

Effects of Thermal Aging on Degradation Mechanism of Flame Retardant-Filled Ethylene-Propylene-Diene Termonomer Compounds

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ABSTRACT: Ethylene-propylene-diene termonomer (EPDM) compounds filled with halogenated (Br and Cl) flame retardants (FRs) and Sb_2O_3 were prepared via melt mixing, and their thermal stability, weight loss, and elemental composition were investigated as a function of aging conditions (temperature: 120–380°C, period: ~100 h, and atmosphere: nitrogen and air). The thermal aging was done with thermogravimetric analysis under both isothermal and nonisothermal conditions and a convection oven. Scanning electron microscopy–energy dispersive spectroscopy was used to study the surface morphology and elemental composition of the thermally aged FRs-filled EPDM compounds. For a better precision of compositional analysis, a laser-induced breakdown spectroscopy (LIBS) was employed in this study. The thermal degradation behavior of EPDM compounds containing halogenated FRs was strongly dependent on the aging atmosphere (N_2 or air) and type of FRs. The weight loss of the EPDM compounds during thermal aging was found to be quite small in the temperature ranges below 190°C, while it was noticeable above the temperature. The LIBS technique can be an effective and promising analysis tools for analyzing the elemental components in a bulk rubber compound. Two possible mechanisms were proposed for the thermal degradation of the EPDM compounds containing brominated FR and Sb_2O_3 . © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41324.

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INTRODUCTION

Rubbers and their compounds show a characteristic elastic nature upon stretching due mainly to the changes in entropic state of the macromolecular chain conformation. They exhibit excellent chemical and thermal stabilities as well as good mechanical properties under dynamic conditions as compared with metals and other counterparts. Because of these unique characteristics of rubbers and their compounds, they have been widely used as secure and promising materials in various fields, such as wire and cable insulation, roof sheeting, extruded profiles, and tires.^{1–3}

Recently, the long-term stability of rubber compounds with improved thermal, chemical, and mechanical properties have been emphasized and requires their applications in more severe environments. In this aspect, it is urgent and critical to develop the tailor-made rubber products for long-term usages with safety guarantee in harsh environments. Especially, fire and

flame retardancy of rubbery materials is one of the most important issues in rubber cable industries.^{4–9}

Flame retardants (FRs) are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing them down or by inhibiting them. They can act in both physical and chemical ways. Many types of them are used in consumer products. They are mainly chlorides and bromides or antimony, aluminum, phosphorous and boron-containing compounds, etc.^{10,11} The FRs can act in a variety of ways: by raising the ignition temperature, by reducing the rate of burning, by reducing flame spread, by reducing smoke generation, by cooling, and by forming protective layer.¹² In typical combustion mechanism of polymer, the thermal degradation mainly occurs as a result of the interaction between the polymer and radiation from the heat source. Depending on the type of material, the diffusion of combustible and incombustible components affects the thermal degradation. The incombustible components prevent the spread of fire but

the combustible components intensify the flame spread rate.^{12,13} It must be emphasized here that the presence of foreign element significantly affects the thermal degradation rate. For the low combustibility of the rubber product, the inherent FR rubbers can be used. However, the inherent FR rubbers are too expensive to be used in the real fields. As one of the alternative methods to solve this problem, the various FRs with low price are added into the rubber compounds. Therefore, it is very important to systematically understand the relationship between the FRs and the combustibility of the corresponding rubber products.

Ethylene-propylene-diene termonomer (EPDM) is one of the distinguished synthetic elastomers with excellent properties that have made significant contributions to many fields. Since EPDM rubber exhibits outstanding resistance to oxidation and ozonization and good weathering performance, it has been often used for a variety of industrial applications such as wire and cable insulation, roof sheeting, extruded profiles, and white tire sidewalls.¹⁻³

Several works have been made on EPDM reinforced with nanofillers or their blend with other polymer systems,¹⁴⁻²² aimed to enhance their mechanical, thermal and flammability behavior. Gang Tang et al.¹⁴ successfully studied the flammability and thermal degradation of a novel intumescent FR (IFR) EPDM compound. They concluded that the combination of microencapsulated ammonium polyphosphate and pentaerythritol, could significantly improve the flame retardancy of IFR-EPDM compounds. Deuri and Bhowmick have studied the aging characteristics of three grades of EPDM having different types of dienes.¹⁵ The findings show that postcuring reactions as well as destruction of crosslinks take place in the aging process and the predominance of the former or latter depends on the structure of dienes. Generally, retention properties of ethylidene norbornene-EPDM are found to be the best. Yu et al. examined the effect of decabromodiphenyl oxide (FR-10) and antimony trioxide (Sb_2O_3) on the flame retardation of EPDM/polypropylene blends. According to their findings, the combination of FR-10 and Sb_2O_3 showed more effective flame retardation than the individual components. But, if too much FR was added, the tensile strength and elongation at break decreased rapidly.¹⁶ Noticeably, little attention has been paid to the durability and the effect of various FRs of EPDM compounds.

The present work is predominantly aimed to understand the thermal degradation mechanism of FR-EPDM compounds. Several representative FR-filled EPDM compounds were prepared by melt mixing. Thermal degradation behavior of the rubber compounds were investigated by thermogravimetric analysis (TGA). The morphology and elemental composition was also analyzed with scanning electron microscopy (SEM)-energy-dispersive X-ray spectroscopy (EDS) and laser-induced breakdown spectroscopy (LIBS) precisely. The weight loss in a convection oven at lower temperature ranges was also monitored as a function of aging period. Finally the possible degradation mechanism of FR-filled EPDM compounds was proposed.

EXPERIMENTAL

Materials and Preparation of Specimen

EPDM (Nordel 4725, DuPont Dow Elastomers) was used as a rubber matrix. An inorganic FR, Sb_2O_3 , was supplied from

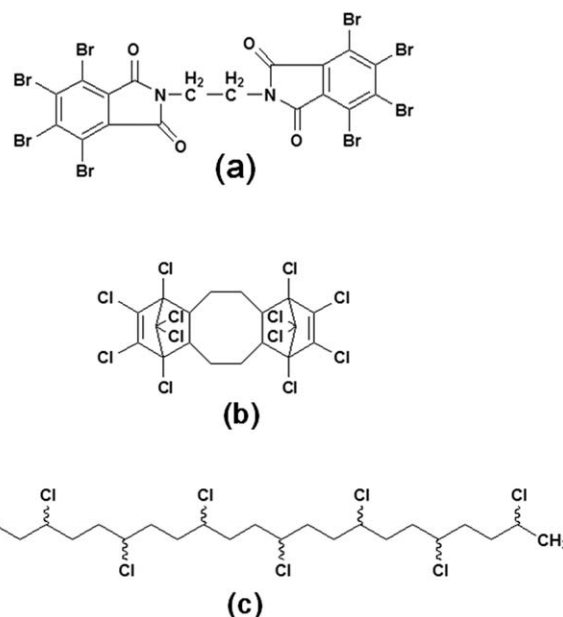


Figure 1. Chemical structure of flame retardants: (a) Saytex BT-93 (Br), (b) Dechlorane plus (Cl_{ar}), and (c) chlorinated paraffin (Cl_{al}).

Sigma Aldrich. Three different kinds of organic FRs were selected in this study. They include an aromatic brominated FR; 4,5,6,7-tetrabromo-2-(2-(4,5,6,7-tetrabromo-1,3-dioxoisindolin-2-yl)ethyl)isoindoline-1,3-dione (Saytex BT93), supplied by Albe marle Corporation, an aromatic chlorinated FR; 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4,7,10-dimethanodibenzo [a,e] cyclooctene (Delchlorna Plus), supplied by Oxychem and an aliphatic chlorinated FR; 2,5,8,11,14,17,20-heptachlorotricosane (chlorinated paraffin), supplied by HBC Chem. The chemical structure of the FRs is represented in Figure 1. A carbon black (N550, Korea Carbon Black, Korea) was loaded by 50 phr. A conventional sulfur curing system [ZnO : 5 phr, stearic acid: 2 phr, aromatic oil: 5 phr, *N*-cyclohexyl-2-benzothiazole sulfonamide (CZ): 1 phr, and sulfur: 1.5 phr] was used. The remaining ingredients for rubber compounds were selected as the typical grade in the rubber industry. The compound composition and designation with major variation components is summarized in Table I.

The compounding procedure is as follows: initially, EPDM was mixed in a Banbury mixer at 140°C for 0.5 min with a rotor speed of 60 rpm using a fill factor of 75%. The various additives including FRs, reinforcing fillers, and processing oils were then added into the rubber and mixed for another 6 min. The curing agents (accelerated sulfur cure system) were added in a two roll-mill (Farrel 8422) at a rotation speed of 15.3 rpm at around 90°C for 10 min. After 24 h, optimum crosslink condition was analyzed by a rheometer (ODR, Alpha Technologies). The optimum conditions were used to vulcanize the prepared samples by a hot-press machine (Caver WMV50H) at pressure of 25 kPa and 170°C temperature.

Characterization

Thermogravimetric Analysis. To understand the thermal degradation behaviors of raw FRs and their compounds, TGA

Table I. Major Composition Variables in Compound Recipe Investigated

Ingredient (phr)	Formulation							
	EP	EP-Sb	EP-Br	EP-Sb-Br	EP-Cl _{ar}	EP-Sb-Cl _{ar}	EP-Sb-Cl _{al}	
Polymer	Nordel 4725 (EPDM)	100	100	100	100	100	100	100
Flame retardant	Sb ₂ O ₃ (Sb)		10		10		10	10
	Saytex BT93 (Br)			50	50			
	Dechlorna plus (Cl _{ar})					50	50	
	Chlorinated paraffine (Cl _{al})							20

measurements were performed under two heating operating conditions: nonisothermal and isothermal. The nonisothermal TGA measurements were performed with sample with mass of 10–12 mg using a Perkin-Elmer thermal analysis instrument. Samples were placed into a platinum pan, and the experiments were conducted in both nitrogen and air atmospheres. Initially samples were heated up to 100°C at a heating rate of 20°C/min. As soon as the system reached the targeted temperatures, they were isothermally kept for 10 min at the set temperatures for evaporating any volatile matters in the samples. After that, the samples were cooled to room temperature at a cooling rate of 20°C/min and then kept for 3 min additionally. Finally, they were heated from room temperature to 600°C at a heating rate of 20°C/min. Three tests were carried out under the same heating rate for each sample, and the characteristic temperatures were reproducible within $\pm 1.0^\circ\text{C}$ limits of experimental errors.

The isothermal tests were carried out in air at a temperature of 190, 220, 250, 280, 300, 330, 340, 350, 360, 370, and 380°C, respectively, for various time intervals using the same TGA instrument (TGA Q50, TA instrument). Before the isothermal test, the samples were heated at a rate of 30°C/min from room temperature up to 120°C and then retained at that temperature for 10 min. Then, heating of the sample was done in order to select the isothermal degradation temperatures. As soon as the system reached the selected temperature, the variations in mass of the samples with respect to the aging time were recorded. Weight loss as a function of temperature or time and the thermal behavior of compounds were monitored. In all cases, the onset decomposition temperature (T_5) was taken at which 5% weight loss occurred, and the temperature corresponding to the maximum value (peak) in derivative thermogram at the maximum degradation temperature (T_{max}).

Convection Oven Aging. For a comparison with results obtained from TGA analysis, various rubber samples of dumbbell-shaped specimens were thermally aged in a convection oven (J-300M, Jisico, Korea) in air at 120, 135, 150, and 165°C for 1, 50, 100, 300, 500, 700, and 1000 h, respectively. The weight loss was monitored with aging conditions using a precise balance.

Scanning Electron Microscope–Energy-Dispersive X-ray Spectroscopy Analysis. Morphological analysis of the rubber compounds before and after aging was conducted by a digital SEM (JEOL JSM 5900, Japan) after cryogenic fracturing of the samples. Prior to the SEM analysis, fractured surfaces of sample

were sputter-coated with a thin gold layer. The images were obtained at the 0° tilt angle with an operating voltage of 15 kV and with an average beam current of 90 mA. For quantitative and qualitative analyses of atomic elements in the specimens, EDX (SUPRA 40VP, Carl Zeiss, Germany) study was carried on the fractured surfaces at the operating voltage of 15 kV. The EDX results of the aged samples for 400 min at 300°C were compared with those of nonaged ones. The result obtained represents the average of five samples.

Laser-Induced Breakdown Spectroscopy. A LIBS equipment was employed to the quantitative analysis of elements such as Sb, Br, and Cl in bulk specimens of EPDM rubber compounds before and after thermal aging. The laser was Brilliant b, Q-switched Nd: YAG and was obtained from Quantel. Using a focal length of 7 cm, a 10 mJ/pulse of energy was forced on a specimen. A cone diameter of 200 μm was used to generate the emission. The generated emission was obtained in plasma state and can be concentrated by the focal lens (7 cm). The LIBS machine comes with a spectroscopy equipped with blazed gratings known as Czerny-Tuner, with total length of 50 cm and positioned at 500 nm. An intensified charge-coupled device was used for photo-detector. The gate width was set to 5 μs as soon as if the detection gate was delayed for 1 μs . He (Helium) gas was supplied for 22.5 L/min using SUS tube (1/4 inch). The detailed principle and procedure of the LIBS is described in our previous work.²³

RESULTS AND DISCUSSION

Thermal Stability of Flame Retardants and Their Compounds

Figure 2 shows the TGA curves of various raw FRs and their mixtures, and the neat EPDM compound (EP) and the corresponding FR-filled EPDM compounds. The major degradation parameters (T_5 , T_{max} , and residue) are also summarized in Table II. The atmospheric condition (air or nitrogen) did not affect much the thermal degradation of the raw FRs and their mixtures. The inorganic Sb₂O₃ was found to be the most stable up to near 600°C, where maximum degradation occurred. Among the organic FRs, the brominated FR showed the highest thermal resistance ($T_5 = 439^\circ\text{C}$ in air), while the aromatic and aliphatic chlorinated FRs (Cl_{ar} and Cl_{al}) showed somewhat lower degradation temperatures of $T_5 = 300$ and 272°C in air, respectively. As can be expected, the aliphatic chlorinated FR showed the lowest thermal resistance. Thus, the thermal stability of the raw FRs was found to be in the order of Sb₂O₃ > Br > Cl_{ar} > Cl_{al}. When the powdery Sb₂O₃ was mixed with halogenated FRs, any

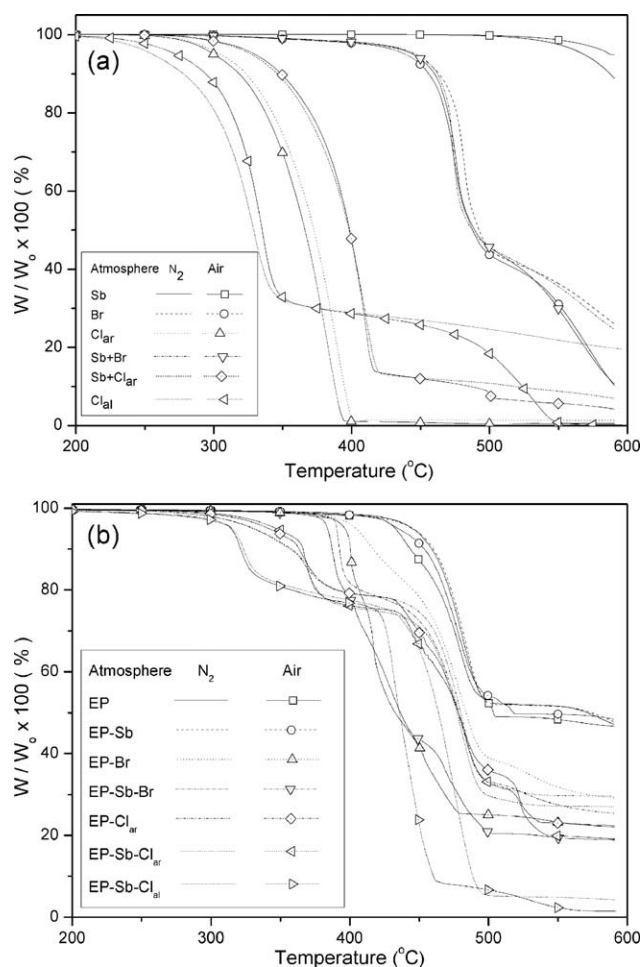


Figure 2. TGA curves of (a) raw FRs and their mixture and (b) the corresponding FR-filled EPDM compounds under air and N_2 condition, respectively.

noticeable change in the thermal degradation temperature was not found, suggesting no chemical reaction among FRs. Nevertheless, the decomposition of all specimens commonly appeared to be slow and steady up to a temperature around 300°C , and thereafter increased more rapidly with increasing temperature.

In the case of rubber compounds, the EP, EP-Sb, EP-Br, and EP-Sb-Br generally showed the higher thermal resistance regardless of atmospheric condition based on the T_5 , probably due to their higher thermal degradation temperature of EPDM ($T_5 = 432^\circ\text{C}$ in air), Br-FR ($T_5 = 439^\circ\text{C}$ in air), and Sb_2O_3 ($T_5 = 580^\circ\text{C}$ in air). When the less stable aliphatic (Cl_{al}) and aromatic (Cl_{ar}) FRs were added in EPDM, the initiation to thermal degradation of compounds (EP- Cl_{ar} , EP-Sb- Cl_{ar} , and EP- Cl_{al}) occurred at the corresponding temperatures. Based on the maximum degradation temperature (T_{max}), the degradation of all compounds roughly remained to be similar the level of degradation of EP (481°C) in N_2 , while a great decrease in T_{max} was observed in air condition for several compounds containing brominated FR (Table II and Figure 2). The observed effect was not noticeable for the compounds (EP- Cl_{ar} and EP-Sb- Cl_{ar}) containing aromatic chlorinated FR (Cl_{ar}), while a considerable effect (but less than that of Br case) was also observed for the compound containing the aliphatic chlorinated FR (Cl_{al}). It was reported that the chemical reaction occurred between the halogenated-RFs and polyethylene matrix²⁴ and other polymer systems.^{25–27} Furthermore, it has been known that the bromine could attack the EPDM rubber in the presence of oxygen.¹ Thus, the observed difference in thermal degradation (T_{max}) of Br and Cl_{al} containing rubber compounds (EP-Br, EP-Sb-Br, and EP- Cl_{al}) between N_2 and air conditions might be due to the chemical attack of halogen to the EPDM matrix in the presence of oxygen. It can be concluded that the thermal degradation behavior of EPDM compounds containing halogenated FRs is strongly dependent on the aging atmosphere and type of FRs.

Table II. The Degradation Temperatures (T_5 , T_{max}) and Residues of Raw FRs and Their Mixtures, and FR-Filled EPDM Compounds Under Air and N_2 Conditions

Materials	T_5 ($^\circ\text{C}$)		T_{max} ($^\circ\text{C}$)		Residue (%)	
	N_2	Air	N_2	Air	N_2	Air
Br	445	439 (−6)	478	474 (−4)	26	10.2 (−15.8)
$\text{Sb}_2\text{O}_3 + \text{Br}$	446	444 (−2)	473	475 (+2)	24.6	10.7 (−13.9)
Cl_{ar}	304	300 (−4)	390	383 (−7)	1.2	0.5 (−0.7)
$\text{Sb}_2\text{O}_3 + \text{Cl}_{\text{ar}}$	327	329 (+2)	409	408 (−1)	6.9	4.2 (−2.7)
Cl_{al}	243	272 (+29)	328	325 (−3)	0.2	0.2 (−)
EP	445	432 (−13)	481	481 (0)	47.2	46.6 (−0.6)
EP-Sb	445	435 (−10)	483	477 (−6)	47.8	48.4 (+0.6)
EP-Br	404	396 (−8)	480	417 (−63)	29.2	22.4 (−6.8)
EP-Sb-Br	390	383 (−7)	480	387 (−93)	25.4	18.9 (−6.5)
EP- Cl_{ar}	330	341 (+11)	481	478 (−3)	29.5	22.1 (−7.4)
EP-Sb- Cl_{ar}	330	347 (+17)	481	482 (+1)	26.9	19.2 (−7.7)
EP-Sb- Cl_{al}	315	314 (−1)	475	432 (−43)	4.2	1.4 (−2.8)

Values in the parentheses are the respective temperature differences (ΔT_5 and ΔT_{max}) between air and N_2 conditions.

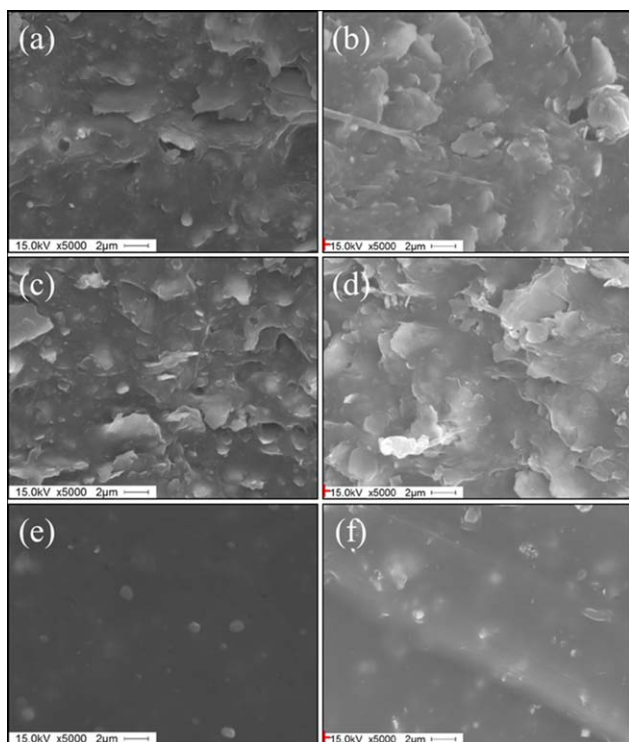


Figure 3. SEM micrographs of the fracture surfaces of FR-filled EPDM compounds before and after aging with isothermal TGA aging at 300°C for 400 min: (a) EP-Sb-Br before aging, (b) EP-Sb-Br after aging, (c) EP-Sb before aging, (d) EP-Sb after aging, (e) EP-Sb-Cl_{al} before aging, and (f) EP-Sb-Cl_{al} after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Morphology and Composition Analysis During Aging

The SEM morphology of five compounds before and after aging at 300°C for 400 min has been shown in Figure 3. EP-Sb-Br and EP-Br shows rougher surfaces of evidencing the traces of presence of Sb₂O₃ and other FRs, but relatively smoother surfaces can be observed for the EP-Sb-Cl_{al}. This could be due to the smaller amount of FR present in the EPDM matrix (Table I). In

general, no striking observations were found on the general morphologies of the samples even after the thermal aging.

To monitor the elements composition, a scanning EDS was carried out for the observed FE-SEM images. Table III represents the results of elemental analysis of four representative compounds (EP-Sb-Br, EP-Sb, EP-Cl_{ar}, and EP-Sb-Cl_{al}) aged in a convection oven at 150°C for 1000 min. The EP-Sb-Br compound showed slightly higher decompositions of Sb₂O₃ and aromatic brominated-RF (Cl_{ar}) compared with those of EP-Sb and EP-Cl_{al}, respectively. However, the EP-Sb-Cl_{al} showed dramatic loss of Sb (88 wt %) and Cl (67 wt %), when aged at 250°C for 150 min. This could possibly be due to severer thermal aging condition involved, which was close to the thermal degradation of chlorinated FR (Cl_{al}) at 243°C under N₂ condition [see Table II and Figure 2(a)]. It could be deduced that the reaction between Sb₂O₃ and aliphatic chlorinated FR might have played effective role in the weight loss.

In the case of the TGA-aged samples at higher temperature of 300°C for 400 min (Table IV), much severe degradations were observed for the FRs. The EP-Sb-Br compound showed a noticeable decomposition of FR along with antimony, indicating a possible reaction that occurred between them. But the chlorinated FRs (Cl_{ar} and Cl_{al}) recorded lower thermal degradation temperature than the brominated FR (Br). Although, the thermal degradation temperature of Br was seen above 400°C, severe degradation of EP-Sb-Br was noted below 400°C typically in air condition. However, the EP-Sb-Cl_{ar} compound did not show corresponding decrease in the weight loss of the raw chlorinated FR (Cl_{ar}). The observed controversial trend might be due to the limitation of SEM-EDS technique, where only smaller regions of the sample surfaces are exposed to examination. This might obviously not represent the bulk concentration of the element in the sample. Due to this limitation of SEM-EDS technique, an attempt was made to precisely analyze the elemental composition in the bulk solid sample by a novel technique, called LIBS. Two wavelengths of 247.9 and 833.5 nm were applied based on internal standard of measurement of atom emission line intensity. The Sb atom emission line was easily observed in air

Table III. EDS Analysis of Unaged and Aged FR-Filled EPDM Compounds by a Convection Oven Aging at 150°C for 1000 min

Compounds	Element	Concentration (wt %/at %)		
		Before aging	After aging	Residue (wt %/at %)
EP-Sb	C	81.8 ± 0.62/97.9 ± 0.08	81.4 ± 1.72/97.8 ± 0.25	99/100
	Sb	18.2 ± 0.62/2.14 ± 0.08	18.6 ± 1.72/2.21 ± 0.25	102/103
EP-Sb-Br	C	64.2 ± 3.09/92.7 ± 0.89	71.1 ± 0.83/94.6 ± 0.20	111/102
	Br	28.7 ± 1.80/6.28 ± 0.64	22.7 ± 0.62/4.55 ± 0.16	79/72
	Sb	7.03 ± 1.58/1.02 ± 0.27	6.23 ± 0.30/0.82 ± 0.04	89/80
EP-Cl _{ar}	C	80.5 ± 1.53/92.4 ± 0.69	82.0 ± 0.57/93.1 ± 0.25	102/101
	Cl	19.5 ± 1.53/7.62 ± 0.69	18.0 ± 0.57/6.93 ± 0.25	92/91
EP-Sb-Cl _{al} ^a	C	74.6 ± 1.66/92.6 ± 0.62	93.9 ± 0.86/98.2 ± 0.27	126/106
	Cl	14.3 ± 1.03/6.02 ± 0.53	4.70 ± 0.67/1.66 ± 0.25	33/28
	Sb	11.2 ± 0.62/1.37 ± 0.10	1.39 ± 0.21/0.14 ± 0.02	12/10

^a Aging condition: 150 min at 250°C.

Table IV. EDS Analysis of Unaged and Aged FR-Filled EPDM Compounds by Isothermal TGA Aging at 300°C for 400 min

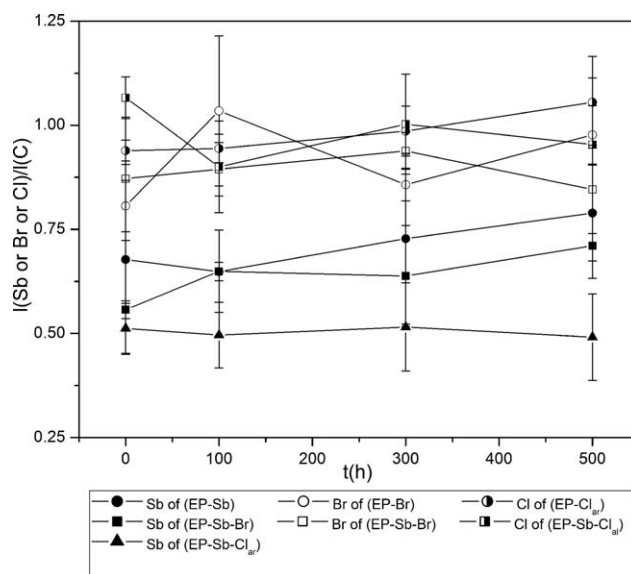
Compounds	Element	Composition (wt %/at %)		Residue (wt %/at %)
		Initial	Aged	
EP-Sb	C	83.54/98.09	81.25/97.76	97/99
	Sb	16.45/1.91	18.74/2.23	113/116
EP-Br	C	76.31/95.54	77.55/95.81	101/100
	Br	23.68/4.46	22.45/4.19	94/93
EP-Sb-Br	C	66.8/93.5	76.1/95.8	114/102
	Br	26.65/5.61	18.29/3.46	68/61
	Sb	6.57/0.91	5.57/0.69	84/76
EP-Cl _{ar}	C	83.03/93.52	85.12/94.40	102/100
	Cl	16.96/6.47	14.88/5.59	87/86
EP-Sb-Cl _{ar}	C	75.88/92.02	77.19/92.35	101/100
	Cl	17.48/7.18	17.22/6.99	98/97
	Sb	6.63/0.79	5.58/0.66	84/83
EP-Sb-Cl _{al}	C	81.47/94.88	83.04/95.65	101/100
	Cl	10.69/4.22	8.71/3.40	81/80
	Sb	7.83/0.89	8.24/0.94	105/104

condition, while halogen elements were not possible to be detected in air condition. Thus, the laser was generated in helium flow medium to prevent any possible interference from air. For a quantitative analysis, the C and Si elements emission lights were detected as a reference peak height for all specimens. The spectrum was observable in the range of 230–270 nm for Sb element and 810–850 nm for halogen elements (Br and Cl). The characteristic primary peak of 259.8 nm for Sb was detected in the EP-Sb-Br, EP-Sb, and EP-Sb-Cl_{al} containing Sb₂O₃. The characteristic peaks of 827.2 and 844.7 nm for Br were detected in the EP-Sb-Br and EP-Br containing brominated FR. The peak for Cl at 837.6 nm was detected in the EP-Sb-Cl_{ar} and EP-Cl_{ar} containing chlorinated FRs. The peaks for standard C was detected at 274.9 and 83.5 nm, and ~250 nm, and for Si at 243.5, 250.7, 251.4, 251.6, 251.9, 252.4, and 252.9 nm. Based on the observed data, it is encouraging to report that the LIBS analysis gives a true representation of the elemental composition in the bulk compounds relative to the EDS analysis.

Figure 4 presents the relative LIBS peak intensity for Sb, Br, and Cl with respect to that of C with aging time in an oven at 150°C for 500 h. This was performed to observe any possible change in atomic losses during the thermal aging. No meaningful change was observed even after 500 h at 150°C. This indicates that the Sb₂O₃ and the other FRs do not decompose to a meaningful level under the given thermal aging condition. Similar trend of the FRs were seen by the measuring the weight loss of specimens aged at the temperature ranges below 165°C (Figure 8). These findings made it interesting to investigate the behavior of the samples at elevated temperature ranges to determine the effect of high temperature (Figure 5) on the acceleration of thermal degradation or on enhancement of chemical reaction among FRs. To investigate the chemical change of samples aged for 400 min at higher temperatures: 190–350°C in the TGA experiments, another set of LIBS experiment was con-

ducted. Figure 5 shows a representative LIBS intensity peak of EP-Sb-Br compound containing both Sb and Br with aging temperature of 190–350°C and time of 400 min. By increasing the aging temperature, the relative LIBS peak intensity of Sb and Br decreased significantly, possibly due to both the thermal degradation of EPDM and brominated FR as well as chemical reactions among the brominated FR, EPDM, and Sb₂O₃.

To clarify the quantitative changes in the loss of elements, the relative peak intensity of each element with respect to that of the standard C is plotted in Figure 6 as a function of aging temperature. A great decrease in relative intensity of the elements: Sb, Br

**Figure 4.** The relative LIBS peak intensity of Sb, Br, and Cl with respect to that of C for various compounds by convection oven aging at 150°C for 500 h.

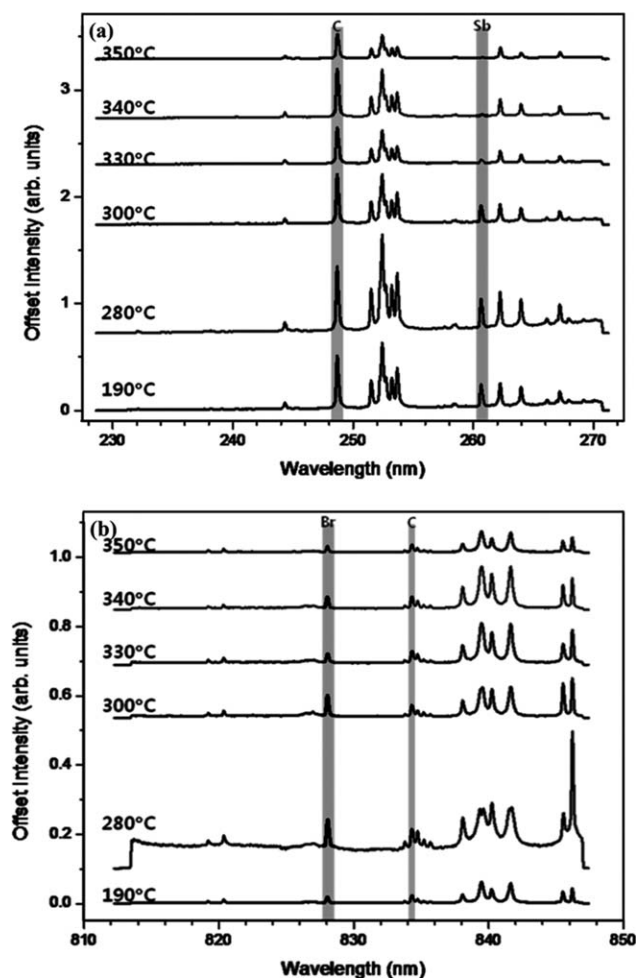


Figure 5. The offset relative LIBS peak intensity of EP-Sb-Br compounds with isothermal TGA aging at 190, 280, 300, 330, 340, and 350°C for 2 h: (a) lower wavenumber of ~ 250 nm and (b) higher wavenumber of ~ 830 nm.

and Cl was found in the EP-Sb-Br and EP-Sb-Cl_{ar}. However, a slight increase was observed in the EP-Sb containing Sb₂O₃ only. As explained earlier, the Sb₂O₃ was found to be stable up to 600°C [Figure 2(a)] and hence the higher thermal stability of EP-Sb. This simply means there was no any significant chemical reaction between EPDM molecules and Sb₂O₃. Another point that worth mention here is that, even though the relative peak ratio did not change much below 300°C, but a dramatic change at higher temperatures was observed thereafter. Again, the raw brominated FR was found to be thermally stable at least up to 400°C (Table II), but a synergy effect of the brominated FR and Sb₂O₃ in the EPDM matrix (EP-Sb-Br) resulted in a dramatic thermal degradation of Br detected around 300°C. This strongly suggests there was a possible chemical reaction among the FRs. Further, it is commendable to state that the presence of Sb₂O₃ alone without brominated FR did not show any thermal degradation up to 400°C. It can therefore be speculated that the dramatic thermal degradation of the brominated FR around 300°C was mainly due to the reaction between Br and EPDM rubber under the oxygen atmosphere.^{24–27} From the above explanation, it can be understood that the elemental composition results

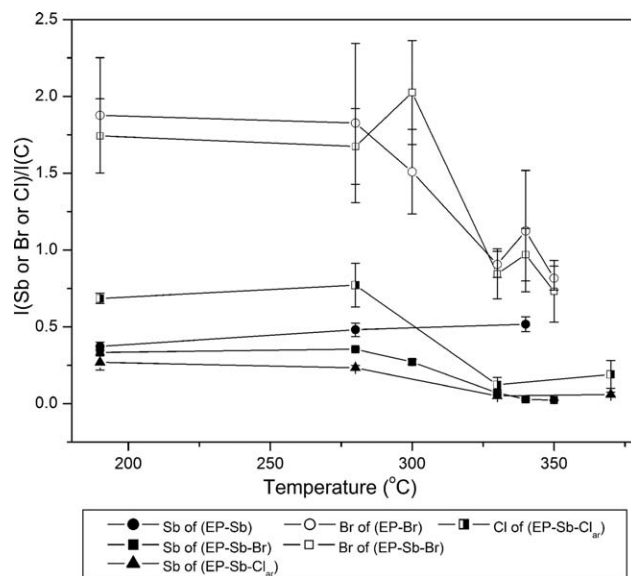


Figure 6. The relative LIBS peak intensity of Sb, Br, and Cl with respect to that of C for various compounds by isothermal TGA aging at 190, 280, 300, 330, 340, and 350°C for 150 min.

obtained by the LIBS technique matches well with the weight loss pattern obtained by the raw FRs and FR-filled EPDM compounds shown in the TGA curves [Figure 2(b)]. At this stage, we confirm that the LIBS can be an effective and promising analysis technique for studying the elemental components in a bulk rubber compound.

Weight Loss Analysis During Aging

Isothermal stability of the specimens at 150, 190, 250, and 300°C were monitored under air condition using TGA and their results are represented in Figure 7. The weight loss by thermal degradation for all the samples was found to be quite low (maximum loss 0.3%) in the temperature range up to 190°C. As can be seen from Figure 7, there is no characteristic difference among the respective weight loss curves of all the specimens, typically within the lower temperature range (150–190°C). However, a big variation in the degradation trend was observed above 190°C. The specimens containing the chlorinated FR (EP-Sb-Cl_{ar} and EP-Cl_{ar}) showed a more rapid weight loss compared to other compounds at higher temperature above 190°C. This might be due to the lower thermal stability of chlorinated FR as already discussed [Figure 2(b) and Table II]. The lower thermal stability of the chlorinated FRs can be ascribed to the possible formation of volatile gases of SbCl₃ and HCl that acted as dehydrating agents in the condense phase during the pyrolysis process and thus facilitated the char formation of the chlorinated FR compound.²⁶ Subsequently, the EP-Sb-Cl_{al} compound containing aliphatic FR (Cl_{al}) with poor thermal stability showed more rapid weight reduction compared to other compounds (EP-Sb-Cl_{ar} and EP-Cl_{ar}) containing aromatic FRs (Cl_{ar}) [Figure 2(a) and Table II].

To examine the weight loss of rubber specimens in convection oven aging conditions, is precisely monitored with thermal aging time, their weights were carefully monitored with thermal aging time, and the results are plotted as weight loss (%) against aging time (h), shown in Figure 8. In the oven aging, the weight

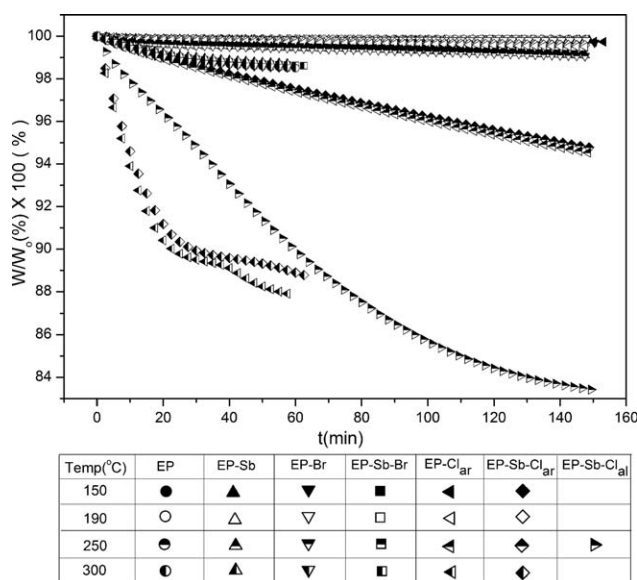


Figure 7. Weight loss curves of EP, EP-Sb, EP-Br, EP-Sb-Br, EP-Cl_{ar}, EP-Sb-Cl_{ar}, and EP-Sb-Cl_{al} compounds by isothermal aging at 150, 190, 250, and 300°C under air for 150 min.

loss of samples were found to be about 1% maximum even after 1000 h at 120, 135, 150, and 165°C respectively. These results are similar to that obtained from the isothermal TGA experiment at 150 and 180°C discussed above (Figure 7). Our studies suggest that there is no clear trend in the weight loss among specimens, which means the rubber compounds were quite stable in terms of weight loss at temperature ranges below 165°C.

Thermal Degradation Mechanism

As already discussed, thermal decompositions (maximum 0.3%) proceeded at somewhat low speed in the aging temperature ranging up to 190°C for all the specimens. However, there was a big difference in the degradation trend above 190°C. To

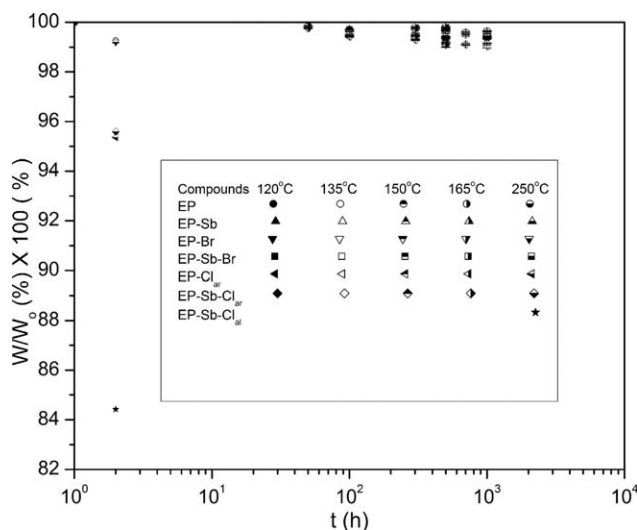


Figure 8. Weight loss of EP, EP-Sb, EP-Br, EP-Sb-Br, EP-Cl_{ar}, EP-Sb-Cl_{ar}, and EP-Sb-Cl_{al} compounds by convection oven aging as a function of aging time at 120, 135, 150, and 165°C, respectively. The results of the isothermal TGA aging at 250°C are also plotted together for a comparison.

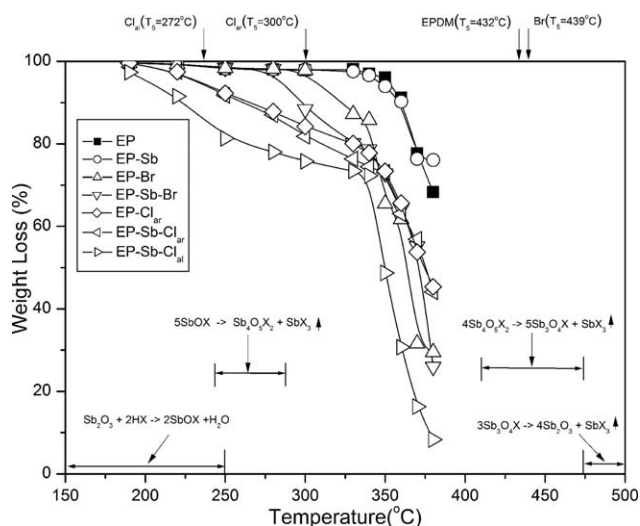


Figure 9. Weight loss of neat EPDM (EP) and FR-filled EPDM compounds with isothermal TGA aging in the aging temperature ranges from 190 to 380°C for 400 min under air condition.

understand the detailed mechanism of thermal degradation at higher temperature ranges, the isothermal aging experiment at temperature range of 190–380°C for the same period of 400 min, was carried out under air condition using TGA and their results are represented in Figure 9.

The degradation of the compounds containing the chlorinated FRs (EP-Sb-Cl_{ar}, EP-Cl_{ar}, and EP-Sb-Cl_{al}) was severer in the temperature ranges of 190–320°C compared to the other compounds, probably because of their lower thermal resistance (notably Cl_{al}). The EP-Sb-Br compound containing brominated FR and Sb₂O₃ showed sizeable decrease above 270°C. The EP-Br containing brominated FR showed a substantial decrease in weight above 300°C. The observed weight loss cannot be explained in terms of the degradation trend of brominated FR, as in the case of the chlorinated FRs, since the brominated FR was stable until around 430°C [Figure 2(b) and Table II]. The degradation of EP-Sb-Br and EP-Br compounds between 270 and 350°C was responsible for the degradation of the EPDM, chiefly by chemical attack of brominated FR.^{24–27}

Even though, both EP-Sb-Br and EP-Br containing the same amount of brominated FR, it was noted that EP-Sb-Br compound showed ample degradation behavior than the EP-Br compound. This clearly indicates that an extra thermal degradation mechanism ensued. The severe thermal decomposition of the sample EP-Sb-Br compound may be as a result of the reaction between Sb₂O₃ and brominated FR in the temperature range of 245–280°C given by the equation²⁹;



The SbBr₃ could evaporate leading to an additional weight loss. The reduction of Sb in the EP-Sb-Br compound has already been confirmed by both the EDS and LIBS element analysis before and after aging. Moreover, the neat EPDM (EP) and EP-Sb compound showed stability behavior until 350°C, where the thermal degradation of the main EPDM matrix was clearly revealed.

Based on the isothermal TGA analysis, two possible mechanisms were proposed which could be used to account for the severe thermal degradation of the rubber compounds containing brominated FR and (EP-Sb-Br and EP-Br). While one was related to a chemical reaction between brominated FR and EPDM rubber matrix at elevated temperatures (noticeable above 190°C), the second was ascribed to the chemical reaction between Sb₂O₃ and brominated FR which produced evaporable compounds such as SbBr₃.

CONCLUSIONS

According to the analysis of the experimental results on thermal aging by convection oven and TGA, elemental analysis by EDS and LIBS, as well as weight loss scrutiny, the following facts were evident in this work.

The thermal stability of the raw FRs was found to be in the order of Sb₂O₃ > Br > Cl_{ar} > Cl_{al}. In the case of rubber compounds, the EP, EP-Sb, EP-Br, and EP-Sb-Br generally showed the higher thermal resistance than EP-Sb-Cl_{ar}, EP-Cl_{ar}, and EP-Sb-Cl_{al}, containing less stable FRs (Cl_{ar} and Cl_{al}) based on T_5 . Based on the maximum degradation temperature (T_{max}), the degradation of all compounds roughly remained to be similar the level of degradation of EP (481°C) in N₂, while a great decrease in T_{max} was observed in air condition for several compounds containing brominated FR. It can be concluded that the thermal degradation behavior of EPDM compounds containing halogenated FRs is strongly dependent on the aging atmosphere and type of FRs.

The elemental composition results obtained by the LIBS technique matches well with the weight loss pattern obtained by the raw FRs and FR-filled EPDM compounds. The LIBS technique can be an effective and promising analysis tools for analyzing the elemental components in a bulk rubber compound.

The weight loss of neat EPDM (EP) and FR-filled EPDM compounds during thermal aging was found to be quite small in the temperature ranges below 190°C, while it was noticeable above the temperature.

Two possible degradation mechanisms were predicted for the rubber compounds containing brominated FR and antimony trioxide (EP-Sb-Br). The first one was attributed to a chemical reaction between brominated FR and EPDM rubber matrix at high temperatures (noticeable over 190°C), while the second involved a chemical reaction between Sb₂O₃ and brominated FR, producing volatile compounds such as SbBr₃. The predicted degradation mechanism could be very useful for future review of FR-filled rubber compounds.

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