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Determination of vulcanization rate constant, crosslink density, and free sulfur content on carbon black filled EPDM

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ABSTRACT

Different ethylene propylene diene monomer (EPDM) composite with the carbon black (CB) variation of 50, 60, and 70 phr (per hundred rubbers) is compounded by using an efficient (EV), semi-efficient (SEV), and conventional (CV) sulfur vulcanization systems. This research aims to investigate the effect of vulcanization systems and carbon black content on the vulcanization rate constant, the crosslink density, and the free sulfur content. This research shows the EV system resulting in the fastest vulcanization rate constant (0.0191/second), the lowest overall crosslink density (0.0022 mol.cm^{-3}), and the highest percentage of free sulfur content in the EPDM vulcanization (0.40 %). The CV system provides the slowest vulcanization rate constant (0.0061/second) and the highest overall crosslink density (0.0034 mol/cm^{-3}). The percentage of free sulfur content in the EPDM vulcanization of CV system is between EV and SEV systems. The SEV system provides the vulcanization with the characteristic of vulcanization rate constant and overall crosslink density between EV and CV systems as well as provides the lowest percentage of free sulfur content (0.29 %). The higher carbon black loading in each vulcanization systems means the lower rate constant of vulcanization and the higher overall crosslink density.

Keywords: EPDM, vulcanization system, crosslink density, free sulfur content.

INTRODUCTION

Vulcanization is a chemical process of treating rubber (natural or synthetic) in order to improve its properties. Sulfur is the commonly used vulcanizing agent. Sulfur based vulcanization system is classified into three types which are conventional (CV), semi-efficient (SEV), and efficient (EV) systems. This classification is based on the level of sulfur and the ratio of accelerators to sulfur: EV>2.5, SEV 0.7-2.5 and CV 0.1-0.6 (Akiba, 1997; Ohnuki, 2015). The vulcanization process allows the polymer to form the various types and number of the crosslink. CV system with a low ratio accelerator to sulfur is dominated by longer flexible polysulfidic crosslink and EV system with a high ratio of accelerator to sulfur mainly gives monosulfide. SEV system that accelerator to sulfur ratio is between CV and EV means the increase of accelerator to sulfur ratio and the shorter increase of monosulfidic and disulfidic crosslink (Rabiei & Shojaei, 2016). Sulfur connects with the molecular chain of rubber to form a crosslink. The amount of crosslink density is defined as the number of crosslink in the polymer per unit volume. Types of vulcanization system have an effect on crosslink density, which can be determined through various methods such as stress-strain relationships, swelling equilibrium by Flory-Rehner equation, and rubber elasticity theory (Yehia & El-Sabbagh, 2007).

During the reaction of vulcanization, the conversion of sulfur to form crosslink may not completely be 100%. The remainder of sulfur which is present in the system is probably in the form of free sulfur. Determination of sulfur residue (free sulfur) in rubber vulcanization provides an overview of the existing vulcanization reaction. The higher vulcanization temperature means the faster decrease of sulfur and the higher vulcanization rate constant (Hasan *et al.*, 2013).

The vulcanization rate of rubber describes the productivity and reactivity of the vulcanization. Estimation of vulcanization reactivity can be performed through many methods. Free sulfur determination and curing curve (torque-time plot of rheograph) are the most common methods in researching vulcanization kinetics. Sirquera & Soares (2003) reported that vulcanization reaction on the natural rubber/mercapto- and thioacetate-modified EPDM blends the system following the first-order reaction.

Recently, Mayasari & Yuniari (2016) investigated the effect of three vulcanization system on the mechanical properties and swelling characteristics. This current research focused on the vulcanization kinetics, crosslink density estimation, and free sulfur determination of carbon black filled EPDM in which different sulfur to accelerator (S/A) and carbon black loading are considered. Crosslink density is determined by Flory Rehner equation employing equilibrium swelling data.

MATERIALS AND METHODS

Materials

EPDM Keltan 4551 A was used in this research. The used additive materials consisted of CB N220 (Ex Korea) as a filler, paraffin wax Antilux 654 A and TMQ as antioxidants, paraffinic oil as a softener, zinc oxide (ZnO) Ex Indoxide, and stearic acid Aflux 42M as activators, tetra methyl thiuram disulfide (TMTD) and mercapto benzo thiazole (MBT) as accelerators, and sulfur Ex Miwon as the agent of vulcanization. Free sulfur determination used sodium sulphite, paraffinic liquid, formaldehyde, acetic acid glacial, sodium thiosulfate, iodine, and amylum whereas swelling experiment applied toluene as solvent.

EPDM Compounds Preparation

In previous publication (Mayasari & Yuniari, 2016), the compounds were prepared and the compounding was performed by two roll mills on laboratory scale (modified with a capacity of 2 kg) and the composition of each ingredient followed the values in formulation Table 1. After homogeneous blend was reached, the compounds were taken out from two roll mills and then cooled and stored in the condition of 23 ± 2 °C for 24 hours. The compounds were vulcanized by compression molding in 170 °C and 150 kg/cm^2 in which the duration of vulcanization was determined by rheometer.

Determination of the vulcanization rate constant

Vulcanization kinetics was researched by using rheometer data. The rate constant was calculated from the torque-time plot (Sirqueira & Soares, 2003; Cifriadi, 2013). The moving die rheometer Gotech M-3000A was used to obtain the curing data at 170 °C. It was assumed that the vulcanization reaction of the EPDM system follows the first-order reaction. The rate equation of the first-order reaction is expressed on Eq. (1) and (2) of which Eq. (2) forms a general expression of linear equation $y=mx+c$ as well as m (slope) will be the vulcanization rate constant (k). Its confirmation is in Figure 1.

$$ln\frac{(M_H-M_L)}{(M_H-M_t)} = k.t \quad (1)$$

$$ln\,(M_H - M_t) = -k.t + \ln\,(M_H - M_L) \quad (2)$$

where M_H is the maximum torque, M_L is the minimum torque, M_t is the torque at cure time t, and k is the vulcanization rate constants. M value chosen to estimate the rate constants is between 25 and 45% of torque changes. The rate constants were obtained by plotting in (M_H - M_t) against t.

Determination of crosslink density

Crosslink density was determined by equilibrium swelling. The swelling experiments were conducted by immersing the rubber sample in toluene at ambient temperature for 72 hours. The weight of rubber sample before and after the immersion was measured. The crosslink density was then calculated based on Flory-Rehner equation (El-Nemr, 2011) as expressed in Eq. (3) and (4),

$$v = -1/V_s\left[\frac{ln(1-V_r)+V_r+X_1V^2{}_r}{V^{1/3}{}_r-V_r/2}\right] \quad (3)$$

where v is the crosslink density; X_1 is the polymer-solvent interaction parameter (X EPDM-toluene = 0.5); V_s is the molar volume of toluene (106.4 cm^3/mol); V_r is the volume fraction of rubber in the swollen specimen; V_r was calculated using the relation

$$Vr = \frac{(D_S-F_fA_W)\rho r^{-1}}{(D_S-F_fA_W)\rho r^{-1}+A_S\rho s^{-1}} \quad (4)$$

where D_S is the swollen weight of the sample; F_f is the fraction in insoluble; A_W is the sample weight; A_S is the weight of the absorbed solvent corrected for swelling increment; ρ_r is the density of rubber; and ρ_S is the density of solvent.

Free sulfur determination

Sulfite method (BS, 1996) was used to determine sulfur. The specimen of EPDM vulcanization was boiled and extracted with a solution consisted of sodium sulfite and liquid paraffin for 4

Table 1. Formulation of EPDM vulcanization.

Materials	EV			SEV			CV		
	EV1	EV2	EV3	SEV1	SEV2	SEV3	CV1	CV2	CV3
	phr	phr	phr	phr	phr	phr	phr	phr	phr
EPDM	100	100	100	100	100	100	100	100	100
CB N220	50	60	70	50	60	70	50	60	70
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1
TMQ	1	1	1	1	1	1	1	1	1
Paraffin wax	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Paraffinic oil	5	5	5	5	5	5	5	5	5
TMTD	1	1	1	1.4	1.4	1.4	0.75	0.75	0.75
MBT	1	1	1	1	1	1	1	1	1
Sulfur	0.8	0.8	0.8	1.7	1.7	1.7	2.5	2.5	2.5

hours. The solution was cooled and then activated with charcoal for 30 minutes. Afterwards, the solution was filtered and then formaldehyde was added and allowed to stand for 5 minutes. Glacial acetic acid and excess iodine solution were then added. The filtrate was titrated with sodium thiosulfate with the starch indicator. The amount of used sodium thiosulfate in the sample titration and the blank were employed to calculate the free sulfur by equation (5):

$$S = \frac{3,2(V_s - V_b)c}{m} x100\% \quad (5)$$

where V_s is the volume of sodium thiosulfate used to titrate the specimen filtrate, V_b is the volume of sodium thiosulfate used to titrate the blank filtrate, *c* is the actual concentration of sodium thiosulfate, and *m* is the specimen weight.

RESULT AND DISCUSSION

Kinetic parameters of vulcanization

Figure 1(a), (b), and (c) shows the confirmation of Eq. (2) for EV system, SEV system, and CV system. The rate constants are obtained by plotting ln (M_H-M_t) against *t*. The slope of the plot of ln (M_H-M_t) versus time is rate constant (*k*) in which it shows a similar pattern on each system. Figure 1(d) shows that EV system has the fastest vulcanization rate than SEV and CV systems. It occurs because the EV system has more amount of accelerator than sulfur and therefore, the process of vulcanization takes place more quickly. The vulcanization rate constant is affected by the amount of accelerator in which increasing accelerator loading gives the higher vulcanization rate constant (Khang & Ariff, 2012). Figure 1(d) shows that vulcanization rate constant decreases with the increasing of carbon black loading. According to Semsarzadeh *et al.* (2005), the rate constant of EPDM/NR increases with increasing of carbon black amount. It is possible that carbon black acts as a catalyst. It is contrary with the phenomenon in this research because greater carbon black is probably hard to disperse into the rubber and unable to function as a catalyst (Hasan *et al.*, 2013).

Crosslink Density

The crosslink density defined in this research is the overall crosslink density. Figure 1 shows that the vulcanization system affects the overall crosslink density. Meanwhile, EV system gives the lowest crosslink density. In the previous research, it is agreed that EV system gives the lowest delta torque (Mayasari & Yuniari, 2016). In the EV system, the optimum cure time is the fastest than the other systems because EV system contains the lowest sulfur concentration. Thus, the time required to achieve optimum cure is shorter and the formed crosslink density is much lower than the others. CV system gives a high crosslink density because it has a high amount of sulfur combined with TMTD accelerator (Dijkhuis *et al.*, 2009) Figure 2 shows that for the overall vulcanization system, the greater carbon black gives the greater crosslink density. It is confirmed that the greater filler loading means the greater delta torque and the greater crosslink density as well (Mayasari & Yuniari, 2016). The degree of cross-linking in filled compounds is greater. Strong bonds are formed between rubber molecules and the surface of carbon black particles (Hartwell, 2003). Carbon black filled with rubber vulcanization has a strong

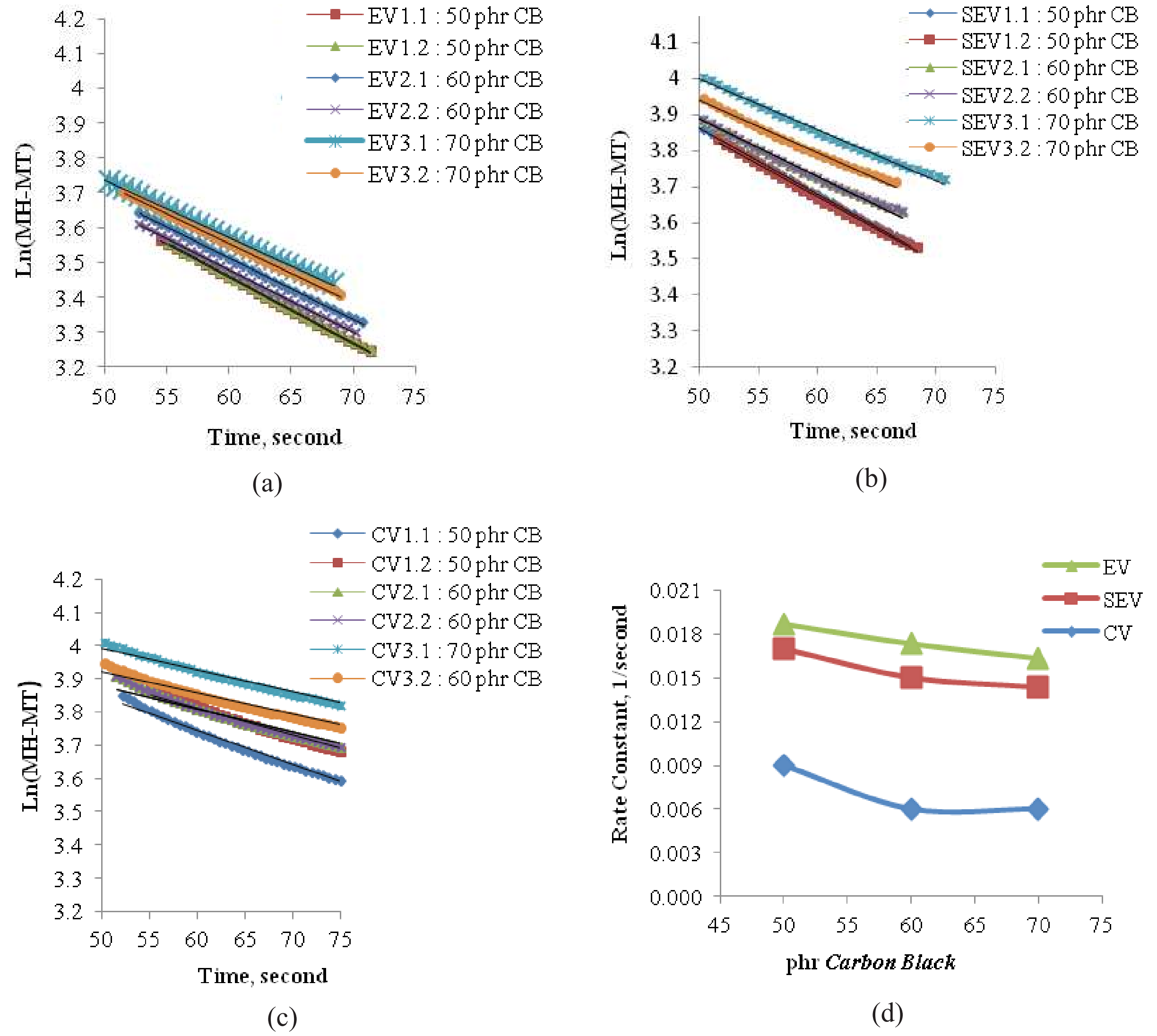

Figure 1. EPDM filled with carbon black at 170°C: (a) EV system; (b) SEV system; (c) CV system; and (d) vulcanization rate constant.

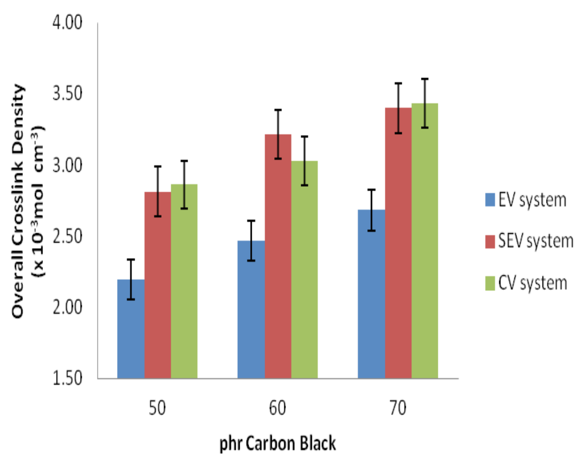

Figure 2. EPDM filled with carbon black in various vulcanization systems: Effect on overall crosslink density.

interaction between rubber molecules and the surface of filler particles (Fei *et al.*, 2012).

Free Sulfur Content

The sulfur content is varied in EV, SEV, and CV vulcanizing system. It is possible that sulfur is not completely consumed during the vulcanization reaction. The remainder of sulfur probably exists in the system as free sulfur. Table 2 shows the non-reactive sulfur (free sulfur) conducted through sulfide method in this experiment.

The EV system gives the highest percentage of free sulfur than SEV and CV systems but provides the least reactive sulfur content. The minimum amount of sulfur in EV system can give high efficiency in producing the cross-linking network (Danwanichakul *et al.,* 2008). Table 2 shows that

Table 2. The total, free sulfur and reactivesulfur contents in EPDM filled with carbon black in various vulcanizing systems.

Formula	Total sulfur (in grams)	Free sulfur (in %)	Free sulfur (in grams)	Reactive sulfur (in grams)
EV 50 phr CB	2.90	0.39	0.01	2.89
EV 60 phr CB	2.74	0.40	0.01	2.73
EV 70 phr CB	2.59	0.39	0.01	2.58
SEV 50 phr CB	6.12	0.29	0.02	6.10
SEV 60 phr CB	5.78	0.30	0.02	5.76
SEV 70 phr CB	5.47	0.29	0.02	5.45
CV 50 phr CB	9.00	0.31	0.03	8.97
CV 60 phr CB	8.49	0.33	0.03	8.46
CV 70 phr CB	8.43	0.33	0.03	8.01

the free sulfur content in each vulcanizing system is not affected by filler loading.

CONCLUSIONS

The research of vulcanization kinetics rate constant, crosslink density, and free sulfur determination of carbon blackfilled EPDM vulcanization have been successfully done. Variations have been made on the sulfur to accelerator ratio (EV, SEV, CV systems) and carbon black loading. The results show that the sulfur to accelerator ratio affects the rate constant, crosslink density, and free sulfur. EV system shows the fastest rate constant of vulcanization, the lowest overall crosslink density, and the highest free sulfur content. The CV system provides the slowest vulcanization rate constant, the highest overall crosslink density, and the lowest free sulfur content of the EPDM vulcanization. The SEV system provides the vulcanization with the characteristic between EV and CV systems. The higher CB loading means the lower vulcanization rate constant and the higher overall crosslink density. The SEV system provides the blend with the characteristic between EV and CV systems. The higher CB loading means the lower rate constant of vulcanization and the higher overall crosslink density.

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