Effect of Hot Air Aging on Properties of EPDM/SmBO$_3$/EVA and EPDM/ATO/EVA Composites

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ABSTRACT: Ethylene–propylene–diene rubber (EPDM)/ samarium borate (SmBO$_3$)/ethylene-vinyl acetate (EVA) copolymer and EPDM/antimony-doped tin oxide (ATO)/ EVA composites are aged at 150°C for different intervals. Surface modification is used to improve filler to matrix interphase. The main aim is to investigate the effect of filler type and vinyl acetate (VA) content in EVA on stability of EPDM composites. It is found that acidic ATO particles can lower pH level of EPDM composites and then promote the degradation of acetic acid during aging. Moreover, when VA content exceeds 14 wt %, the instable VA content causes more acetic acids escape during aging. With the increasing of aging time, EPDM/SmBO$_3$ control and EPDM/SmBO$_3$/EVA composites tend to become darker while EPDM/ATO and EPDM/ATO/EVA composites would become yellow. And the color change is correlated well with the variation of carbonyl index. The chemical crosslink points prevent crystals in EVA from melting at aging temperature (150°C), and the variation of crosslink density influences the crystallinity during aging. The tendency of tensile strength is well consistent with that of swelling ratios, and electric properties are correlated with increased polar groups and crystallinity. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3277–3289, 2011

Key words: ethylene–propylene–diene rubber; ethylene-vinyl acetate copolymer; hot air aging; carbonyl index; swelling ratio; mechanical and electric properties

INTRODUCTION

The copolymerization of ethylene and propylene leaves ethylene–propylene–diene rubber (EPDM) saturated main chain, which endows EPDM excellent resistance to heat, oxidation, electricity, and polar solvent.[1,2] However, the copolymerization can inhibit the crystallization of ethylene chain in EPDM, leading to few crystals in EPDM. Thus, it is necessary to reinforce it to expand its usage.[3–5] In the recent years, there were growing interests in two kinds of inorganic fillers, samarium borate (SmBO$_3$)[6] and antimony-doped tin oxide (ATO),[7] which possess excellent electromagnetic properties.

We have reported that the addition of SmBO$_3$ and ATO can both reinforce the EPDM and endow EPDM with other properties.[8,9] Because the tensile strength of EPDM/SmBO$_3$ and EPDM/ATO composites is not satisfactory, we plan to further reinforce it. Generally, there are two main ways to reinforce EPDM to obtain optimal mechanical properties: adding inorganic fillers, such as carbon black[10], silica,[11]

and clay[12]; blending with crystalline resins [polyethylene (PE) and polypropylene].

Commonly, crystal lattices not only withstand forces at room temperature and then reinforce EPDM composites, but also melt under cure temperature of EPDM composites, which boost the fluidity of EPDM. So the addition of crystal resins can reinforce EPDM/filler and at the meantime increase the fluidity of EPDM/filler/resin composites.

There are a lot of literatures reporting the reinforcement of EPDM by blending with polyolefins. And some of them emphasize how blend ratio and cure system affect properties of EPDM/polyolefin composites.[13,14] However, there are few reports regarding the reinforcement of EPDM/SmBO$_3$ and EPDM/ATO composites by blending ethylene-vinyl acetate copolymer (EVA).[15] In our previous work, we found that there are crystal lattices in EVA at room temperature to withstand forces and then reinforce EPDM composites. Moreover, the properties of EPDM/filler/EVA composites can also be influenced by the varied content of vinyl acetate (VA).

VA groups are instable in the presence of heat, and there are few reports regarding how SmBO$_3$ and ATO particles affect thermal stability of EPDM composites. There are few literatures reporting the effect of VA content and filler type on properties of EPDM during aging. Thus, it is necessary for

TABLE I
EPDM Composites Formulation (phr)

Sample no.	EPDM	EVA14	EVA18	EVA28	SmBO$_3$	ATO	ZnO		DCP	RD	MB
A	100	–	–	–	30	–	5	1	4	0.5	0.5
B	80	20	–	–	30	–	5	1	4	0.5	0.5
C	80	–	20	–	30	–	5	1	4	0.5	0.5
D	80	–	–	20	30	–	5	1	4	0.5	0.5
E	100	–	–	–	–	30	5	1	4	0.5	0.5
F	80	20	–	–	–	30	5	1	4	0.5	0.5
G	80	–	20	–	–	30	5	1	4	0.5	0.5
H	80	–	–	20	–	30	5	1	4	0.5	0.5

practical users to know how VA content and filler type influence the time-dependent changes of mechanical and electric properties of EPDM/SmBO$_3$/EVA and EPDM/ATO/EVA composites.[16]

In this study, EPDM/SmBO$_3$ and EPDM/ATO composites incorporated with three types of EVA are aged in hot air at 150°C for different intervals. The main aim is to investigate the effect of filler type and VA content in EVA on stability of EPDM composites. Swelling ratio and differential scanning calorimetry (DSC) measurement are applied to monitor the time-dependent changes of mechanical properties of composites. Color difference and electric properties of EPDM composites are also evaluated during aging.

EXPERIMENTAL

Materials

The rubber used in this study is ethylene–propylene–diene monomer (EPDM J-4045) containing 5-ethylidene-2-norbornene (ENB) as diene, which is manufactured by Jilin Petrochem., SINOPEC. The EPDM consists of 52.0 wt % ethylene, 40.3 wt % propylene, and 7.7 wt % ENB. Three commercial EVA copolymers with different VA contents are used for investigation. EVA 14-2 (VA content 14 wt %) and EVA 18-3 (VA content 18 wt %) are produced by Beijing Organic Chemical Plant, China, whereas EVA KA-31 (VA content 28 wt %) is produced by Sumitomo Chemical (Japan). They are all supplied in granular forms. For convenience, we define EVA 14-2, EVA 18-3, and EVA KA-31 as EVA14, EVA18, and EVA28, respectively.

Compounding ingredients, such as dicumyl peroxide, zinc oxide, stearic acid, 2-mercapto benzimidazole (antioxidant MB), and polymerized 2, 2, 4-trimethyl-1, 2-dihydroquinoline (antioxidant RD) are of industrial grade. SmBO$_3$ particles are prepared by sol–gel method, and ATO particles are prepared by coprecipitation method. The commercial name of *bis*(-3-(triethoxysilyl)propyl) tetrasulfide, obtained from Nanjing Shuguang Chemical Group Co., is

KH845-4, and molecular structure of KH845-4 is listed below:
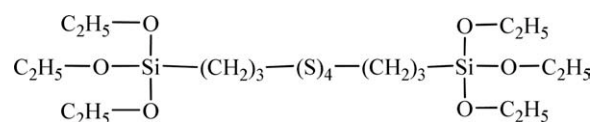
Sample preparation

Surface modification of SmBO$_3$ and ATO

In this work, KH845-4 is applied for the surface treatment of the SmBO$_3$ and ATO particles, respectively. The content of coupling agent is 1% by weight (wt %) of particle amount. For instance, 1.0 g of KH845-4 is mixed with 100 mL ethanol. SmBO$_3$ (100 g) is then added into the solution with a further 30 min stirring to ensure a uniform distribution of the coupling agent on the SmBO$_3$ surface. The treated SmBO$_3$ particles are then dried at 60°C for 4 h in an oven until weight remained constant. Similarly, ATO particles are treated in the method mentioned earlier.

Compounding of EPDM/SmBO$_3$ and EPDM/ATO vulcanizates

According to ISO2393, EPDM is first blended with EVA above the melting temperature (120°C) of EVA. The obtained blends are cooled to room temperature, mixed with cure ingredients, and treated with SmBO$_3$ 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 are vulcanized in an electrically heated press at 180°C and 10.0 MPa for 15 min. Vulcanizates are conditioned for 24 h before testing.

Hot air aging

Sheets and dumbbells samples of EPDM, with smooth surface, prepared above are both placed in a hot air aging testing chamber 401A (JiangDu Mingzhu Testing Machinery Co., China) with air blowing for aging testing at different intervals of time up

to 14 days, where the temperature is $(150 \pm 1)°C$. All conditions in the hot air aging refer to ISO188.

Fourier transform infrared spectroscopy

FTIR spectra of EPDM/EVA/SmBO$_3$ and EPDM/EVA/ATO composites before and after aging are obtained by attenuated total reflectivity with a resolution of 4 cm^{-1} in the range of 600–4000 cm^{-1} in NEXUS 670 spectrometer (Nicolet, USA).

Colorimetric measurement

The surface of EPDM/EVA/filler composites before and after aging is determined according to ISO 7724 by CR-300 model colorimeter (Konica Minolta, Japan). Lightness (L) and chromacity coordinates (a and b) are measured. The total color change (ΔE) is calculated using the following equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \qquad (1)$$

where $+\Delta L =$ lighter, $-\Delta L =$ darker, $+\Delta a =$ redder, $-\Delta a =$ greener, $+\Delta b =$ yellower, $-\Delta b =$ bluer.

DSC measurement

The melting behaviors of EVA and EPDM composites are evaluated using Q200 type of DSC instrument (TA). Samples (EPDM composites) weighing about 10 mg are first heated from 30 to 150°C with a heating rate of 40°C/min and then are held at 150°C for 3 min to eliminate the effect of thermal history. In the next cooling step, the samples are cooled from 150 to 0°C by a cooling rate of 10°C/min. Finally, the samples are heated again from 0 to 150°C by a heating rate of 20°C/min. The argon purge gas with a flux of 50 mL/min is used to prevent oxidative degradation of samples during the heating run.

$$X_c = \frac{\Delta H}{\varphi \times \Delta H^*} \times 100\% \qquad (2)$$

where ΔH^* is the enthalpy of fusion of the perfect PE crystal and ΔH is the enthalpy of fusion of the EVA after eliminating thermal history, EPDM/SmBO$_3$/EVA, and EPDM/ATO/EVA samples. The value of ΔH^* for PE is 277.1 J/g.[17] φ is the weight fraction of EVA in EPDM composites.

Swelling ratio measurement

According to ISO 10147, EPDM specimens are immersed in xylene for 7 days. The calculation of swelling ratio is shown below:

$$SR = [(W_g - W_d)/(W_o - W_e)] \times K + 1 \qquad (3)$$

where SR is the swelling ratio, W_g the weight of swollen gel after the immersion period, W_d the weight of dried gel, W_o the weight of polymer in the specimen being used, W_s the weight of specimen being tested, $W_e = W_s - W_d$, weight of xylene in swollen gel, K the ratio of density of polymer to that of the solvent at the immersion temperature.

The density of xylene is 0.88g/cm^3 and that of EPDM specimens is measured according to ISO 2781. The equation of density is listed as following:

$$\delta = \rho \frac{m_1}{m_1 - m_2} \qquad (4)$$

where ρ is the density of water, m_1 is the weight of sample in the air, and m_2 is the weight of sample in the water.

Mechanical properties

Test specimens are cut off from vulcanized sheets, more than 24 h after vulcanization. The tensile test is carried out according to ISO37 using a CMT 5254 type electromechanical universal testing machine (Shenzhen SANS Testing Machine Co., China) at a stable rate of 500 mm/min. The Shore A hardness of the specimens is measured using a LX-A rubber Shore A hardness degree tester (JiangDu Mingzhu Testing Machinery Co., China) according to ISO7619-1.

Electrical property measurement

Measurement of volume resistivity. The volume resistivity of composites is measured at room temperature by a high-insulation resistance meter (Shanghai Precision and Scientific Instrument Co., China), following IEC60093.
Measurement of dielectric constant and dielectric loss. The dielectric constant and dielectric loss are measured at 10 MHz (Agilent 4294A precision impedance analyzer, USA), following IEC60250.
Measurement of AC dielectric strength. The dielectric strength at 50 Hz is determined following IEC 60243-1. The voltage source is a YOJ–10 kVA step-up transformer (Xuzhou Power Transformer Factory, China). The voltage on the circular sample with diameter of 100 mm increases from zero until dielectric failure of the test specimen occurs. The power rating for this test is 1 kV/s for voltages under 20 kV and 2 kV/s for voltages above 20 kV.

RESULTS AND DISCUSSION

FTIR spectra of EPDM/EVA/filler composites before and after aging

FTIR spectroscopy has been successfully applied to detect the products and evaluate mechanism of
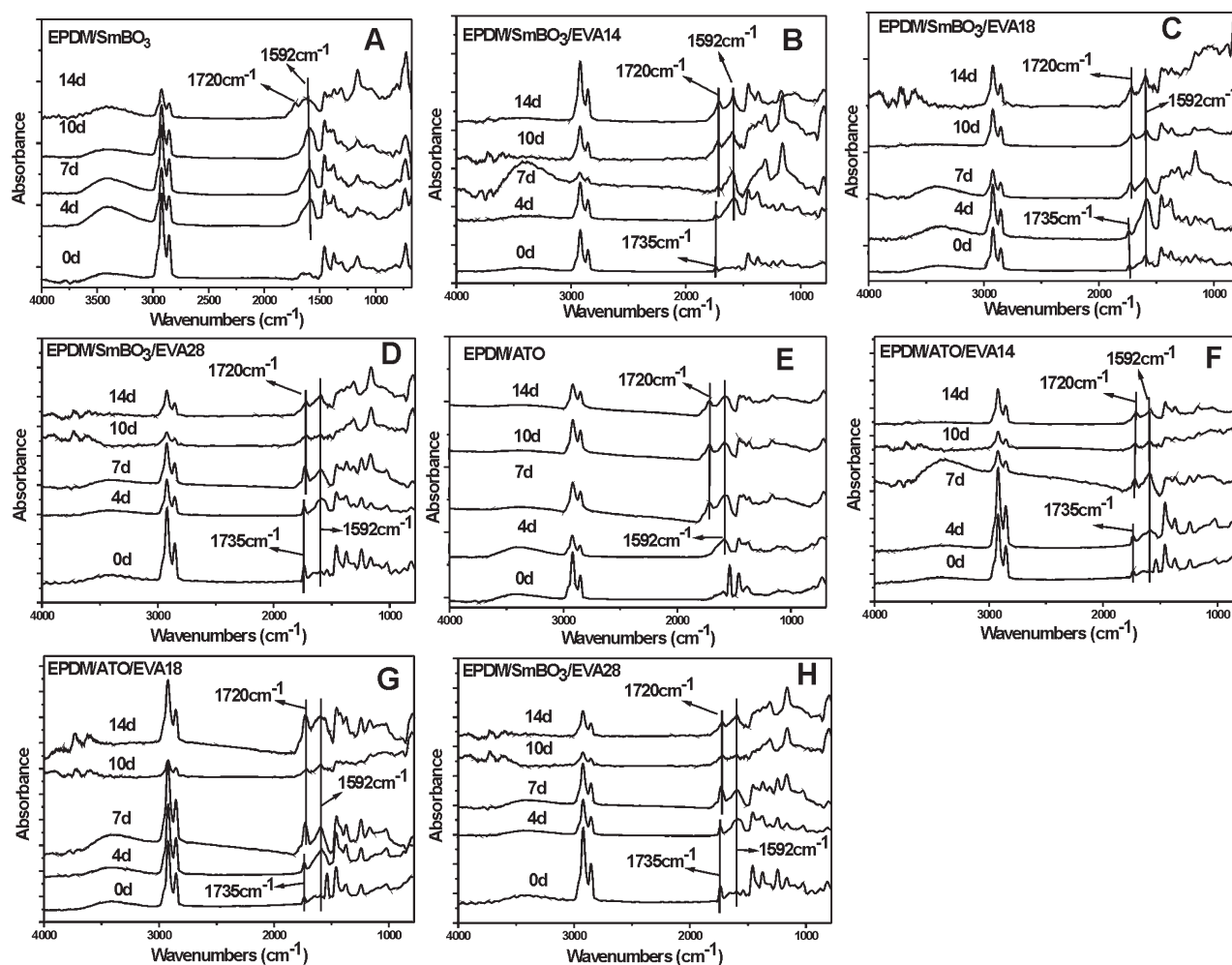
Figure 1 FTIR spectra of EPDM composites before and after hot air aging: (A) EPDM/SmBO$_3$; (B) EPDM/SmBO$_3$/EVA14; (C) EPDM/SmBO$_3$/EVA18; (D) EPDM/SmBO$_3$/EVA28; (E) EPDM/ATO; (F) EPDM/ATO/EVA14; (G) EPDM/ATO/EVA18; (H) EPDM/ATO/EVA28.

polymers during degradation.[18] According to Figure 1, after 4 days of aging, the absorption peak of carboxylate anions appears at 1592 cm^{-1}, for EPDM/SmBO$_3$ and EPDM/ATO control, respectively. Moreover, there is characteristic peak of ketones at 1720 cm^{-1} for EPDM/SmBO$_3$ control after 14 days of aging and for EPDM/ATO control after 7 days of aging, indicating that the formation of ketones in EPDM/ATO control is earlier to be detected than that in EPDM/SmBO$_3$ control. As for EPDM/filler/EVA composites, before aging, there is absorption peak at 1735 cm^{-1}, assigned to stretching vibration of C—O in EVA. After 7 days of aging, the peak at 1735 cm^{-1} disappears, and there appears peak at 1720cm^{-1}. This is because the VA groups can decompose during ageing and form ketones according to Eq. (9). Figure 1(B,C,F,G,H) also shows a absorption peak in the region of 3600–3200 cm^{-1} in 7 days which disappears in 10 and 14 days samples. Absorption peak in the region of 3600–3200 cm^{-1} is possibly ascribed to the —OH and —COOH absorption. It is indicated that with the increase of age-

ing, carboxyl and hydroxyl groups can first emerge in 7 days and further react to form other substance in the rest of ageing time, resulting in the appearance of peak in 3600–3200 cm^{-1} only at 7 days.[11]

The simplified mechanism of ketones is listed in Eq. (5)[8] in Figure 2.[19–21] P radicals are first formed through H abstraction when EPDM samples are thermo-oxidatively aged and then easily react with oxygen to produce polymeric peroxy (ROO radicals) radicals. These ROO radicals can react further with ROO radicals to form ketone.

In our previous work,[9] it is reported that the pH level of treated SmBO$_3$ is alkaline (pH = 7.8); in contrast, treated ATO particles is acidic (pH = 5.0). It seems that acidic ATO can promote formation of ketones. In other words, low-pH value facilitates the formation of ketones in EPDM composites. This is possible that the formation of oxidative products is easier in acidic system of EPDM composites.

Because of the VA groups, there is characteristic absorption peak of carbonyl group at around 1735

$$RH \xrightarrow{\text{heat}} R\bullet + H\bullet \tag{5}$$

$$R\bullet + H\bullet + O_2 \xrightarrow{\text{heat}} ROOH \tag{6}$$

$$2ROOH \xrightarrow{\text{heat}} RO\bullet + H_2O + ROO\bullet \tag{7}$$

$$\overset{\overset{\displaystyle OO\bullet}{|}}{\sim\!\!\sim\!\!\sim CH}\sim\!\!\sim\!\!\sim + ROO\bullet \xrightarrow{\text{heat}} \sim\!\!\sim\!\!\sim \overset{\overset{\displaystyle O}{\|}}{C}\sim\!\!\sim\!\!\sim + ROH + O_2 \tag{8}$$

$$\text{(9)}$$

Figure 2 Simplified mechanism of EVA degradation.

cm^{-1} in EPDM/EVA/SmBO$_3$ and EPDM/EVA/ATO composites before aging. The simplified degradation mechanism of EVA is exhibited in Eq. (9) in Figure 2.

Generally, the degradation of EVA undergoes a pyrolysis involving two-step decomposition: an acetate pyrolysis of copolymer, forming a polyunsaturated linear hydrocarbon and mainly acetic acid.[22] Moreover, oxidative degradation also occurs during aging and contributes to the loss of acetoxy groups of VA units.[23,24]

To characterize the variation of carbonyl groups of EPDM/EVA composites during aging, the increase of absorbance in carbonyl region is measured by FTIR. And carbonyl index is applied to follow the process of hot air aging and defined as the ratio of the peak area between 1800 and 1500 cm^{-1} ($A_{1800-1500}$) and the absorption of the peak at 1463 cm^{-1} (A_{1463})[25]:

$$CI = A_{1800-1500}/A_{1463} \tag{5}$$

The CI of EPDM/EVA/SmBO$_3$ and EPDM/EVA/ATO composites is shown in Figure 3. Clearly, the

CI of EPDM/SmBO$_3$ composites all increases with increasing aging time, and EPDM/SmBO$_3$/EVA composites possess higher CI than EPDM/SmBO$_3$ control before and through the hot air aging. This phenomenon can be explained by the fact that there are double bonds in VA groups, which elevate the CI of EPDM/SmBO$_3$/EVA composites. In addition, according to literature,[8] ATO possesses characteristic absorption peak between 1500 and 1800 cm^{-1}, leading to the initial CI value of EPDM/ATO.

Although EVA14 possesses the lowest VA content before aging, the CI of EPDM/SmBO$_3$/EVA14 is higher than that of other two EPDM/SmBO$_3$/EVA composites after 7 days of aging.

For EPDM/SmBO$_3$/EVA composites, there are three competing factors influencing the CI: the initial VA content, the formed oxidative products containing (C=O), and the acetic acids released during hot air aging. The higher initial VA groups and generated oxidative products pose positive effect on the rise of CI, while instable VA groups are likely to pyrolyze, releasing acetic acids and then decrease the CI during hot air aging.

It seems that when VA contend exceeds 18 wt %, the effect of released acetic acid plays more remarkable effect than other two factors, making the CI of EPDM/SmBO$_3$/EVA18 and EPDM/SmBO$_3$/EVA28 lower than that of EPDM/SmBO$_3$/EVA14 composites at the same aging time.

Compared to alkaline SmBO$_3$, acidic ATO particles can promote the pyrolysis of VA groups in EPDM/EVA, making CI of EPDM/ATO/EVA all lower than that of EPDM/ATO control. This is consistent with literature that the decomposition rate of acetic acid grows with decreasing pH value of system.[26]
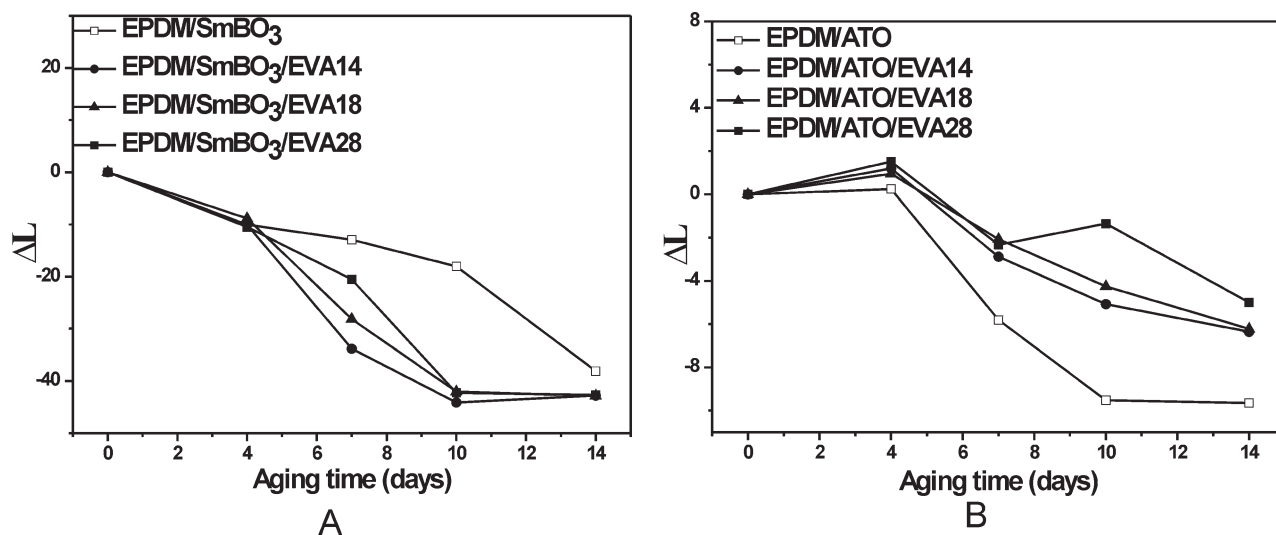
In terms of EPDM/ATO composites, the CI of EPDM/ATO/EVA composites is all higher than that

Figure 3 Carbonyl index of EPDM composites before and after hot air aging: (A) EPDM/SmBO$_3$ composites; (B) EPDM/ATO composites.

Figure 4　Color change of EPDM composites: (A) ΔE of EPDM/SmBO$_3$ composites; (B) ΔE of EPDM/ATO composites.

of EPDM/ATO control at the beginning of aging. However, the CI of EPDM/ATO/EVA composites increases slower than that of EPDM/ATO control during aging. In other words, compared to alkaline SmBO$_3$, acidic ATO particles can promote the pyrolysis of VA groups in EPDM/EVA, making CI of EPDM/ATO/EVA all lower than that of EPDM/ATO control. This is consistent with literature that the decomposition rate of VA grows with decreasing pH value of system.[26]

Moreover, with the increase of VA content, CI rises much slower. There are also three competing factors influencing the CI of EPDM/ATO/EVA composites: the initial VA groups in EVA, loss of acetic acid, and formation of oxidative products containing (C=O). It seems that in the presence of acidic ATO (pH = 5.0), when VA content exceeds 14 wt %, the acetate pyrolysis of EVA is promoted, accelerating

the generation of acetic acid during hot air aging. This is ascribed to the fact that acidic ATO particles can lower the pH level of system, which raises the decomposition rate of VA.

Colorimetry measurement of EPDM/EVA/filler composites before and after aging

In practical use, it is necessary to consider the color change of specimens during aging. The color difference of EPDM specimens before and after hot air aging is presented in Figures 4–7. It is apparent that the total color difference (ΔE) of EPDM/SmBO$_3$ and EPDM/ATO composites increases sharply in the first 7 days of aging and then stays little changed in the last 7 days of aging.

According to Eq. (1), for EPDM/SmBO$_3$, the trend of ΔE is correlated with the lightness factor (ΔL),

Figure 5　Color change of EPDM composites: (A) ΔL of EPDM/SmBO$_3$ composites; (B) ΔL of EPDM/ATO composites.
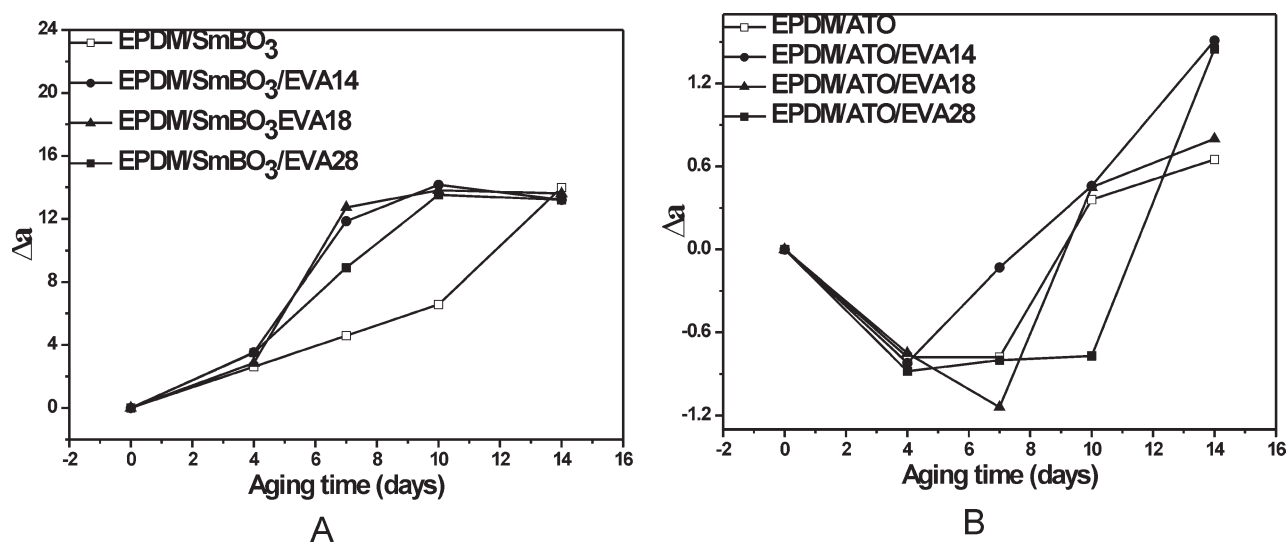
Figure 6 Color change of EPDM composites: (A) Δa of EPDM/SmBO$_3$ composites; (B) Δa of EPDM/ATO composites.

while the ΔE of EPDM/ATO is mainly determined by the Δb. This is because the SmBO$_3$ is light color filler and ATO is deep color filler. Thus, the decreased lightness of EPDM/EVA/SmBO$_3$ would be more remarkable than that of EPDM/EVA/ATO composites. By comparison, during hot air aging, EPDM/EVA/ATO become yellow due to chromophore formation.[27]

The variation of ΔE in EPDM/SmBO$_3$/EVA composites is higher than that in EPDM/SmBO$_3$ control, while EPDM/ATO/EVA composites exhibit lower ΔE than EPDM/ATO control. This can be explained by the varied CI. Because carbonyl groups are chromophore, the higher amount of carbonyl groups causes greater change of ΔE. Moreover, the higher VA content indicates more acetic acid lost during aging, resulting in lower ΔE change. Thus, with the

increase of VA content, the ΔE change of EPDM/filler/EVA composites is less remarkable than that of EPDM/filler control.

Effect of hot air aging on crystallization of EVA in EPDM/EVA/filler composites

Table II lists DSC characteristics of EPDM/EVA/filler composites before and after aging. It is indicated that the peak melting temperature (T_m^{peak}), melting enthalpy (ΔH), and degree of crystallinity (X_c) of EPDM/EVA/filler composites increases gradually in the first 10 days of aging and drops drastically in the last 4 days of aging.

It should be noted that the aging temperature in this study is 150°C, which is higher than the temperature of melting peak (T_m^{peak}) of EVA copolymers in
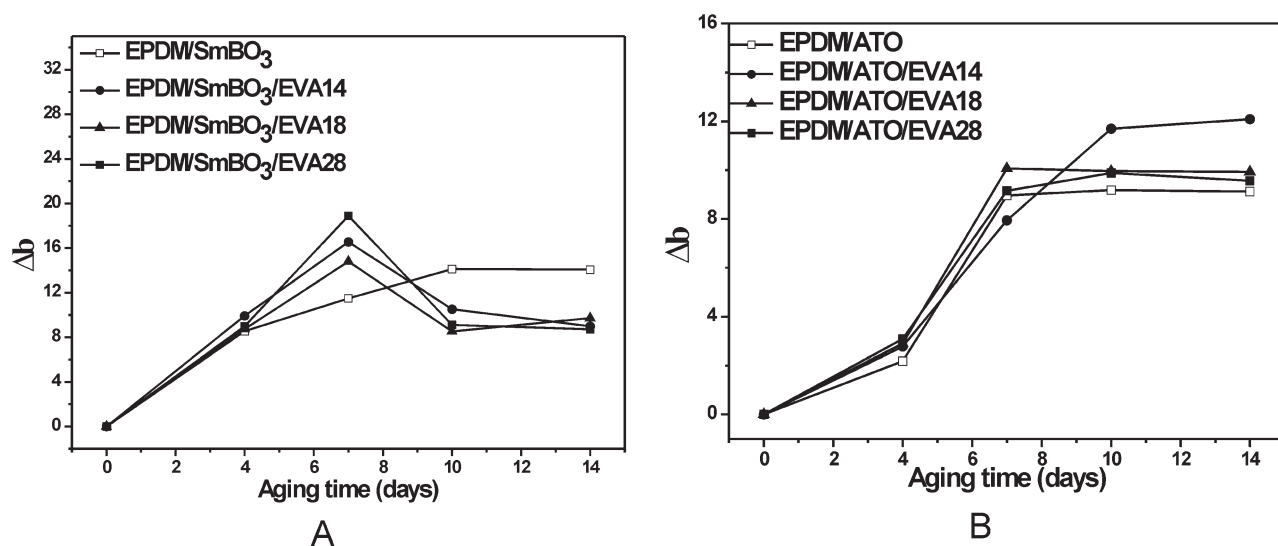
Figure 7 Color change of EPDM composites: (A) Δb of EPDM/SmBO$_3$ composites; (B) Δb of EPDM/ATO composites.

TABLE II
DSC Characteristics of EPDM Composites Before and After Hot Air Aging

Sample	Aging time (days)	T_m^{peak} (°C)	ΔH (J/g)	X_c (%)
EPDM/SmBO₃/EVA14	0	76.9	6.1	15.4
	4	78.9	8.2	20.9
	7	77.1	6.5	16.5
	10	79.1	8.2	20.9
	14	75.1	5.5	14.0
EPDM/SmBO₃/EVA18	0	74.6	5.4	13.9
	4	76.8	6.6	16.8
	7	75.0	5.7	14.5
	10	77.6	7.5	19.1
	14	74.1	5.2	13.2
EPDM/SmBO₃/EVA28	0	60.8	2.8	7.2
	4	62.8	4.4	11.2
	7	61.0	2.9	7.4
	10	85.7	9.8	24.9
	14	80.9	6.7	17.0
EPDM/ATO/EVA14	0	75.8	6.7	17.1
	4	76.0	7.6	19.3
	7	75.3	7.0	17.8
	10	76.4	7.6	19.3
	14	72.1	3.3	8.4
EPDM/ATO/EVA18	0	75.2	6.2	15.8
	4	77.7	7.4	18.8
	7	74.3	5.7	14.5
	10	78.6	8.7	22.1
	14	74.2	5.5	14.0
EPDM/ATO/EVA28	0	59.3	3.5	8.8
	4	64.7	5.0	12.7
	7	62.1	3.3	8.4
	10	88.0	11.2	28.5
	14	78.1	6.1	15.5

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

EPDM/filler/EVA composites. So, it is the chemical crosslink points in EPDM composites that prevent the crystals from melting during aging. Generally, the aging process is accompanied by chain crosslinking and scission, which are two competing factors affecting the total chemical crosslink points. In one aspect, the increase of chemical crosslink density can fasten the crystals and raise the crystallinity. In another aspect, when the number of chemical crosslink points exceeds certain critical point, the motion of ethylene chains is restricted, leading to the decrease of crystallinity.

In the first 4 days of aging, the growth of T_m^{peak} and crystallinity of EVA copolymer in EPDM/filler/EVA is mainly due to the fact that secondary crystallization of short-chain segments in EVA copolymer can obtain sufficient mobility under 150°C and be incorporated in existing lamelles or to nucleate new crystallites, causing the rise of crystallinity. This trend is consistent with previous reports.[15,18,24]

It is reported that EPDM undergoes predominantly chain scission during the early stages of the degradation process and crosslinking during the latter stage of aging.[28] The dropped crystallinity of EVA copolymer in EPDM/filler/EVA between 4 and 7 days of aging is caused by the decrease of chemical crosslink points in EPDM/filler/EVA composites. The decreased chemical crosslink points can facilitate the motion of ethylene chains and make crystals of EVA in EPDM/filler/EVA partially melt under 150°C.

In the range of 7–10 days, the risen T_m^{peak} and crystallinity of EVA copolymer in EPDM/filler/EVA are possibly ascribed to the grown chemical crosslink points, which can restrict the motion of ethylene chains and prevent crystals of EVA in EPDM/filler/EVA composites from melting.

The drop of crystallinity in the last 4 days of aging is explained by the further grown chemical crosslink points in EPDM/filler/EVA composites. The increased chemical crosslink points hinder the packing of ethylene chains into crystals, resulting in the lower crystallinity of EVA in EPDM/filler/EVA.

Effect of hot air aging on swelling ratio of EPDM/EVA/filler composites

Generally, the chemical crosslink points formed during vulcanization can prevent the EPDM from swelling in xylene. In addition, EVA crystallizes at room temperature. Because the xylene is not polar solvent, the interaction of xylene with EVA cannot damage the crystals of EVA at room temperature.[29] In this way, the crystals of EVA can be considered as physical crosslink points at room temperature, which act the same role as chemical crosslink points in preventing the EPDM composites from swelling. Because of high VA (28%) content, EVA28 samples has low crystallinity. So has EVA samples having high VA content (28%) has high swelling.

Swelling ratio is an indirect method of chemical and physical crosslink points: the higher the swelling ratio is, the fewer amounts of chemical and physical crosslink points exist. Figure 8 exhibits swelling ratios of EPDM composites during hot air aging. Conspicuously, the swelling ratio of EPDM/SmBO₃ control rises during the first 10 days of aging and then declines in the next 4 days of aging. There are no physical crosslink points in EPDM/SmBO₃ control, and so the trend of swelling ratio is an inverse ratio of that of chemical crosslink points of EPDM/SmBO₃ control. In this way, the trend of swelling ratio indicates that the chemical crosslink density of EPDM/SmBO₃ control decreases in the first 10 days of aging and then increases in the next 4 days of aging. This phenomenon indicates that there are two degradation stage of EPDM, which is consistent with literatures.[30]
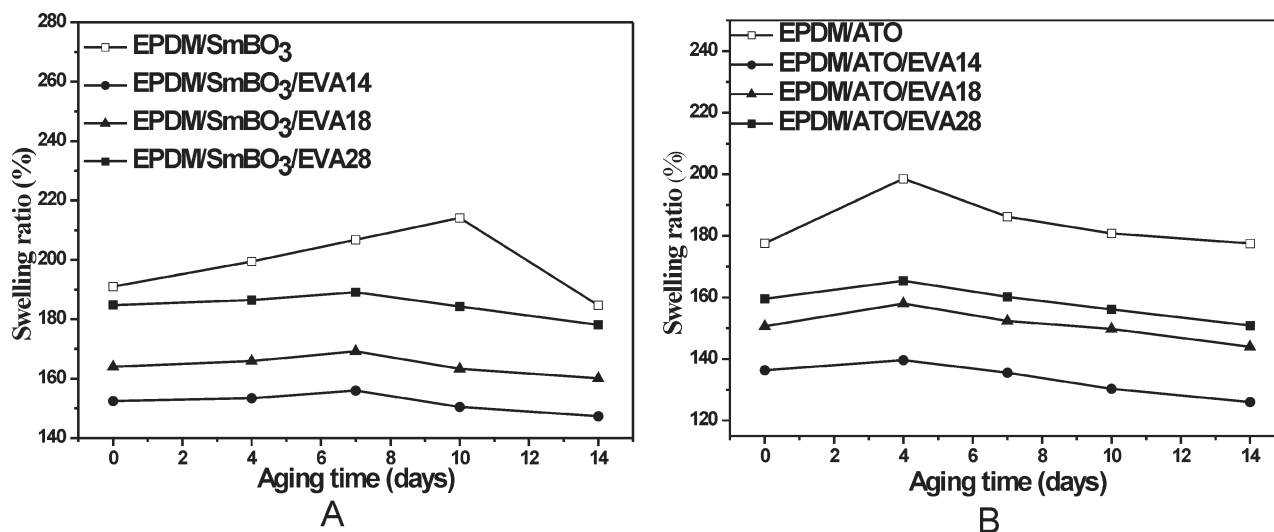
Figure 8 Swelling ratio of EPDM composites: (A) EPDM/SmBO₃ composites; (B) EPDM/ATO composites.

In terms of EPDM/ATO control, the change in swelling ratio reveals that the chemical crosslink points decrease in the first 4 days of aging and then increase in the next 10 days of aging. Apparently, the first stage of degradation of EPDM/ATO control is shorter than that of EPDM/SmBO₃, which indicates that acidic ATO can accelerate the degradation of EPDM by some degree. This is explained by the fact that acidic ATO particles could not scavenge acids formed during aging just like alkaline SmBO₃ particles did.

As for EPDM/EVA/filler composites, because the xylene is not polar solvent, and the interaction of xylene and EVA cannot damage the crystals of EVA at room temperature.[27] In this way, the crystals of EVA are considered as physical crosslink points at room temperature, which act the same role as chemical crosslink points in preventing the EPDM composites from swelling. So, there are two competing factors influencing the swelling ratios of EPDM/filler/EVA composites: chemical and physical crosslink points.

The crystallinity of EPDM/SmBO₃/EVA composites has the upward trend in the first 4 days of aging and goes down in the next 3 days, meaning the amount of physical crosslink points first increases and then decreases. In addition, the swelling ratios of EPDM/SmBO₃/EVA composites grow gradually during the first 7 days of aging, indicating the decreased number of physical and chemical crosslink points. Thus, it seems that the chemical

TABLE III
Mechanical Properties of EPDM/SmBO₃ Composites Before and After Hot Air Aging

Sample	Aging time (days)	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)
EPDM/SmBO₃	0	55	2.95 ± 0.27	169 ± 51
	4	54	2.38 ± 0.31	109 ± 24
	7	54	2.19 ± 0.24	95 ± 27
	10	53	1.60 ± 0.33	39 ± 2
	14	64	2.40 ± 0.22	57 ± 11
EPDM/SmBO₃/EVA14	0	66	3.74 ± 0.21	184 ± 28
	4	69	3.30 ± 0.09	58 ± 9
	7	70	2.64 ± 0.10	23 ± 13
	10	77	3.62 ± 0.26	31 ± 3
	14	64	3.74 ± 0.31	88 ± 7
EPDM/SmBO₃/EVA18	0	65	3.47 ± 0.05	193 ± 43
	4	68	3.19 ± 0.06	76 ± 4
	7	69	2.65 ± 0.09	22 ± 3
	10	75	3.30 ± 0.07	32 ± 2
	14	62	3.40 ± 0.50	46 ± 6
EPDM/SmBO₃/EVA28	0	62	3.04 ± 0.48	198 ± 51
	4	66	2.99 ± 0.40	72 ± 18
	7	67	2.06 ± 0.07	19 ± 12
	10	75	3.45 ± 0.14	29 ± 6
	14	66	3.59 ± 0.19	88 ± 4

TABLE IV
Mechanical Properties of EPDM/ATO Composites Before and After Hot Air Aging

| Sample	Aging time (days)	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)
EPDM/ATO	0	55	2.36 ± 0.3	165 ± 52
	4	55	1.55 ± 0.54	73 ± 13
	7	56	1.94 ± 0.12	68 ± 18
	10	64	2.07 ± 0.22	41 ± 10
	14	70	2.20 ± 0.17	41 ± 14
EPDM/ATO/EVA14	0	64	3.63 ± 0.47	180 ± 33
	4	63	2.46 ± 0.24	104 ± 19
	7	65	2.76 ± 0.11	49 ± 12
	10	70	2.84 ± 0.39	25 ± 10
	14	72	3.42 ± 0.54	33 ± 7
EPDM/ATO/EVA18	0	62	4.00 ± 0.15	173 ± 23
	4	61	1.92 ± 0.30	92 ± 7
	7	62	2.13 ± 0.10	47 ± 7
	10	67	2.70 ± 0.08	23 ± 5
	14	72	2.93 ± 0.24	36 ± 6
EPDM/ATO/EVA28	0	61	2.96 ± 0.22	107 ± 16
	4	56	1.91 ± 0.08	95 ± 9
	7	58	1.97 ± 0.07	72 ± 3
	10	60	2.17 ± 0.28	30 ± 7
	14	68	2.69 ± 0.25	39 ± 8
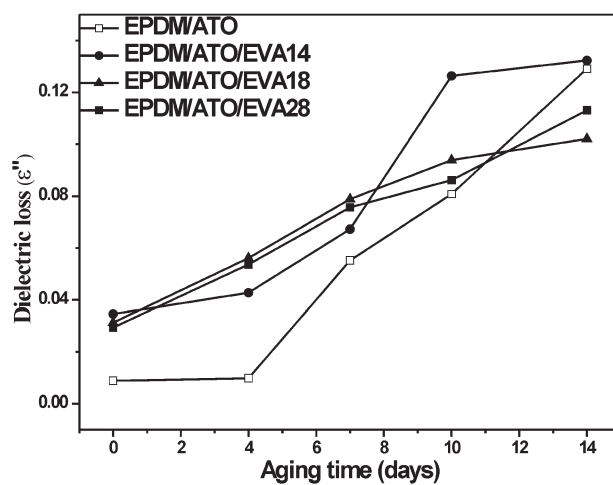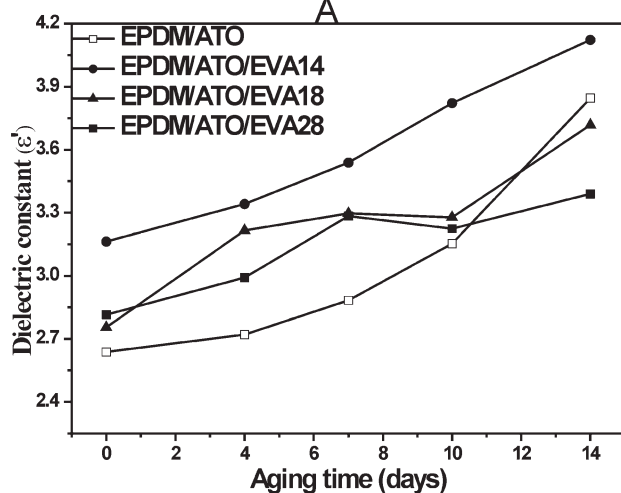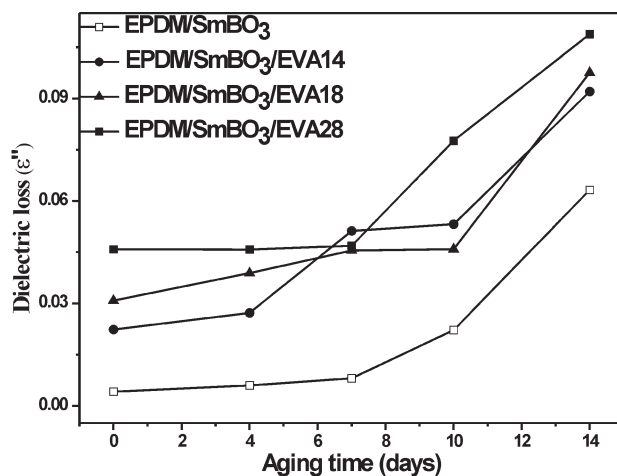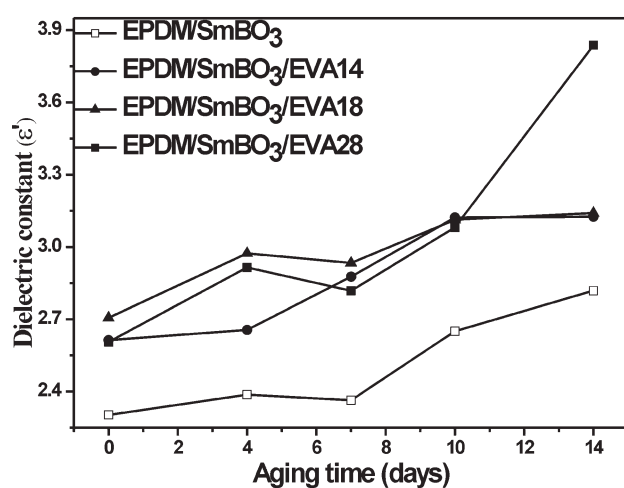
Figure 9 Dielectric constant and loss of EPDM composites: (A) dielectric constant of EPDM/SmBO$_3$ composites; (B) dielectric loss of EPDM/SmBO$_3$ composites; (C) dielectric constant of EPDM/ATO composites; (D) dielectric loss of EPDM/ATO composites.

TABLE V
Volume Resistivity of EPDM/SmBO₃ Composites Before and After Hot Air Aging

Aging time (days)	Volume resistivity (Ω m)			
	EPDM/SmBO₃	EPDM/SmBO₃/EVA14	EPDM/SmBO₃/EVA18	EPDM/SmBO₃/EVA28
0	1.08×10^{15}	2.16×10^{15}	1.82×10^{14}	9.44×10^{13}
4	8.73×10^{14}	1.69×10^{15}	1.72×10^{14}	6.53×10^{13}
7	5.45×10^{14}	1.04×10^{15}	1.16×10^{14}	1.39×10^{13}
10	5.23×10^{14}	6.22×10^{14}	1.54×10^{13}	1.80×10^{12}
14	1.58×10^{14}	1.93×10^{14}	1.04×10^{13}	1.43×10^{12}

crosslink points descend in the first 7 days of aging and play more remarkable effect on swelling ratio than physical crosslink points did, leading to the rise of swelling ratios.

The crystallinity of EPDM/SmBO₃/EVA experiences an increase between 7 and 10 days of aging and fell in the next 4 days of aging, while their swelling ratios all decrease. So, it seemed that the chemical crosslink points takes the main effect on swelling ratios of EPDM/SmBO₃/EVA composites, in spite of the varied crystallinity of EVA in EPDM/SmBO₃/EVA.

As for EPDM/ATO control, the curve of swelling ratio shows that the chemical crosslink points decrease in the first 4 days of aging and then increase in the next 10 days of aging. The first stage of degradation of EPDM/ATO control is obviously shorter than that of EPDM/SmBO₃, which means that ATO accelerates the degradation of EPDM to some extent compared to SmBO₃. This is explained by the fact that acidic ATO particles cannot promote the degradation of VA groups compared to alkaline SmBO₃ particles.[26]

In the first 4 days of aging, the crystallinity of EPDM/filler/EVA composites has the upward trend, meaning increased physical crosslink points. By comparison, the swelling ratios of EPDM/filler/EVA composites rise a little. In this way, it seems that the chemical crosslink points fall in the first 4 days of aging. In the next 10 days of aging, crystallinity of EPDM/SmBO₃/EVA fluctuates, but their swelling ratios drop gradually. This phenomenon indicates that in the last 10 days of aging the chemical crosslink points of EPDM/SmBO₃/EVA increased, resulting in the decreased swelling ratios.

Effect of hot air aging on mechanical properties of EPDM composites

Mechanical properties of EPDM composites at various aging time are shown in Tables III and IV. It is clear that the addition of EVA enhances the hardness and tensile strength of EPDM/filler/EVA composites before aging. This is because ethylene chains of EVA can crystallize in EPDM/filler/EVA composites, resulting in the rise of hardness and tensile strength.

The hardness and tensile strength of EPDM/SmBO₃ control decrease in the first 10 days of aging and increase in the next 4 days of aging. This trend is correlated with that of swelling ratios. The higher swelling ratio means lower chemical crosslink points in EPDM/SmBO₃ control.

The hardness of EPDM/SmBO₃/EVA reaches the highest value at the 10th day of aging, which is explained by the relatively higher crystallinity at the 10th day of aging. In another aspect, the tensile strength of EPDM/SmBO₃/EVA decreases slightly in the first 7 days of aging and then increases in the next days. This is in line with the trend of swelling ratios. The higher swelling ratio reflects lower physical and chemical crosslink points in EPDM/SmBO₃/EVA composites.

As for EPDM/ATO control and EPDM/ATO/EVA composites, the trend of hardness and tensile strength is also correlated with that of swelling ratio. In addition, the decreased amplitude of tensile strength of EPDM/ATO control and EPDM/ATO/EVA composites is more remarkable than that of EPDM/SmBO₃ control and EPDM/SmBO₃/EVAcomposites. This is ascribed to the fact that acidic

TABLE VI
Volume Resistivity of EPDM/ATO Composites Before and After Hot Air Aging

Aging time (days)	Volume resistivity (Ω m)			
	EPDM/ATO	EPDM/ATO/EVA14	EPDM/ATO/EVA18	EPDM/ATO/EVA28
0	2.91×10^{15}	2.97×10^{15}	3.08×10^{14}	2.05×10^{13}
4	7.24×10^{15}	2.12×10^{15}	1.85×10^{14}	1.67×10^{13}
7	4.28×10^{14}	1.26×10^{15}	1.37×10^{14}	1.27×10^{13}
10	6.96×10^{13}	5.14×10^{14}	4.49×10^{13}	5.49×10^{13}
14	4.42×10^{13}	7.72×10^{13}	3.48×10^{13}	7.32×10^{12}

TABLE VII
Dielectric Strength of EPDM/SmBO$_3$ Composites Before and After Hot Air Aging

Aging time (days)	Dielectric strength (MV m^{-1})			
	EPDM/SmBO$_3$	EPDM/SmBO$_3$/EVA14	EPDM/SmBO$_3$/EVA18	EPDM/SmBO$_3$/EVA28
0	33.6	29.6	28.5	28.3
4	34.0	26.6	27.3	27.8
7	33.3	30.8	28.3	28.2
10	29.4	30.3	31.5	30.0
14	27.9	30.8	31.3	32.6

ATO particles can promote the decomposition of VA groups, while alkaline SmBO$_3$ particles cannot. Thus, the decreased amplitude of tensile strength of EPDM/ATO/EVA is greater than that of EPDM/SmBO$_3$/EVA.

Effect of hot air aging on dielectric constant and loss at 10 MHz of EPDM composites

The relative dielectric constant is a measure of the energy stored in a sample during a cyclic electric excitation.[30] Generally, the dielectric constant of a material is mainly dependent on the polarization of molecules, and the dielectric constant increases (or decreases) with increasing (or decreasing) polarizability.[31]

Figure 9 shows curves of dielectric constant and loss of EPDM composites during aging at 10 MHz. At the beginning of aging, it is noted that the addition of EVA enhances the dielectric constant and loss of EPDM composites to some extent. This is attributed to the fact that the polarity of EVA is often higher than polarity of EPDM molecule due to polar VA groups.[32]

It is revealed from Figure 8 that the dielectric constant of EPDM composites increases with the increasing aging time. A large amount of polar groups is generated during aging, which has been mentioned earlier. Thereby, there are more dipoles aligning to cyclic electric excitation, causing dielectric constant of EPDM composites rise during aging.[33]

The dielectric loss is a measure of the energy lost into a system during cyclic electric excitation.[34,35] The more polar groups aligning in cyclic electric excitation mean more energy lost during such excita-

tion. Thereby, the dielectric constant and loss of EPDM composites all increase during aging.

Effect of hot air aging on dielectric strength and volume resistivity of EPDM composites

Tables V–VIII show dependence of dielectric strength and volume resistivity of EPDM/SmBO$_3$/EVA and EPDM/ATO/EVA composites on aging time, respectively. The volume resistivity of EPDM/SmBO$_3$ and EPDM/ATO composites falls with the increasing aging time. Resistivity is often used to characterize the resistance which the material exhibits to the passage of current. With the growing of aging time, there are more polar groups formed, indicating more conductive channels present in matrix. And the grown such pathways facilitate passage of current and then reduce volume resistivity of composites.

The dielectric strength of EPDM/SmBO$_3$ and EPDM/ATO control has downward trend with the increasing aging time. Generally, the tendency of dielectric strength is also related to the varied polar groups. The higher amount of polar groups demonstrates more energy is stored. Thus, less energy is needed to penetrated samples.

In terms of EPDM/SmBO$_3$/EVA and EPDM/ATO/EVA composites, the dielectric strength experienced upward tendency during aging. In addition to polar groups, the crystallinity of EVA in EPDM/filler/EVA composites can also influence the dielectric strength of EPDM composites. During aging, the crystallinity has the upward trend. The rise of crystallinity indicates more crystals existing in EPDM/filler/EVA composites. Such crystals inhibit the

TABLE VIII
Dielectric Strength of EPDM/ATO Composites Before and After Hot Air Aging

Aging time (days)	Dielectric strength (MV m^{-1})			
	EPDM/ATO	EPDM/ATO/EVA14	EPDM/ATO/EVA18	EPDM/ATO/EVA28
0	24.3	21.1	21.4	22.9
4	14.7	22.5	22.1	24.8
7	11.8	30.3	29.2	20.5
10	12.9	32.6	31.2	27.9
14	12.2	33.9	32.1	28.4

penetration. In this way, more energy is needed, and the dielectric strength of EPDM/filler/EVA composites increases.

CONCLUSIONS

The pH level of fillers and VA content affects the properties of EPDM/filler/EVA composites during hot air. Compared to alkaline SmBO$_3$ particles, acidic ATO particles can promote the decomposition of VA during aging, reflected by the CI.

Moreover, when VA content exceeds 18 wt % (for EPDM/SmBO$_3$/EVA composites) and 14 wt % (for EPDM/ATO/EVA composites), the released acetic acids play dominant effect on CI of EPDM composites during aging. As for cooler difference, EPDM/SmBO$_3$ control and EPDM/SmBO$_3$/EVA composites tend to become darker while EPDM/ATO and EPDM/ATO/EVA composites is more yellow. And the color change is correlated well with the variation of CI.

The EPDM/filler control experiences two stages: chain scission and crosslink. And the first stage of degradation of EPDM/ATO is shorter than that of EPDM/SmBO$_3$ control, because acidic ATO can promote the decomposition of VA groups during aging and accelerate the degradation to some extent.

The crystals of EVA in EPDM/filler/EVA composites are regarded as physical crosslink points, which can be influenced by chemical crosslink points. When chemical crosslink points decrease, the crystals become easier to melt under 150°C. But in the latter stage of aging, the increase of chemical crosslink points hinders the packing of ethylene chains and then lower the crystallinity of EVA in EPDM/filler/EVA composites.

The tensile strength is correlated with the swelling ratios by some degree. The electric properties of EPDM/filler control are related to the amount of polar groups formed during aging, which is shown by CI. In addition to polar groups, the electric properties of EPDM/filler/EVA composites are also affected by varied crystallinity of EVA in EPDM/filler/EVA composites.

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