Effect of natural zeolite as substrate filler on the properties of NBR/EPDM blend

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ABSTRACT

The NBR/EPDM blend has great ozone, oil, and heat resistance. Carbon black is the most common used filler material for rubber goods. But, it is less environmentally friendly and less healthy friendly. In this study, it would be studied the use of natural zeolite as a substitute for the filler. This blend was carried out by a two-roll mill and tested by rheometer and tensile strength tester. From the research that has been done, it was known that vulcanizate with carbon black was better than all of the vulcanizate using zeolite as filler substitute. Vulcanizate with CB provided the fastest curing time, the fastest reaction speed and also the best mechanical properties. Vulcanization with the 10 phr zeolite gives the optimum curing time and the best mechanical properties compared to the substitution of other fillers. This shows that 10 phr zeolite (16.7%) can be a suitable filling material for NBR/EPDM blend.

Keywords: NBR/EPDM, zeolite, filler, natural.

INTRODUCTION

Synthetic rubber is derived from petroleum. It is made to overcome the weaknesses of natural rubber. Nitrile butadiene rubber (NBR) has good solvent and oil resistance properties but has poor heat and ozone resistance. NBR is synthetic rubber containing acrylonitrile (ACN) and butadiene which determines its polarity and also the heat and oil resistance (Jovanović *et al.*, 2009; Indrajati *et al.*, 2012; Kantala *et al.*, 2009; Jovanović *et al.*, 2013). Ethylene diene monomer butadiene rubber (EPDM) is a nonpolar synthetic rubber that has ethylidene-2-norbornene (ENB) content. The higher the ENB content, the more sensitive EPDM to thermal oxidation, and the easier to degrade. EPDM has good ozone and heat resistance but is less resistant to nonpolar solvents (Jovanović *et al.*, 2013; Ning *et al.*, 2014; Mayasari & Yuniari, 2016). Nowadays, researchers try to blend two or more rubber to get excellent rubber properties. The blend of rubber can improve the weakness of one rubber by the excellence of another rubber. The blend of NBR and EPDM can produce composites with better heat, oil, and ozone resistance than NBR or EPDM composites separately as previous research by Jovanović *et al.* (2013).

Carbon black (CB) is commonly used as filler in making rubber goods because it has good properties and cheap. CB can improve the mechanical properties of rubber goods (Jovanović *et al.*, 2013). However, various types of pollution arise in the process of making CB, which can be a problem for the environment. In addition, CB dust can

cause serious health impact. Therefore, nowadays, many efforts are attempted to substitute CB such as activated carbon (Marlina *et al.*, 2014), clay (De Sousa *et al.*, 2011), silica (Ahmed *et al.*, 2013), and zeolite (Pajarito *et al.*, 2017).

Zeolite is an alumina-silicate-hydrate mineral that has a structure in three dimensions and contains alkaline-earth cation. It can be derived from natural and synthetic ingredients. Zeolites in nature are generally pure, easily available and inexpensive. It is widely used in the environmental, petroleum, chemical, and agricultural industries (Rianto *et al.*, 2012; Wustoni *et al.*, 2011; Fang *et al.*, 2015). Nowadays, the zeolite is widely developed and investigated as a filler, such as for NR/NBR blend (Siriyong & Keawwattana, 2012), NBR (Petrova *et al.*, 2015), NR (Pajarito *et al.*, 2017). Zeolite can be used directly or with activation, both physically (Wiyantoko *et al.*, 2017) and chemically (Aidha, 2013; Utami, 2017). It has good thermal resistance, high surface area and has the ability to absorb polymers. Because zeolite is a kind of silica (inorganic silica), so it can be used as rubber filler (Fang *et al.*, 2015). However, research on the NBR/EPDM rubber blend with zeolite as fillers is still limited, especially using modified zeolite.

In this present study, zeolite was combined with CB as filler in the NBR/EPDM blends. The effect of zeolite substitution was studied in the terms of the cure characteristics and mechanical properties of the NBR/EPDM blend. These information are valuable in

determining the suitable filler for NBR/EPDM blend.

MATERIALS AND METHODS

Materials

The materials used in this study were NBR (ACN 48.5%, Krynac 4975 F), EPDM (ENB 8.7%, Keltan 4551 A), carbon black N330 High Abrasion Furnace (HAF) (OCI, Korea), and natural zeolite from local market in Klaten, Indonesia as filler, paraffinic oil (Indrasari), paraffin wax (Antilux 654 A) as antioxidant, stearic acid Aflux 42 M (Rhein Chemie), and zinc oxide (ZnO, Indoxide) as activator, 6PPD (Starchem) as antiozonant, 2,2'-dithiobis(benzothiazole) (MBTS) Kemai as accelerator, and sulfur (Miwon) as vulcanizing agent.

Methods

Modification of zeolite

Zeolite was modified by activated the natural zeolite physically by ground it in the mortar, then it was heated in an oven 100 °C for 6 hours.

Rubber blends preparation

NBR, EPDM, and additives were weighed according to the formulation in Table 1 and were blended using a two-roll mill. The NBR/EPDM compound were conditioned for 24 hours at room temperature. The compounds were then tested with a rheometer MDR Gotech 3000 A to determine the curing time of the compound and it was vulcanized by hydraulic press according to the time of the test results from the rheometer. The filler material was varied by 100% of CB, 91.2% of CB (5 phr zeolite), and 83.3% of CB (10 phr zeolite) for both unmodified zeolite and modified zeolite.

Curing characteristics

The curing characteristics of NBR/EPDM blend can be studied from rheometer data. The compounds were tested by rheometer Gotech M-3000A in 160 °C within fixed angle and frequency of 3 deg. and 100 cps, respectively. The elastic torque (S'), viscous torque (S''), scorch time (ts_2), and optimum curing time (tc_{90}) were obtained. From these data, the cure rate index of compound can be studied. Cure rate index (CRI) can be calculated with equation (1).

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

The curing kinetics of NBR/EPDM compound also can be seen from the results of the rheometer test. The rate constant (k) can be calculated by equation (2) as in the previous study (Yuniari *et al.*, 2016)

$$\ln \frac{(M_H - M_L)}{(M_H - M_t)} = kt \quad (2)$$

The rate constant is obtained from the plot results from $\ln(M_H - M_t)$ results in a first order curing reaction which is indicated by a straight line.

Mechanical properties

The mechanical properties of the NBR/EPDM blend were studied using the tensile strength tester Kao Tieh to observe the tensile strength, elongation of the break, and tear strength.

RESULTS AND DISCUSSION

Curing Characteristics

The curing process is an important stage that comes at the final stage in making rubber goods. At this stage, rubber compounds are heated within certain time, curing agents work onto the rubber molecular chains and crosslink one chain to another and form a network at the final. Heat is transferred through the surface into rubber material to become a strong elastic material (Jovanović *et al.*, 2013).

The curing curve of the NBR/EPDM compound is shown in Figure 1. On this curve, it is already known that the curing process of the compound is divided into 3 stages, i.e. induction period, curing and overcure. Induction period is the initial stage, in which no vulcanization reaction takes place. Crosslinks are mainly formed from interaction between rubber and filler, or often called by physical crosslink. In this period, rubber compound should have better flow properties because it must fill the mold cavities within short time. Thus, the physical crosslink will play important role in compound flow characteristic. Higher physical crosslink hinders the compound to flow. The next phase is the curing phase in which vulcanization reaction takes place and crosslink increase rapidly. The rubber compound becomes harder and elastic. The last phase is overcure or the maturation phase of resulted crosslinks with prolong heating. Rubber compound responds differently with prolong heating after curing phase, namely reversion, equilibrium, and marching. These phenomena depends on the type of accelerator and sulphur ratio in the formulation. Reversion occurs when crosslinking decrease dramatically with the prolong heating after the curing phase. Equilibrium is indicated by the stable crosslink with prolong heating, and the marching is marked by increasing crosslinks over prolong heating (Leroy *et al.*, 2013; Indrajati *et al.*, 2014; Karaağaç *et al.*, 2009). In the induction phase, addition of zeolite does not influence the graph. But in the curing phase, the higher addition of zeolite, the lower torque. The lower line from addition of 10 phr zeolite shows the lower crosslink happened. In the overcure phase, the addition of zeolite does not affect the graph. All compounds show the marching phenomena.

Scorch time (ts_2) gives a sign for the end of the induction phase. It means that at $t > ts_2$, the vulcanization reaction takes place and crosslinks start to form. When compound reach scorch time, it will nearly stop to flow. Therefore, scorch time is often related to the scorch safety in which a safe time span for the compound before its molecules chain start to crosslink. The optimum curing time (tc_{90}) is the time needed to achieve the desired properties of final rubber goods. The optimum curing

Table 1. Formulations of NBR/EPDM composites.

Materials	NEZ0	NEZ 5	NEZ 5M	NEZ 10	NEZ 10M
NBR	50	50	50	50	50
EPDM	50	50	50	50	50
HAF CB N330	60	55	55	50	50
Zeolite	0	5	0	10	0
Modified zeolite	0	0	5	0	10
Zinc Oxide	5	5	5	5	5
Stearic acid	1	1	1	1	1
Paraffinic oil	2	2	2	2	2
Paraffinic Wax	0.5	0.5	0.5	0.5	0.5
6 PPD Vulkanox	5	5	5	5	5
MBTS	1.5	1.5	1.5	1.5	1.5
Phenolic resin	1	1	1	1	1
Sulfur	1.5	1.5	1.5	1.5	1.5

time is taken when the compound is 90% mature. Because if we use t_{c100} , we need extra energy thus higher cost. And, we give some time span to the rubber goods before they use (during storage they will mature slowly by the heat). So, when they are applied, they are in very good state. Figure 2 depicts the scorch and optimum curing time of the blends. It is clearly seen (Figure 2a) that 5 phr zeolite gives the longest scorch times either modified or unmodified. Further addition of zeolite (10 phr) has markedly reduced scorch time for both types of zeolite. Generally, the addition of zeolite rises the optimum cure time (t_{c90}) and modification of zeolite does not affect it, as seen on Figure 2b. This probably deals with the nature of silica, the main substance presented on zeolite that tends to

reduce the cure rate of rubber. Silica absorbs accelerators so that their amount are reduced and lowers the cure rate. While the curing time with 100% of CB gives the fastest time (326 seconds) compared to the compound with CB and zeolite fillers. The addition of 10 phr zeolite without modification gives the lowest optimum curing time (341 seconds) compared to the substitution of other fillers. This can be affected by material compatibility. Modification of zeolite does not show an effect on the scorch time and optimum curing time. The addition of 5 phr zeolite increases the scorch time but 10 phr zeolite does not affect the scorch time. The addition of 5 phr zeolite is more suitable than 10 phr zeolite.

Crosslinking in rubber can be monitored through

Figure 1. Curing curve of NBR/EPDM compound.

Figure 2. Scorch time (a) and optimum curing time (b) of NBR/EPDM compound.

the rheometer torques changes. Crosslink formation stiffen the compound, then increase the torque. Minimum torque (ML) is a rough description of compound viscosity and related to the physical crosslinking. High ML will give negative impact to the compound during processing since it has high viscosity that leads to a slow flow (Indrajati *et al.*, 2014). ML of the blends is comparable, thus it can be concluded that incorporation of zeolite does not change compound viscosity. The highest crosslink numbers formed during curing phase is monitored through the maximum elastic torque (MH). The addition of 5 phr zeolite, both modified and unmodified, results in comparable crosslink numbers, but further addition of zeolite (10 phr) tends to reduce it. Modification of zeolite does not give significant effect to the crosslink. Crosslink density of rubber is often measured from the torque delta (MH-ML). The higher the delta MH and ML, the more crosslinking is formed (Nabil *et al.*, 2013). It is clearly seen on Table 2 that incorporation of zeolite in the formulation does not result in an increase of crosslink density. Moreover, 10 phr zeolite tends to decrease the crosslink density to certain level. This is probably related to the nature of silica that presents in higher amount in zeolite. Silica is known to retard the cure by absorbing the accelerator. Thus, it reduces the amount of accelerator involved in the curing phase and leads to a low crosslink density formation.

From the rheometer data, the minimum torque value (ML) and maximum torque value (MH) of the viscous element (S'') and an elastic element (S') of the rubber material are known. Rubber has viscoelastic properties whose ratio is represented by $\tan \delta$ (damping factor). Table 2 shows that $\tan \delta$ MH is inversely proportional to delta torque. The higher the $\tan \delta$ MH, the less crosslinking is formed (Nabil *et al.*, 2013). The viscoelastic curve of the NBR/EPDM compound is shown in Figure 3. Figure 3 shows that all compounds have an elastic area (S') larger than the viscous (S'') region, this illustrates that the compound has high viscosity.

The cure rate index and the rate constant of curing can be seen from the rheometer test results. The curing

rate index (CRI) shows the speed of the cure of compound which can be calculated from equation (1). While the reaction kinetics can be illustrated by the constant rate calculated from equation (2). From equations (1) and (2), the CRI values and constants rate are shown in Table 3.

From Table 3, it is known that CRI is directly proportional to the constant rate. The higher CRI, the faster vulcanization speed, so the time needed for curing is low. High constant rate indicates that the rubber matrix and filler material are easier to react. In Table 3, it is known that NEZ 0 (60 phr CB), composite with all of the carbon black as filler, gives the highest constant rate compared to compounds with zeolite as substitute filler. The compound with 5 phr modified zeolite gives higher reaction speed than 5 phr unmodified zeolite, while the compound with 10 phr unmodified zeolite gives a slightly higher constant rate than modified zeolite. It may happen because the physical treatment given to zeolite does not affect the bond between zeolite and the rubber matrix.

Mechanical Properties

The rubber compounds with formulation given in Table 1 are then vulcanized to produce NBR/EPDM composites. The composites are then tested to determine their mechanical properties, including tensile strength, elongation, and tear strength. The mechanical properties of NBR/EPDM composites are shown in Figure 4.

From Figure 4, it is known that CB, as filler, provides the best mechanical properties, both from tensile strength, elongation, and tear strength. Carbon black can be easily dispersed into the rubber matrix so that composite has high mechanical property (Jovanović *et al.*, 2013). The high physical properties of the composite with 100% of CB filler is in accordance with the rheometer results which indicate that 100% of CB provides the highest delta torque that correlates with its mechanical properties (Alam *et al.*, 2014). Zeolite as a substitute for filler does not provide significantly different results between 5 phr and 10 phr zeolite for tensile strength. Whereas, 10 phr unmodified zeolite gives the highest elongation and tear strength. This

Figure 3. $\tan \delta$ curve of NBR/EPDM compound.

Table 2. Rheometer torques and tan delta of NBR/EPDM blends.

Compound ID	S'MH kgf.cm	S'ML kgf.cm	S''MH kgf.cm	S''ML kgf.cm	tan δ (MH)	tan δ (ML)	S'(MH-ML) kgf.cm
NEZ 0	45.09	7.74	13.40	6.62	0.29	0.86	37.35
NEZ 5	45.10	8.08	12.33	6.97	0.27	0.86	37.02
NEZ 5M	44.85	7.66	12.63	7.12	0.28	0.93	37.20
NEZ 10	37.20	6.50	11.53	6.18	0.31	0.95	30.70
NEZ 10M	36.93	7.44	11.95	6.75	0.32	0.91	29.49

Table 3. Results of the maturation velocity index calculation and reaction speed constants.

Composite	CRI	Constant rate, k (s ⁻¹)
NEZ 0	0.35	0.0118
NEZ 5	0.30	0.0079
NEZ 5M	0.31	0.0080
NEZ 10	0.33	0.0084
NEZ 10M	0.28	0.0073

is in accordance with previous studies which found that CB substitution with 8 phr zeolite produced the best tensile strength (Fang *et al.*, 2015). The modification of zeolite which does not show an enhancement of the mechanical properties is possible because physical modification just minimizes the size but does not makes a better bond

between zeolite and the rubber matrix. Modifications to zeolite are expected not only to enlarge the area but also to increase the interaction between zeolite and rubber. So that chemical modification is needed to improve zeolite as filler.

Figure 4. Mechanical properties of NBR/EPDM composite (a) tensile strength, (b) elongation at break, (c) tear strength.

CONCLUSIONS

From the research that has been done, it is known that carbon black as filler gives better properties than carbon black substitute by zeolite. Compound with 100% of CB provides the fastest curing time (326 seconds), the highest curing rate index (0.35), the highest constant rate (0.0118 s^{-1}), and also the best mechanical properties (tensile strength 103.3 kg/cm^2 , elongation 170%, and tear strength 37.9 kg/cm). Compound with substitute 10 phr zeolite (16.7%) gives the higher optimum curing time (342 seconds), the higher cure rate index (0.33), the higher constant rate (0.0084 s^{-1}), and also higher mechanical properties (tensile strength 65.5 kg/cm^2 , elongation 131%, and tear strength 25 kg/cm) than other substitution fillers. Physical modification of zeolite does not give a significant effect on rheology and mechanical properties of NBR/EPDM compound. The substitution of 10 phr zeolite (13.4%) can be a suitable filler for NBR/EPDM blend. However, research on modification of zeolite as a filler material needs to be continued to obtain filler properties that are closer to carbon black.

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