CURING CHARACTERISTIC OF VARIOUS ACCELERATORS ON NATURAL RUBBER/CHLOROPRENE RUBBER BLENDS

KARAKTERISTIK CURING KOMPON TERHADAP BERBAGAI JENIS AKSELERATOR PADA CAMPURAN KARET ALAM DAN KARET KLOROPRENE

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Abstract

The effects of the various accelerator of natural rubber (NR) and chloroprene (CR) blends on the cure characteristics was investigated in this paper. Blending process of elastomers NR and CR were prepared by using laboratory two-roll mill. Several types of an accelerator, namely diphenyl guanidine (DPG), 2-mercaptobenzothiazol (MBT), N-tert-butyl-2-benzothiazyl sulphenamide (TBBS), ethylene thiourea (ETU), and tetramethyl thiuram monosulfide (TMTM) was used to find out curing characteristics of compound NR/CR (coded A, B, C, D, E). Rheology was studied with a rheometer. Research results show that type of used accelerator and vulcanization temperature influenced scorch time (ts_2), optimum vulcanization time (tc_{90}) and cure rate index (CRI) of NR/CR rubber blends.

Keywords: accelerator, chloroprene rubber, curing characteristic, natural rubber, scorch time

Abstrak

Penelitian ini bertujuan untuk mengetahui pengaruh dari berbagai jenis akselerator pada campuran karet alam (NR) dan karet kloroprene (CR) terhadap karakteristik curing kompon. Proses pencampuran elastomer NR dan CR menggunakan two-roll mill skala laboratorium. Beberapa jenis akselerator, yaitu diphenyl guanidine (DPG), 2-mercaptobenzothiazol (MBT), N-tert-butyl-2-benzothiazyl sulphenamide (TBBS), ethylene thiourea (ETU), and tetramethyl thiuram monosulfide (TMTM) digunakan untuk mengetahui karakteristik curing kompon NR / CR (kode A, B, C, D, E). Rheologi dipelajari dengan menggunakan alat rheometer. Hasil penelitian menunjukkan bahwa tipe akselerator dan suhu vulkanisasi mempengaruhi waktu scorch, waktu optimum vulkanisasi dan laju vulkanisasi campuran NR/CR.

Kata kunci: akselerator, karet kloroprene, karakteristik curing, karet alam, waktu scorch

INTRODUCTION

Elastomer blends are being widely used for various applications in the rubber industry to generate optimum compromise in compound physical properties, processability and cost. A blend can propose a set of characteristics that can give it the potential of entering application area not possible with either of the elastomers comprising the blend (Ismail & Leong, 2001).

There have been many studies on rubber blending to improve product quality, namely synthetic rubber mixed with natural rubber (NR) to improve its properties. Mixing of one or several elastomers may improve the physical or chemical properties of the mixture. For example, blends of NR with choloprene rubber (CR) are noted for good weather resistance because NR fail from weather, ozone, oil, thermal properties and poor flame (Ramesan et al, 2005). Several studies have shown that synthetic rubber and natural rubber blends can improve mechanical properties such as ozone resistance (Indrajati & Sholeh, 2016).

In the vulcanization process, additives such as activators, fillers, accelerators, vulcanization materials, and softeners are needed. Fillers are classified into two, namely carbon black and non-black fillers such as silica. Carbon black (CB) is a filler that is widely used because of its nature as an amplifier (Mayasari & Yuniari, 2016b). This type of carbon black will affect the strength of vulcanizates, especially tensile strength and elastic modulus. Each type of CB contributes to different mechanical properties that are affected by surface area (Omnès et al., 2008). Besides CB, fillers can also come from clay groups, including kaolin, bentonite, and so on.

Characteristics of rubber products are controlled by the usage of fast-, moderate-, or slow-speed accelerators and three different vulcanization systems. Conventional vulcanization (CV) system has the highest sulfur to accelerator ratio, leading to the formation of predominantly polysulfide cross-link (Azar & Sen, 2017).

Accelerators play an important role in the vulcanization process of rubber. It is used to speed up the process, and in addition, accelerators affect the physical and chemical properties of vulcanisates (Alam et all., 2012). The use of two or more accelerators simultaneously is more advantageous for technological applications because the accelerator combination system shows higher vulcanization activity (synergism) than a single accelerator separately (Alam et al., 2012). The choice of accelerator must be appropriate to obtain good vulcanization properties because the accelerator gives a different response to each rubber.

Accelerators are generally organic compounds used in the compounding process to accelerate the vulcanization reaction of compounds by sulfur. According to chemical structure, accelerators are classified in to thioureas, thiazole, guanidines, sulfenamides, dithocarbamates, di- or polyamine, and thiuram (Table 1).

Table 1. Chemical Classes of Accelerators (Todeschini et al., 2014)

Chemical class	Chemical name	Abbre-viation
Thioureas	ethylenethiourea	ETU
	N,N'-diphenylthiourea	DPTU
Sulfenami-des	N-tert-butyl-2 benzothiazol-sulfenamide	TBBS
Guanidines	Diphenyl guanidine	DPG
	Di-o-toluylguanidine	DOTG
	N-cyclohexyl-2-benzothiazol-sulfenamide	CBS
Thiazoles	2,2-dithiobis benzothiazole	MBTS
	2-Mercaptobenzo thiazole	MBT
Dithiocarbamates	zinc bis(dibutyl dithiocarbamate)	ZDBC
	zinc bis(diethyl dithiocarbamate)	ZDEC
Thiurams	Tetramethylthiu-ram disulfide	TMTD
	Tetramethylthiu-ram monosulfide	TMTM
Di- or polyamine	hexamethylene diamine	HMDA
	hexamethylene tetraamine	HEXA

Accelerators can be used single, binary or more. Accelerators can act as primary accelerators and secondary accelerators. Primary accelerators show scorch delay (slow to delayed fast) and sec- ondary accelerators are scorchy (fast curing) (Sisanth et al, 2016). The Thiazole and Sulfenamide groups act as prime accelerators while Guanidine, Thiuram, and Dithiocarbamate groups are commonly used as secondary accelerators, to activate primary accelerators and to increase reaction speed.

Formela et al., (2015) investigated the effect of different types of vulcanization accelerators on reclaimed rubber. Authors attained optimum vulcanization time (tc_{90}) and cure rate index (CRI) of investigated materials significantly depended on the type of accelerator. Indrajati & Dewi (2019) studied the effect of accelerator pairs in natural rubber compounds. MBTS and CBS in combination with DPG are used as accelerator system with certain amount. The result of study showed that the elastic rheometric torques (M_L and M_H) were affected by the accelerator type and concentration.

CR are homopolymers of chloroprene. The polymer chains have an almost entirely *trans*-1-4-configuration (Ismail & Leong, 2001). CR is also cross-linked with metal oxides systems, based on magnesium oxide/zinc oxide (Sisanth et al, 2016). CR is used to increase oil and thermal resistance of NR. While the addition of NR to CR will increase elasticity and flexibility at low temperatures. Solubility is one of important factors in mixing two or more ingredients, since all materials should be mixed homogeneously to avoid uneven distribution between different phases. Differences in polarity can also increase interface voltage that can reduce mechanical properties (Zhang et al., 2008). To overcome this problem, it is necessary to provide the right compatibilisator or accelerator.

Curing characteristic of rubber compound is used to indicate the vulcanization reaction that expressed by torque-time curve from rheometer (Yuniari et al., 2016). Cure kinetics of rubber compound are measured by a variety of methods. Some of these methods are hardness, measuring tensile modulus, swelling methods, differential scanning calorimetry (DSC) analysis, stress relaxation measurements, chemical analysis which are often based on the determination of the rate of free sulfur disappearance, and measurements of different crosslink types but the common method in the rubber industry is based on rheometry because of practical uses (Fathurrohman et al., 2015). Study of free sulfur determination was used in the analysis of the vulcanization kinetics by Hasan et al., (2013b) which results showed that vulcanization kinetics of NR was influenced by vulcanization temperature, rubber mixing process and ingredients mixing sequence in rubber compounding.

Previous research on NR and CR blending have been done previously with *gebang* fiber and silica-based fly ash (Kongvasana et al., 2011). The results of the study showed that resistance to aging, oil, and ozone increased. The use of organomodified montmorillonite (OMMT) in the CR/NR mixture also gave good results of reversion resistance (Zhang et al., 2008). In 2017, Azar studied the effects of accelerators on network structure, cross bond density, resistance to aging from CR / NR (Azar & Sen, 2017). NR's blending ratio with CR is also known to provide different vulcanisate properties (Salleh et al., 2016).

In this research, rheometer method was used in the analysis of the curing characteristics on NR/CR blend with five types of commonly used vulcanization accelerators were used namely diphenyl guanidine (DPG), 2-mercaptobenzothiazol (MBT), N-tert-butyl-2-benzothiazyl sulphenamide (TBBS), ethylene thiourea (ETU), and tetramethyl thiuram monosulfide (TMTM).

MATERIAL AND METHOD

Material

The materials used in this study include natural rubber (NR) supplied by PTPN IX, synthetic rubber chloroprene (CR) Baypren 220, zinc oxide activator (ZnO) Indoxide supplied from Bratachem, MgO (magnesium oxide), stearic acid Rhein Chemie, parrafinic wax Antilux 654 A, carbon black (CB) N330 with particle size 26-30nm ex. OCI as filler, paraffinic oil from Indrasari as plasticizer, 6PPD ex.Starchem as an antioxidant, accelerator MBT, TBBS, ETU, TMTM and DPG (Shandong Shianxian) and sulfur from Miwon as vulcanization materials

Instrument

The tools used in the study include process aids and test equipment, including process equipment (laboratory two-roll mill), process aids (rheometer Moving Die Rheometer Gotech 3000 A, analytic balance, compound cutting knives). Rubber compound formulations are shown in Table 2.

Table 2. Rubber compound formulation

	Rubber compound (phr*)				
Material	**A**	**B**	**C**	**D**	**E**
CR	25	25	25	25	25
NR	75	75	75	75	75
Zinc Oxide	5	5	5	5	5
MgO	3	3	3	3	3
Stearic Acid	3	3	3	3	3
CB N330	50	50	50	50	50
Paraffinic Oil	5	5	5	5	5
Paraffinic Wax	0.5	0.5	0.5	0.5	0.5
6 PPD Vulkanox	5	5	5	5	5
DPG	2	0	0	0	0
MBT	0	2	0	0	0
TBBS	0	0	2	0	0
ETU	0	0	0	2	0
TMTM	0	0	0	0	2
Sulfur	2	2	2	2	2

*part per hundred rubber

Method

CR, NR, and additives were sequentially mixed in a two-roll mill until the rubber compound became plastic. The rubber compound was then conditioned on a conditioning room at 23 ± 2 ºC for 24 hours. After that, a rheometer test was carried out at 140, 150, and 160ºC. Data obtained from the test included maximum (M_H) and minimum torque (M_L), delta torque (M_H -M_L), scorch time (ts_2) and optimum vulcanization time (tc_{90}). Cure rate index (CRI) was calculated following a previously published equation (1) (Marković, et al., 2007)

$$CRI = \frac{100}{tc_{90}-ts_2} \qquad (1)$$

The maturation kinetics was used to predict the optimum ripening time through a kinetic model based on experimental results. In general, chemical reaction models are expressed in differential equations as presented in equation (2) (Mayasari & Yuniari, 2017):

$$\frac{d\alpha}{dt} = k\ (T).f(\alpha) \qquad (2)$$

where t is time, T is temperature and α is a conversion obtained from the rheometer data, calculated by equation (3) (Mayasari & Yuniari, 2017):

$$\alpha = \frac{M_t-M_L}{M_H-M_L} \qquad (3)$$

The Mt value used is a difference in torque of 25%up to 45% (Semsarzadeh et al., 2005). Reaction vulcanization is assumed to be a first-order reaction and proportional to the material fraction that is not cross-linked (1-α), then:

$$f(\alpha) = (1-\alpha) \qquad (4)$$

The substitution of equation (4) to equation (2) results in equation (5) (Mayasari & Yuniari, 2017):

$$\frac{d\alpha}{(1-\alpha)} = k(T).dt \qquad (5)$$

Integration of equation (5) produces:

$$ln\frac{1}{(1-\alpha)} = kt \qquad (6)$$

The substitution of equation (3) into the equation (6) results in equation (7) (Semsarzadeh et al., 2005):

$$ln\frac{M_H-M_L}{M_H-M_t} = kt \qquad (7)$$

From equation (7) a graph is generated and k is obtained which is a speed constant reaction.

RESULT AND DISCUSSION

Figure 1 and Figure 2 describe the relationship the torque changes (curing curve) during the MDR measurement and data from curing curve are presented in Table 3. It consist three regions that reflect the reaction stages taking place during vulcanization, i.e. induction period, curing period and over cure (Indrajati & Dewi, 2019) as depicted in Figure 1 and Figure 2.

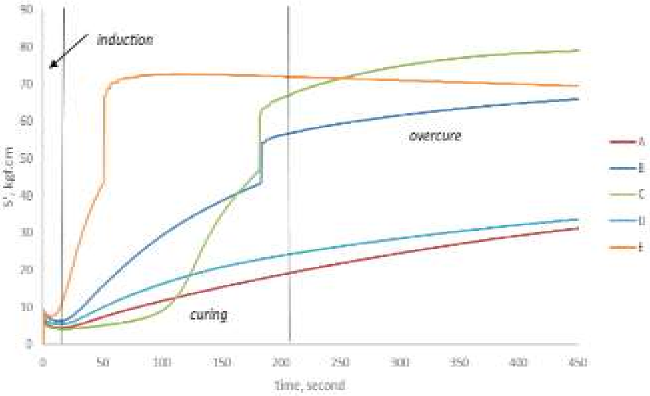

Figure 1. Curing curve NR/CR at 140℃

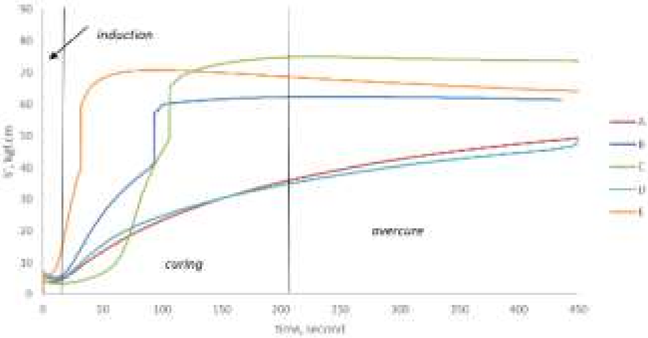

Figure 2. Curing curve NR/CR at 150℃

The induction period is the time when the vulcanization reaction has not been started yet. In this period, physical linkages are mostly formed as a result of the interaction between rubber and filler particles, and the chain entanglement as well (Indrajati & Dewi, 2019). Scorch time (ts_2) and minimum torque (M_L) are often used to characterize the induction period. Scorch time mark of the vulcanization onset. When the vulcanization temperature increased from (140ºC to 150ºC) then the scorch time decreased, the vulcanization reaction takes place immensely fast. The results are in accordance with Hasan et al. (2013a).

Next stage is the curing reaction period, during which the cross linking network starts and the stiffness of rubber are increased (Fathurrohman et al., 2015). The reaction occurs between rubber and sulfur molecules to form sulfide (mono-, di- or poli-) bonds (Mayasari & Yuniari, 2016a). The third region is the over cure period that may occur as equilibrium, reversion, or marching cure behaviors, according to the compound characteristics (Fathurrohman et al., 2015).

Characteristics of vulcanization of NR/CR composites at 140, 150, and 160℃ are presented in Table 3. Vulcanization temperature influenced the scorch time (ts_2), optimum vulcanization time (tc_{90}). Rubber compound E with TMTM as accelerator resulted in the fastest scorch time and optimum curing time, while C with TBBS as accelerator resulted in the longest scorch time. The type of used accelerator evidently influenced the scorch time (t_2) (Formela et al., 2015). This was due to the chemical nature of used accelerators. TBBS accelerated systems present two functions during vulcanization of rubber compounds. Firstly, it retard the vulcanization that increases the scorch time and has positive influence on safe processing of rubber compounds. Secondly, TBBS take effect with zinc oxide to form sulfuric complex that accelerates polysulfidic cross-links formation (Formela et al., 2015).

Rubber compound D with ETU as accelerator resulted in the longest optimum curing time. Scorch time is the time when the rubber can still be formed. The optimum time is recorded at the time when the rubber compound reaches maturation. Table 3. shows that the optimum curing time (tc_{90}) and scorch time (ts_2) decreased with increasing the temperature of vulcanization. In general, faster optimum time is preferred because it means lower energy is used during the rubber production. On the other hand, higher temperature (means higher energy) causes faster scorch time and curing time. Therefore, an optimum condition is worth to find (Kinasih et al., 2015).

Table 4 shows the experimental data of minimum torque (M_L), maximum torque (M_H), and delta torque at three different vulcanization temperature, obtained from the rheometry. Maximum torque for different accelerators shows a trend decrease with increasing temperature, may it cause the effectiveness at cross-linking bonds decreases by intramolecular cyclization of sulphurs (Semsarzadeh et al., 2005). In TBBS as accelerator provide the compound with the highest delta torque. ETU provide the compound with the lowest delta torque. Delta torque is the difference of the minimum torque (M_L) and the maximum torque (M_H). The delta torque related with the crosslink density of the rubber compound.

Table 3. Characteristics of vulcanization of NR/CR composite

vulcanizate	vulcanization temperature					
	140℃		150℃		160℃	
	ts_2 (s)	tc_{90} (s)	ts_2 (s)	tc_{90} (s)	ts_2 (s)	tc_{90} (s)
A	43	481	20	370	20	246
B	29	259	16	101	15	110
C	78	266	43	127	26	120
D	35	456	22	405	13	422
E	11	49	8	37	8	64

Table 4. Minimum torque, maximum torqoue, delta torque at 140℃, 150℃, 160℃

Vulcanizate	Vulcanization Temperature								
	140℃			150℃			160℃		
	ML kgf.cm	MH kgf.cm	delta torque kgf.cm	ML kgf.cm	MH kgf.cm	delta torque kgf.cm	ML kgf.cm	MH kgf.cm	delta torque kgf.cm
A	4.305	35.51	31.205	3.7	49.195	45.495	4.065	55.075	51.01
B	6.185	65.875	59.69	5.26	62.645	57.385	5.83	61.345	55.515
C	4.02	79.325	75.305	3.31	74.925	71.615	3.49	59.815	56.325
D	5.35	38.03	32.68	4.655	50.1	45.445	5.125	49.74	44.615
E	8.345	72.65	64.305	6.925	71.585	64.66	6.49	69.58	63.09

The cure rate index represents the speed of reaction during curing process. The cure rate index (CRI) can be calculated from equation (1) and shown in Table 5.

Table 5. Cure rate index (CRI)

vulcanizate	vulcanization temperature		
	140℃	150℃	160℃
A	0.228	0.286	0.442
B	0.435	1.176	1.053
C	0.532	1.190	1.064
D	0.238	0.261	0.244
E	2.632	3.448	1.786

Table 5 shows that the cure rate index commonly increases with the increasing of vulcanization temperature. Figure 3 shows the speed constant of the vulcanization reaction of the rubber NR/CR composite at 140, 150, and 160°C. Composite NR/CR with DPG accelerator (A) has the lowest rate constant when compared to other NR/CR composites. Composite NR/CR with accelerator TMTM (E) has the highest speed constant reaction at all vulcanization temperatures. The higher vulcanization temperature, the higher speed constant reaction.

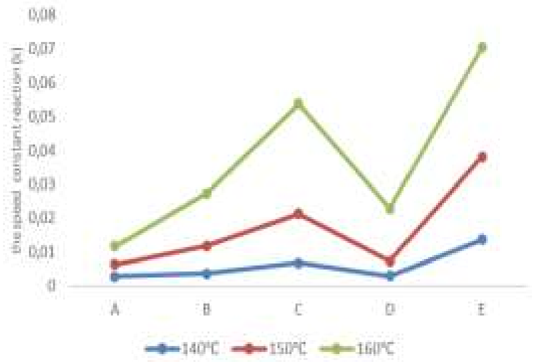

Figure 3. Speed constant of the vulcanization reaction of composite NR/CR

CONCLUSION

We have studied the curing characteristic of NR/CR-based rubber compounds using five different type of accelerators namely diphenyl guanidine (DPG), 2-mercaptobenzothiazol (MBT), N-tert-butyl-2-benzothiazyl sulphenamide (TBBS), ethylene thiourea (ETU), and tetramethyl thiuram monosulfide (TMTM). Rheology was studied with a rheometer. Research results show that type of used accelerator and vulcanization temperature influenced scorch time (ts_2), optimum vulcanization time (tc_{90}) and cure rate index (CRI) of NR/CR rubber blends. The speed constant reaction increases with the increase in vulcanization temperature.

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