

Flame Retardation of Polypropylene: Effect of Organoantimony Compounds on the Flammability and Thermal Behavior

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Synopsis

Triphenylstibinedibromide and its derivatives with tribromo-, trichloro-, and pentachlorophenols have been used as flame-retardant additives for polypropylene. Maximum limiting oxygen index of 31.5 against 18.2 for unfilled polypropylene was obtained in a sample containing 10 phr of triphenylstibinedibromide. However, V-0 rating in UL-94 test was observed in 20 phr flame-retardant-filled polypropylene sample, while V-2 rating was obtained even at 5 phr flame-retardant level. Thermal behavior of flame-retardant-filled polypropylene was also studied in air atmosphere by thermogravimetric analysis, and an attempt has been made to correlate the flammability with the thermal behavior. The residue obtained in isothermal treatment at 450°C for ½ hour in air was analyzed for antimony and halogen which establishes the role of these flame retardants in vapor phase.

INTRODUCTION

In the last decade a large number of flame-retardant additives based on phosphorus and antimony compounds have been developed for polypropylene.¹ In phosphorus compounds, both inorganic and organic phosphorus compounds have been used and the studies show that organophosphorus compounds containing halogen are more effective compared to other phosphorus compounds. Among the antimony compounds, the most favored is Sb_2O_3 , which has been used along with some halogen-containing compounds, such as chlorinated hydrocarbons,²⁻⁶ octaphenylene dioxide, dimers of hexachlorocyclopentadiene,⁶ hexa- and tetrachlorophthalimides,⁷ tetrabromobisphenol A-bis(dibromopropyl ether) and decabromodiphenyl ether,⁸ and Diel's-Alder adduct of chlorinated cyclopentadiene with polyunsaturated cycloaliphatic compounds along with decabromodiphenyl ether.⁹

The main disadvantages of such Sb-halogen systems are: (i) Higher loading of flame retardant to impart an optimal level of flame retardancy, resulting in adverse effects upon mechanical properties. (ii) Sb_2O_3 is a high melting solid and thus cannot be mixed homogeneously in the base polymer, hence, poor flame-retardant and mechanical properties.¹⁰

Keeping in mind the above problems, it was considered of interest to develop some new low melting halogenated antimony compounds as flame retardants for polypropylene.

Organoantimony compounds generally have a low melting point as compared to inorganic Sb compounds. So far, no organoantimony compound has

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been reported as a flame retardant for polypropylene. However, in the patent literature,¹¹⁻¹⁴ the use of some organoantimony compounds (e.g., triphenylstibine, triphenylstibinedichloride, etc.) as flame retardants for polyesters, polyethylene, and epoxy resins has been revealed.

The present paper deals with the application of halogenated organoantimony compounds as flame retardants for polypropylene.

Polypropylene was melt-blended with 5–20 phr of organoantimony compounds, viz., triphenylstibinedibromide and its derivatives of tribromo-, trichloro-, and pentachlorophenol. The flammability and thermal behavior of flame-retardant-filled polypropylene was studied.

EXPERIMENTAL

Materials

Polypropylene "Koylene M3030" was obtained from Indian Petrochemicals Ltd., Baroda, India. Triphenylstibinedibromide (Ph_3SbBr_2) was prepared by the reported method¹⁵ and its derivatives with tribromo-, trichloro-, and pentachlorophenols [$\text{Ph}_3\text{Sb}(\text{tbp})_2$, $\text{Ph}_3\text{Sb}(\text{tcp})_2$, and $\text{Ph}_3\text{Sb}(\text{pcp})_2$, respectively], were prepared by reacting Ph_3SbBr_2 and the respective phenols in 1:2 molar ratio in the presence of triethylamine, a deprotonating agent, using benzene as a solvent. The detailed method of the syntheses has been reported earlier.¹⁶

Sample Preparation

The different compositions were prepared by dry blending and were then extruded through a single screw extruder Betol BM1820 at a screw speed of 40 rpm, keeping the temperature profiles 200° (first zone); 210° (second zone); 200° (third zone); and 200°C (die zone) and L/D of die, 20.

The extrudates were then chopped in a granulator and dried overnight in a vacuum oven at 80° C. Samples of the size 16.1 × 1.1 × 0.6 cm for various tests, were prepared by using a Windsor injection moulding machine keeping the machine settings as follows: Rear zone, 200°; front zone, 210°; nozzle, 80°; and mold, 27°C; injection speed, 4–5 cm/s; cycle time, 60 s; and injection pressure, 80 kg/cm².

Evaluation of Samples

Limiting oxygen index (LOI) was determined on a Stanton Redcroft FTA flammability unit as per the ASTM D-2863.

In vertical flame test, the samples were exposed vertically to a small Bunsen Burner flame for 10 s and then evaluated as per the UL-94 specification.

In smoke-density measurements, the samples were ignited in the flammability test equipment for 20 s at an oxygen index 1% higher than that of the LOI of the respective sample and left to burn for 3 min.¹⁷ Smoke was allowed to enter a smoke-density chamber and the % obscuration was directly noted from the recorder.

Thermogravimetric analysis of the filled polypropylene was carried out in air (25 mL/min) on a Stanton Redcroft TG-750 thermobalance at a heating

rate of 10°C/min. The activation energy (E^*) of thermal decomposition was calculated by using Coats and Redfern equation¹⁸ by plotting

$$\log[1 - (1 - \alpha)^{1-n}]/T^2(1 - n) = A \text{ versus } \frac{1}{T} \times 10^3$$

when $n \neq 1$, if $n = 1$ then $A = -\log[-\log(1 - \alpha)]/T^2$, where α is the function decomposed at a temperature T and n is the order of reaction. For a number of assumed values of n a number of such relationships are plotted by using the computational approach and the correct value of n for a given thermal decomposition reaction gives a best fit straight line. The E^* is then calculated from the equation

$$E^* = 2.303 mR$$

where m is the slope of the straight line and R is the gas constant.

RESULTS AND DISCUSSION

Flammability

Incorporation of organoantimony compounds even at low additive level, increased the LOI of filled polypropylene to a considerable extent (Table I), compared to conventional Sb_2O_3 /halogen and phosphorus-based flame-retardant formulations. The addition of 10 phr of $\text{Ph}_3\text{SbBr}_2(\text{P}_{12})$ only, raised the LOI of polypropylene to 31.5 from 18.2, whereas in other conventional flame-retardant systems the LOI of 26 to 28 is reported at a loading of 25–26% for Sb_2O_3 /halogen systems,^{19–21} and the LOI of 28–29.5 for phosphorus-based flame retardants at a concentration of 25–30%.^{22–25} The response of LOI to flame retardants' concentration shows (Fig. 1) that initially there is an increase in LOI which levels off at higher flame-retardant loading; there is even a slight decrease in the LOI of Ph_3SbBr_2 -filled polypropylene at higher concentration (15–20 phr).

In UL-94 flame test, a V-2 rating was observed at only 5 phr additive level in all formulations, whereas for V-0 rating a loading of 20 phr of these compounds was required. This indicates the superior performance of these organoantimony compounds at low additive levels compared to the conventional flame-retardant systems, where a loading of 35–40% is required for Sb_2O_3 /halogen²⁶ and 12.5–30% for phosphorus-based flame retardants (e.g., phosphine oxides, phosphonium halides, and ammonium polyphosphate^{25,27}) for obtaining V-0 rating.

Apparently, there seems to be no correlation between LOI and UL-94 test. Although in the Ph_3SbBr_2 -filled polypropylene series the sample P_{12} has higher LOI compared to the sample P_{14} , it has a V-2 rating compared to the latter which has V-0 rating in the UL-94 test. The other flame-retardant-filled polypropylene samples P_{24} , P_{34} , and P_{44} have V-0 rating at LOI values 30.4, 26.8, and 22.2, respectively, which is less than that of P_{12} (LOI 31.5).

Results of the UL-94 test appear to be independent of the type of flame retardant, whereas a comparison of the effect of the nature or type of flame

TABLE I
Flame Retardance of Organoantimony Compounds-Filled Polypropylene

Additive (phr)	Sample code	Elemental analysis of sample		LOI	UL-94	Smoke density %
		Sb %	Cl/Br %			
1 —	P ₁	—	—	18.2	Failed	2
2 Ph ₃ SbBr ₂	5	1.13	1.49	25.9	V-2	10
	10	2.16	2.84	31.5	V-2	26
	15	3.10	4.07	31.2	V-2	32
	20	3.96	5.20	30.3	V-0	46
3 Ph ₃ Sb(tbp) ₂	5	0.57	2.26	23.8	V-2	22
	10	1.09	4.30	25.9	V-2	42
	15	1.57	6.18	29.6	V-2	52
	20	2.00	7.89	30.4	V-0	62
4 Ph ₃ Sb(tcp) ₂	5	0.79	1.36	23.0	V-2	20
	10	1.49	2.59	24.1	V-2	44
	15	2.13	3.72	25.3	V-2	56
	20	2.73	4.76	26.8	V-0	62
5 Ph ₃ Sb(pcp) ₂	5	0.65	1.91	23.0	V-2	26
	10	1.25	3.65	24.8	V-2	52
	15	1.80	5.24	25.8	V-2	62
	20	2.30	6.64	27.2	V-0	74

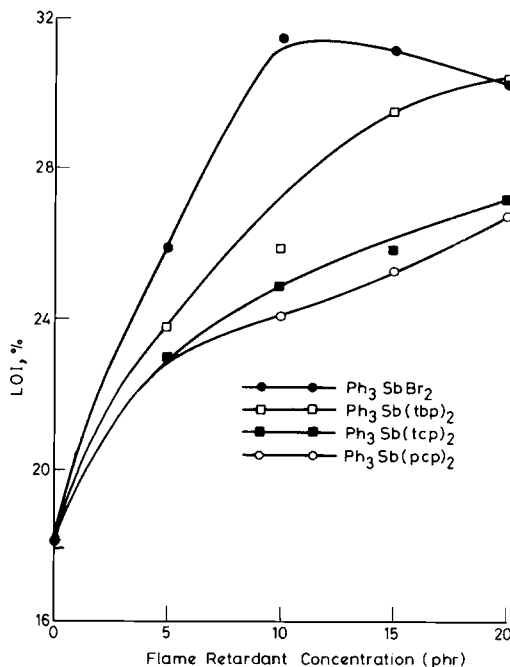


Fig. 1. LOI response to flame-retardant concentration (phr).

retardant on LOI reveals that: (a) a flame retardant having halogen attached directly to Sb is more effective than one attached to a phenyl ring (Ph_3SbBr_2 versus $\text{Ph}_3\text{Sb}(\text{tbp})_2$). (b) $\text{Ph}_3\text{Sb}(\text{tbp})_2$ is found to be more effective than $\text{Ph}_3\text{Sb}(\text{tcp})_2$, the chloro derivative.

The smoke density of the filled sample is higher than the unfilled sample, which increases further with increased flame-retardant concentration. The increase in the amount of smoke might be due to the formation of aromatic hydrocarbons during the decomposition of flame retardants.

THERMAL DECOMPOSITION STUDIES

Thermal behavior of organoantimony compound-filled polypropylene was studied by thermogravimetric balance in air atmosphere, and the results are presented in Table II.

The addition of these compounds in polypropylene shifts the onset of degradation to higher temperature. There is an increase in the temperature of extrapolated beginning of major weight loss (T_i) by 22 to 43°C, depending upon the type of flame retardant and its concentration (Table II). The maximum increase in the initial degradation temperature was observed in polypropylene compositions containing Ph_3SbBr_2 and $\text{Ph}_3\text{Sb}(\text{tbp})_2$, namely for P_{11} and P_{14} , the T_i was 327 and 318°C, and for P_{21} and P_{24} , T_i was 326 and 313°C, respectively.

Interestingly, the neat Ph_3SbBr_2 compound completely degraded in the temperature range of 235–265°C, which is even earlier than the T_i of unfilled polypropylene (264°C). However, in $\text{Ph}_3\text{Sb}(\text{tbp})_2$, $\text{Ph}_3\text{Sb}(\text{tcp})_2$, and

TABLE II
Thermal Behavior of Organoantimony Compounds-Filled Polypropylene in Air

Sample	Major weight ^a loss region		T_f , °C	D'_{max} , °C	Rate of maximum weight loss % min ⁻¹	Weight loss at		E^* kcal/mol	Residue (°C)
	T_i , °C	T_f , °C				300°C	400°C		
P ₁	264	387		339	8.8	30.0	96.5	14.5	0(467)
P ₁₁	327	405		384	15.5	12.0	89.0	16.2	0(431)
P ₁₄	318	407		384	15.5	10.5	84.5	14.1	0(429)
P ₂₁	326	406		384	17.1	10.0	92.0	17.8	2.5(457)
P ₂₄	313	408		375	12.5	15.5	86.5	14.1	4.5(485)
P ₃₁	318	401		384	16.8	13.0	89.5	16.2	2.0(490)
P ₃₄	306	397		375	11.5	18.5	83.5	15.1	5.0(513)
P ₄₁	309	410		384	10.5	16.0	85.5	14.3	0(494)
P ₄₄	306	419		384	9.5	18.5	81.0	11.5	7.5(540)

^a T_i , Temperature of extrapolated beginning of major weight loss region, T_f , Temperature of extrapolated end of major weight loss region.

$\text{Ph}_3\text{Sb}(\text{pcp})_2$ the degradation temperature range matches well with that of unfilled polypropylene.

The increased T_i of the filled system, compared to that of unfilled polypropylene or of the additive indicates that the mode of decomposition changes in the flame-retardant polypropylene.

The filled polypropylene continues undergoing a slow but uninterrupted thermal decomposition up to 420°C, with a retarded rate of decomposition as evident by the higher amount of residue left at 300 and 400°C in the flame-retardant-filled polypropylene (Table II), thus, indicating some interaction between flame retardant and polymer in condensed phase. Initially, at 300°C there is more weight loss at higher additive levels (20 phr) compared to low additive loadings (5 phr) in flame-retardant-filled polypropylene, except Ph_3SbBr_2 -filled system. However, around 400°C the maximum residue is obtained at higher additive loading (20 phr).

Further, the maximum decomposition temperature is different depending upon the composition (Table II). In Ph_3SbBr_2 - and $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene the D'_{max} observed at 384°C against 339°C for unfilled polypropylene, which was independent of the flame retardants' concentration. The $\text{Ph}_3\text{Sb}(\text{tbp})_2$ and $\text{Ph}_3(\text{tcp})_2$ also increased the D'_{max} to 384°C at 5 phr loading, however, it shifted to lower temperature (375°C) at higher additive loading (20 phr).

The Ph_3SbBr_2 -filled polypropylene is completely volatilized, like unfilled polypropylene by 430°C. However, in other flame-retardant-filled polypropylene, a little amount of residue is left, which increases upon increasing the flame retardants' concentration. The maximum amount of final residue was retained by a polypropylene sample filled with 20 phr $\text{Ph}_3\text{Sb}(\text{pcp})_2$. From this data, it is evident that the antimony in Ph_3SbBr_2 -filled polypropylene has been transferred completely into the flame front, while in other flame-retardant-filled systems the residue is much less than the amount incorporated. This established the vapor phase mechanism of these flame retardants.

Moreover, the activation energy (E^*) of oxidative pyrolysis of polypropylene (14.5 kcal/mol) increases in the presence of flame retardants at 5 phr additive level, except in $\text{Ph}_3\text{Sb}(\text{pcp})_3$ -filled system, where the E^* decreases over unfilled polypropylene (Table II). But at higher flame-retardant concentration E^* decreases.

ISOTHERMAL TREATMENT OF FLAME-RETARDANT POLYPROPYLENE

In order to establish the mechanism of flame retardation by these organo-antimony compounds, the elemental analyses of the char, obtained by isothermal treatments of polypropylene samples at 450°C for half an hour (the temperature was selected on the basis of TG studies) were carried out (Table III). The results show that almost all the antimony volatilized during combustion, but, the halogen could not be detected in the residue.

The amounts of antimony volatilized during combustion show that the higher the LOI of the system, the larger the amounts of antimony moving

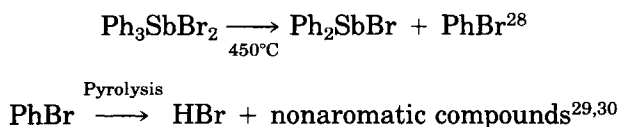
TABLE III
Isothermal Treatments of Flame-Retardant Polypropylene at 450°C for ½ Hour

Sample	Char %	Elemental analysis, %		Amount of Sb volatilized %
		Sample Sb	Char Sb	
P ₁₁	2.0	1.13	0.14	87.6
P ₁₂	2.5	2.16	0.11	95.0
P ₁₃	2.5	3.10	0.22	93.0
P ₁₄	3.0	3.96	0.36	91.0
P ₂₁	4.5	0.57	0.09	84.1
P ₂₂	6.2	1.09	0.17	84.4
P ₂₃	7.9	1.57	0.22	86.0
P ₂₄	9.1	2.00	0.25	87.5
P ₃₁	4.0	0.79	0.14	82.1
P ₃₂	5.8	1.49	0.25	83.2
P ₃₃	6.6	2.13	0.34	84.1
P ₃₄	8.0	2.73	0.38	86.1
P ₄₁	6.2	0.65	0.18	72.3
P ₄₂	7.5	1.25	0.33	73.6
P ₄₃	8.9	1.80	0.46	74.5
P ₄₄	10.5	2.30	0.58	74.8

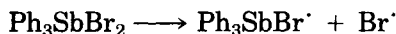
into the flame front (Fig. II). This suggests that compounds operative in vapor phase are more efficient flame retardants for polypropylene.

The greater influence of Ph₃SbBr₂, flame retardant in polypropylene (where Br is directly attached to Sb) compared to aromatic bromine in Ph₃Sb(tbp)₂ is further supported from the lower content of Sb present in the residue of Ph₃SbBr₂-filled polypropylene. The effectiveness of Br over Cl in these flame-retardant systems can also be seen from the antimony content analyzed from the residue (Table III), which shows that the greater amount of antimony is volatilized in the bromine containing flame retardants.

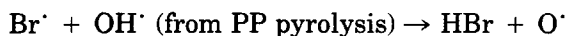
The flame retardants used in the present study presumably decompose to some active species, which interrupt the initiating free radicals produced during pyrolysis of polypropylene. Thus, the decomposition of Ph₃SbBr₂-filled polypropylene and its flame-retardant action is given below:



In addition to this, the following reaction may also occur:



The polypropylene upon oxidative pyrolysis gives H[·] and OH[·] which plays a vital role in chain scission and the chain branching during the thermal degradation of polypropylene.^{31,32} These radicals interact with Br[·]:



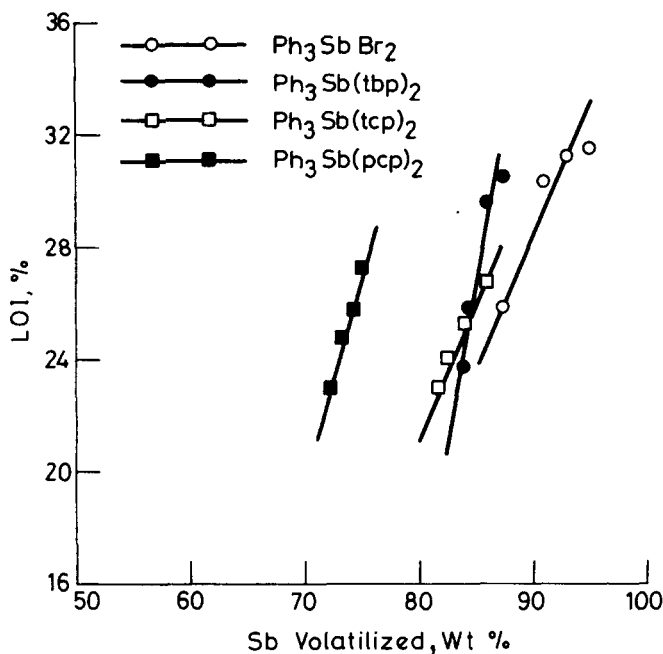
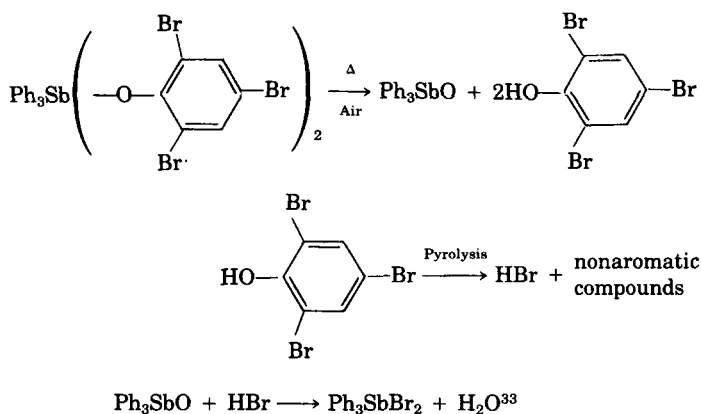


Fig. 2. LOI versus antimony content in the residue obtained from flame-retardant polypropylene, after heating isothermally at 450°C for ½ hour.

The HBr and Br· so formed may act as free radical quenchers. The decomposition of other flame retardants, viz. Ph₃Sb(tbp)₂, Ph₃Sb(tcp)₂, and Ph₃Sb(pcp)₂ occurs through the cleavage of Sb—O bond.¹⁶



The higher efficiency of Ph₃SbBr₂ may be due to its mode of decomposition, where Sb and Br are released simultaneously at lower temperatures by the cleavage of Sb—Br bond due to low bond dissociation energy [314 ± 5 kJ/mol].³⁴ However, in Ph₃Sb(tbp)₂, Sb is released by the cleavage of Sb—O bond comparatively at higher temperatures, due to higher bond dissociation energy (372 ± 84 kJ/mol),³⁴ and Br from C—Br bond at lower temperature (bond dissociation energy, 280 ± 2 kJ/mol),³⁴ and hence the chances of the reaction of Sb and Br are less in this case.

CONCLUSIONS

Among the various organoantimony flame retardants studied, the triphenylstibinedibromide has been found to be a highly efficient flame retardant for polypropylene at low additive levels. Only at 5 phr loading can these flame retardants give V-2 rating, in other words, self-extinguishing polypropylene can be produced. The mode of action of these flame retardants seems to be in the vapor phase.

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