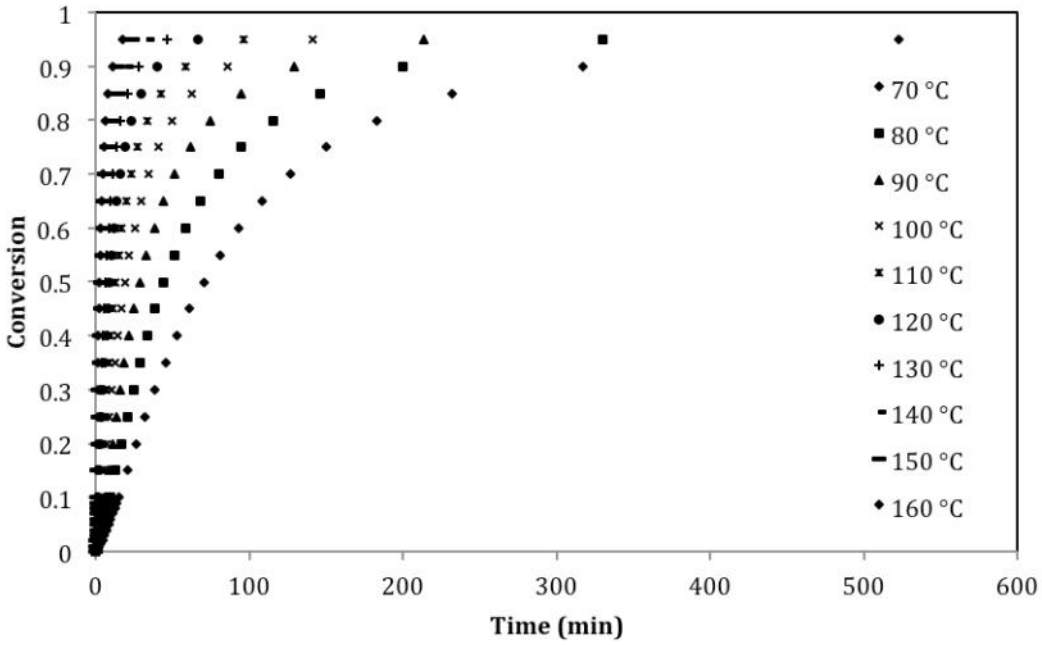

Figure 5. Curing time of EPDM thermal insulation as a function of conversion

Tabel 4. The mechanical properties of EPDM thermal insulation at various temperatures

Temperature, °C	70	130	140	150	160
Hardness (shore A)	65 ± 0.49	71 ± 0.63	72 ± 0.40	72 ± 0.40	72 ± 0.40
Tensile strength (MPa)	6.60 ± 0.56	19.27 ± 1.13	18.82 ± 1.39	16.84 ± 1.67	18.68 ± 0.85
Elongation at break (%)	1000 ± 8.00	750 ± 18.86	680 ± 12.47	610 ± 28.28	630 ± 4.71
Modulus at 300% (MPa)	2.20 ± 0.30	4.38 ± 0.12	5.08 ± 0.04	4.97 ± 0.12	5.54 ± 0.08

EPDM thermal insulation with neglecting small quantities can be described as:

$$t = 4.5746x10^{-6} \exp\frac{5570}{T}\int_0^{\alpha}\frac{d\alpha}{\alpha^{0.26}(1-\alpha)^{1.65}} \quad (6)$$

The Equation 6 was assumed that thermal insulation is a thin rubber product with the thickness 1-2 mm. So, the thickness of rubber was not affected to cure time [8]. The predicted results were shown in Figure 5 which provides information for the actual curing characteristic of EPDM thermal insulation.

The optimum curing time (t_{90}) of EPDM thermal insulation was determined by Equation 6 when the conversion is 90%. The other method to determine $t_{90}$was determined by using Arrhenius equation [3,14]:

$$t_r = t\exp\left|\frac{E_a}{R}\left(\frac{1}{T_r}-\frac{1}{T}\right)\right| \quad (7)$$

where t_r is equivalent cure time at temperature T_r and E_a was obtained from autocatalytic model in Table 2. The results between autocatalytic model (Equation 6) and Arrhenius model (Equation 7) and experiment are listed in Table 3. The results show that the t_{90} of EPDM thermal insulation was obtained from model are almost similar with experiment results.

3.3. Mechanical properties of EPDM thermal insulation

The mechanical properties of EPDM thermal insulation, i.e. hardness, tensile strength, elongation at break, and modulus 300% at various temperatures, were listed in Table 4. The mechanical properties at temperature 160 °C have excellent properties. These results were similar with another author that used silica as filler or EPDM thermal insulation for case-bonded solid rocket motors, because silica particles have silanol groups on their surface. This typical structure gives hydrophobic nature to this class of silica and these silanol groups are reactive sites for surface treatment [15]. Composite propellants generally are cured between 40 and 60 °C [16]. Meanwhile, LAPAN (Indonesia) used 70 °C in hydroxyl-terminated polybutadiene (HTPB) processing as the best curing temperature [17]. So, the temperature 70 °C was chosen to compare the mechanical properties of EPDM thermal insulation with different temperatures. The optimum curing time at temperature 70 °C was obtained from the autocatalytic model (Equation 7).

The hardness of rubber could be used to predict the optimum cure time in rubber industry, but this technique is based on trial and error. The hardness value in this study was used to confirm the optimum curing time. The hardness of EPDM thermal insulation is almost similar at different temperatures. The hardness at temperature 70 °C is smaller, but to a relatively small degree. It indicated that the optimum cure times from rheometry analysis were correct, because the hardness of rubber related to crosslink density [11]. The tensile strength and modulus at 300% of the EPDM thermal insulation were almost similar at different temperatures, except at temperature 70 °C, while the elongation at breaking point decreased with increasing temperature of vulcanization. The decrease in the values of elongation at break with increasing vulcanization temperatures is the resulting of higher cross-linking [18]. The small value of the tensile strength and Modulus 300% at temperature 70 °C were caused of smaller cross-linking, although the hardness values were comparable.

4. Conclusions

In this paper, the optimum curing time were predicted by using autocatalytic model. The cure kinetic parameters were obtained from the rheometry analysis. The curing characteristic of EPDM thermal insulation has a good agreement with the model parameters determined from autocatalytic model equations and the suitability of this model in characterizing the cure kinetics. The activation energy was determined from the autocatalytic model is 46.3661 kJ.mol^{-1}. The predictions of optimum curing time provide information for the production of EPDM thermal insulation. The mechanical properties of EPDM thermal insulation were almost similar at different temperature, especially for hardness, except at temperature 70 °C.

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