# Development of Halogen-Free Flame-Retardant Thermoplastic Elastomer Polymer Blend

**Kiran Pal,[1] J. N. Rastogi[2]**

[1]Defence Research & Development Organization, CFEES, Min. of Defence, Delhi 110054, India
[2]Department of Chemistry, M. M. Post Graduate College, Modi Nagar, 201204, U.P. India

**Abstract:** Ethylene-propylene diene rubber (EPDM) and isotactic polypropylene (iPP) blends have widest industrial applications that require a degree of flame retardancy. Halogen-free intumescent technology based on phosphorous salt is a significantly advanced approach to make the polymer flame-retardant. Both ammonium polyphosphate and ethylenediamine phosphate are important intumescent compounds. Their combination with carbonific and spumific agents were studied in binary blends of EPDM/PP. The polymer system was vulcanized online during melt mixing. Intumescent flame-retardant polymer systems exhibit good flame-retardancy with optimum comparable physiomechanical, electrical, and fluid resistance properties, including lower smoke emission, which is essential to protect people because the visibility remains unaffected in the event of fire. Pronounced charring and intumescent effect appear to enhance the flame-retardancy of the polymers. Possible expected intumescent mechanism is proposed based on the nonpyrolysis mechanism for the flame-retarded polymer and the intumescent components. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 407–415, 2004

**Key words:** ethylene-propylene diene terpolymer (EPDM); isotactic polypropylene (iPP); flame retardant; intumescent char; limiting oxygen index (LOI)

## INTRODUCTION

In recent years, elastomer-plastic blends have become technologically interesting for use as thermoplastic materials. These materials exhibit some of the physical properties of conventional elastomers at serviceable temperatures and are processible at elevated temperatures.[1–2] Ethylene–propylene diene terpolymer (EPDM) was applied because of simple synthetic process and good weather resistance. Because the processibility is not very good, polypropylene (PP) is used to modify EPDM.[3–6]

Because all carbon-containing polymers are organic, they burn under one or more set of conditions. Polymers, being solid, do not burn clearly; it is the volatile products of thermal decomposition that burn. The flame is self-propagating when the heat of combustion is sufficient to maintain an adequate supply of decomposition products as fuel.[7] The process of spreading a flame over the surface of a polymer material is considered a continuous diffusion ignition process for the gaseous state of the polymer's degradation products. Heat from a flame, radiating on the surface edge of a material, warms up a layer of polymer material to the temperature at which gasification starts. The gaseous fuel products then diffuse from the surface into the oxidizing atmosphere. The self-accelerating exothermal oxidation of the fuel is generated in the gaseous phase. In this way, a continuous spread of flame is proceeded.[8]

The objective of the flame-retarding polymers is to increase the resistance of the material to ignition and to reduce the flame spread with minimal degradation of its properties. Addition of flame-retardant material to polymer will suppress the propagation of flame.[9] These change the combustion characteristics of the polymeric material so that it will be more difficult to ignite. Once ignition has occurred, addition of flame-retardant material will cause the flame to die out or cause the material to burn more slowly so that the flame spread, rate of heat release, or both will be substantially lowered.

Recent research[10–18] has shown halogen-free flame-retardant intumescent-based technology that is an alternative to both halogenated and inorganic flame-retardant for development of flame-retardant polymers. Intumescent char is an effective technical approach to develop the flame-retardant products with low overall fire hazard. The intumescent effect is achieved by using the following three basic ingredients in the polymer system:

Catalyst: This usually consists of the salt of an inorganic non-volatile acid.

Carbonific compounds: A source of carbon, these are polyhydroxy compounds.

Spumific compounds: A source of noncombustible gases.

Intumescent flame-retardant agents function is defined as follows.

In the first stage, the effect of intense heat causes the inorganic salt to decompose to the acid (e.g., ammonium dihydrogen phosphate)

$$NH_4H_2PO_4 \xrightarrow{\Delta} NH_3 + H_3PO_4$$
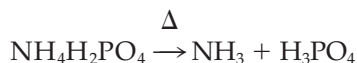
The components of the intumescent mixture start to soften. The acid esterifies the polyhydroxy compound to give the polyester (e.g., pentaerythritol)

$$C_5H_8(OH)_4 + H_3PO_4 \rightarrow C_5H_8(OH)_4H_3PO_4$$
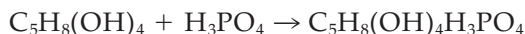
The acidified carbonific mixture melts and decomposes. The polyol ester breaks down to acid, water, and a carbonaceous residue.

$$C_5H_8(OH)_4H_3PO_4 \xrightarrow{\Delta} H_3PO_4 + H_2O + C$$
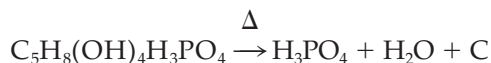
Simultaneously, the spumific compound supplying blowing agent decomposes and the gases generated expand the molten carbonaceous mass, for example,

$$C_nH_{(2n-1)}Cl \xrightarrow{\Delta} HCl + C$$
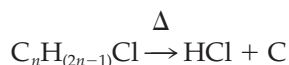
which acts as an excellent thermal insulator between the substrate and heat, which prevents the temperature of the substrate from raising under a fire situation.

## EXPERIMENTAL

To examine the efficiency of different flame-retardant additives, 14 sample formulations were prepared with different concentrations. Ten sample formulations were prepared by incorporating 10, 20, 30, 40, and 45 wt % of each, hostaflam 462 (ammonium polyphosphate microencapsulated with melamine resin) and amgard NL (ethylenediamine phosphate and silica amorphous), in the binary blend of EPDM/PP and designated as $FRA_1$, $FRA_2$, $FRA_3$, $FRA_4$, $FRA_5$ and $FRB_1$, $FRB_2$, $FRB_3$, $FRB_4$, $FRB_5$, respectively.

Four intumescent formulations were prepared by incorporating the combination of (1) hostaflam/melamine/pentaerythritol, (2) hostaflam/melamine/crystalline wax, (3) hostaflam/dicyandiamide/pentaerythritol, and (4) amgard/melamine/pentaerythritol in the ratio of 3:1:1 into the EPDM/PP polymer blend and accordingly the samples are designated as $FRC_1$, $FRC_2$, $FRC_3$, and $FRC_4$ (Table II).

A plain EPDM/PP 50/50 vulcanized blend was also prepared with the same thermal history to compare the results and the sample designated as control sample. In all the flame-retardant formulations, blend composition of EPDM/PP was kept constant at 50:50 as selected on the basis of optimum mechanical properties of the blends containing different proportions prepared in this study by mixing 10, 20, 30, 40, and 50 wt % of isotactic polypropylene (iPP) with EPDM (Tables I and IV).

Blend compositions were prepared by melt-mixing techniques in an internal mixer of a torque Haake Rheocord, RC-90, having sigma type of screws. Following conditions were used for blending: charge weight = 185 g; screw speed = 80 rpm; Bowl temperature = 190°C; total time of blending = 10 min.

The materials were dried in a vacuum oven at 80°C for 24 h. The EPDM and iPP and other formulating ingredients including thermal stabilizer and antioxidant were fed into a mixing bowl of the internal mixer in torque rheometer-90 under load. Melt mixing and blending were done under identical conditions. At the start of the fifth minute of blending cycle, the phenolic curative and accelerator were introduced into the blend and the vulcanization of EPDM was monitored on line until the torque stabilization was obtained. Mixing was continued without interruption for 10 min to obtain the maximum consistency of the total mixture.

The chopped granules were compression molded by using an automatic hydraulic compression-molding machine under maximum pressure of 30 MPa at a temperature of 185–190°C. Molding was done in a frame-type mold (8 in. × 8 in. × 3 mm dimensions) between stainless steel glazing sheets. The compression-molded sheet was conditioned at 23 + 2°C for 24 h and then the sheet was used to prepare the specimens for test and evaluation.

### Flammability test

Limiting oxygen index (LOI), which measures the flammability of a material, was evaluated by using a Stanton Red craft FTA flammability test unit in accordance to ASTM D-2863. Specimens measuring 150 × 6.5 × 3 mm were used in the test. LOI is a numerical measure of polymer flammability and this numerical value was calculated quantitatively as follows:

$$LOI (\%) = 100 \times O_2/O_2 + N_2$$

**TABLE I**
**Composition of EPDM and PP Binary Blends (wt % wise)**

| Sample design | EPDM | IPP | N-Phenyl 2-naphthylamine[a] | Zinc stearate[b] | Stearic acid[a] | Stannous chloride[c] | TNPP[b] | Dimithylol phenolic resin[a] | ZnO[d] |
|---|---|---|---|---|---|---|---|---|---|
| EPDM$_{90}$ PP$_{10}$ | 90 | 10 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 7.5 | 20.0 |
| EPDM$_{80}$ PP$_{20}$ | 80 | 20 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 7.5 | 20.0 |
| EPDM$_{70}$ PP$_{30}$ | 70 | 30 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 7.5 | 20.0 |
| EPDM$_{60}$ PP$_{40}$ | 60 | 40 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 7.5 | 20.0 |
| EPDM$_{50}$ PP$_{50}$ | 50 | 50 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 7.5 | 20.0 |
| EPDM$_{50}$ PP$_{50}$ | 50 | 50 | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | — | — |

[a] Wt % based on EPDM.
[b] Wt % based on PP.
[c] Wt % based on EPDM/PP.
[d] Wt % based on dimethylol phenolic resin.

where $O_2$ is the volume concentration of oxygen, $N_2$ is the volume concentration of nitrogen, and the value of LOI is read directly from the digital meter.

Vertical flammability test was conducted according to UnderWriter's laboratory test 94 (UL-94), which relates to fire safety materials (Table III).

**Smoke generation/density**

Smoke generated during the pyrolysis of the specimen was determined in accordance to ASTM D-2843, applicable to measuring and observing the relative amounts of smoke obscuration produced by burning or decomposition of plastics. Smoke generation was measured in terms of the loss of light transmission through a collected volume of smoke produced on burning a sample under controlled conditions. A 25 × 25 × 6 mm test specimen was used in the test (Table III).

**Physiomechanical properties**

Specific gravity was measured by displacement method in accordance to ASTM D-792. Change in weight of the specimen in liquid media (butyl acetate) was taken. Hardness was measured by a shore hardness durometer (shore D) according to ASTM D-2240. Heat distortion temperature was measured by ASTM D-648 under 4.6 kg/cm$^2$ load and heating rate of 120°C/h. Vicat softening temperature was measured by ASTM D-1525 under 1 kg load and heating rate of 50°C per h. Tensile properties were measured by ASTM D-638 by Instron Universal testing machine model 4302. Specimens were evaluated at a crosshead speed of 5 mm/min up to stress yield and then 50 mm/min until failure. Izod impact resistance-notched was measured by ASTM D 256 by using a CEAST impact tester. Accelerated heat aging of the test specimens was carried out as per BIS 5831. The test specimens were suspended in an electrically heated

**TABLE II**
**Composition of Flame-Retardant EPDM and PP Blend (wt % wise)**

| Sample design | EPDM | (iPP) | Hostaflam 462 | Amgard NL | Melamine | Pentaerythritol | Dicyndiamide | Crystalline wax |
|---|---|---|---|---|---|---|---|---|
| FR.A$_1$ | 50 | 50 | 10 | — | — | — | — | — |
| FR.A$_2$ | 50 | 50 | 20 | — | — | — | — | — |
| FR.A$_3$ | 50 | 50 | 30 | — | — | — | — | — |
| FR.A$_4$ | 50 | 50 | 40 | — | — | — | — | — |
| FR.A$_5$ | 50 | 50 | 45 | — | — | — | — | — |
| FR.B$_1$ | 50 | 50 | — | 10 | — | — | — | — |
| FR.B$_2$ | 50 | 50 | — | 20 | — | — | — | — |
| FR.B$_3$ | 50 | 50 | — | 30 | — | — | — | — |
| FR.B$_4$ | 50 | 50 | — | 40 | — | — | — | — |
| FR.B$_5$ | 50 | 50 | — | 45 | — | — | — | — |
| FR.C$_1$ | 50 | 50 | 27 | — | 9 | 9 | — | — |
| FR.C$_2$ | 50 | 50 | 27 | — | 9 | — | — | 9 |
| FR.C$_3$ | 50 | 50 | 27 | — | — | 9 | 9 | — |
| FR.C$_4$ | 50 | 50 | — | 27 | 9 | 9 | — | — |

[a] Ingredients were taken wt % based on EPDM and PP.
[b] Vulcanizing/processing agents were added wt % wise as above TABLE I.
[c] TiO$_2$ kept constant at wt % 2.5.

## TABLE III
### Effect of Different Concentrations of Flame-Retardant Agents and Their Combination on Flammability and Oxygen Index

| Sample No. | Sample design | LOI | UL-94 rating | Smoke density |
|---|---|---|---|---|
| 1 | $EPDM_{100}$ | 16.4 | $V_2$ | 64.19 |
| 2 | $PP_{100}$ | 17.1 | $V_2$ | — |
| 3 | EPDM/PP | 16.5 | $V_2$ | 51.06 |
| 4 | $FRA_1$ | 18.2 | $V_2$ | 40.06 |
| 5 | $FRA_2$ | 21.6 | $V_2$ | 31.15 |
| 6 | $FRA_3$ | 24.7 | $V_1$ | 25.66 |
| 7 | $FRA_4$ | 28.2 | $V_0$ | 22.33 |
| 8 | $FRA_5$ | 29.8 | $V_0$ | 20.25 |
| 9 | $FRB_1$ | 18.0 | $V_2$ | 41.55 |
| 10 | $FRB_2$ | 21.0 | $V_2$ | 32.32 |
| 11 | $FRB_3$ | 23.5 | $V_1$ | 26.66 |
| 12 | $FRB_4$ | 26.9 | $V_0$ | 22.05 |
| 13 | $FRB_5$ | 28.4 | $V_0$ | 19.85 |
| 14 | $FRC_1$ | 27.6 | $V_0$ | 15.14 |
| 15 | $FRC_2$ | 26.8 | $V_1$ | 18.5 |
| 16 | $FRC_3$ | 27.4 | $V_0$ | 16.0 |
| 17 | $FRC_4$ | 27.0 | $V_0$ | 15.37 |

oven and the temperature of the oven was thermostatically controlled at $125 \pm 1°C$ for 168 h (7 days). The changes in the above-mentioned mechanical properties after aging were evaluated.

## Fluid and temperature resistance properties

Oil resistance was measured by ASTM D-3182. Water resistance was measured by ASTM D-47. Temperature resistance was measured by aging the samples in an air oven at 105°C for 7 days. After every 24 h, samples were taken out, cooled, and weighed. Electrical properties were measured by breakdown voltage and insulation resistance, conducted in accordance to ASTM D-149 and ASTM D-257, respectively (Tables VI–IX).

## RESULTS AND DISCUSSION

Flammability results of the samples in which hostaflam 462 and amgard NL were incorporated indicated that LOI values increased as their concentration in the sample formulations increased. Although both hostaflam 462 and amgard NL reduce flammability of EPDM/PP blend at equal levels of loading, LOI values are higher in the presence of hostaflam 462 (ammoniumpolyphosphate) as compared to amgard NL (ethylenediamine phosphate and silica).

The LOI values of all four intumescent formulations designated $FRC_1$, $FRC_2$, $FRC_3$, and $FRC_4$ were observed higher than the formulations in which hostaflam 462 and amgard NL were used alone at about similar concentrations. In these samples, rate of flame propagation and amount of smoke generated on burning were also observed as minimal compared to other samples designated as FRA and FRB series, including control EPDM/PP blend. On comparison of LOI values at an equal level of loading, maximum value was obtained in formulation containing hostaflam, melamine, and pentaerythritol. Hostaflam also gave a higher value as compared to amgard NL in combination with melamine and pentaerythritol.

Functional mechanism of an intumescent flame-retardant polymer formulation may be suggested as represented in Figures 1 and 2.

A series of processes are occurring during pyrolysis and combustion, including decomposition of ammonium polyphosphate with release of ammonia and water, phosphorylation of the pentaerythritol and thermooxidation of organic polymer, dehydration, decomposition, crosslinking, carbonization, and formation of char structure.

The role of melamine is believed to facilitate the phosphorylation to serve as a blowing agent in the intumescent formulation as a part of the volatiles emitted during pyrolysis, which includes $H_2O$, CO, $CO_2$ $NH_3$, and hydrocarbons all serving to foam the char. On comparing the effectiveness of melamine and dicyandiamide at equal loading, a higher value of LOI was obtained in the presence of melamine.

On examining the effectiveness of pentaerythritol and crystalline wax as carbonific agents, it was found that pentaerythritol gave a higher LOI value as compared to crystalline wax at the equal loading of both

## TABLE IV
### Physiomechanical Properties of Vulcanized and Unvulcanized EPDM/PP Blends

| Blend system | Sample designation | Wt % EPDM rubber | Wt % PP plastic | Hardness shore D | Tensile stress at yield (MPa) | Tensile stress at break (MPa) | Elongation at break (%) | Specific gravity (gm/cm$^3$) | HDT at actual load (°C) |
|---|---|---|---|---|---|---|---|---|---|
| Vulcanized blends | $EPDM_{90} PP_{10}$ | 90 | 10 | — | 9.6 | 9.0 | 180 | 0.876 | — |
| | $EPDM_{80} PP_{20}$ | 80 | 20 | — | 10.3 | 9.5 | 250 | 0.881 | — |
| | $EPDM_{70} PP_{30}$ | 70 | 30 | 44 | 12.4 | 11.3 | 310 | 0.884 | 46 |
| | $EPDM_{60} PP_{40}$ | 60 | 40 | 48 | 14.9 | 14.0 | 340 | 0.887 | 58 |
| | $EPDM_{50} PP_{50}$ | 50 | 50 | 52 | 16.5 | 15.4 | 390 | 0.891 | 62 |
| Unvulcanized | $EPDM_{50} PP_{50}$ | 50 | 50 | 52 | 15.4 | 14.6 | 350 | 0.889 | 60 |

**TABLE V**
**Physiomechanical Properties of Different Flame-Retardant EPDM/PP Blends**

| Sample design | Hardness shore D | | Tensile stress at yield (MPa) | | Tensile stress at break (MPa) | | Elongation at break (%) | | HDT at actual load (°C) | | Vicat softening temp. (°C) | | Izod impact notched Type A (J/m) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unaged | Aged | Unaged | Aged | Unaged | Aged | Unaged | Aged | Unaged | Aged | Unaged | Aged | Unaged | Aged |
| EPDM/PP | 52 | 54 | 16.5 | 17.2 | 15.4 | 17.0 | 350 | 320 | 62 | 70 | — | — | 210 | 190 |
| $FRA_1$ | 54 | 56 | 16.1 | 18.4 | 15.4 | 17.5 | 330 | 300 | 65 | 75 | 104.5 | 110.0 | 200 | 180 |
| $FRA_2$ | 54 | 56 | 15.5 | 17.5 | 14.0 | 16.8 | 320 | 280 | 65 | 76 | 104.7 | 111.5 | 180 | 155 |
| $FRA_3$ | 55 | 57 | 13.9 | 16.7 | 12.5 | 16.0 | 300 | 280 | 66 | 80 | 105.0 | 115.0 | 150 | 125 |
| $FRA_4$ | 56 | 57 | 12.2 | 16.0 | 10.2 | 15.3 | 290 | 260 | 66 | 82 | 105.0 | 115.0 | 130 | 118 |
| $FRA_5$ | 58 | 60 | 12.0 | 15.0 | 10.5 | 14.1 | 260 | 250 | 68 | 85 | 107.0 | 118.0 | 120 | 102 |
| $FRB_1$ | 54 | 56 | 16.0 | 18.1 | 14.5 | 17.0 | 320 | 300 | 65 | 80 | 105.0 | 114.0 | 200 | 180 |
| $FRB_2$ | 55 | 58 | 15.4 | 17.0 | 13.0 | 15.9 | 320 | 290 | 66 | 81 | 105.0 | 115.0 | 185 | 150 |
| $FRB_3$ | 55 | 58 | 13.0 | 17.0 | 11.5 | 16.0 | 300 | 270 | 66 | 83 | 106.0 | 115.0 | 150 | 115 |
| $FRB_4$ | 56 | 60 | 13.0 | 15.8 | 11.5 | 14.5 | 280 | 260 | 66 | 86 | 106.5 | 117.0 | 125 | 100 |
| $FRB_5$ | 58 | 60 | 12.5 | 15.0 | 10.0 | 14.0 | 250 | 240 | 68 | 83 | 106.5 | 117.0 | 113 | 90 |
| $FRC_1$ | 55 | 56 | 12.5 | 14.5 | 10.2 | 13.6 | 280 | 240 | 67 | 81 | 104.0 | 113.0 | 140 | 108 |
| $FRC_2$ | 55 | 56 | 12.3 | 14.0 | 10.2 | 13.2 | 300 | 260 | 66 | 80 | 103.0 | 112.0 | 135 | 105 |
| $FRC_3$ | 55 | 56 | 12.0 | 14.5 | 10.0 | 13.4 | 290 | 250 | 66 | 81 | 103.0 | 113.0 | 140 | 100 |
| $FRC_4$ | 55 | 58 | 12.0 | 14.5 | 10.0 | 13.5 | 290 | 250 | 66 | 81 | 104.0 | 113.0 | 130 | 100 |

the compounds. Pentaerythritol, $C (CH_2OH)_4$, has four primary hydroxl groups which are all esterifiable with catalyst $(NH_4PO_3)_n$, resulting in a good amount of char that protects the solid surface of the polymer against oxidation.

Intumescent formulations gave a $V_0$ rating, which indicated that in the presence of melamine/dicyandiamide affects the mechanism of flame propogation. Both act as spumific agents by evolution of noncombustible gases such as $NH_3$, HCN, etc., which diluted the oxygen supply in the event of flaming of polymer resulting in extinguishing the flame at an early stage. Both hostaflam and amgard showed a $V_0$ rating at a loading of 27.0 wt % with a combination of carbonific and spumific agent, whereas they each give a $V_0$ rating at 40–45 wt % loading when used alone. Formulations in which intumescent agents were used showed better intumescent property and slow rate of flame propagation compared to other formulations as visualized during vertical flammability testing. After glow, an expected source of back burn is also observed as almost nil.

Smoke density is very important in any kind of flaming because more deaths are caused by smoke rather than by burns. Visibility becomes poor due to smoke; hence, the victim may not be able to escape in the event of fire. The results have shown that smoke density decreases with increasing concentration of hostaflam 462 as well as amgard NL in the EPDM/PP blend.

In the intumescent formulations designated $FRC_1$, $FRC_2$, $FRC_3$, and $FRC_4$, wherein hostaflam/amgard was incorporated with a combination of spumific and carbonific agents, smoke density is reduced between 63.8 and 70.3% as compared to EPDM/PP control

blend. This could be explained as nitrogen-containing noncombustible gases produced by the decomposition of ammonium polyphosphate/ethylenediamine phosphate and melamine/dicyandiamide. Nitrogen-containing gases are reported as a smoke suppressant. It is believed that they can also act chemically and physically in the gas phase. The physical effect takes place mainly by shielding the polymer substrate with heavy nitrogen-containing gases against thermal attack. They also dilute the smoke gases and reduce the smoke density. Chemically, in the gas phase, it eliminates either soot precursors or the soot itself. Removal of soot precursors may occur by oxidation of the aromatic species.

In all the intumescent formulations, it is also found that, when these samples are exposed to flame only, a very little amount of smoke is released in the early stage of flaming and the smoke density remains low for a long time, whereas dense black smoke is produced very rapidly with the usual EPDM/PP blend. Valuable time for escape or rescue is thus gained in the event of fire; this is an important advantage of intumescent-type flame-retardant additives. This would be due to their mode of action (i.e., formation of a protective charred layer over the surface of the substrate).

The results of the specific gravities of different EPDM/PP blends and their variation with blend composition have shown gradual and marginal increase in specific gravity with increasing PP contents in EPDM. At 50% concentration of PP, it increased from 0.87 to 0.891 $gm/cm^3$. The increase in specific gravity with increasing content of rigid PP is quite expected as the specific gravity of pure PP (0.905 $gm/cm^3$) is greater than plain EPDM (0.87 $gm/cm^3$). Changes in specific

**TABLE VI**
**Percentage Weight and Thickness Change of Different Samples After Immersion in Oil at Different Time Intervals**

| Sample design | Weight change at different time intervals (%) | | | | Change in thickness (%) after 24 h |
|---|---|---|---|---|---|
| | 4 h | 8 h | 12 h | 24 h | |
| $EPDM_{100}$ | 20.25 | 35.50 | 45.35 | 60.50 | 35.6 |
| $PP_{100}$ | 00.05 | 00.09 | 00.10 | 00.35 | — |
| EPDM/PP | 12.30 | 18.22 | 25.75 | 35.10 | 24.5 |
| $FRA_1$ | 10.37 | 15.50 | 18.20 | 29.92 | 15.2 |
| $FRA_2$ | 10.50 | 14.20 | 20.10 | 35.35 | 17.5 |
| $FRA_3$ | 11.25 | 15.70 | 21.80 | 40.60 | 18.9 |
| $FRA_4$ | 11.75 | 16.20 | 22.60 | 45.80 | 20.1 |
| $FRA_5$ | 12.50 | 16.60 | 23.00 | 48.50 | 22.3 |
| $FRB_1$ | 11.50 | 16.30 | 24.10 | 52.30 | 22.6 |
| $FRB_2$ | 11.70 | 16.00 | 23.20 | 43.70 | 20.0 |
| $FRB_3$ | 10.50 | 15.20 | 21.75 | 39.80 | 18.8 |
| $FRB_4$ | 10.20 | 14.60 | 20.10 | 33.60 | 17.6 |
| $FRB_5$ | 09.40 | 14.00 | 19.70 | 29.90 | 15.4 |
| $FRC_1$ | 11.30 | 15.10 | 21.60 | 33.80 | 16.6 |
| $FRC_2$ | 10.35 | 15.25 | 20.10 | 32.50 | 16.1 |
| $FRC_3$ | 10.10 | 14.50 | 19.80 | 30.10 | 15.7 |
| $FRC_4$ | 11.65 | 14.80 | 19.60 | 33.70 | 16.3 |

gravity on blending of PP with EPDM may be due to the changes in crystallinity by the combined effect of EPDM/PP.

Hardness shore D values increase with increasing PP content in the blend. The hardness values are also increased on increasing the percentage loading of flame-retardant additives in polymer.

Tensile properties were characterized by measuring stress at break, yield stress, and corresponding elongation as a function of blend composition. Breakage usually occurred at low elongation just above the yield point where stress began to decrease. Yield stress usu-

**TABLE VII**
**% Weight-Change of Different Samples After Treatment in Boiling Water at Different Time Intervals**

| Sample design | Weight change at different time intervals (%) | | | |
|---|---|---|---|---|
| | 4 h | 8 h | 12 h | 24 h |
| $EPDM_{100}$ | 0.00 | 0.00 | 0.00 | 0.98 |
| $PP_{100}$ | 0.00 | 0.00 | 0.00 | 0.77 |
| EPDM/PP | 0.55 | 0.90 | 0.90 | 2.55 |
| $FRA_1$ | 0.95 | 0.95 | 1.19 | 1.75 |
| $FRA_2$ | 0.90 | 0.95 | 1.25 | 1.90 |
| $FRA_3$ | 0.95 | 0.93 | 1.35 | 2.00 |
| $FRA_4$ | 1.15 | 1.20 | 1.50 | 2.18 |
| $FRA_5$ | 1.10 | 1.25 | 1.60 | 2.25 |
| $FRB_1$ | 0.85 | 0.95 | 1.00 | 1.90 |
| $FRB_2$ | 0.97 | 1.05 | 1.10 | 2.25 |
| $FRB_3$ | 1.17 | 1.10 | 1.10 | 2.28 |
| $FRB_4$ | 1.30 | 1.38 | 1.30 | 2.35 |
| $FRB_5$ | 1.32 | 1.30 | 1.30 | 2.42 |
| $FRC_1$ | 1.10 | 1.18 | 1.32 | 1.60 |
| $FRC_2$ | 0.90 | 0.90 | 1.05 | 1.84 |
| $FRC_3$ | 0.90 | 0.90 | 1.15 | 1.95 |
| $FRC_4$ | 1.10 | 1.15 | 1.25 | 2.15 |

ally occurred higher than stress at break. Blending the different percentages of PP in EPDM, tensile properties of the blends are significantly affected and increases over the entire studied range of blend composition. However, after incorporation of flame-retardant additives/fillers, the tensile properties of all the formulations are reduced as increasing the percentage of their loading. At 45 wt % loading of hostaflam in EPDM/PP blend, the percentage of elongation is obtained 260 at 12 MPa tensile yield stress, and in the case of amgard, it was obtained 250 at 12.5 MPa yield stress. However, in all the intumescent formulation, percentage of elongation was obtained in optimum range between 280 and 300 at equal concentration.

Heat distortion temperature is increased as increasing the PP content in the EPDM. In all the EPDM/PP flame-retardant formulations, heat distortion temperature is also increased with increasing the amount of flame-retardant additives. It is expected that the inclusion of PP in EPDM rubber resulted in an increase in stiffness, thereby increasing the HDT values. The same view is expected when flame-retardant additives are incorporated in the combined EPDM/PP blend.

Vicat softening temperature of all the blend compositions increased in the same gradual fashion and this increasing effect is attributed to the expected factors.

The variation in results of Izod impact strength, independent of the specimen thickness, is decreased with increasing the flame-retardant additives/filler concentration in the blends. The energy absorbed during impact is dissipated by yielding, crazing, creation of new crack surface, and the kinetic energy of the broken specimen. It is expected that on addition of flame-retardant additives in the EPDM/PP blend,

**TABLE VIII**
**Percentage Weight Loss of Different Samples at Different Time Intervals After Heating in Oven for 7 Days**

| Sample designation | % Weight change at different time interval (days) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| EPDM/PP | 0.26 | 0.28 | 0.31 | 0.31 | 0.33 | 0.33 | 0.32 |
| FRA$_1$ | 0.64 | 0.83 | 0.89 | 0.92 | 0.93 | 0.93 | 0.93 |
| FRA$_2$ | 0.63 | 0.83 | 0.87 | 0.91 | 0.92 | 0.95 | 0.95 |
| FRA$_3$ | 0.60 | 0.77 | 0.82 | 0.86 | 0.86 | 0.91 | 0.91 |
| FRA$_4$ | 0.57 | 0.73 | 0.77 | 0.81 | 0.83 | 0.88 | 0.88 |
| FRA$_5$ | 0.55 | 0.68 | 0.76 | 0.80 | 0.82 | 0.86 | 0.86 |
| FRB$_1$ | 0.59 | 0.75 | 0.80 | 0.85 | 0.91 | 0.92 | 0.93 |
| FRB$_2$ | 0.58 | 0.76 | 0.80 | 0.87 | 0.91 | 0.92 | 0.92 |
| FRB$_3$ | 0.55 | 0.77 | 0.80 | 0.85 | 0.91 | 0.92 | 0.92 |
| FRB$_4$ | 0.53 | 0.76 | 0.78 | 0.85 | 0.91 | 0.91 | 0.92 |
| FRB$_5$ | 0.43 | 0.50 | 0.62 | 0.69 | 0.81 | 0.90 | 0.90 |
| FRC$_1$ | 0.81 | 0.90 | 0.92 | 0.94 | 0.96 | 0.96 | 0.97 |
| FRC$_2$ | 0.80 | 0.91 | 0.93 | 0.94 | 0.95 | 0.95 | 0.98 |
| FRC$_3$ | 0.82 | 0.91 | 0.94 | 0.96 | 0.98 | 0.98 | 0.99 |
| FRC$_4$ | 0.81 | 0.90 | 0.93 | 0.93 | 0.94 | 0.94 | 0.98 |

brittleness increases as increasing the additives concentration. At 45 % wt loading of hostaflam and amgard, the values were obtained at 120 and 113 J/m, respectively, as compared to the control EPDM/PP blend of 210 J/m.

From the study of physiomechanical properties, it is revealed that in all the flame-retardant formulations, heat distortion temperature, vicat softening temperature, and hardness are increased as increased the concentration of flame-retardant additives in the binary blend of EPDM/PP. The same trend was obtained when the above properties after thermal aging of the test specimen were determined. It may be due to the finding that on thermal aging both PP and EPDR undergo thermooxidative degradation. The degradation process can cause both chain session and crosslinking. In the PP, the tertiary hydrogen atoms present are most labile and mainly responsible for thermooxidative attack. In EPDR, the presence of double bonds is mainly responsible for thermooxidative attack. However, aging impact rigidity in the system and the aged samples show higher hardness, heat distortion, and vicat softening values than unaged samples.

On comparing the property profile of unvulcanized and vulcanized EPDM/PP blend composition (Table IV) as determined in the study, it was found that all the physiomechanical properties are enhanced on vulcanization. This is due to the fact that unvulcanized EPDR is not strong, does not maintain its shape after

**TABLE IX**
**Breakdown Voltage and Insulation Resistance of Different Samples**

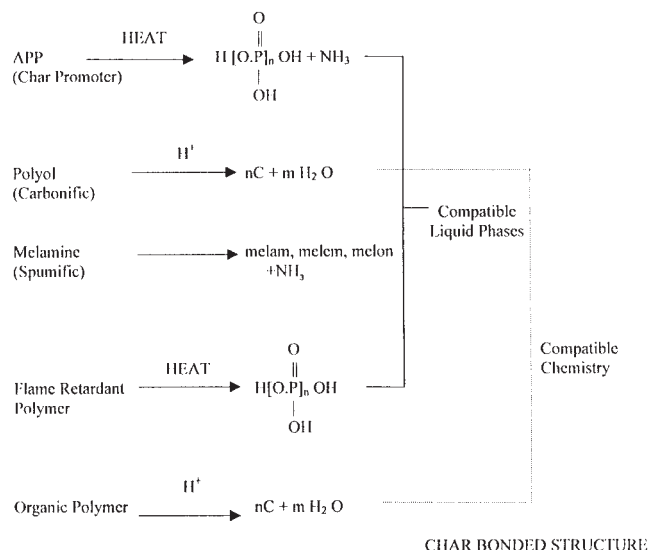| Sample designation | Breakdown voltage (kV) | Insulation resistance (Ohms) |
|---|---|---|
| EPDM/PP | 24.0 | $3.0 \times 10^{12}$ |
| FRA$_1$ | 28.0 | $3.5 \times 10^{12}$ |
| FRA$_2$ | 30.0 | $4.0 \times 10^{12}$ |
| FRA$_3$ | 33.0 | $4.2 \times 10^{12}$ |
| FRA$_4$ | 35.0 | $4.5 \times 10^{12}$ |
| FRA$_5$ | 38.0 | $4.8 \times 10^{12}$ |
| FRB$_1$ | 28.0 | $3.6 \times 10^{12}$ |
| FRB$_2$ | 30.0 | $3.6 \times 10^{12}$ |
| FRB$_3$ | 30.0 | $3.4 \times 10^{12}$ |
| FRB$_4$ | 28.0 | $3.2 \times 10^{12}$ |
| FRB$_5$ | 25.0 | $3.2 \times 10^{12}$ |
| FRC$_1$ | 30.0 | $3.8 \times 10^{12}$ |
| FRC$_2$ | 30.0 | $3.5 \times 10^{12}$ |
| FRC$_3$ | 30.0 | $3.5 \times 10^{12}$ |
| FRC$_4$ | 28.0 | $3.5 \times 10^{12}$ |



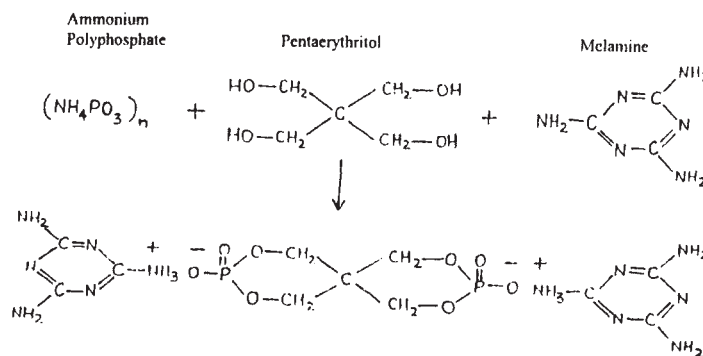**Figure 1** Schematic chemistry of organic polymer intumescent char-forming interaction.

**Figure 2** Chemical reaction mechanism of intumescent flame-retardant agents.

a large deformation, and can be very tacky. In the EPDM/PP blend, the rubber phase is vulcanized dynamically during online melt mixing to give particulate vulcanized rubber phase morphology. The vulcanized rubber particles remain stable during melt processing of the blends, resulting in improvement in compatibility of the combined EPDM/PP polymer blend. During dynamic vulcanization, the EDPM and PP have to undergo a phase inversion to maintain the thermoplasticity of the blend and during this process the rubber phase is vulcanized to give a fine particulate vulcanized rubber phase of stable domain morphology resulting in improvement in all the physiomechanical properties.

Formulations containing hostaflam additive show a positive trend in breakdown voltage as well as in insulative resistance, whereas amgard additive shows a negative trend. It is clear from the results that increasing the amount of hostaflam increases both the breakdown voltage and the insulative resistance values.

Both the FRA and the FRB series of sample formulation, which contain hostaflam 462 and amgard NL, respectively, showed higher oil absorption as compared to plain EPDM/PP blend, while this is lower than pure EPDM. All intumescent-based formulations showed low oil absorption than control EPDM/PP blend. In hostaflam sample formulations, oil absorption increases with increasing additive concentration, while it decreases in amgard formulation as a result of increasing additive concentration. The same trend was also obtained in change of thickness.

All the sample formulations showed low water absorption as compared to EPDM/PP control blend. Formulation with amgard showed higher weight as compared to hostaflam at equal levels of additive loading. Minimum increase in weight is observed in formulation $FRC_1$ among all the samples. It is concluded that all the samples showed $2.0 \pm 0.4\%$ increase in weight after 24 h.

On evaluating the resistance to temperature, $0.94 \pm 0.05\%$ weight loss was observed after oven aging at $105°C$ for 168 h (7 days) in all the sample formulations.

## CONCLUSION

The objective of development of flame-retardant polymers is to increase the resistance of polymers to ignition and to reduce flame propogation/speed with minimum degradation of properties. The use of flame-retardant polymers is to minimize the fire risk associated with their use in a specific application and may prevent a small fire that could become a major catastrophe.

Halogen-free intumescent flame-retardant polymer containing EPDM/PP blend to which additives based on phosphorous [i.e., ammonium polyphosphate (hostaflam 462) and ethylenediamine phosphate (amgard NL)] were mixed in different proportions and in combination with pentaerythritol/crystalline wax as char forming and melamine/dicyandiamide as blowing agent and were studied to improve flame-retardancy of EPDM/PP blend. Studies have revealed that intumescent polymer blend systems offered good flame-retardancy with optimum comparable physiomechanical, electrical, and fluid-resistance properties including low emission of smoke on burning, an additional advantage of intumescent flame-retardant additives. Low generation of smoke does not affect the visibility for a longer time, thus, valuable time for escape or rescue is gained in the event of fire. Phosphorous compounds promote char formation in the polymer. Polymer blend systems filled with intumescent components exhibit more pronounced charring and intumescence effect when the blend systems. come in contact with heat and flame, resulting in flame-retardancy of the polymer. More char-producing mechanism and intumescence phenomenon are effective ways of protecting the combustible material from heat and flame. Both melamine and diacynadiamide as blowing agent and pentaerythritol and crystalline wax as carbonific agents are considered satisfactory in intumescent formulation. However, melamine/pentaerythritol represents better flame retardancy; this was also supported by the evidence of thermal analysis and char morphology studies. It is also revealed from the present study that the

vulcanization process improved the mechanical properties of the EPDM/PP blend and the flame-retardant additives employed in the study accelerate the crosslinking process in this thermoplastic elastomer blend. It is concluded in this study that an intumescent technology is a viable halogen-free flame-retardant approach for development of flame-retardant polymeric materials with balanced mechanical properties and low emission of smoke and toxicants.

## References

1. Rader, C. P. Modern Plastics; Greene, R., Ed., New York, 1992.
2. Thomas, D. A., Sperling, L. H. Polymer Blends; Newman, S., Paul, D. R., Eds.; Academic Press: New York, 1978; Vol. 2.
3. Haiqing, Hu; Hongge, Guo; EPDM/PP Blending Thermoelastomer CA:130:154792; Qingdao Institute of Chemical Technology: Qingdao shandong 266042, Republic of China 1999.
4. Ishikawa, M., Sugimoto, M., Inoune, T. J Appl Poly Sci 1996, 62, 1495.
5. Rader, C. P.; Abdou-Sabet, S. Two-Phase Elastomeric Alloys (EPDM-Polypropylene blends); Montesano Chemical Co., Akron, OH, 1998.
6. Morton Brown, A. Schulman. IEEE Elect Insul January/February, 1994.
7. Landrock, H. Handbook of Plastics Flammability and Combustion toxicology; Noyes Publications: Park Ridge, NJ, 1983.
8. Aseeva, R. M., Jaikov, G. E. Combustion of Polymer Materials; Hanser Publishers: Munich Vienna/New York, 1985.
9. Fire, F. L. Combustability of Plastics—Flame Retardant and Flame Retarded Plastics; Van Nostrand Reinhold Publication: New York, 1991.
10. Vandersall, H. L. J Fire Flammability 1971, 2,97.
11. Mortin Rieber, H. W. Sehiffer, International Plastics Flammability Handbook; Hanser Publishers: New York; 1983.
12. Green, J. J Fire Sci. 1996, 14, (5), 353.
13. Huggard M.T. Plas Eng November 1993, 29–31.
14. Ballisteri, A.; Montaudo, G.; Puglisi, C.; Scamporino, E.; Vitallini, D. J Appl Poly Sci 1983, 28, 1743.
15. Camino, G., Costa, L. Fire Retardant Polymers Rev Inorg Chem 1986, 8, 69–100.
16. Davis, J., Huggard, M. The Technology of Halogen Free Flame Retardant Additives for Polymer System; The Sixth Annual BCC Conference on Flame Retardancy, May 24, 1995, Stamford, CT; Business Communication Co. Inc.: Norwalk, CT.
17. Bugajny, M., Michel Le Bras and Serge Bourbigot Fire Mater 23, 49–51 (1999).
18. Hem Lewin: J. Fire Sci, 17, Jan./Feb. 1999.