The Blending of EPDM/NR with Maleic Anhydride as Compatibilizer: Comparing the Effect of Accelerators on Cure Characteristic and Mechanical Properties

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Abstract: The blending of ethylene propylene diene monomer/natural rubber (EPDM/NR) needs much attention because of their incompatibility. In this work, the influence of accelerator type on cure characteristics and mechanical properties of 60/40 EPDM/NR blend was investigated. The compounds were prepared by controlling the migration of curative and using maleic anhydride as the compatibilizer. Three types of accelerators were studied: 2,2'-dithiobis(benzothiazole) (MBTS), the combination of MBTS and tetramethyl thiuram disulfide (TMTD), and n-tert-butyl-2-benzothiazolesulfenamide (TBBS). The cure characteristic, mechanical properties, and morphology of the composites had been investigated by rheometer, tensile testing machine, hardness durometer and scanning electron microscope (SEM). Blending of EPDM/NR with various accelerator gave different composite characteristics. MBTS, used in single or binary accelerator system, provided good mechanical properties. TBBS gave the longest scorch time, the lowest crosslink density and poor mechanical properties, except tear strength. Binary accelerator, MBTS/TMTD, provided the lowest processing time and the highest cure rate, but not significantly different from MBTS. Binary accelerator gives the best aging resistance and compatibility blend. These results correspond well with SEM micrograph. From the study, it can be concluded that binary accelerator system was the proper accelerator for EPDM/NR blend.

Keywords: ethylene propylene diene monomer (EPDM); natural rubber (NR); accelerator; compatibilizer; maleic anhydride

INTRODUCTION

Nowadays, study about the blending of two polymers or more is interesting. The blends are developed to meet the desired product. Ethylene Propylene Diene Rubber (EPDM) is a synthetic rubber having good ozone and aging resistance (because its unsaturation sites are in the side chain and not in the backbone), good chemical and weathering resistance, and has a low specific gravity. The most commonly used diene–monomer is 5-ethylidene-2-norbornene (ENB). The commonly used of EPDM are in automotive, building and construction, cable insulation and jacketing [1-3]. However, EPDM has poor mechanical properties [3-4].

Therefore, it is necessary to mix EPDM with other material to strengthen its mechanical properties. This study used natural rubber (NR) to improve its mechanical properties. NR has good processing characteristics and also dynamic and mechanical properties. But, NR has low oil and heat resistance and also has high gas permeability. It also easy to be deteriorated by ozone because the main chain of NR is highly unsaturated [5-6]. The EPDM phase that finely dispersed in unsaturated rubber provides good internal antioxidant that more effective than conventional antioxidant such as N-(1,3-dimethylbutyl)-N’-phenyl-p-phenylene-diamine (6PPD) [7]. In the blending of EPDM/NR, NR is expected to improve the mechanical properties of the product, and EPDM is expected to improve the heat and oil resistance of the product. So that the blend has a good mechanical properties, oil resistance, and heat resistance. The application of this product such as hose and conveyor belt, especially for high-temperature application and also in the automotive application.
The blending of EPDM/NR is an interesting field because it can provide the product with superior properties. It is also can reduce the production cost because NR is less expensive than EPDM. But, in the manufacture of EPDM/NR blends, some conditions need attention. The EPDM rubber is saturated rubber thus non-reactive, and natural rubber is highly unsaturated and reactive. Because of the difference in chemical reactivity, NR has a higher crosslinking rate. NR and EPDM also have incompatibility cure rate. The higher solubility of many curatives in NR than EPDM could reduce the crosslink density of EPDM, NR is highly crosslinked, and EPDM is poorly crosslinked. Many attempts to improve cure compatibility had been made such as using compatibilizer, accelerators, and controlling the migration of curative [8-9].

Compatibilizer is used as the compatibilizing agent to make better dispersion among the rubber blends. This study used maleic anhydride as a compatibilizer. Maleic anhydride is commonly used by grafting it onto the polymer matrix. Accelerator is defined as the chemical added to a rubber compound to increase the speed of vulcanization and to permitting lower temperature vulcanization with greater efficiency. An accelerator can be used as a single, binary, or triplet accelerator. The suitable binary accelerator systems used in the vulcanization of diene rubber and butyl rubber are slow curing accelerator. Primary accelerator is an accelerator with a slow cure rate. Primary accelerator is commonly reacted with another faster accelerator type that becomes the secondary accelerator. The cure characteristics and the processing safety of the compounds are strongly influenced by the accelerators [9-11].

TMTD is an accelerator from thiuram groups, MBTS from the mercapto group and TBBS from the sulfenamide group. MBTS used as a primary accelerator and it can be used as a single or binary. TMTD, ultra-fast accelerator, can be used as a primary or secondary accelerator. TBBS is classified as a delayed action accelerator that involves a long vulcanization process [10-11]. Accelerators used in this study are shown in Table 1.

The sequence and technique of rubber blending also influence the cure characteristics and mechanical properties of the blends [12]. This study was done by controlling the migration of curative as the method from previous researchers [8-9]. The blending of EPDM/NR by controlling the migration of curative give better cure characteristics and mechanical properties than simple blending [7]. Preheating compound is needed to improve the crosslink distribution by curative migration to higher phase from the EPDM phase in unsaturated natural rubber [13].

The EPDM/NR blends had been studied by some researchers with methyl methacrylate-butadiene-styrene (MBS) [2], maleic anhydride (MAH) as compatibilizer [8], MBTS/ZDEC [9], TBBS [5,14], MBT [2,8,15], MBTS [15], TMTD as accelerators [2,7,11,15], and controlling the migration of curative [5,9,13]. Based on our knowledge, no research has been published about the influence of different accelerator on EPDM/NR blend by controlling the curative migration with maleic anhydride as the compatibilizer. The goal of this study is

Table 1. Compound formulation of EPDM blends

<table>
<thead>
<tr>
<th>Materials</th>
<th>Compound (part per hundred resin, phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MB</td>
</tr>
<tr>
<td>EPDM</td>
<td>60.0</td>
</tr>
<tr>
<td>CB N220</td>
<td>60.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>TMQ</td>
<td>1.0</td>
</tr>
<tr>
<td>Paraffinic wax</td>
<td>0.5</td>
</tr>
<tr>
<td>Paraffinic oil</td>
<td>5.0</td>
</tr>
<tr>
<td>MBTS</td>
<td>1.5</td>
</tr>
<tr>
<td>TBBS</td>
<td>-</td>
</tr>
<tr>
<td>TMTD</td>
<td>-</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Fig 1. Structure of (a) 2,2-dithiobis(benzothiazole) (MBTS), (b) N-tert-butyl-2-benzothiazole sulphonamide (TBBS) and (c) tetramethyl thiuram disulfide (TMTD) of the blends [12].
to investigate the effect of some accelerators on the cure characteristics and mechanical properties of EPDM/NR blends. This study used MBTS, MBTS/TMTD and TBBS as accelerators with the molecular structure as shown in Fig. 1. It is important to know the suitable accelerator for EPDM/NR blends to get the more efficient process and reduce the cost. This is the second publication of this project. The first publication is focused on the thermal degradation [16].

**EXPERIMENTAL SECTION**

**Materials**

EPDM Keltan 4551 A (ENB 8.7%, ML(1+4) 125 °C) and NR (SIR 20) by PTPN IX was used in this study. Carbon black (CB) N220 (Korea) used as filler, paraffin wax (Antilux 654 A) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ, Kemai) as antioxidants, paraffinic oil (Indrasari, Semarang) as softener, zinc oxide (ZnO, Indoxide) and stearic acid (Aflux 42M) as activators, MBTS (Shandong Sianxian), TBBS (Shandong Sunshine), TMTD (Starchem) as accelerators, MAH (Justus), dicumyl peroxide (DCP) (Sigma Aldrich), and sulfur (Miwon) as a vulcanizing agent.

**Instrumentation**

The equipment used in this study were processed equipment and testing equipment. The processed equipment consisting of the two-roll mill, MDR rheometer Gotech 3000 A moving die rheometer, and hydraulic press Toyoseiki A-652 200 500. The testing instrument used were Kao-Tieh tensile strength tester, hardness durometer (shore A), and SEM SNE 3200 M.

**Procedure**

**Compound preparation**

Formulation of the composites in this experiment is given in Table 1 and 2 as the previous publication [16]. The compounds were prepared using two-roll mill (modified with the capacity of 2 kg). EPDM blends (Table 1) were mixed (total mixing time about 20 min) with sequence EPDM, ZnO, stearic acid, CB and paraffinic oil, paraffin wax and TMQ, accelerators, then sulfur. NR compounds (Table 2) were mixed with sequence NR, CB, MAH, DCP (total mixing time about 10 min). EPDM compounds were tested by the rheometer at 170 °C to calculate the preheated time. The preheated time for EPDM compounds before mixed with NR are shown in Table 3 based on 0.75 ts2.

The EPDM compounds were preheated in a hydraulic press under a pressure of 150 kg/cm². The preheated EPDM were cooled in an open atmosphere. The blend compounds (EPDM and NR) were then mixed in the two-roll mill about 3 min. The rubber compounds were stood overnight before vulcanized. The compounds were tested by the rheometer. Then, it was vulcanized using an electrically heated hydraulic press under a pressure of 150 kg/cm² with the determined optimum cure time (t90) by rheometer at 160 °C.

**Curing characteristic**

The cure and dynamic characteristics of the compounds were calculated from the torque-time curves taken from experiments performed at 150 and 160 °C by the rheometer. Data from the rheometer can be used to predict the curing kinetics using a kinetic model based on experimental results. Chemical reactions can be modeled in eq. (1).

\[
\frac{d\alpha}{dt} = k(T).f(\alpha)
\]

The degree of conversion (\(\alpha\)) in curing reaction is defined from rheometer as follows [17]:

\[
\alpha = \frac{M_1 - M_L}{M_H - M_L}
\]

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**Table 2. Compounds formulation for NR blends**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Compound (part per hundred resin, phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM</td>
<td>MB 60.0</td>
</tr>
<tr>
<td>N 220</td>
<td>MB 20.0</td>
</tr>
<tr>
<td>MAH</td>
<td>3.0</td>
</tr>
<tr>
<td>DCP</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Table 3. Preheated time for EPDM compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>64</td>
</tr>
<tr>
<td>MBTM</td>
<td>30</td>
</tr>
<tr>
<td>TB</td>
<td>56</td>
</tr>
</tbody>
</table>

*t\(p\) = preheated time
where \( M_t \) is the torque at a time \( t \), \( M_L \) and \( M_H \) are the minimum and maximum torque. \( M \) values between 25 and 45% of torque change were chosen to estimate the rate constants in this work [18]. Vulcanization reaction is assumed to follow first-order and proportional to the fraction of material which is not crosslinked \((1 - \alpha)\), given:

\[
f(\alpha) = (1 - \alpha)
\]

(3)

By substituting eq. (3) to eq. (1), given:

\[
\frac{d\alpha}{(1 - \alpha)} = k(T) \, dt
\]

(4)

Integrating eq. (4) given:

\[
\ln\left(\frac{1}{(1 - \alpha)}\right) = kt
\]

(5)

By substituting eq. (2) to eq. (5) given:

\[
\ln\left(\frac{M_{H} - M_{L}}{M_{H} - M_{L}}\right) = kt
\]

(6)

Rearrangement equation

\[
\ln(M_{H} - M_t) = \ln(M_{H} - M_L) - kt
\]

(7)

By plotting \( \ln(M_{H} - M_t) \) against the time \( t \), the rate constant \( k \) could be obtained from the slope of the line.

**Mechanical properties**

The mechanical testing such as tear strength (according to ISO 34), tensile strength and elongation at break (according to ISO 37) were carried out by Kao-Tieh tensile strength tester. The hardness testing (according to ISO 48) was carried out by hardness durometer shore A.

**Morphological**

The morphological examination was done by SEM SNE 3200 M. The dried samples were sputter-coated by gold before SEM analysis.

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### RESULTS AND DISCUSSION

#### Cure and Dynamic Characteristics

The vulcanization characteristics of EPDM/NR compounds with carbon black filler material were determined by the Gotech rheometer MDR 3000 A. Rheometer provides a digital output of curing characteristics and processability such as scorch time \((t_{s2})\), optimum cure time \((t_{90})\), and dynamic properties as shown in Table 4 and Table 5.

Table 4 shows that EPDM/NR compounds in this experiment have fast scorch and optimum curing time. It happens due to the presence of preheating step, where the formation of the active substance sulfurating agent needs a little time to react with allylic hydrogen in the NR molecules [13]. MBTS/TMTD gave the lowest scorch time and optimum cure time. This result suitable with the previous research that the compound processability of the binary accelerator is lower than single accelerator [9]. TBBS gave the longest scorch time that means the safest processing time. Safety processing time is a time when the compound still can be formed and still plastic; compounds will be safe if being worked below the scorch time. Scorch time indicates that the

<table>
<thead>
<tr>
<th>Code</th>
<th>( t_{s2} ) (sec)</th>
<th>( t_{90} ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150 °C</td>
<td>160 °C</td>
</tr>
<tr>
<td>MB</td>
<td>161</td>
<td>101</td>
</tr>
<tr>
<td>MBTM</td>
<td>171</td>
<td>84</td>
</tr>
<tr>
<td>TB</td>
<td>718</td>
<td>397</td>
</tr>
</tbody>
</table>

#### Table 5. Dynamic characteristics of EPDM/NR compounds

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Compound</th>
<th>S'ML (kgf.cm)</th>
<th>S'MH (kgf.cm)</th>
<th>S'ML (kgf.cm)</th>
<th>S'MH (kgf.cm)</th>
<th>tan δ</th>
<th>tan δ</th>
<th>delta torque (kgf.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>MB</td>
<td>6.56</td>
<td>17.89</td>
<td>5.33</td>
<td>4.97</td>
<td>0.81</td>
<td>0.28</td>
<td>11.33</td>
</tr>
<tr>
<td></td>
<td>MBTM</td>
<td>3.77</td>
<td>14.54</td>
<td>3.72</td>
<td>3.24</td>
<td>0.99</td>
<td>0.22</td>
<td>10.77</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>2.75</td>
<td>5.88</td>
<td>3.33</td>
<td>3.53</td>
<td>1.21</td>
<td>0.6</td>
<td>3.13</td>
</tr>
<tr>
<td>160</td>
<td>MB</td>
<td>6.28</td>
<td>15.9</td>
<td>4.93</td>
<td>5.51</td>
<td>0.78</td>
<td>0.35</td>
<td>9.62</td>
</tr>
<tr>
<td></td>
<td>MBTM</td>
<td>4.25</td>
<td>15.98</td>
<td>4.35</td>
<td>4.67</td>
<td>1.02</td>
<td>0.29</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>3.79</td>
<td>7.1</td>
<td>3.88</td>
<td>4.37</td>
<td>1.02</td>
<td>0.62</td>
<td>3.31</td>
</tr>
</tbody>
</table>
plastic material is converted become chemically elastic [3]. TBBS is an accelerator from sulfenamide group that has delayed action and involves a long vulcanization process. It needs a long time to form a sulfuring agent by reacting with the ZnO, and then it reacts with the polymer chain [11,15]. This result similar to the previous research by Sae-oui et al. [15]. MBTS is an accelerator from thiazole group that has ultra-fast speed and being used as a primary accelerator. Hence the MBTS gives fast scorch time both in MB and MBTM compounds. At the lower vulcanization temperature, the compounds need longer curing time than at higher vulcanization temperature. The higher vulcanization temperature, the shorter scorch time and the optimum cure time reached. Higher temperature gave more heat means energy that makes the particles move faster. Therefore, the required time for the reaction was shorter.

Table 5 shows the dynamic properties of EPDM/NR compounds. Rubber is a viscoelastic material that has elastic elements ($S'$) and viscous elements ($S''$) influencing its flow properties. MH is a maximum torque and ML is a minimum torque. A maximum torque (MH) considered being the stiffness or shear modulus of the vulcanized rubber at the vulcanization temperature [13]. Minimum elastic torque ($S''\text{ML}$) also related to shear modulus and degree of crosslinking of the compound [9,13,16].

Table 6. Rate constant, $k$ of EPDM/NR compounds

<table>
<thead>
<tr>
<th>Code</th>
<th>$150 , ^\circ\text{C}$</th>
<th>$160 , ^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>0.0025</td>
<td>0.0097</td>
</tr>
<tr>
<td>MBTM</td>
<td>0.0038</td>
<td>0.0104</td>
</tr>
<tr>
<td>TB</td>
<td>0.0005</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

$S''\text{ML}$ is a minimum viscous torque and related to the security process and the damping characteristics of a rubber compound. The damping characteristics is a ratio of the viscous element and the elastic element. Damping factor ($\tan \delta$) was determined by divided $S''$ with $S'$. $\tan \delta \,(\text{ML})$ is a loss tangent in the compound, and $\tan \delta \,(\text{MH})$ is a loss tangent at vulcanizate. The damping factor ($\tan \delta$) is inversely proportional to the crosslinking degree. Lower damping factors indicate greater crosslinking degree [5] as shown in Table 6. TBBS gave the greatest damping factor and the lowest delta torque, while MB and MBTM gave no significant difference in delta torque. The damping factor is shown in Fig. 2.

Fig. 2 shows that the different accelerator used gave the different viscoelastic properties of the compounds. MB compound is dominated by the elastic element ($S' > S''$), MBTM has more viscous element than MB compound, and TB tends to dominated by viscous element ($S'' > S'$). Compound with great elasticity has

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**Fig 2.** The damping factor ($\delta$) of the EPDM/NR composites
poor flow properties [9]. The vulcanization temperature changes the proportion of viscous and elastic element in the rubber compound. Higher vulcanization temperature gives more elastic element than the viscous element. It may happen because high vulcanization temperature results faster scorch time so that the viscous element decrease.

**Cure Kinetics**

Rheometer gave the cure rate shown in Fig. 3. The composites with higher vulcanization temperature (160 °C) result in higher cure rate than lower vulcanization temperature. MBTS/TMTD give the highest cure rate, followed by MBTS and TBBS. TBBS is an accelerator from sulfenamide group that has delayed action, hence the cure rate is the lowest.

Rate constant (k) of EPDM/NR compounds by plotting from eq. (7) are shown in Table 6. Higher vulcanization temperature gives higher rate constant. At high temperature, the collision of the particles became faster hence the reaction rate increases. Rate constant also represents the cure rate. Binary accelerator MBTS/TMTD gave the highest constant rate, while TBBS gave the lowest constant rate. Using of two or more accelerators simultaneously are more profitable for technological applications. Their combination showed a higher vulcanization activity (synergism) rather than a single accelerator separately [9]. MBTS and TMTD can react to form the DMTBD as studied by Bergendorff et al. The reaction between MBTS and TMTD results in the formation of DMTBD as seen in Fig. 4 [19].

**Mechanical Properties**

EPDM/NR compounds were vulcanized at 160 °C, and the result of the mechanical test is shown in Fig. 5. Fig. 5 shows that EPDM/NR composites have good mechanical properties. It may happen because there are preheating time before the compounds were vulcanized. Preheating time results more homogeneous crosslinking and good mechanical properties [13]. MBTS gave the highest hardness and tensile strength, the lowest elongation and tear strength. MBTS/TMTD gave the same hardness with MBTS composite and gave no significant difference in tensile strength. TBBS gave the lowest hardness and tensile strength, the highest elongation and tear strength.
Fig 5. Mechanical properties of EPDM/NR composites: (a) hardness, (b) tensile strength, (c) elongation, and (d) tear strength

The hardness of the vulcanizate depends on the hardness of the components. Tensile strength is related to the resistance material to the load. Hardness and tensile strength are related to crosslinking density [20]. Higher crosslinking density indicated that the molecules of material are tight, rigid and hard [21]. TBBS gave the lowest crosslinking density so that TBBS gave the lowest hardness and tensile strength. MBTS, used in single or as a binary accelerator, gave high hardness to the composites.

The elongation is related to the flexibility or elasticity of the sample upon stretching till failure. Elongation at break indicates the elasticity, flexibility, and ductility of the vulcanizates [13]. Elongation decrease with increasing of tensile strength. Elongation increase with the decreasing of crosslinking density because the high amount of crosslinking density makes more difficult to stretch the material [22]. Tear strength proportionate with the elongation properties. TBBS gave the highest elongation and tear strength followed by MBTS/TMTD and MBTS.

The composites also aged and the results are shown in Fig. 5. After aging test, all composites become harder. Tensile, elongation, and tear strength are reduced. This reduction could be attributed to the oxidation of polymer. Oxidation can result in chain scissions which made fewer entanglements, then decreases the tensile strength, elongation at break, and tear strength [11]. The test result that MBTS/TMTD gave the lowest reduction of mechanical properties (6.5% hardness; 10.8% tensile; 12.2% elongation; 10% tear). It shows that binary accelerators give better resistance to aging than the single accelerator.

Morphology

Morphology determines the extent of the compatibility of the blend. The phase structure is influenced by several factors, such as the composition, blend ratio, viscosity of each component, surface characteristics, and compounding process. The composition of the blends is the primary factor that determines the morphology.
Fig. 6 shows the morphology of EPDM/NR composites with 60 phr CB filler. The dark regions represent NR, and the lighter regions represent EPDM [23]. The dispersion was not uniform, but the combination of MBTS/TMTD gave more homogeneous and compatible composite than others. Binary accelerator results in better filler dispersion in the rubber matrix.

CONCLUSION

Blending of EPDM/NR with various accelerators gave different composite characteristics. Vulcanization temperature at 160 °C gave better cure characteristic than 150 °C. Binary accelerator, MBTS/TMTD, resulted the lowest scorch and optimum curing time. Binary accelerator gave the highest cure rate and constant rate (0.0038 sec⁻¹ at 150 °C and 0.0104 sec⁻¹ at 160 °C), but not significantly different with MBTS. MBTS/TMTD and MBTS resulted good mechanical properties (hardness 62 shore A, tensile strength 86 and 81 kg/cm², tear strength 22 and 24 kg/cm, elongation 356 and 385%). TBBS gave the longest scorch time, the lowest crosslink density and mechanical properties except for the tear strength. Binary accelerator results in better aging resistance and compatibility blend. These results correspond well with SEM micrograph of the fractured surfaces of tensile strength. From the study, the suitable vulcanization temperature for EPDM/NR was 160 °C with a binary accelerator of MBTS/TMTD.

ACKNOWLEDGMENTS

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