Reinforcement Effect of MAA on Nano-CaCO₃-Filled EPDM Vulcanizates and Possible Mechanism

YABIN ZHOU, SHIFENG WANG, YINXI ZHANG, YONG ZHANG
Research Institute of Polymer Materials, Shanghai Jiao Tong University, 200240 Shanghai, People’s Republic of China

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ABSTRACT: Methacrylic acid (MAA) was used as in situ surface modifier to improve the interface interaction between nano-CaCO₃ particle and ethylene–propylene–diene monomer (EPDM) matrix, and hence the mechanical properties of nano-CaCO₃-filled EPDM vulcanizates. The results showed that the incorporation of MAA improved the filler–matrix interaction, which was proved by Fourier transformation infrared spectrometer (FTIR), Kraus equation, crosslink density determination, and scanning electron microscope (SEM). The formation of carboxylate and the participation of MAA in the crosslinking of EPDM indicated the strong filler–matrix interaction from the aspect of chemical reaction. The results of Kraus equation showed that the presence of MAA enhanced the reinforcement extent of nano-CaCO₃ on EPDM vulcanizates. Crosslink density determination proved the formation of the ionic crosslinks in EPDM vulcanizates with the existence of MAA. The filler particles on tensile fracture were embedded in the matrix and could not be observed obviously, indicating that a strong interfacial interaction between the filler and the matrix had been achieved with the incorporation of MAA. Meanwhile, the presence of MAA remarkably increased the modulus and tensile strength of the vulcanizates, without negative effect on the high elongation at break. Furthermore, the ionic bond was thought to be formed only on filler surface because of the absolute deficiency of MAA, which resulted in the possible structure where filler particles were considered as crosslink points. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 1226–1236, 2006

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INTRODUCTION

Except for a few rubbers like natural rubber and chloroprene rubber that can be reinforced by self-crystallization in tensile process, most rubbers must be reinforced by fillers before practical application. A number of fillers have been used as reinforcing agents, such as carbon black,¹,² silica,³–⁵ and montmorillonite.⁶ As mineral filler, CaCO₃ has been used only as bulking agent mainly reducing the cost of rubber products. With the development of technology in particle fining and especially in surface modification, CaCO₃ is used as a reinforcing agent. Surface modification can decrease the surface energy and polarity of inorganic fillers, thus reducing the aggregation tendency of filler particles in rubber matrix. As a result, good dispersion and large interfacial area can be obtained, leading to better reinforcement of CaCO₃ on rubbers.

Many surface modifiers have been used to treat CaCO₃, including coupling agents,⁷,⁸ surfactants,⁹,¹⁰ and reactive polymers.¹¹ Among them, stearic acid is a very important anionic surfactant and is often used to treat CaCO₃.¹² Its carboxyl
terminals can be coupled to the filler surface with ionic bonds and the alkyl terminals are oriented in directions outward the surface. As a result, the particle surface of CaCO₃ is modified from hydrophilic to hydrophobic, which reduces the filler–filler interaction and favors the even dispersion of CaCO₃ in matrix. Because of lack of any active functional group, strong interaction can not be obtained between stearic acid and matrix, only to reduce the surface energy of filler and to improve the dispersion.

Unlike stearic acid, methacrylic acid (MAA) is an unsaturated carboxylic acid which contains two functional groups, that is, a carboxyl and a carbon–carbon double bond in each molecule. The carboxyl group on MAA could react with the active functional groups on the surface of nano-CaCO₃, mainly Ca²⁺ ion, which is similar to the reaction between stearic acid and CaCO₃. Moreover, the carbon–carbon double bond on MAA can participate in the crosslinking reaction of ethylene–propylene–diene monomer (EPDM) induced by dicumyl peroxide (DCP), and hence, bonded to the crosslink network in EPDM vulcanizates. As a result, a strong interfacial interaction between nano-CaCO₃ and the EPDM matrix can be obtained.

In fact, in a study of CaCO₃-filled polypropylene (PP), some kind of unsaturated carboxylic acid similar to MAA, such as acrylic acid (AA), has been used to modify CaCO₃. A strong interaction between CaCO₃ and PP could be realized through the grafting polymerization of AA to PP initiated by DCP. However, the incorporation of DCP would unavoidably initiate the degradation of PP, which would worsen the mechanical properties of compound.

In this study, MAA was used to in situ modify nano-CaCO₃ when blending with EPDM to strengthen filler–matrix interaction and result in excellent mechanical properties. To prove the strong interaction between the filler and the matrix, Fourier transformation infrared spectrometer (FTIR), Kraus equation, crosslink density determination, and scanning electron microscope (SEM) had been used successfully. The remarkable improvement in modulus for filled vulcanizates with MAA also proved our assumption effectively. Meanwhile, other mechanical properties, such as tensile strength and tear strength are also increased. Furthermore, the ionic bond is thought to be formed only on filler surface because of the absolute deficiency of MAA, which results in the possible structure where filler particles are considered as crosslink points.

### EXPERIMENTAL

#### Materials

Ethylene–propylene–diene monomer rubber (EPDM), ND 4770R, is a semicrystalline rubber with ethylene content of 70% and supplied by Du Pont Company, USA. Nano-CaCO₃ without surface modification was supplied by Shanghai Yaohua Nano-Tech Ltd., China. All the chemicals, including MAA and DCP, were used as received.

#### Sample Preparation

According to the typical formulation showed in Table 1, EPDM and nano-CaCO₃ were mixed in a HAAKE Rheometer RC90 (Haake Company, Germany) at 40 °C with a rotor speed of 60 rpm. EPDM was plasticized in the rheometer for 2 min at first, and then mixed with nano-CaCO₃ and MAA for 6 min, followed by addition of DCP and mixed for 2 min. The resultant composite was sheeted on a two-roll mill at room temperature and compression molded at 170 °C for 10 min to obtain vulcanizates.

#### Measurements

**Fourier Transformation Infrared Spectrometer**

Infrared transmission spectra were obtained using an FTIR spectrometer (model Paragon 1000, PerkinElmer Corp). The scan range was from 4400 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. Samples of CaCO₃ powder were prepared by milling CaCO₃ with KBr and compressed to a KBr disc for testing. Samples of EPDM gum, compound, and vulcanizates were pressed to thin films for testing.

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**Table 1. Typical Formulation**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Content (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM (ND 4770R)</td>
<td>100</td>
</tr>
<tr>
<td>Nano-CaCO₃</td>
<td>Variable (0–100)</td>
</tr>
<tr>
<td>MAA</td>
<td>Variable (0–6)</td>
</tr>
<tr>
<td>DCP</td>
<td>1</td>
</tr>
</tbody>
</table>

phr, parts per hundred parts of rubber (by weight); MAA, methacrylic acid; DCP, dicumyl peroxide.
Transmission Electron Microscope

Transmission electron microscope (TEM) images were taken in H-800 microscope (Hitachi, Japan) with an accelerator voltage of 120 kV. Thin sections (~100 nm) of the specimens were cryo-cut with a diamond knife at about 120 K and used without staining.

Determination of Crosslink Density

The crosslink density was determined using an equilibrium swelling method. Vulcanizate samples were swollen in toluene at 25 °C for 72 h to achieve equilibrium swelling. The weight of the samples was recorded under swollen conditions. Then the samples were dried in a vacuum oven at 80 °C for 48 h to remove all the solvent, and weighed again. The volume fraction of rubber swollen in the gel, $V_r$, which was used to represent the crosslink density of the vulcanizates, was determined by the following equation:

$$V_r = \frac{m_0 \phi(1-x)/\rho_r}{m_0 \phi(1-x)/\rho_r + (m_1 - m_2)/\rho_s}$$

where $m_0$ is the sample mass before swelling, $m_1$ and $m_2$ are the sample masses before and after drying, $\phi$ is the mass fraction of rubber in the vulcanizates, $x$ is the mass loss of the gum EPDM vulcanizates during swelling, and $\rho_r$ and $\rho_s$ are the rubber and solvent density, respectively. To distinguish ionic crosslinks from covalent crosslinks, the samples were swollen in a mixture of toluene and chloroacetic acid for 5 days to destroy ionic crosslinks, followed by swelling in toluene for 2 days and weighed, then vacuum dried and reweighed.\textsuperscript{15} $V_{r1}$ was calculated from eq 1, which represents the covalent crosslink density. $V_{r2}$, which was calculated by subtracting $V_{r1}$ from $V_r$, was used to represent the ionic crosslink density.

Scanning Electron Microscope

The morphology of EPDM vulcanizates was studied using a SEM, S-2150 (Hitachi Japan). Samples were tensile fractured and covered with a thin gold layer before observation.

Measurement of Mechanical Properties

Tensile properties and tear strength were measured using an Instron 4465 tester at a crosshead speed of 500 mm/min, according to ASTM D412 and ASTM D624, respectively. Shore A hardness was determined using a Shore A sclerometer, according to ASTM D2240.

RESULTS AND DISCUSSION

Morphology of MAA-CaCO₃ in Rubber Matrix

The TEM photographs of uncoated and MAA-coated nano-CaCO₃ particles in vulcanizates are shown in Figure 1. Both micrographs are in two magnifications of 10,000 and 50,000 times.

It is seen in Figure 1(a) that the uncoated cubic nano-CaCO₃ particles are aggregated in vulcanizates with an irregular shape, which is attributed to its high surface energy. For MAA-coated nano-CaCO₃ particles, a lot of aggregates are also found and no obvious improvement in...
dispersion is detected than uncoated nano-CaCO₃, as shown in Figure 1(b). It is mostly because of the too short carbon chain in MAA molecule, which can not reduce the high energy of nano-CaCO₃ particles effectively, and hence, does not play a remarkable insulation effect among filler particles.

FTIR Analysis

MAA is a difunctional carboxylic acid which has a terminal double bond in the molecule. It is highly reactive in the presence of free radicals and readily reacts to form crosslink with both saturated and unsaturated elastomers. Figure 2 shows the FTIR spectra of EPDM, MAA, CaCO₃, and their compound and vulcanizates.

Curve (a) in Figure 2 is the spectrum of the EPDM gum with characteristic absorbing peaks at 2924 and 2854 cm⁻¹ generated from C–H asymmetric and symmetric stretching vibrations of the methylene group. The characteristic peak at 1466 cm⁻¹ is due to the scissoring vibration of CH₂. The peak at 1376 cm⁻¹ is ascribed to the symmetric deformation vibration of the methyl group. The band at 722 cm⁻¹ is ascribed to the C–H bending vibration of (CH₂)ₙ when the n value is not smaller than four. Curve (b) in Figure 2 is the spectrum of MAA. It is known that the liquid methacrylic acid is likely to form dimer because of the strong hydrogen bond among the molecules. The strong association reaction between hydroxide and carbonyl will extend the hydrogen band to nearly 2500 cm⁻¹. As a result, the stretching vibration band of hydroxyl will be observed at 3300–2500 cm⁻¹. The broadband at 948 cm⁻¹ is ascribed to the O–H bending vibration. The bands at 1696 and 1636 cm⁻¹ are due to C=O strong stretching vibration and C=C stretching vibration, respectively. The C=O stretching vibration bands are from 1250 to 1400 cm⁻¹. Moreover, the band at 810 cm⁻¹ is ascribed to the out-of-plane bending vibration in H₂C–CH. Curve (c) in Figure 2 is the spectrum of CaCO₃. The strong and broad peak at 1485–1417 cm⁻¹ is due to the C–O stretching vibration.

Curves (d) and (e) in Figure 2 are the spectra of the EPDM/CaCO₃/MAA compound and vulcanizates, respectively. When the EPDM is mixed with CaCO₃ and MAA, most characteristic peaks of the components did not change, except for the band at 1696 cm⁻¹. At the same time, a new band at 1564 cm⁻¹ is observed, which is ascribed to the formation of carboxylate, that is, the (Ca²⁺)(OOC) band. The bonding between Ca²⁺ and OOC homogenized the C=O and C=O in carboxyl. As a result, the peak at 1696 cm⁻¹ disappeared, which is as-

![Figure 2. Transmission FTIR spectra of (a) EPDM, (b) MAA, (c) CaCO₃, (d) EPDM/CaCO₃/MAA compound, and (e) EPDM/CaCO₃/MAA/DCP vulcanizates.](image-url)
cribed to the C=O strong stretching vibration. Compared with the spectrum of compound, the spectrum of vulcanizates has a significant change in the peak of 1640 cm\(^{-1}\). The relative intensity of C=O absorption at 1640 cm\(^{-1}\) becomes weak obviously, which indicates that the carbon–carbon double bonds have reacted to a great extent in the vulcanization process.

**Extent of Reinforcement**

The chemical reactions between MAA and CaCO\(_3\) as well as between MAA and EPDM have been proved by FTIR, which indicates that a strong interaction exists between CaCO\(_3\) and EPDM through the bridge effect of MAA. In this section, the extent of reinforcement is assessed by using the Kraus equation\(^{16}\), as the following:

\[
V_{ro} = \frac{d\rho_p^{-1}}{d\rho_p^{-1} + A_s\rho_s^{-1}}
\]

where \(V_{ro}\) is the volume fraction of rubber in the solvent-swollen unfilled vulcanizates and is given as following.

Since eq 2 has the general form of an equation for a straight line, a plot of \(V_{ro}/V_{rf}\) as a function of \(f/(1-f)\) should give a straight line, and its slope will be a direct measurement of the reinforcing ability of the filler.

The Kraus plots for filled vulcanizates with incorporation of MAA are shown in Figure 3. It can be seen that the slope changed from a positive value to a negative value when MAA was introduced into the system, indicating the presence of MAA could enhance the reinforcement effect of nano-CaCO\(_3\) on EPDM.

**Ionic Crosslink and its Density**

DCP can initiate the crosslink reaction of EPDM as well as the polymerization of MAA, including both homo polymerization and graft polymerization.\(^{17}\) To investigate the effect of MAA on the crosslink structure in the DCP-cured nano-CaCO\(_3\)-filled EPDM vulcanizates, the crosslink densities of ionic and covalent bonds were measured by using an equilibrium swelling method. The values of \(V_r\) (representing the gross crosslink density of the vulcanizates) and \(V_{r1}\) (representing covalent crosslink density of the vulcanizates) were calculated according to eq 1. \(V_{r2}\) (representing ionic crosslink density of the vulcanizates) was calculated by subtracting the covalent crosslink density from the gross crosslink density.

![Figure 3. \(V_{ro}/V_{rf}\) versus \(f/(1-f)\) for vulcanizates in toluene with incorporating MAA.](image)

![Figure 4. Effect of nano-CaCO\(_3\) content on crosslink density of EPDM vulcanizates (EPDM/CaCO\(_3\)/MAA/DCP = 100/variable/2 wt % of CaCO\(_3\)/1).](image)
Figure 4 shows the effect of CaCO₃ content on the crosslink densities of EPDM vulcanizates, where CaCO₃ is in situ modified with 2 wt % of MAA. It is seen that the gross crosslink density of EPDM vulcanizates increases monotonously with increasing CaCO₃ content and this change is mostly attributed to the increase in ionic crosslink density. In fact, the incorporation of CaCO₃ and MAA reduces the covalent crosslink density of EPDM vulcanizates. When CaCO₃ content is more than 20 phr (parts per hundred parts of rubber (by weight)), the covalent cross-link density begins to decrease.

Figure 5 shows the effect of MAA content on the crosslink density of the EPDM vulcanizates. At a given filler content of 60 phr, both the gross crosslink density and ionic crosslink density increase with the incorporation of MAA, while the covalent crosslink density exhibits a slight decrease. With the further increase in MAA content, no distinct change is observed in ionic crosslink density. It is concluded that the incorporation of MAA into CaCO₃/EPDM generates ionic crosslinks. However, the ionic crosslink density in vulcanizates could not increase sequentially with increasing MAA content.

SEM Micrographs of Tensile Fracture Surface

SEM images of tensile fracture surfaces of EPDM vulcanizates are shown in Figure 6. It can be seen in Figure 6(a) that nano-CaCO₃ particles incline to aggregate. Some holes and exposed particles left after the filler particles were pulled out from the matrix when the stress was applied. The failure occurred at the filler–matrix interface, indicating the weak interfacial adhesion between the filler and the matrix. However, the pull-out phenomenon of filler particles is not observed on the tensile fracture surface of vulcanizates with MAA. The filler particles in Figure 6(b) are embedded in the matrix and can not be observed obviously, indicating that a strong interfacial interaction between the filler and the matrix has been achieved with the incorporation of MAA. The failure occurred at the matrix because of strong adhesion between the filler and the matrix. In tensile test, the particle covered by a layer of the matrix was pulled out together with the matrix. As a result, the tensile fracture surface of vulcanizates with MAA is much coarser than that without MAA, indicating the failure surface of vulcanizates with the presence of MAA.

Figure 6. SEM micrographs of tensile fracture surface of EPDM vulcanizates filled with 60 phr CaCO₃. (a) Without MAA and (b) with MAA.
Mechanical Properties

Effect of MAA Content on Mechanical Properties

Figure 7 shows the effect of MAA content on the mechanical properties of nano-CaCO$_3$-filled EPDM vulcanizates. It is found that the modulus of vulcanizates is increased with the incorporation of MAA. As is discussed above, the incorporation of MAA builds the strong connection between filler particle and rubber matrix, which results in the formation of ionic crosslink and the increase in gross crosslink density, and hence, the increase in the modulus of vulcanizates. With the increase in MAA content, the modulus at 100% elongation increases, and the modulus at 300% increases more significantly and reaches the maximum value of 13.6 MPa when the MAA content is 2 phr, then decreases gradually thereafter (it is still more than 10 MPa even when the MAA content is 6 phr), which is nearly corresponding to the change in gross crosslink density. Furthermore, the tensile strength increases with increasing MAA content, and reaches the maximum value when the MAA content is 1.2 phr. In the range of MAA content from 2 to 6 phr, all the vulcanizates have the tensile strength more than 23 MPa. The elongation at break of EPDM vulcanizates substantially increases with increasing MAA content, and reaches its maximum value at the MAA content of 4.8 phr, which is 21% higher than that of the EPDM vulcanizates without MAA. The tear strength of vulcanizates increases by 34% when the MAA content increases from 0 to 1.2 phr. With the further increase in MAA content, the tear strength does not increase anymore. Generally, the incorporation of MAA further reinforces the EPDM vulcanize after nano-CaCO$_3$. It appears to be an effective way to obtain high elongation at break, meanwhile remarkably increasing the modulus and tensile strength of nano-CaCO$_3$-filled EPDM vulcanizates.

Effect of Nano-CaCO$_3$ Content on Mechanical Properties

Figure 8 shows the effect of nano-CaCO$_3$ content on the mechanical properties of EPDM vulcanizates.
Figure 8. Effect of nano-CaCO$_3$ content on the mechanical properties of EPDM vulcanizates: (a) modulus at 100%, (b) modulus at 300%, (c) tensile strength, (d) elongation at break, and (e) tear strength.
the vulcanizates without MAA. It is clear that the incorporation of MAA always increases the modulus of vulcanizates, no matter how much CaCO₃ is incorporated. The tensile strength increases with increasing filler content, and reaches its maximum value of 25.6 MPa at 60 phr filler content, which is 51% higher than that of the filled vulcanizates without MAA. The elongation at break increases significantly and reaches the maximum value of 654% when the nano-CaCO₃ content is 20 phr, and decreases gradually thereafter (although it is still over 450% even when the nano-CaCO₃ content is 100 phr). The tear strength of the vulcanizates increases by about 139% when the nano-CaCO₃ content increases from 0 to 100 phr.

**Stress–Strain Behavior**

It is well known that the stress–strain curves of the filled vulcanizates are affected by the crosslink density of rubber matrix, the size of agglomerates formed by filler, and matrix–filler interaction. These effects can be controlled by adjusting the curing agent content and filler particle size and by introducing a surface modifier.

Figure 9 shows the stress–strain curves for nano-CaCO₃-filled EPDM vulcanizates. The initial slopes of the curves for filled vulcanizates increase with the incorporation of MAA, indicating the presence of MAA increases the initial modulus of nano-CaCO₃-filled vulcanizates. It is not similar to the results of common coupling agent. When the coupling agents were introduced to particle surface, a hydrophilic characteristic of the particle was changed into a hydrophobic one, which reduced the filler–filler interactions via reduced agglomerate size formed by filler particles, leading to the decrease of tensile modulus, which is known as Payne effects. Unlike common coupling agents, MAA has two functional groups in each molecule. The carboxyl group can react with the functional groups on the surface of CaCO₃ particle, and the carbon–carbon double bond can participate in the crosslink reaction and can be grafted to the polymer crosslink network. As a result, a strong interfacial interaction between nano-CaCO₃ particle and the matrix is achieved by using MAA as coupling agent, resulting in the higher modulus of vulcanizates with the presence of MAA. Moreover, it is an interesting phenomenon that an inflection point is observed in the stress–strain curve of vulcanizates containing MAA, which is seen more clearly in Figure 10.

In filled vulcanizates without MAA, there are only covalent crosslinks. With the extension progress of tensile samples, more covalent crosslinks are subjected to the stress, resulting in a monotonous increase of $d\sigma/d\varepsilon$ value. According to the structural model of unsaturated carboxylate-reinforced vulcanizates, the schematic presentation of possible structure in filled vulcanizates with MAA is shown in Figure 11. Besides covalent crosslink, another kind of crosslink structure probably exists in MAA in situ modified nano-CaCO₃-filled vulcanizates. Unlike the structure in unsaturated carboxylate-reinforced vulcanizates, the ionic bond is formed only on filler surface, because MAA is absolutely deficient compared with nano-CaCO₃.

Figure 9. Stress–strain curves of EPDM vulcanizates with incorporating MAA (EPDM/CaCO₃/MAA/DCP = 100/60/1.2/1).

Figure 10. The first derivative of stress–strain curves of EPDM vulcanizates filled with 60 phr CaCO₃ with incorporating MAA and gum vulcanizates.
As shown in Figure 11(b), the filler particle can be bonded on the crosslink network via one or several ionic bonds. When three or more MAA molecules are bonded to a same filler particle through ionic bond, this filler particle can be considered as a crosslink point, which is completely different from the covalent crosslink, and even different from the ionic crosslink in unsaturated carboxylate-reinforced vulcanizates. For unsaturated carboxylate-reinforced vulcanizates, the ionic bond can be re-formed after being destroyed in tensile process, which might account for the loss of modulus. As a result, no similar inflection point was observed in the stress–strain curve of unsaturated carboxylate-reinforced vulcanizates. For filled vulcanizates with MAA, the decrease of $d\sigma/d\varepsilon$ at certain elongation is thought to be associated with the destroying of filler crosslink, which can not be re-formed like ionic bond in unsaturated carboxylate-reinforced vulcanizates. The following increase of $d\sigma/d\varepsilon$ value corresponds to the effect of covalent crosslink on modulus.

The effect of nano-CaCO$_3$ content on $(d\sigma/d\varepsilon)-\varepsilon$ curves of filled vulcanizates with MAA is shown in Figure 12. It can be seen that peak position is shifted to low strain region with the increase in

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![Figure 11](image1.png)

![Figure 12](image2.png)
filler content, and this shift can be seen more clearly in Figure 13. With increasing filler content, the proportion of EPDM matrix in vulcanizates decreases rapidly, leading to a relatively higher strain being applied to the EPDM matrix, because the filler is usually thought to be rigid and undeformable in a tensile process. It means the vulcanizates with higher filler content will reach the critical point of strain at lower macroscopical strain, and then the filler crosslink begins to be destroyed. The test results in Figure 13 fairly conform to the above analysis.

CONCLUSIONS

The incorporation of MAA improved the interfacial interaction between nano-CaCO3 particles and EPDM matrix, so as to enhance the mechanical properties of filled vulcanizates. The formation of carboxylate and the participation of MAA in the crosslink of EPDM indicated the strong filler–matrix interaction from the aspect of chemical reaction. Kraus equation proved that MAA enhanced the reinforcement extent of nano-CaCO3 on EPDM vulcanizates. Crosslink density determination proved the formation of the ionic crosslinks in EPDM vulcanizates with MAA. The tensile failure occurred at the matrix, indicating that the strong adhesion between the filler and the matrix was achieved by incorporating MAA. Furthermore, the presence of MAA remarkably increased the modulus and other mechanical properties. As a result, EPDM vulcanizates exhibited high strength, high modulus, and high elongation at break. The tensile strength of filled vulcanizates with MAA had the maximum value of 25.6 MPa at 60 phr filler content, which was 51% higher than that of filled vulcanizates without MAA. Furthermore, the ionic bond was thought to be formed only on filler surface because of the absolute deficiency of MAA, which resulted in the possible structure where filler particles were considered as crosslink points.

REFERENCES AND NOTES
