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Effect of vulcanization system and carbon black on mechanical and swelling properties of EPDM blends

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ABSTRACT

EPDM (Ethylene propylene diene monomer) is one of synthetic rubber that widely used in automotive. It must be vulcanized and added by other materials before used. The aim of this study is to investigate the effect of vulcanization system and the addition of carbon black (CB) to the mechanical properties and swelling characteristic of EPDM. This research used three vulcanization system: conventional vulcanization (CV), efficient vulcanization (EV), and semi-efficient vulcanization (SEV) with the variation of carbon black 50, 60, and 70 phr (per hundred resin). This research showed that EV system resulted faster vulcanization time and lower delta torque than SEV and CV systems. This system also performed the highest tensile strength, elongation, and tear strength, while SEV system resulted the highest hardness. Furthermore, the conventional vulcanization system resulted the lowest swelling index.

Keywords: vulcanization system, EPDM, efficient, semi-efficient, conventional.

INTRODUCTION

Ethylene-Propylene-Diene-Rubber (EPDM) is a type of synthetic rubber which has a good resistance to chemical, weathering, and aging. EPDM is widely used in automotive. EPDM is obtained by polymerizing ethylene and propylene with a little amount of a diene. Sulphur vulcanization in EPDM allowed by the diene-monomers in the main chain (Dijkhuis *et al.*, 2009; Nabil *et al.*, 2013).

Sulphur is one of vulcanizing agent and plays an important role in the process of vulcanization. Sulphur vulcanization systems are classified as efficient (EV), semi-efficient (SEV), and conventional (CV). Efficient vulcanization system (EV) is characterized by a high ratio of accelerators to sulphur (> 2.5) which produces a high percentage of monosulfidic in the formation of the crosslink. Conventional vulcanization system (CV) has a low ratio of accelerators to sulphur (0.1 to 0.6), which produces a high percentage of polysulfidic, while the semi-efficient vulcanization system (SEV) is in between of them, which is characterized by the moderate ratio of accelerators to sulphur (0.7 to 2.5) (Dijkhuis *et al.,* 2009). Yuniari *et al.* (2013) found that the different sulphur loading gave different result for the vulcanizate. Some vulcanization systems; conventional (CV), efficient (EV) also affected on the process of thermal degradation (Yahya *et al.*, 2011).

Some additional materials such as filler, accelerator, vulcanization agent, activator, antioxidant, and softener are added during the vulcanization process to improve the properties of the vulcanizate. Carbon black (CB), the most widely used filler in rubber industry is a reinforcing filler. It is applied in rubber to improve strength and mechanical properties of the vulcanizates. The surface of CB can absorb the rubber molecules, it can increase the formation of bound rubber (Hasan *et al.*, 2012). The formation of crosslink between EPDM and carbon black depend on the type and amount of carbon black. The amount of filler affect the tensile strength and the curing characteristics of elastomer (Litinov *et al.*, 2011; Formela & Haponiuk, 2014). The relationship between the crosslink density, network structure and mechanical properties of CB reinforced EPDM had been investigated by Dijkhuis *et al.* (2009).

Accelerator is used to accelerate the vulcanization process and improve the properties of the vulcanizate. Accelerator can be used a single or binary system. However, the usage of binary accelerator is preferable because the combination system of accelerator showed higher activity than a single accelerator separately (Indrajati & Sholeh, 2014).

This study will evaluate the effect of the vulcanization system (CV, SEV, EV) and CB addition on EPDM in order to determine the best vulcanization system and CB loading to produce the desired product.

MATERIALS AND METHODS

Materials

Synthetic rubber EPDM Keltan 4551 A was used in this study. The additive materials used were 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 42 M as activators, tetramethylthiuram disulphide (TMTD) and mercaptobenzothiazole (MBT) as accelerators, and sulphur Ex. Miwon as a vulcanization agent. The formulation used in this study are presented in Table 1.

Methods

Equipment used in this study were two roll mills (modified with a capacity of 2 kg), Toyoseiki A-652 200 500 hydraulic press, Kao Tieh tensile strength tester, Gotech 3000A moving die rheometer (MDR), and Tecklock hardness tester.

Compounds were made by mixed the materials using two roll mills equipment with time taken and sequence show on Table 2.

After homogeneous blend was reached, the compounds were taken out from two roll mills then cooled and stored in conditions 23±2°C for 24 h. The compounds were vulcanized by compression molding in 170ºC and 150 kg/cm², the duration of vulcanization was determined by rheometer.

The cure characteristics were obtained using a rheometer, which was used to determine the scorch time (ts_2), cure time (t_{90}), cure rate index (CRI), maximum torque (mH), minimum torque (mL). Cure rate index (CRI) calculated based on the difference of the optimum time with scorch time according to equation (1). Maximum torque and minimum torque are used to calculate delta torque by equation (2)

$$CRI=100/(t_{90}-ts_2) \quad (1)$$

$$\text{Delta torque} = mH-mL \quad (2)$$

Tests conducted on vulcanizates were tensile strength and elongation at break according to ISO 37, hardness according to ISO 48, and tear strength according to ISO 34.

Swelling test was performed for 72 h at 23±2°C according to ISO 1817. The change in mass was calculated by equation (3).

$$\text{Swelling index (\%)} = [(W_1-W_0)/W_0] \times 100 \quad (3)$$

Where W_1 is the mass of test piece after swelling, W_0 is the mass of test piece before swelling.

Table 1. Formulation of rubber vulcanizates with various vulcanization systems and carbon black loading.

Materials	EV			SEV			CV		
	ET1	ET2	ET3	ST1	ST2	ST3	CT1	CT2	CT3
	phr	phr	phr	phr	phr	phr	phr	phr	phr
EPDM	100	100	100	100	100	100	100	100	100
Carbon black (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	0.5	0.5	0.5
Sulphur	0.8	0.8	0.8	1.7	1.7	1.7	2.5	2.5	2.5

Table 2. Time taken and sequence of EPDM vulcanizates.

Ingredients	Time (approximately), min
EPDM	5
ZnO	4
Stearic acid	4
Carbon black + paraffinic oil	9
TMQ	3
Paraffin wax	2
TMTD and MBT	2
Sulphur	3
Total	32

RESULTS AND DISCUSSION

Curing Characteristics

The important parameters of the vulcanization process such as the optimum time (t_{90}), scorch time (ts_2), cure rate index (CRI), and torque of the vulcanizate can be known from the rheometer. The optimum time (t_{90}) is the time to cure vulcanizate 90%. Scorch time (ts_2) is an indicator of the processing safety. Curing characteristics of vulcanizates are presented in Table 3.

The fastest optimum vulcanization time (t_{90}) and the highest CRI have resulted from EV vulcanization system, then SEV and CV. These results are consistent with the research conducted by Minnath *et al.* (2011), the increasing of CRI is proportional to the decreasing of vulcanization reaction time. This is because the EV system has 2.5 phr ratio accelerator to sulphur, which contains at least 0.8 phr sulphur and more accelerator. Thus, the time required for the formation of crosslink between EPDM with sulphur become short, so that the curing time is the fastest. Then, the SEV vulcanization system with an amount of sulphur as 1.7 phr, and CV vulcanization system with an amount of sulphur as 2.5 phr. The increasing amount of sulphur loading increasing the time needed to form the crosslink. Table 2 shows that the optimum time will increase with the increasing of CB content. This phenomena possibly state that the more CB added, the more time was needed to absorb the rubber molecules to its surface.

Fig. 1 shows that the EV system gives the lowest delta torque, then SEV and CV. According to the research conducted by Dijkhuis *et al.* (2009), increasing the amount of CB proportional to the increasing of the delta torque. The density of crosslinking increase with the increasing of the number of CB, which is the bonding between polymer with CB can increase the torque (Li *et al.*, 2008). Torque is the amount of force needed in compounding process. Therefore, the delta torque would be proportionate with the curing time, the amount of sulphur and the amount of CB addition.

Table 3. Curing characteristics of EPDM vulcanizates.

Code	ts_2, s	t_{90}, s	CRI, s^{-1}
EV 50 phr	36	265	0.44
EV 60 phr	33	302	0.37
EV 70 phr	38	307	0.37
SEV 50 phr	31	381	0.29
SEV 60 phr	28	436	0.24
SEV 70 phr	27	422	0.25
CV 50 phr	32	1036	0.10
CV 60 phr	36	1591	0.06
CV 70 phr	36	1742	0.06

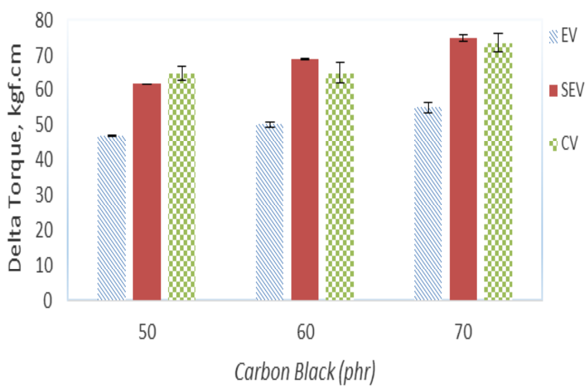

Fig. 1. Effect of vulcanization systems and carbon black on torque.

Mechanical Properties of EPDM Vulcanizate

The mechanical properties of the vulcanizate are very important to be known because it is associated with the quality of rubber products. Mechanical properties are presented in Fig. 2-6.

Hardness of EPDM vulcanizate

Hardness is one of the requirements needed in the manufacture of engineering products. Hardness of the vulcanizate depends on the hardness of components (Yuniari *et al.*, 2013). Fig. 2 shows the minimum hardness obtained from the EV vulcanization system. While the results of SEV and CV vulcanization system have not much difference. The previous study by Dijkhuis *et al.* (2009) got that the hardness from EV lower than SEV and CV. Hardness increases with the increasing amount of crosslink. Yuniari *et al.* (2013) also got the same results, hardness increases with the increasing amount of sulphur. This happens because the high density crosslink showed the tightly of that material molecules so that it more rigid and hard.

The vulcanizate's hardness increases with the increasing of CB loading. The increasing of hardness possibly due to CB as a reinforcing filler (strengthening the mechanical properties). The surface area of CB takes effect on hardness because its outer surface allows the bond formation of and keep the bound not moving. The increasing of CB make the space on the rubber become full so that the rubber vulcanizate becomes stiffer (Hasan *et al.*, 2011).

Tensile strength of EPDM vulcanizate

Tensile strength is statically mechanical testing by means of samples drawn by the load. The tensile strength of vulcanizate is presented in Fig. 3. The lowest tensile strength has resulted from CV vulcanization system, then SEV and then EV, as the previous study conducted by Dijkhuis *et al.* (2009). Tensile strength increases with the increasing of the crosslink density, but at an optimum level of filler, it will decrease (Dijkhuis *et al.*, 2009; Li *et al.*, 2008). Vulcanization system and the type of rubber determine the formation of the crosslink density. High crosslink density indicates that the material is tight and rigid, so the elasticity and tensile strength decrease.

Tensile strength increases with the addition of CB, but at some point, it will decrease. Increasing the number of bounds between the CB and the rubber molecules can increase the tensile strength (Li *et al.*, 2008) and the increasing of hardness can decrease the tensile strength of vulcanizate (Hasan *et al.*, 2011).

Elongation of EPDM vulcanizate

Elongation is interpreted as the resistance of material to elastic deformation (Yuniari *et al.*, 2013). Fig. 4 shows that the lowest elongation has resulted from CV vulcanization system. These results are consistent with the previous study conducted by Dijkhuis *et al.* (2009). The elongation of EPDM vulcanizates proportionate with the tensile strength. Elongation decreases with the increasing of crosslink density because the greater amount of crosslink make the material more difficult to be stretched (Dijkhuis *et al.*, 2009). EV vulcanization system produces higher elongation at break than SEV and CV. EV vulcanization system with the high amount of accelerator result more monosulfidic bonding (Ahmed *et al.*, 2012).

Elongation decreases with the addition of

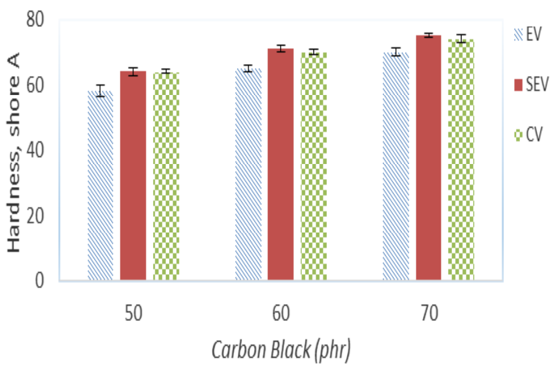

Fig. 2. Effect of vulcanization system and carbon black on hardness.

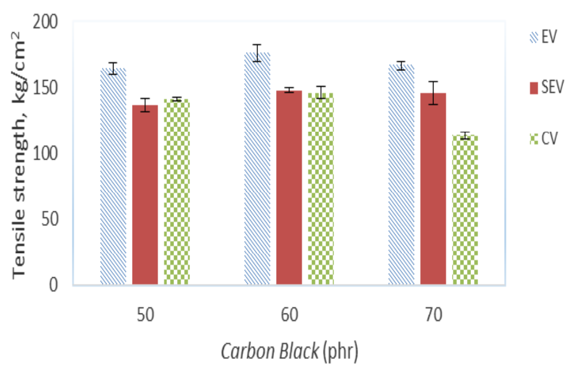

Fig. 3. Effect of vulcanization systems and carbon black on tensile strength.

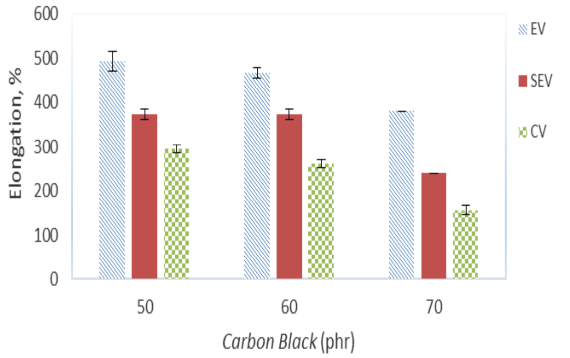

Fig. 4. Effect of vulcanization systems and carbon black on elongation of EPDM.

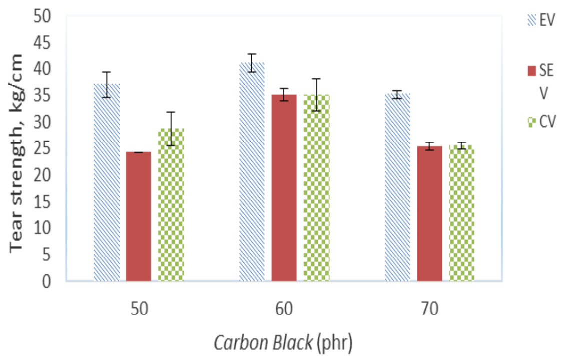

Fig. 5. Effect of vulcanization systems and carbon black addition on tear strength.

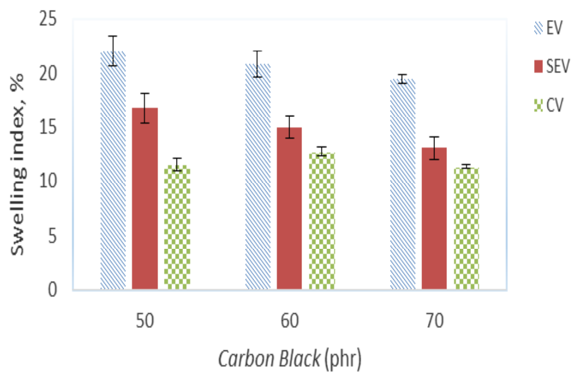

Fig. 6. Effect of vulcanization systems and carbon black on swelling index.

CB. The amount of CB makes vulcanizates stiffer so that the elasticity and tensile strength decrease (Li *et al.*, 2008).

Tear Strength of EPDM Vulcanizate

Tear strength of the vulcanizate proportionate with the elongation properties. Fig. 5 shows the highest tear strength has resulted from EV vulcanization system. Generally, tear strength is correlated with the amount of polysulfidic crosslink, while monosulfidic crosslink produces more brittle vulcanization. This study give same result with the studied by Dijkhuis *et al.* (2009) where the polysulfidic crosslink didn't show a big effect on the material tear strength.

Tear strength increases from the addition of 50 phr to 60 phr and then decreases at the addition of 70 phr of CB. The increasing of stiffness makes the vulcanizate more difficult to be ripped so that the tear strength increases (Hasan *et al.,* 2011). However, at a certain point, vulcanizate will be fatigue, so that it will easy to be ripped.

Swelling characteristics of EPDM vulcanizate

Swelling occurs because of the expansion of polymer and the availability of more free volume to facilitate the mass transfer of solvent (Yuniari & Sarengat, 2013).

Vulcanization system is closely related to the formation of crosslink density. Fig. 6 shows that the EV vulcanization system produces higher swelling index than the SEV and CV vulcanization system. Swelling index is correlated with the crosslink density, the swelling indeks increases with the decreasing of the crosslink density. This condition due to the process of vulcanization forming polar bond that has an impact on increasing the resistance of swelling (Yuniari *et al.*, 2013). Crosslink hamper the elongation of rubber induced by swelling. As a result, the diffusion of the solvent into the gap between the molecules becomes difficult, thus decrease the percentage of swelling and prevent the occurrence of the chain termination (Indrajati *et al.*, 2012).

CONCLUSIONS

This research showed that EV, SEV, and CV vulcanization system performed in a blend of EPDM give varying results on the cure characteristics, mechanical properties and swelling characteristics. EV vulcanization system gives the faster vulcanization time (265 s) and lower delta torque (46.93 kgf.cm) than SEV and CV vulcanization systems. The highest mechanical properties of tensile strength (176.19 kg/cm^2), elongation (493.33 %) and tear strength (41.12 kg/cm) were obtained by EV vulcanization system. While the highest hardness (75 shore A) was obtained by SEV vulcanization system. The lowest swelling index (11.36 %) was achieved by CV vulcanization system. In general, EV vulcanization system is better and more suitable than SEV and CV for EPDM. However, if the vulcanizates require high resistance to oil, CV is the most appropriate vulcanization system.

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