Non-Halogen-Containing Flame-Retardant Ethylene–Propylene Copolymer Compositions for Cable Insulation with Nitrogen- and Sulfur-Containing Fire Retardants

M. S. KARAIVANONA, K. M. GJUROVA

University "Prof. As. Zlatarov," Department of Organic Chemistry, Central Research Laboratory, 8010 Bourgas, Bulgaria

Received 24 January 1996; accepted 24 August 1996

ABSTRACT: The effects of ammonium salts of sulfaminic acids, containing aliphatic and arylaliphatic hydrocarbon chains, respectively, in a combination with inorganic fire retardants and fillers, on the properties of ethylene–propylene copolymer compositions (EPCC) for cable insulation were studied. The additive action of the organic fire retardants and antimony oxide in a weight ratio of 3:1 was proved. EPCC indicated a limited oxygen index (LOI) of 37–39% and a diminished smoke release and belonged to UL class zero. The thermal destruction of the system consisting of a copolymer blend and fire retardant, as well as the individual organic and inorganic fire retardants, was studied using dynamic thermal analyses (DTA, TG, DTG). The combination of fire retardants caused a decrease of both the heat release and weight loss over the EPCC surface. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 581–588, 1997

Keywords: fire retardant; ammonium salts of sulfaminic acids; ethylene–propylene copolymer; cable insolution; oxygen index; smoke release; thermal analysis

INTRODUCTION

Polyolefins, such as the copolymers of ethylene and propylene, are among the most widely produced materials for the preparation of plastics. A number of valuable properties including frost hardiness, high elasticity, excellent dielectric characteristics, easy processability, and low price result in the application of these prominent materials in both technology and everyday life. The unique electrochemical properties of the polyolefins also lead to their wide utilization in the corresponding industry. This kind of application is, however, associated with a diminished flammability of the polyolefins to a certain level, depending on the operating conditions.

The earliest investigations on reducing the flammability of polyolefins date back to the mid-1950s, and the research has developed in two stages: A number of publications on the selection of new fire retardants and their course of action combined with a chemical modification of the polyolefins appeared in the literature up to the mid-1970s. An extensive research on the mechanism of action of the fire retardants (FR) marked the second stage of this development.

A number of chloro-, bromo-, and phosphorus-containing organic compounds, as well as metal hydroxides, etc., have been studied as FR for polyolefins, particularly ethylene–propylene copolymers. Other additives, such as nitrogen- and sulfur-containing FR which are mostly nontoxic, have been covered to a lesser degree.

Among the nitrogen-containing compounds, triallylisocyanurate, the 1,3,5-triazine derivative, and a polyfunctional compound containing imide groups have been studied.[1] Flame-retardant and thermally stable compositions based on the ethylene–vinyl acetate copolymer, 1,3,5-tris-(3,5-di-*tert*-butyl-4-hydroxybenzoyl)isocyanurate, sulfur-containing esters, and aluminum or magnesium

Correspondence to: M. S. Karaivanona
Contract grant sponsor: Ministry of Science Education and Technology, Bulgaria

hydroxides,[2] as well as inorganic FR and zinc compounds[3] have been employed for cable and wire insulation. An elastomeric composition with a low flammability and smoke release, based on the ethylene–propylene rubber contained, modified by oleinic acid aluminum hydroxide thrihydrate (AHT), Me_2SiCl_2, and $RMeSiCl_2$, was also used for cable insulation.[4] A flame-retardant polyolefinic composition containing thiobis-phenols and magnesium hydroxide treated superficially by silane and, consequently, by aliphatic acids and their salts was also developed.[5] A halogenated cyclic hydrogen carbonate combined with antimony oxide (AO) were introduced into ethylene–(ethylidene–norbornene)–propylene terpolymers and the flammability characteristics of the composition obtained were studied.[6] Also, the terpolymer mentioned above, as well as the melamine-modified ethylene–propylene copolymer,[7] were blended with ammonium polyphosphate, condensation products of formaldehyde with five-membered heterocyclic (thio)ketones, containing two or more nitrogen atoms, and triazine derivatives in a search for the optimum properties. A nonflammable ethylene–propylene copolymer composition (EPCC) contained the cyanurochloride–tribromo–(methyl–ethylidene)–bisphenol oligomer and AO and had a diminished smoke release.[8] Tris-(2,3-dibromopropyl)phosphate and dinonylphosphate ester were also employed as FR.[9] The thermal degradation of both the crosslinked and noncrosslinked chlorsulfonated polyethylene containing modifying additives, such as magnesium oxide, diphenyldiamine, chloroparafin, SiO_2, AO, etc., was studied.[10]

The present work is a continuation of our previous research on the preparation of a flame-retardant EPCC for cable insulation, Dutral Co 034, containing ammonium salts of bromosulfaminic and bromonitrosulfonic acids.[11] The purpose of the research was to study the influence of ammonium salts of sulfaminic acids, containing aliphatic and arylaliphatic hydrocarbon chains, on the physicomechanical, electrical, and thermal properties as well as the flammability characteristics of EPCC. A combination of nitrogen–sulfur-containing and inorganic fire retardants and, also, fillers was selected in order to improve the flammability characteristics of EPCC.[11,12]

EXPERIMENTAL

Materials

Organic Fire Retardants

Two ammonium salts of oligomeric sulfaminic acids based on nitrooligomers of 1,4-*cis*-isoprene rubber SKI-3 (SA-SKI-3) and butadiene–styrene rubber Bulex-1500 (SA-L), respectively, were prepared by a two-stage synthetic procedure. A nitration of the elastomer or the corresponding latex by nitric acid resulted in a preparation of nitrooligomers, which was followed by an interaction of the latter with ammonium hydrogen sulfite. As a result, ammonium salts of sulfaminic acids were obtained.[13,14] SA-SKI-3 has 16.1% N and 23.0% S, respectively, in a weight ratio of N : S of 1 : 1.4–1.5. The investigated ammonium salts with aliphatic and arylaliphatic hydrocarbon chains consists of $—SO_3NH_4$, $—NHSO_3NH_4$, and *sec*-OH functional groups. These salts combined with ammonium sulfate (2 : 1 weight ratio) were introduced as additives to the ethylene–propylene rubber (EPR).

Inorganic Fire Retardants and Fillers

Aluminum hydroxide thrihydrate—Martinal 104-C (AHT)

Calcium carbonate (precipitated)

Zinc borate (ZB)

Antimony oxide, Sb_2O_3 (AO).

EPR, weight parts (phr)

Ethylene–propylene rubber (EPR) Dutral Co 034	90
Polyethylene OB 20-108	10
Fillers	100–200
Plasticizers	8–20
Antiaging agents	1–3
Curing group	5–8
Fire retardants (FR)	5–25.

The blends were prepared using laboratory rollers of 350/500 mm size in a two-stage procedure. First, the EPR was blended with polyethylene for 3–5 min at 100–120°C. Then, the ingredients were introduced into the blend for 15–20 min at 50–60°C. Samples of 100 × 100 × 3 mm dimensions were cut from the blend and subjected to curing in a laboratory press at 115°C for 30 min under a pressure of 22 MPa. The physicomechanical properties were examined with a dynamometer type WPM (Germany).

Thermal Studies

These studies were conducted by using OD-102 derivatograph (F. Paulik, J. Paulik & L. Erdey) under the following conditions: for EPCC: temperature range 25–550°C, heating rate of 6°C/min, air atmosphere (static); for the FR: temperature range 25–1000°C; heating rate of 10°C/min.

Characteristic Tests

The limited oxygen index (LOI) was determined, according to ASTM 2863-77, using a DIG OXIMETER unit, with sample dimensions 100 × 100 × 3 mm. The flame resistance was evaluated, according to the UL-94 standard (vertical method) with the same sample size. The smoke-release parameters were estimated in a smoke camera equipped with an optical cell, according to ASTM 662E. The following parameters were determined: $D_{S_{max}}$ (maximum optical density); R (velocity of smoke distribution, %/min); CST (coefficient of smoke transparency); and D_S at t_{16} (s).

RESULTS AND DISCUSSION

The preparation of flame-retardant EPCC represents a challenging research problem, since the introduction of additives or fillers into the elastomeric composition is likely to disrupt the whole set of physicomechanical parameters. Therefore, the selection of efficient FR is associated with their properties as flame-retardant compounds, as well as their influence on the mechanical characteristics of the corresponding compositions.

Influence of the Fire Retardants on the Physicomechanical and the Electrical Characteristics of EPCC

The ethylene–propylene copolymer Dutral Co 034 was selected for the preparation of the compositions for cable and wire insulation because of its excellent dielectric properties, thermal stability, and the possibility of diminished smoke release when combined with FR.

The first set of compositions was prepared in order to establish convenient methods for studying the influence of the organic additives, such as SA-SKI-3 and SA-L combined with AHT (200 phr) and ZB (10 phr) on the physicomechanical characteristics of EPCC. The increase of SA-L concentration within 5–20 phr was found to result in an increased relative elongation from 295 to 360%, respectively, whereas SA-SKI-3 did not have a significant effect (Fig. 1, curves 1 and 4). The higher relative elongation corresponded to a lower scleroscope hardness (Shore A), as shown in Figure 1 (curves 2 and 5), probably due to the plasticizing effect of the FR studied. In our previous work,[15] the plasticizing effect of SA-SKI-3 was proved in compositions based on polychloroprene. Accordingly, the decrease of the tensile strength was not surprising in the EPCC examined (Fig. 1, curves 3 and 6); however, the corresponding values did conform to the technical requirements. An increase of the tensile strength from 4.5 to 6.0–6.2 MPa was observed, provided that the content of the plasticizer Sunpar was decreased from 10 to 6 phr for EPCC containing SA-SKI-3 and SA-L separately.

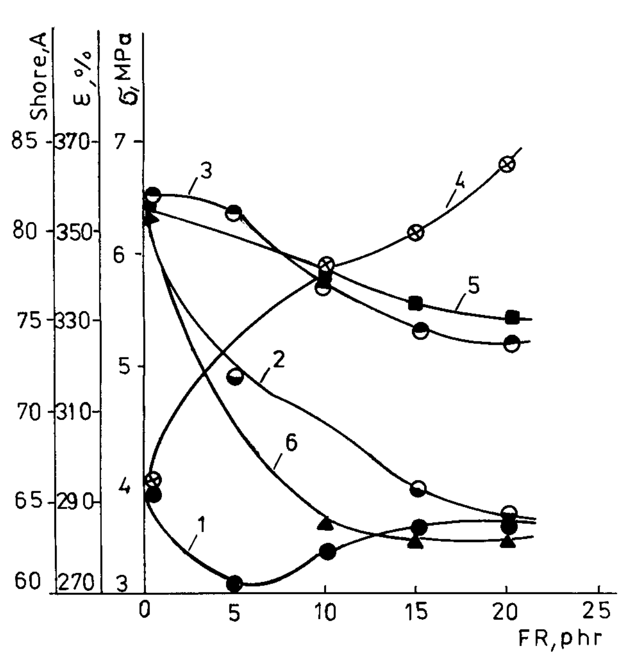

Figure 1 Influence of SA-SKI-3 and SA-L on the physicomechanical parameters of flame-retardant EPCC containing 200 phr AHT and 10 phr ZB: (1) relative elongation (SA-SKI-3), %; (2) scleroscope hardness, Shore A (SA-SKI-3); (3) tensile strength (SA-SKI-3), MPa; (4) relative elongation (SA-L), %; (5) scleroscope hardness, Shore A (SA-L); (6) tensile strength (SA-L), MPa.

The combination of the organic additives and AO, regarding their influence on the physicomechanical parameters of EPCC, was also studied in the presence of the mineral fillers AHT and calcium carbonate. No significant change of these parameters was observed as SA-SKI-3 (10–20 phr) and AO (3–5 phr) were introduced (Table I, blends 10 and 13). The complete substitution of AHT for calcium carbonate, however, resulted in a decrease of both the relative elongation and ten-

Table I Composition and Some Physicomechanical Properties of Flame-retardant Ethylene–Propylene Copolymer Blends Containing SA-SKI-3 and SA-L Fire Retardants

	Blend No.								
No. Fire-retardant Filler (phr)	1	2	3	4	10	11	12	13	17
1. SA-SKI-3	—	—	—	—	10	25	25	20	—
2. SA-L	—	—	—	—	—	—	—	—	15
3. Antimony oxide (AO)	—	—	—	8	3	—	—	5	5
4. Aluminum hydroxide trihydrate "Martinal 104-C" (AHT)	—	200	—	200	200	150	100	200	200
5. Calcium carbonate precipitated	—	—	200	—	—	50	100	—	—
6. Zinc borate (ZB)	—	10	10	10	10	10	10	10	10
7. Tensile strength (MPa)	5.5	6.5	4.0	6.8	5.5	5.4	5.5	4.9	3.4
8. Relative elongation (%)	400	295	195	287	264	262	245	252	335
9. Scleroscope hardness, Shore A	78	82	77	78	70	65	66	67	75

sile strength. The combination of AHT–calcium carbonate (1 : 1 wt ratio) was found to preserve the physicomechanical characteristics of EPCC (Table I, blend 12).

The effects of the organic additives synthesized for the first time by us[13,14] on the characteristics of EPCC have not been studied so far. Therefore, the heat aging and the electrical properties were also examined. The compositions containing SA-SKI-3 were found to be resistant toward heat aging (Table II) and they indicated good dielectric characteristics, such as specific volume resistivity (1.8×10^{14}–2.9×10^{14} Ω cm^{-1}). The values of these parameters were within the corresponding range indicated by the technical specifications for EPCC. The influence of SA-L in concentrations of 10–20 phr was found to be similar to SA-SKI-3 and the corresponding values were, approximately, the same.

Effect of the Fire Retardants on the Flammability Characteristics of EPCC

EPCC based on polyolefins are known to release a significant amount of volatile products on burning, which requires an introduction of mineral fillers. The selected compositions contained the organic additives and, also, AHT or a combination of AHT and calcium carbonate (up to 200 phr), as well as ZB (10 phr) (Table I). The ammonium salts of the organic acids used (SA-SKI-3 and SA-L) are nontoxic.

The independent influence of each FR and filler on LOI was studied (Table III). The LOI of the composition without any additives and fillers was found to be 21%. It increased gradually and reached 27% in the presence of ZB. The introduction of SA-SKI-3 (25 phr) and AHT (200 phr) resulted in an LOI of 30–31%. The combination of AHT with AO gave an LOI of 29%, whereas in the presence of AHT and SA-SKI-3 or AHT and calcium carbonate, only a slight increase was observed (Table III, blends 4, 11, and 12).

The LOI reached values of 30–36% as the concentration of SA-SKI-3 was increased from 5 to 20 phr. The upper concentration of SA-SKI-3 established was 15–20 phr (Table III, blend 8). The binary system SA-SKI-3/AO in concentrations of 15–20 and 3–5 phr, respectively, showed additive fire-retarding properties, with the LOI reaching 37.5% (Table III, blends 10 and 13). A similar dependence was also observed in the presence of SA-L as an organic additive. The LOI was 37% with SA-L (15 phr) only, whereas SA-L in a combination with AO (5 phr) gave an LOI of 39% (Table III, blends 15 and 17).

The determination of the smoke-release characteristics of EPCC provides additional information about the specific influence of FR. The smoke release determined by an evaluation of the parameter $D_{S_{max}}$ was found to increase slightly as SA-SKI-3 was introduced alone or in a combination with ZB (Table IV, blends 11-A and 12-A). AHT introduction decreased the smoke release significantly, unlike calcium carbonate (Table IV, blends 2 and 3). $D_{S_{max}}$ values decreased from 137 to 52 and 44 in the presence of both SA-SKI-3 (20 phr) and the binary system SA-L/AO, respectively (Table IV, blends 8 and 10). The additive effect of the binary system SA-L/AO was observed again with respect to the value of $D_{S_{max}}$, which decreased to 34 with an LOI of 39% (Table IV,

Table II Effect of SA-SKI-3 on Heat Aging and the Specific Volume Resistivity of Flame-retardant EPCC

No. Properties	Standard	Blend No. 1	2	3	4	5	6	7	8	9	10	11	12	13
1. Heat aging after 168 h at 135°C														
$K_{\text{tensile strength}}$ (%)	± 30	+2	−4.8	+11	−5.8	−7.2	−8.8	−5.7	−6.0	−5.8	−7.8	−7.4	−7.3	−12.2
$K_{\text{relative elongation}}$ (%)	± 30	−2.5	−9.6	−4	−10.1	−10.5	−14.1	−14.2	−20.7	−18.4	−14.5	−8.9	−9.7	+10.9
2. Specific volume resistivity ($\Omega\ cm^{-1} \cdot 10^{14}$)	1.0	2.9	2.5	—	—	1.6	1.5	1.8	1.1	1.2	—	—	2.5	1.9

Table III Effect of SA-SKI-3 and SA-L on Some Thermal and Combustion Characteristics of Fire-retardant EPCC

Fire-retardant filler (phr)	Blend No. 1	3	15A	2A	2B	4	11A	12A	2	11	5	6	7	8	9	12	10	13	14	15	16	17
SA-SKI-3	—	—	—	—	—	—	25	25	—	—	5	10	15	20	25	25	10	20	—	—	—	—
SA-L	—	—	15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10	15	20	15
AO	—	—	—	—	—	8	—	—	—	—	—	—	—	—	—	—	3	5	—	—	—	5
AHT	—	—	—	—	200	—	—	—	200	150	200	200	200	200	200	100	200	200	200	200	200	200
Calcium Carbonate Precipitate	—	200	—	—	—	200	—	—	—	50	—	—	—	—	—	100	—	—	—	—	—	—
ZB	—	10	10	10	—	10	—	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
LOI (%)	21	23	23	24	29	29	29	30	31	33	30	33	36	35.5	34	32	35	37.5	35	37	36	39
UL-94	—	—	—	—	—	—	—	—	—	—	0	0	0	0	0	0	0	0	0	0	0	0
$\Delta M_{480°}$[a] (%)	88	35	79	81	51	80	—	52	51	—	—	—	—	—	49	49	—	46	50	—	—	45

[a] SA-SKI-3, 87%; SA-L, 86%; AO, 1%; AHT, 32%; Calcium carbonate precipitate, 1%; ZB, 25%.

Table IV Effect of SA-SKI-3 and SA-L on the Smoke-release Characteristics of Fire-retardant EPCC

Fire-Retardant Filler (phr)	Blend No.													
	1	2A	12A	11A	3	2B	2	9	8	10	14	15	16	17
SA-SKI-3	—	—	25	25	—	—	—	25	20	10	—	—	—	—
SA-L	—	—	—	—	—	—	—	—	—	—	10	15	20	15
AO	—	—	—	—	—	—	—	—	—	—	3	—	—	5
AHT	—	—	—	—	—	200	200	200	200	200	200	200	200	200
Calcium Carbonate Precipitate	—	—	—	—	200	—	—	—	—	—	—	—	—	—
ZB	—	10	10	—	10	—	10	10	10	10	10	10	10	10
$D_{s_{max}}$ (maximum optical density)	137	234	161	149	142	95	70	80	52	44	72	73	72	34
R (velocity of smoke distribution, %/min)	42	120	42	61	56	28	29	29	22	21	14	12	9	2
CST (coefficient of smoke transparency)	20	138	25	34	33	8	6.5	12	4.8	5.5	7.5	4	5	2
D_s at $t_{16\,s}$	2.9	2.0	3.8	2.9	2.4	4.0	3.9	3.2	3.1	2.3	2.8	3.3	2.9	3.0

blend 17). The parameters R and CST decrease significantly to 28 and 6.5, respectively (compared to blend 1) after introduction of AHT (Table IV, blends 2B, 2). When EPCC consist of 10–15 phr of SA-L (blends 14–16), R and CST continue to diminish from 14 to 9 and 7.5 to 5. The best characteristics were obtained with the system SA-L/AO/AHT, when they reach to the value of 2. The parameters D_S at t_{16} (s) for optimal blends (Table IV, blends 15 and 17) are not changed considerably toward the initial composition (blend 1).

In conclusion, the organic ammonium salts were found to act as additive fire retardants when combined with AO in a weight ratio of 3 : 1 with an upper concentration of both the fire retardants of 15–20 phr. Each composition studied contained also AHT (up to 200 phr) and ZB (10 phr) as fillers.

Effect of the Fire Retardants on the Thermal Characteristics of EPCC

The studies on the thermal destruction of the systems, consisting of a polymer and FR, provide valuable information about the initial (and crucial) stages of burning. Correlations between some thermal characteristics and the flammability parameters, such as LOI and smoke release, have been observed in most cases.[16–19] This, in turn, reveals information about the total mechanism of action of FR used.

Starting Materials

The initial blend without FR added was characterized by a certain thermooxidative decomposition within 245–480°C (Fig. 2, curve 1). The weight loss at 480°C ($\Delta M_{480°C}$) determined by the TGA scan was found to reach 88% with respect to the initial sample weight as shown in Table III. According to the TGA data, FR can be selected which have the same temperature range of gas release as that of the polymeric composition.[19] FR are known to release mostly nonflammable gases and the endothermic effects are predominant. AHT (Fig. 3, curve 1) undergoes a dehydration within the 240–350°C temperature range, which is accompanied by a strong endothermic effect. Thus, AHT is a powerful potential coolant of the system at the initial stage of the destruction of EPCC. The dehydration of ZB (Fig. 3, curve 2) is characterized by a significantly weaker endothermic effect at ca. 220°C. Calcium carbonate (curve 3), in turn, decomposes endothermally with a release of CO_2 at much higher temperature (over

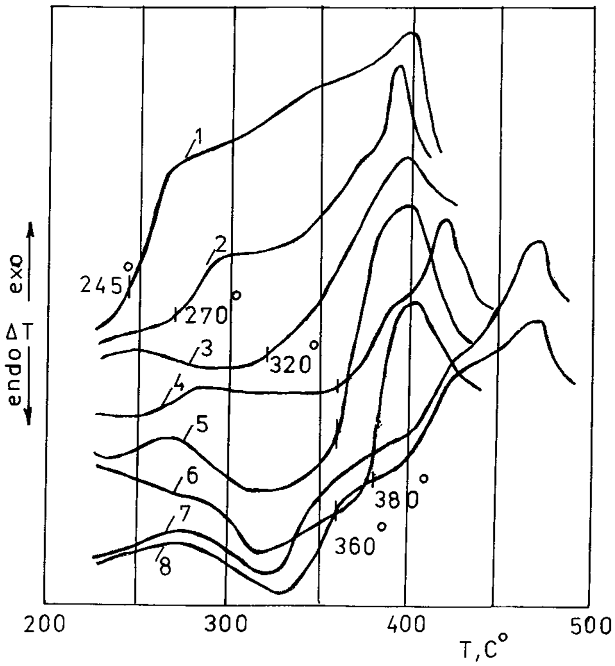

Figure 2 DTA scans of flame-retardant EPCC (for the corresponding blend numbers, refer to Tables I and III): (1) initial EPR blend (without FR added), blend 1; (2) ZB (10 phr) (blend 2A); (3) AHT (200 phr) (blend 2B); (4) SA-SKI-3 (25 phr), ZB (10 phr) (blend 12A); (5) AHT (200 phr), ZB (10 phr) (blend 2); (6) SA-SKI-3 (25 phr), ZB (10 phr), AHT (200 phr) (blend 9); (7) SA-SKI-3 (20 phr), AO (5 phr), AHT (200 phr), ZB (10 phr) (blend 13); (8) SA-L (15 phr), AO (5 phr), AHT (200 phr), ZB (10 phr) (blend 17).

700°C) and serves as an inert filler only. Among the inorganic fillers, only AO is characterized by an exothermic effect on heating (curve 4). Both the organic additives SA-SKI-3 and SA-L (curves 5 and 6) undergo a two-stage decomposition accompanied by strong endothermic effects at ca. 360° and 460°C and a release of nonflammable gases, such as ammonia and sulfur dioxide.

EPCC Containing FR

The fire retardants studied caused a significant decrease and a shift of the exothermic effects, accompanying the thermal oxidation toward higher temperatures in most of the EPCC (Fig. 2). A comparison of the LOI values with the thermal characteristics (Table III; Fig. 2) revealed that the compositions 9, 13, and 17 (curves 6–8) of the high LOI indicated the most pronounced changes of the thermal properties. The onset of the exothermic effects was shifted significantly from 245°C to ca. 380°C. The basic weight loss at 480°C was decreased from 88% to ca. 45%; therefore, the total gas release was reduced. The best results were obtained for compositions 9, 13, and 17 (curves 6–8) containing the organic FR whose action covered the whole temperature range of decomposition of the initial blend. These data were found to correlate with the flammability characteristics mentioned above, thus giving a more profound understanding about the predominant mechanism of the fire retardation. The FR system affects mostly the thermal balance and the gas composition immediately over the EPCC surface. Besides, the endothermic reactions prevail over the exothermic effects at the crucial initial stages of destruction of the composition.

The organic FR ammonium salts SA-L, consisting of sulfonic and sulfaminic groups, in the

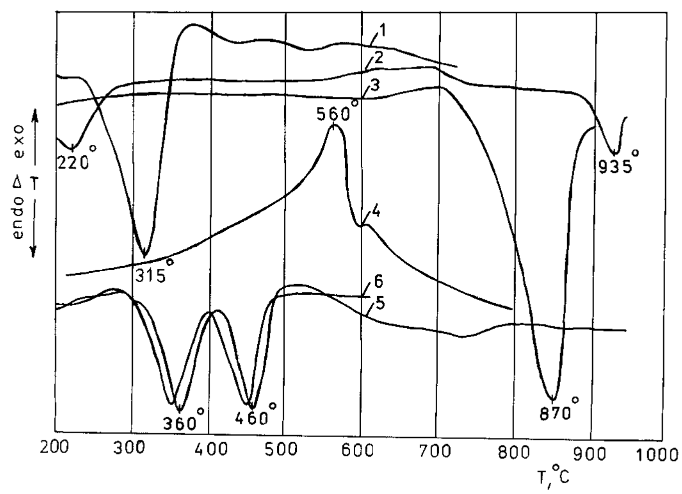

Figure 3 DTA scans of FR for flame-retardant EPCC: (1) AHT; (2) ZB; (3) $CaCO_3$; (4) AO; (5) SA-SKI-3; (6) SA-L.

process of their decomposition, release nonflammable gases such as sulfur dioxide and ammonia. The first one is the bigger concentration of the ammonia (weight ratio N : S is 1 : 1.5). The action of the two FR causes a significant decrease of smoke release of the system as a result of the interaction of the part of generated sulfur dioxide with AO to form nonvolatile antimonyl–sulfur compounds. It is known that ammonia possesses the possibility to diminish fire as do SO_2, CO_2, and nitrogen.[19] On the other side, AHT releases water vapors, which isolate the EPCC surface from the atmospheric oxygen.

The above-stated confirms once again that organic ammonium salts are found to act as an effective additive FR when they are combined not only with AO but also with AHT. Nitrogen–sulfur-containing FR combined with AO were found to be more efficient than were the bromo–nitrogen–sulfur-containing ones,[11] particularly with respect to the smoke-release and heat-release characteristics. Probably it was due to the high smoke release ($D_{S_{max}}$) of the simultaneous elimination of HBr and nitrogen oxides separated from one of the FR nitro groups. These gases have an oxydative effect in the temperature range within 200°C where the EPCC oxidative decomposition begins.

CONCLUSIONS

1. Ammonium salts of aliphatic and arylaliphatic nitrogen-containing sulfonic acids combined with antimony oxide act as fire retardants and exhibit a plasticizing effect in the ethylene–propylene copolymer compositions (EPCC).
2. Flame-retardant ethylene–propylene copolymer compositions containing 15–20 wt parts of the ammonium salts combined with 3–5 wt parts antimony oxide, 200 wt parts aluminium thrihydrate, and 10 wt parts of zinc borate were prepared for cable insulation. These compositions show good physicomechanical and dielectric properties.

REFERENCES

1. K. Hiroshi and M. Chiaki, Jpn. Pat. 56-90845 (1981).
2. Y. Yasuaki, K. Shiguru, and T. Norio, Jpn. Pat. 03-37909 (1991).
3. N. Kyoshi and F. Shunichi, Jpn. Pat. 03-197539 (1991).
4. A. G. Grigorian, V. E. Milkin, A. T. Merkulova, V. H. Volokhin, and M. A. Shenker, *Plast. Massi,* **41,** 31–33 (1991).
5. H. Akihiro, T. Masami, and Y. Yasuaki, Jpn. Pat. 01-302610 (1989).
6. Hitachi Cable, Ltd., Japan Synthetic Rubber Co., Jpn. Pat. 58-216305 (1983).
7. T. Nobuya, A. Shinichi, and F. Toru, Jpn. Pat. 04-146944 (1992).
8. Y. Yasuaki, Y. Hideki, K. Hiromi, and F. Kenji, Jpn. Pat. 61-97343 (1986).
9. L. Peters, U.S. Pat. 3,279,929 (1966).
10. V. V. Bogdanova, I. A. Klimotsova, and M. A. Shashkina, *Vestsi Akad. Navuk Belarusi Ser. Khim. Navuk,* **2,** 110–112 (1992).
11. M. S. Karaivanova and K. M. Gjurova, *J. Appl. Polym. Sci.,* **49,** 159–167 (1993).
12. E. Leonelli and F. Tonioli, *Kautschuk Gummy Kunstoffe,* **44**(10), 960–962 (1992).
13. M. S. Karaivanova and Iv. Mladenov, Bulg. Pat. 39,549 (1985).
14. M. S. Karaivanova and Iv. Mladenov, Bulg. Pat. 94,167 (1991).
15. M. S. Karaivanova, D. Bajdarov, Y. Patov, and Iv. Bajdarova, *Wiss. Zeit. Tech. Hochschule Merseburg,* **33**(3), 523–532 (1991).
16. D. W. Van Krevelen, *Adv. Chem. Therm. Stable Polym.,* 119 (1977).
17. V. M. Bhatnager and I. M. Vergnand, *J. Therm. Anal.,* **27,** 159 (1983).
18. S. H. Zeronian, M. S. Ellison, and K. Alger, *J. Appl. Polym. Sci.,* **25,** 1311 (1980).
19. V. I. Kodolov, *Gorjuchest i Ognestoikost Polimernich Materialov,* Khimia, Moscow, 1980, pp. 184–185.