

Combined Effect of VA Content and pH Level of Filler on Properties of EPDM/SmBO₃ and EPDM/ATO Composites Reinforced by Three Types of EVA

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ABSTRACT: This study investigates the interaction of vinyl acetic (VA) content of ethylene-vinyl acetate (EVA), pH level of Samarium borate (SmBO₃), and Sb-doped SnO₂ (ATO) on reinforcement of peroxide-cured ethylene-propylene-diene rubber (EPDM)/SmBO₃ and EPDM/ATO composites. It was found that EVA could both reinforce mechanical properties of EPDM, and enhance fluidity of gum during processing. During vulcanization, the interaction of VA groups and pH value of filler particles can influence the crosslink density of EPDM composites. In alkaline EPDM/SmBO₃/EVA, VA groups could hydrolyze to produce polyvinyl alcohol and reduce pH level of medium by consuming OH⁻. When dispersed in acidic EPDM/ATO/EVA, VA groups could generate polyunsaturated bonds and acetic acid during vulcanization. The double bonds could react with dicumyl peroxide (DCP) and then boost crosslink efficiency of EPDM composites. Moreover, acetic acid and reduction of pH value could make DCP decompose into ions, and lower crosslink

density of EPDM composites. In addition to the contribution of crosslink density, EVA could crystallize in EPDM composites to reinforce EPDM composites. Electric properties of EPDM were also affected. Surface and volume resistivity of EPDM composites decreased with the rise of VA content. As for EPDM/SmBO₃/EVA composites, the growth of VA groups could boost dielectric constant and loss, decrease dielectric strength, due to the enhancement of polarity and reduction of crosslink density. In terms of EPDM/ATO/EVA composites, the EPDM/ATO/EVA14 possesses the highest dielectric constant and loss, and the lowest dielectric strength, because of the competing effect of VA content and crosslink density. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1741–1749, 2010

Key words: ethylene-propylene-diene rubber; ethylene-vinyl acetate copolymer; cure properties; mechanical properties; electric properties

INTRODUCTION

Ethylene-propylene-diene rubber (EPDM) consisted of ethylene, propylene, and unsaturated diene has become one of the fastest growing synthetic rubbers.^{1,2} Because of the copolymerization of ethylene with propylene, EPDM possesses low crystallinity and can not be self-reinforced like natural rubber, chloroprene rubber and so on. Thus, it is interesting to blend EPDM with crystalline resin, which could crystallize in EPDM and then reinforce EPDM composites.

The traditional crystalline resins used to reinforce EPDM include: polyethylene (PE)³ and polypropylene (PP).^{4,5} But there are fewer reports regarding the reinforcement of ethylene-vinyl acetate (EVA) copolymers on EPDM composites. EVA has been widely used as films, coatings, foams, cables, and hot-melt adhesives by the introduction of VA groups. The properties of

EVA can be varied by different comonomer ratio. At low VA content, the copolymers were more analogous to polyethylenes, and possess enough ability to crystallize. However, at high VA content, the VA groups could prevent polyethylene chains from packing into the crystal lattices.⁶ It is reported that the increase of crystallinity of EVA could enhance the hardness and tensile strength of EVA resin.^{7,8}

In our previous work,⁹ it is found that the different synthesis process could endow SmBO₃ and ATO particles with different pH level, which could affect the vulcanization,¹⁰ and evaluated the effect of SmBO₃ and ATO on reinforcement of EPDM composites. What's more, the coupling agents also influence the vulcanization of rubber composites and then enhance the mechanical properties of rubber composites.^{11–15} To further reinforce the mechanical properties of EPDM/SmBO₃ and EPDM/ATO, three types of EVA with varied VA content were blended with EPDM composites.

In this study, we focus on reinforcement of EPDM/SmBO₃ and EPDM/ATO composites by EVA and evaluate the combined effect of filler type and

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TABLE I
EPDM Composites Formulation (phr)

| Sample No. | EPDM | SmBO ₃ | ATO | EVA14 | EVA18 | EVA28 | ZnO | SA | DCP | RD | MB |
|------------|------|-------------------|-----|-------|-------|-------|-----|----|-----|-----|-----|
| A | 100 | 30 | – | – | – | – | 5 | 1 | 4 | 0.5 | 0.5 |
| B | 80 | 30 | – | 20 | – | – | 5 | 1 | 4 | 0.5 | 0.5 |
| C | 80 | 30 | – | – | 20 | – | 5 | 1 | 4 | 0.5 | 0.5 |
| D | 80 | 30 | – | – | – | 20 | 5 | 1 | 4 | 0.5 | 0.5 |
| E | 100 | – | 30 | – | – | – | 5 | 1 | 4 | 0.5 | 0.5 |
| F | 80 | – | 30 | 20 | – | – | 5 | 1 | 4 | 0.5 | 0.5 |
| G | 80 | – | 30 | – | 20 | – | 5 | 1 | 4 | 0.5 | 0.5 |
| H | 80 | – | 30 | – | – | 20 | 5 | 1 | 4 | 0.5 | 0.5 |

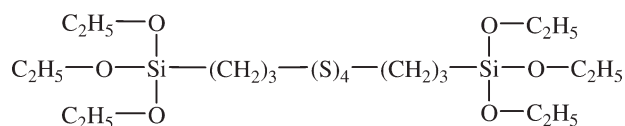
VA content on Mooney viscosity, cure, mechanical, and electric properties of EPDM composites.

EXPERIMENTAL

Materials

The rubber used in this study was ethylene-propylene-diene monomer (EPDM J-4045) containing 5-ethylidene-2-norbornene (ENB) as diene, which was manufactured by Jilin Petrochem., Sinopec. The EPDM consisted of 52.0 wt % ethylene, 40.3 wt % propylene, and 7.7 wt % ENB. Three commercial EVA copolymers with different VA contents were used for investigation. EVA14-2 (VA content 14 wt %) and EVA18-3 (VA content 18 wt %) were produced by Beijing Organic Chemical Plant, China; whereas EVAKA-31 (VA content 28 wt %) was produced by Sumitomo Chemical (Japan). The Melt Flow Rate (MFR), given by manufacturer, of EVA14-2, EVA18-3, and EVAKA-31 is 2 g/10 min, 3 g/10 min, and 7 g/10 min, respectively. They were all supplied in granular forms. For convenience, we define EVA14-2, EVA18-3, and EVAKA-31 as EVA14, EVA18, and EVA28, respectively.

Compounding ingredients, such as dicumyl peroxide (DCP), zinc oxide (ZnO), stearic acid (SA), 2-mercapto benzimidazole (antioxidant MB), and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (antioxidant RD) were of reagent grade. SmBO₃ particles were prepared by sol-gel method and ATO particles were prepared by coprecipitation method. The chemical/commercial name of KH845-4, obtained from Nanjing Shuguang Chemical Group Co., is bis-(3-(triethoxysilyl)propyl)tetrasulfide and structure of KH845-4 is listed below:



Sample preparation

Surface modification of SmBO₃ and ATO

In this work, KH845-4 was applied for surface treatment of the SmBO₃ and ATO particles, respectively, according to literature.⁹

Compounding of EPDM/EVA/SmBO₃ and EPDM/EVA/ATO vulcanizates

According to ISO2393, EPDM was firstly blended with EVA above the melting temperature of olefin, and then were mixed with treated SmBO₃ and ATO, respectively, by a two roll mixing mill (Shanghai Rubber Machinery Works, China).

The formulations of EPDM composites are displayed in Table I. Mixes were vulcanized in an electrically heated press at 180°C and 10 MPa for 15 min. Vulcanizates were conditioned for 24 h before testing

Testing procedures

Curing characterizations

Curing properties of EPDM gums were characterized at 180°C by an intelligent computer moving die rheometer (MDR) 2000 (Wuxi Liyuan Electronic & Chemical Equipment Co., China) with the arc of oscillation 1°.

Mooney viscosity

After mixing, the Mooney viscosity (ML₁₊₄^{100°C} and ML₁₊₄^{125°C}) of the compounds was measured by a Mooney viscometer MV-97 (Kunshan Huakun Electronic Equipment Co., China), following ISO 289.

DSC measurement

The melting behaviors of EVA copolymers and EPDM composites were evaluated using Pyris1 type of DSC instrument produced by PerkinElmer. Samples weighting about 10 mg were tested with a heating rate of 20°C/min, and argon purge gas with a flux of 20 mL/min was used to prevent oxidative degradation of samples during the heating run. Here the scanning range was from 30 to 150°C. The relative crystallinity (Xc) of the samples was calculated with the following expression:

$$X_c = \frac{\Delta H}{\phi \times \Delta H^*} \times 100\% \quad (1)$$

TABLE II
DSC Characteristics of EVA Copolymers

| Sample | T_m^{onset} (°C) | T_m^{peak} (°C) | T_m^{final} (°C) | ΔH (J/g) | Xc (%) |
|--------|---------------------------|--------------------------|---------------------------|------------------|--------|
| EVA14 | 61.3 | 89.7 | 95.5 | 78.9 | 28.5 |
| EVA18 | 54.2 | 86.1 | 94.5 | 59.6 | 21.5 |
| EVA28 | 34.2 | 71.8 | 83.1 | 32.6 | 11.8 |

T_m^{onset} , onset melting temperature; T_m^{peak} , peak position in melting temperature range; T_m^{final} , final melting temperature; ΔH , enthalpy of fusion; Xc, relative crystallinity.

Where ΔH^* is the enthalpy of fusion of the perfect polyethylene (PE) crystal and ΔH is the enthalpy of fusion of the EVA, EPDM/SmBO₃/EVA, and EPDM/ATO/EVA samples. The value of ΔH^* for PE is 277.1 J/g.¹⁶ ϕ is the weight fraction of EVA in EPDM composites.

Crosslink density

Crosslink density of EPDM specimens was measured by the solvent swell method. EPDM samples were immersed in toluene for 72 h at room temperature. The crosslink density was determined by the Flory-Rehner equation:¹⁷

$$v = -\frac{1}{V} \left[\frac{\ln(1 - V_R) + V_R + \mu V_R^2}{V_R^{1/3} - \frac{V_R}{2}} \right] \quad (2)$$

Where v is the crosslink density (mol cm⁻³), V_R is the volume fraction of EPDM rubber after immersion in toluene, V is the molar volume of toluene (cm³ mol⁻¹), μ is the interaction parameter between rubber and toluene (0.49).¹⁶

Scanning electron microscopy

The dispersion of filler was carried out by scanning electron microscopy (SEM) (JEOL JSM-5900, Japan). The samples were fractured in liquid nitrogen, and then fracture surface was sputtered with a thin layer of gold to avoid electrical charging during examination.

Mechanical properties

Test specimens were cut off from vulcanized sheets, more than 24 h after vulcanization. The tensile and tear tests were carried out according to ISO37 and ISO 34 using a CMT 5254 type electromechanical universal testing machine (Shengzhen SANS Testing Machine Co., China) at a stable rate of 500 mm/min. The Shore A hardness of the specimens was measured using a LX-A rubber Shore A hardness degree tester (Jiangsu Mingzhu Testing Machinery Co., China) according to ISO 868.

Electric properties

Volume and surface resistivity. The volume and surface resistivity of composites were measured at room temperature by a high-insulation resistance meter (Shanghai Precision & Scientific Instrument Co., China) following IEC 60,093.

Dielectric constant and dielectric loss. The dielectric constant and dielectric loss were measured at 10 MHz (Agilent 4294A precision impedance analyzer, America) following IEC 60,250.

Dielectric strength. The dielectric strength was determined following IEC 60,243-1. The voltage source is a YOJ – 10kVA step-up transformer (Xuzhou Power Transformer Factory, China). The voltage on the circular sample with diameter of 100 mm is increased from zero until dielectric failure of the test specimen occurs. The power rating for this test was 1 kV/s for voltages under 20 kV, and 2 kV/s for voltages up to 20 kV.

RESULTS AND DISCUSSION

DSC measurement of EVA copolymers and EPDM composites

Table II shows DSC characteristics of EVA copolymers. It is clear that with the ascend of VA content, onset melting temperature (T_m^{onset}), peak melting temperature (T_m^{peak}), final melting temperature (T_m^{final}), melt enthalpy (ΔH) and crystallization degree (Xc) all descend. The Xc increased from 11.8% at 28 wt % VA content to 28.5% at 14 wt % VA content.

It is shown from Table III that EPDM/SmBO₃ and EPDM/ATO possess no melting peak. With the rise of VA content, T_m^{onset} , T_m^{peak} , T_m^{final} , ΔH and Xc of EPDM composites filled with EVA all drop. What's more, the value of T_m^{onset} , T_m^{peak} , T_m^{final} , ΔH and Xc of EPDM composites are lower than those of EVA resins to some extent. Take the EVA14 for example, the Xc falls from 28.5 wt % in the form of granule to 15.4% in EPDM/SmBO₃/EVA14.

TABLE III
DSC Characteristics of Crosslinked EPDM Composites

| Sample | T_m^{onset} (°C) | T_m^{peak} (°C) | T_m^{final} (°C) | ΔH (J/g) | Xc (%) |
|-------------------------------|---------------------------|--------------------------|---------------------------|------------------|--------|
| EPDM/SmBO ₃ | – | – | – | – | – |
| EPDM/SmBO ₃ /EVA14 | 42.8 | 76.9 | 84.8 | 42.7 | 15.4 |
| EPDM/SmBO ₃ /EVA18 | 42.3 | 74.6 | 80.5 | 38.4 | 13.8 |
| EPDM/SmBO ₃ /EVA28 | 42.9 | 60.8 | 69.4 | 20.0 | 7.2 |
| EPDM/ATO | – | – | – | – | – |
| EPDM/ATO/EVA14 | 41.8 | 75.8 | 82.9 | 47.5 | 17.1 |
| EPDM/ATO/EVA18 | 40.9 | 71.2 | 78.6 | 43.7 | 15.8 |
| EPDM/ATO/EVA28 | 42.4 | 59.3 | 69.5 | 24.4 | 8.8 |

T_m^{onset} , onset melting temperature; T_m^{peak} , peak position in melting temperature range; T_m^{final} , final melting temperature; ΔH , enthalpy of fusion; Xc, relative crystallinity.

TABLE IV
Effect of VA Content on Mooney Viscosity of EPDM Composites

| Sample | SmBO ₃ | | ATO | |
|--------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| | ML ₁₊₄ ^{125°C} | ML ₁₊₄ ^{100°C} | ML ₁₊₄ ^{125°C} | ML ₁₊₄ ^{100°C} |
| EPDM Control | 33.7 | 57.9 | 33.0 | 52.7 |
| EPDM/EVA14 | 29.3 | 52.4 | 27.4 | 48.0 |
| EPDM/EVA18 | 27.8 | 47.4 | 22.1 | 45.7 |
| EPDM/EVA28 | 22.3 | 40.0 | 18.7 | 39.3 |

Mooney viscosity measurement

The combined effect of filler and EVA type on Mooney viscosity is shown in Table IV. It can be seen that the addition of EVA14, EVA18, and EVA28 could all decrease Mooney viscosity at 100 and 125°C of EPDM/SmBO₃ and EPDM/ATO. Among them the EVA28 could greatly reduce the Mooney viscosity at 125°C of EPDM/SmBO₃ and EPDM/ATO from 33.7 to 22.3, and 33.0 to 18.7 Mooney units, respectively. This is attributed to the fact that the T_m^{final} of those copolymers is lower than 100°C, which is listed in Table IV. Thereby the EVA copolymers which melted totally at 100 and 125°C could endow the EPDM/SmBO₃ and EPDM/ATO more fluidity, which could facilitate the manufacturing process.

According to MFR data mentioned in material section, the increased VA content would also lower the MFR of EVA copolymer. This is because VA groups could enlarge the gap between ethylene chains and then facilitate the chain motion at test temperature of MFR measurement. In this way, the Mooney viscosity of EPDM would also be cut down due to the rising fluidity caused by grown VA content.

In addition, the increase of test temperature, from 100°C to 125°C, could further lower the Mooney viscosity of EPDM/SmBO₃ and EPDM/ATO. This is ascribed to the fact that macromolecular chains would gain much more mobility at relatively higher temperature, so EPDM composites exhibited higher Mooney viscosity at 125°C than at 100°C. And the enhanced fluidity of gum could facilitate the manufacture process at 180°C.¹⁸

Cure properties of EPDM mixes

The rheographs, cure characteristics and crosslink density of EPDM composites with EVA copolymers are shown in Figures 1, 2 and Table V. The initial decline of torque could be explained by the softening of the EPDM/EVA blend caused by heating. Then, torque soars because of the formation crosslinking bonds.¹⁴ Obviously, ultimate cure state of EPDM/SmBO₃/EVA vulcanizates indicated by max-

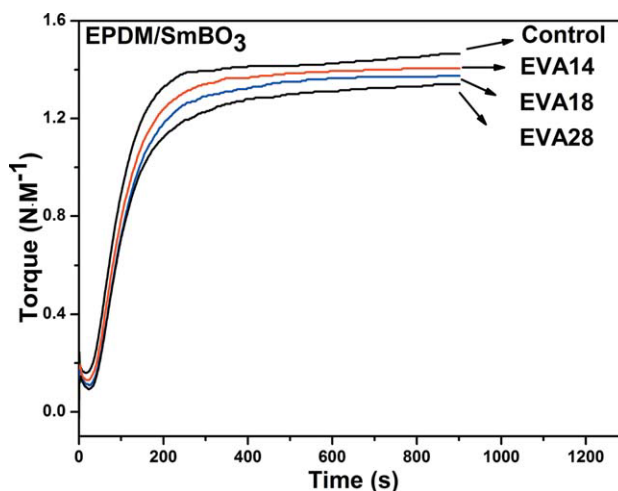


Figure 1 Effect of VA content on cure curves of EPDM/SmBO₃/EVA composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

imum torque (M_H), cure rate, and crosslink density follow the order: vulcanizate with EPDM/SmBO₃ > EPDM/SmBO₃/EVA14 > EPDM/SmBO₃/EVA18 > EPDM/SmBO₃/EVA28, whereas M_H and cure rate of EPDM/ATO/EVA vulcanizates follow the order: EPDM/ATO > EPDM/ATO/EVA28 > EPDM/ATO/EVA18 > EPDM/ATO/EVA14.

It is reported that in the presence of thermo, the acetate in EVA copolymers would decompose into a polyunsaturated linear hydrocarbon and to release mainly acetic acid in neutral or acidic condition.⁷ When dispersed in alkaline condition, EVA would partially hydrolyze and produce polyvinyl alcohol, according to eq. (3).¹⁹ What's more, DCP, which is

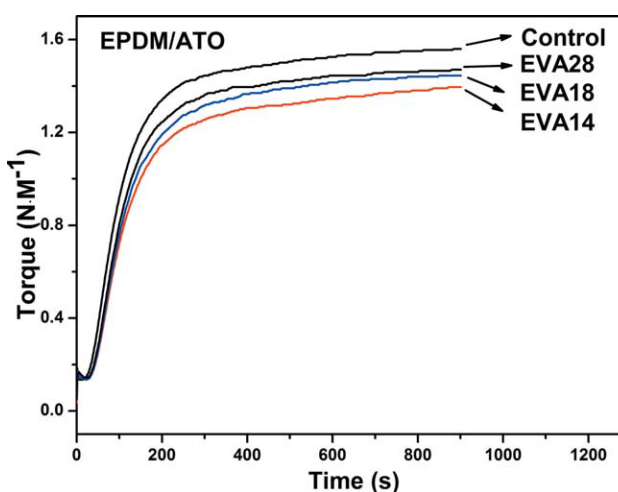


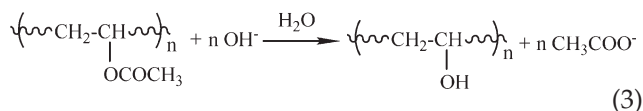
Figure 2 Effect of VA content on cure curves of EPDM/ATO/EVA composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Effect of VA Content on Cure Characteristics and Crosslinking Density of EPDM Composites

| Sample | M_L (Nm) | t_{ML} (min) | M_H (Nm) | t_{MH} (min) | t_{s2} (min) | t_{90} (min) | Cure rate (Nm min ⁻¹) | Crosslink density (mol cm ⁻³) |
|-------------------------------|---------------|-------------------|---------------|-------------------|-------------------|-------------------|--------------------------------------|--|
| EPDM/SmBO ₃ | 0.16 | 0.25 | 1.47 | 14.27 | 0.88 | 3.43 | 0.0934 | 0.000863 |
| EPDM/SmBO ₃ /EVA14 | 0.15 | 0.30 | 1.43 | 14.31 | 0.95 | 3.77 | 0.0914 | 0.000795 |
| EPDM/SmBO ₃ /EVA18 | 0.15 | 0.32 | 1.42 | 14.42 | 1.00 | 4.05 | 0.0901 | 0.000686 |
| EPDM/SmBO ₃ /EVA28 | 0.15 | 0.35 | 1.40 | 14.53 | 1.06 | 4.68 | 0.0882 | 0.000592 |
| EPDM/ATO | 0.14 | 0.12 | 1.56 | 15.42 | 0.82 | 4.27 | 0.0928 | 0.000992 |
| EPDM/ATO/EVA14 | 0.14 | 0.35 | 1.36 | 14.55 | 1.02 | 5.40 | 0.0859 | 0.000819 |
| EPDM/ATO/EVA18 | 0.14 | 0.37 | 1.41 | 14.68 | 0.98 | 4.97 | 0.0887 | 0.000961 |
| EPDM/ATO/EVA28 | 0.14 | 0.42 | 1.47 | 15.05 | 0.93 | 4.62 | 0.0909 | 0.001081 |

M_L : minimum torque; t_{ML} : time to minimum torque; M_H : maximum torque; t_{MH} : time to maximum torque; t_{s2} : scorch time; t_{90} : optimum cure time; Cure rate: $(M_H - M_L)/(t_{MH} - t_{ML})$.

sensitive to acid, would generate ions rather than radicals when pH value of cure system is lower than 7.²⁰



Because the SmBO₃ particles are alkaline,⁹ EVA would hydrolyze and produce polyvinyl alcohol rather than double bonds and acetic acid, and lower the pH value of EPDM composites by consuming OH⁻.¹⁹ So, more VA groups indicate more OH⁻ would be consumed. In other words, the pH level of EPDM/SmBO₃/EVA would be decreased by the growing amount of VA groups. And lower pH value means DCP is more likely to decompose into ions, which can not participate into cure and then reduce the M_H , cure rate, and crosslink density of EPDM/SmBO₃/EVA composites.

EVA would decompose into double bonds and acetic acid in the presence of acidic ATO particles.⁹ Therefore, there are two competing factors influencing the vulcanization: the double bonds and the acetic acid. The double bonds would react with peroxide radicals, followed by transfer of the radical to another chain, which would form a new crosslink to increase crosslink efficiency of EPDM composites.²¹⁻²³ The acetic acid would make DCP decompose into ions rather than radicals and then retard the vulcanization of EPDM composites.^{9,20} It seemed that when VA content in EVA is no more than 14%, it was the acetic acid played the main effect on vulcanization of EPDM/EVA/ATO composites. What's more, when VA content reaches 18 wt %, the effect of double bonds would counteract with that of acetic acid to some degree, making the crosslink density of EPDM/ATO/EVA18 more higher than EPDM/ATO/EVA14. Moreover, when VA content is 28 wt % in EVA, it was the double bonds that took the main effect on vulcanization of EPDM composites.

In this way, the M_H , cure rate, and crosslink density of EPDM/ATO/EVA follow the order: EVA/ATO/EVA28 > EVA/ATO > EVA/ATO/EVA18 > EVA/ATO/EVA14.

The acetic acid and double bonds are two competing factors influencing the vulcanization of EPDM/EAA/composites. It seemed that when VA content is below 28 wt %, EVA from the first year of aging,

Scorch time is the time taken for the minimum torque value to increase by two units. It is an indicator of premature vulcanization of the matrix. It is revealed from Table V that ATO could reduce scorch time of EPDM, because particles with low pH can reduce scorch time owing to the possibility of matrix crosslinking while mixing.²⁴ What's more, the increase of VA content can prolong the scorch time of EPDM/SmBO₃/EVA composites, but shorten that of EPDM/ATO/EVA composites. In other words, with the increase of VA content, the scorch safety of EPDM/SmBO₃/EVA become better, while that of EPDM/ATO/EVA worse. This trend was consistent with trend of cure rate: the gum, which cured slower would possess better scorch safety.

Filler dispersion and mechanical properties of EPDM vulcanizates

Filler dispersion could influence the mechanical properties of EPDM vulcanizates to some extent. Scanning electron micrographs (Fig. 3) shows the effect of VA content on filler dispersion of EPDM composites. Apparently, the variation of VA content did not influence the filler aggregation and dispersion. This is because the VA groups posed little effect on the strong hydrogen bonding formed by hydroxyl on filler surface.

It is revealed that the phase morphologies of EPDM composites exhibit a high degree of cocontinuity. This is because that the main component of EVA is ethylene chains, which possess good compatibility with EPDM, copolymer of ethylene and propylene.²⁵

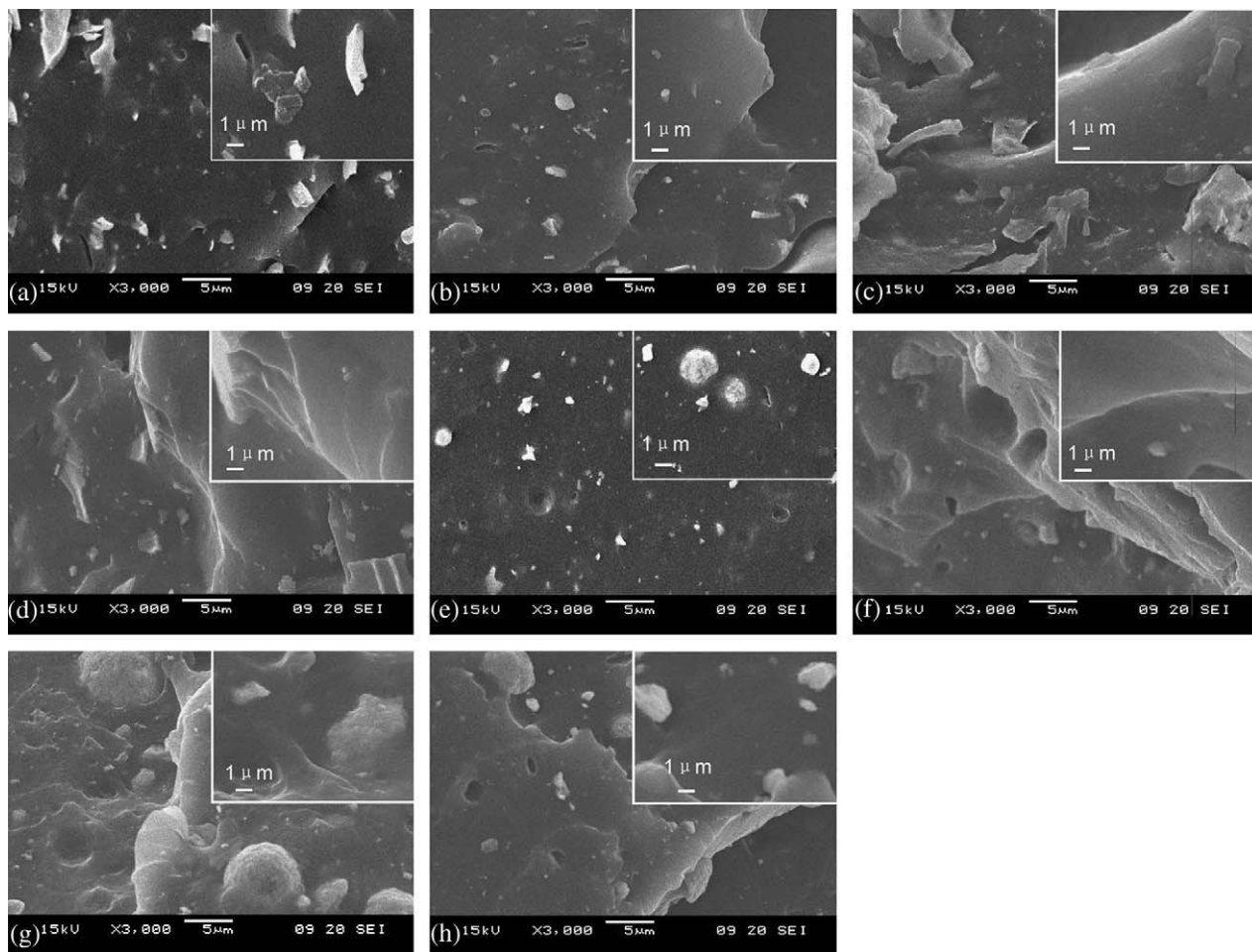


Figure 3 SEM micrographs of rubber vulcanizates with different fillers and EVA resin: (a) EPDM/ SmBO_3 ; (b) EPDM/ SmBO_3 /EVA14; (c) EPDM/ SmBO_3 /EVA18; (d) EPDM/ SmBO_3 /EVA28; (e) EPDM/ATO; (f) EPDM/ATO/EVA14; (g) EPDM/ATO/EVA18; (h) EPDM/ATO/EVA28.

Data of mechanical properties of EPDM/ SmBO_3 /EVA and EPDM/ATO/EVA composites with various VA content of EVA are listed in Table VI. The addition of EVA copolymers could enhance hardness, tensile and tear strength of EPDM/ SmBO_3 and EPDM/ATO composites. With the increase of VA content, the hardness, tensile, and tear strength of EPDM/ SmBO_3 /EVA composites all fall, while those

of EPDM/ATO/EVA composites follow the order: EPDM/ATO/EVA18 > EPDM/ATO/EVA14 > EPDM/ATO/EVA28. Among them, the EVA14 could have EPDM/ SmBO_3 and EPDM/ATO reinforced from 2.95 MPa and 2.36 MPa to 3.74 MPa and 3.63 MPa, respectively, and could at the meantime improve the processing of EPDM composites filled with EVA by curtailing Mooney viscosity of those composites.

TABLE VI
Effect of VA Content Mechanical Properties of EPDM Composites

| Sample | Hardness Shore (A) | Tensile strength (MPa) | Elongation at break (%) | Tear strength (kN m^{-1}) |
|------------------------------|-----------------------|---------------------------|----------------------------|---|
| EPDM/ SmBO_3 | 55 | 2.95 | 169 | 8.72 |
| EPDM/ SmBO_3 /EVA14 | 65 | 3.74 | 184 | 11.64 |
| EPDM/ SmBO_3 /EVA18 | 64 | 3.47 | 193 | 11.16 |
| EPDM/ SmBO_3 /EVA28 | 62 | 3.04 | 198 | 10.73 |
| EPDM/ATO | 55 | 2.36 | 165 | 8.91 |
| EPDM/ATO/EVA14 | 62 | 3.63 | 180 | 9.87 |
| EPDM/ATO/EVA18 | 63 | 4.00 | 173 | 13.19 |
| EPDM/ATO/EVA28 | 61 | 2.96 | 95 | 11.26 |

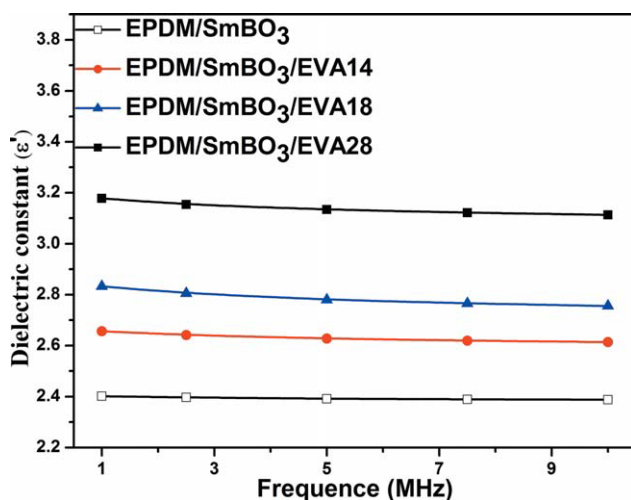


Figure 4 Effect of VA content on dielectric constant of EPDM/SmBO₃/EVA composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Due to little discrepancy among dispersion and size of SmBO₃ and ATO, it is concluded that mechanical properties of EPDM are largely dependent on crosslink density.²⁶ According to literature, the crystallinity of EVA would influence the mechanical properties of EVA resin.⁷ The increase of VA content could retard the vulcanization of EPDM/SmBO₃/EVA composites, and then reduce the crosslink density. What's more, the increased VA groups would also hinder the arrangement of ethylene chain into crystal lattice and then decrease the crystallinity of EVA shown in Table III. Thus, from the combined view of crosslink density and crystallinity, the increase of VA content would decrease the hardness, tensile, and tear strength of EPDM/SmBO₃/EVA composites. In addition, the increasing VA content would make the crosslink density of EPDM composites descend, so there are less C—C linkages to restrict the macromolecular motion, leading to the rise of elongation at break of EPDM/SmBO₃/EVA composites.

In terms of EPDM/ATO/EVA composites, the trend of crosslink density follows the order: EPDM/ATO/EVA28 > EPDM/ATO > EPDM/ATO/EVA18 > EPDM/ATO/EVA14, while that of crystallinity obeys the sequence: EPDM/ATO/EVA14 > EPDM/ATO/EVA18 > EPDM/ATO/EVA28 > EPDM/ATO. Thereby, there are two competing factors affecting mechanical properties of EPDM/ATO/EVA composites: crosslink density of EPDM and crystallinity of EVA. Clearly, it is the crystallinity that made the major contribution on mechanical properties of EPDM/ATO/EVA, making EPDM/ATO/EVA18 the highest hardness, tensile and tear strength among EVA copolymers.

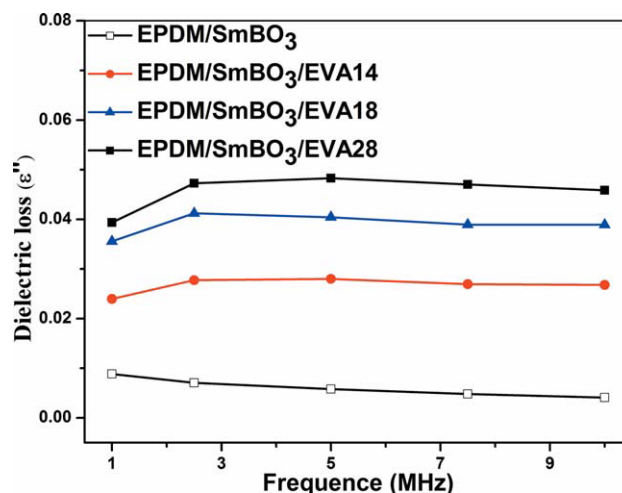


Figure 5 Effect of VA content on dielectric loss of EPDM/SmBO₃/EVA composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Electric properties of EPDM vulcanizates

Dielectric constant and loss of EPDM vulcanizates

EPDM is regarded as an insulator just like most polymers.²⁷ The relative dielectric constant and loss, which are utilized to characterize molecular relaxations, were measured. The relative dielectric constant is a measure of the energy stored in a sample during a cyclic electric excitation. The relative dielectric loss is a measure of the energy lost into a system during cyclic electric excitation.²⁸

Figures 4–7 show curves of dielectric constant and loss of EPDM/SmBO₃/EVA and EPDM/ATO/EVA composites in the range of frequency from 1 to 10 MHz. It is clear that the dielectric constant and loss

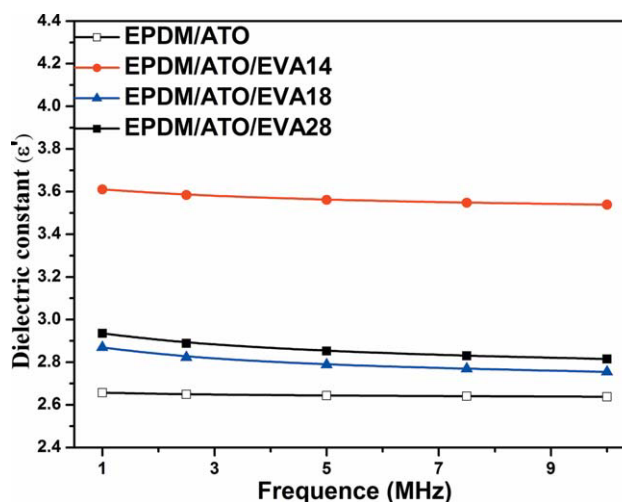


Figure 6 Effect of VA content on dielectric constant of EPDM/ATO/EVA composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

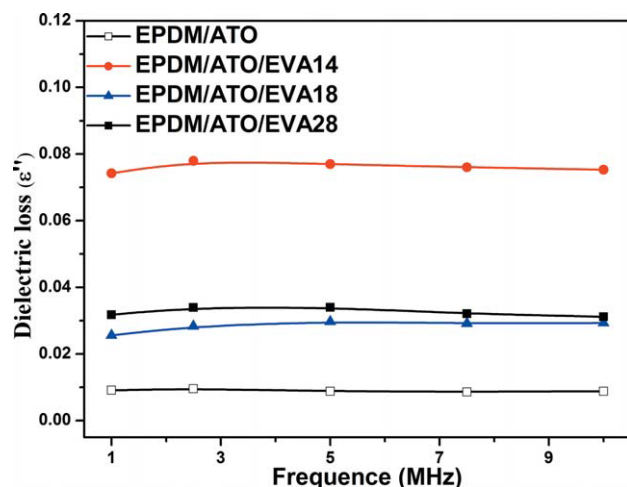


Figure 7 Effect of VA content on dielectric loss of EPDM/ATO/EVA composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of EPDM/SmBO₃/EVA increase with the increasing VA content. The reason is that the increase of VA content would increase the dipole polarity of composite, and lower the crosslink density of EPDM composites. VA groups possess higher polarity than ethylene chains, and crosslink points would hinder the motion of dipoles. Therefore, the ascending of VA content would make more dipoles aligning to cyclic electric excitation, and the descending of crosslink density would enhance the mobility of dipoles, both of which would boost the dielectric constant and loss.²⁹

Apparently, the EPDM/ATO/EVA14 possesses the highest value of dielectric constant and loss than other EPDM/ATO/EVA composites. And the dielectric constant and loss of EPDM/ATO/EVA18 and EPDM/ATO/EVA28 are almost the same. This phenomenon lies in the two competing factors: amount of polar groups and crosslink density. The increasing VA groups could not only provide more dipoles but also enhance the crosslink density of EPDM/ATO/EVA composites. So it seemed that the effect of crosslink density on dielectric constant counter-

acted with that of VA groups by some degree, leading to drop of dielectric constant and loss of EPDM/ATO/EVA18 and EPDM/ATO/EVA28 composites.

Volume and surface resistivity and dielectric strength of EPDM vulcanizates

Table VII shows dependencies of dielectric strength, surface and volume resistivity of EPDM composites on VA content of EPDM/SmBO₃/EVA and EPDM/ATO/EVA composites. It is found that the increase of VA content could lower the surface and volume resistivity of EPDM composites. Resistivity is a measure of the resistance the material exhibits to the passage of current. More VA content means more interconnective pathways or conductive channels in matrix. And the increase of such pathways indicates easier current carrier motion, which could facilitate passage of current and reduce surface and volume resistivity of composites.³⁰

The dielectric strength of EPDM/SmBO₃/EVA14 decreased with the increase of VA content, while that of EPDM/ATO/EVA14 possesses the relatively the lowest dielectric strength among EPDM/ATO/EVA copolymers. Generally, the dielectric strength is correlated with two factors: dielectric constant and crosslink density. The higher the dielectric constant means more energy stored, which makes perforation in composites easier. The more the crosslink points are, the easier the penetration would become. The increased VA content would lower the crosslink density and boost the dielectric constant of EPDM/SmBO₃/EVA composites, leading to the decrease of dielectric strength. Additionally, the decrease of dielectric strength is not obvious when the VA content exceeded 18 wt %.

In terms of EPDM/ATO/EVA, the crosslink density followed the order: EPDM/ATO/EVA28 > EPDM/ATO > EPDM/ATO/EVA18 > EPDM/ATO/EVA14. EPDM/ATO possesses no polar VA groups and the relatively higher crosslink density, so the dielectric strength of EPDM/ATO is the highest among other EPDM/ATO/EVA composites. In terms of EPDM/ATO/EVA composites, it seemed

TABLE VII
Effect of VA Content Resistivity and Dielectric Strength of EPDM/EVA/Filler Composites

| Sample | Surface resistivity (Ω) | Volume resistivity (Ωm) | Dielectric strength (kV m ⁻¹) |
|-------------------------------|-------------------------|-------------------------|---|
| EPDM/SmBO ₃ | 1.31 × 10 ¹⁰ | 2.61 × 10 ¹⁵ | 33.6 |
| EPDM/SmBO ₃ /EVA14 | 4.46 × 10 ¹⁰ | 1.08 × 10 ¹⁵ | 29.6 |
| EPDM/SmBO ₃ /EVA18 | 4.23 × 10 ¹⁰ | 1.82 × 10 ¹⁴ | 28.5 |
| EPDM/SmBO ₃ /EVA28 | 5.39 × 10 ¹⁰ | 9.44 × 10 ¹³ | 28.3 |
| EPDM/ATO | 9.24 × 10 ¹⁰ | 2.91 × 10 ¹⁵ | 24.3 |
| EPDM/ATO/EVA14 | 1.39 × 10 ¹¹ | 2.97 × 10 ¹⁵ | 21.1 |
| EPDM/ATO/EVA18 | 1.15 × 10 ¹¹ | 3.08 × 10 ¹⁴ | 22.1 |
| EPDM/ATO/EVA28 | 1.54 × 10 ¹¹ | 2.05 × 10 ¹³ | 22.9 |

that the crosslink density played the more remarkable effect than that of VA groups. Thereby, the dielectric strength of EPDM/ATO/EVA composites rises with the increased VA content.

CONCLUSIONS

The crystalline EVA resins could not only melt above 100°C to increase the fluidity of EPDM gums but also reinforce the EPDM/SmBO₃ and EPDM/ATO composites by crystallizing in EPDM composites. The interaction of VA groups and pH level of filler particles have significant influence on vulcanization of EPDM/SmBO₃/EVA and EPDM/ATO/EVA composites.

It was found that in the presence of alkaline SmBO₃ particles, the VA groups would hydrolyze to produce polyvinyl alcohol, and lower the pH value, which would make DCP decompose into ions and then retard the vulcanization of EPDM/SmBO₃/EVA composites. By comparison, in the presence of acidic particles, The VA groups could decompose into a polyunsaturated linear hydrocarbon and to release mainly acetic acid. The generated double bonds could react with DCP to promote crosslink efficiency of EPDM/ATO/EVA composites. The acetic acid could also make DCP decompose into ions and then retard the vulcanization of EPDM/ATO/EVA composites. It seemed that it is the formed double bonds posed more remarkable effect on the vulcanization of EPDM/ATO/EVA composites. Therefore, the M_H and cure rate of EPDM/ATO/EVA ascended with the increasing VA content.

The VA content also affects the crystallinity of EVA in EPDM/filler/EVA composites. What's more, the combined effect of crystallinity and crosslink density would contribute to the variation of mechanical and electrical properties of EPDM/SmBO₃/EVA and EPDM/ATO/EVA composites.

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