

# Flame Retardation of Polypropylene: Effect of Organoantimony Compounds on the Structural and Mechanical Properties

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## Synopsis

Structural properties of polypropylene (PP) filled with flame-retardant (FR) organoantimony compounds, viz., triphenylstibinedibromide and triphenylantimony (V) derivatives of tribromo-, trichloro-, and pentachlorophenols at 5–20 phr additive loading, were investigated through differential thermal analysis (DTA), and X-ray diffraction (XRD) studies. Incorporation of flame retardant in PP has decreased the melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H_f$ ) of PP. Crystallization peak and the onset temperature, crystallization rate and crystallite size are also influenced by the addition of these compounds. The percent crystallinity obtained by XRD is in good agreement with that obtained by DTA. The tensile properties of the flame-retardant-filled PP are also studied, and an attempt has been made to correlate the tensile properties with that of structural changes in polypropylene. Fracture mechanism of flame-retardant-filled PP has been investigated with the help of a scanning electron microscope.

## INTRODUCTION

The addition of fillers to polypropylene makes it possible to achieve high performance polypropylene plastics for various applications.<sup>1–8</sup> For example, the use of talc considerably increases polypropylene stiffness, improves dimensional stability, and reduces creep at high temperature, though the impact strength decreases.<sup>9</sup> However, the addition of these fillers also affects the structural properties of the filled system.<sup>10–13</sup> Beck and Ledbetter<sup>10</sup> have found that the addition of aluminium dibenzoate, potassium benzoate, etc. as nucleating agents in polypropylene increases the crystallization peak temperature and the crystallization rate, resulting in an increase in the yield stress and the initial modulus with a decrease in percent yield strain. Similar findings were also reported by Gupta et al.,<sup>11</sup> where the addition of HDPE to PP/glass fiber composites increased the tensile strength and the initial modulus with an increase in the crystallization peak temperature and the crystallinity. Stehling et al.<sup>12</sup> have attributed the changes in impact strength of polypropylene upon blending with poly(ethylene-co-propylene) rubber and HDPE to the variations in morphology as observed by scanning electron microscopy.

Thus, it is of technical importance to study the structural behavior of the filled polypropylene, which will be helpful in understanding the mechanical properties of the system. The present work deals with the effect of halogenated

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organoantimony compounds, viz., triphenylstibinedibromide and triphenylantimony (V) derivatives of tribromo-, trichloro-, and pentachlorophenols used at 5, 10, 15, and 20 phr additive levels in polypropylene, on its structural and mechanical properties.

The effect of halogenated organoantimony compounds based flame retardants upon the melt flow behavior and on the flammability and thermal behavior of polypropylene have been communicated elsewhere.<sup>14,15</sup>

## EXPERIMENTAL

### Materials

Polypropylene "Koylene M3030" (MFI 3.0) was obtained from IPCL, Baroda, India. Triphenylstibinedibromide ( $\text{Ph}_3\text{SbBr}_2$ ) was prepared by a reported method.<sup>16</sup> The synthesis of the derivatives of triphenylantimony (V) with tribromo-, trichloro-, and pentachlorophenols [compounds namely  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ ,  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ , and  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ ] has been communicated elsewhere.<sup>17</sup>

### Blending and Injection Molding

The flame retardants were dry-blended with polypropylene at various additive levels ranging between 5 and 20 phr (Table I), and then extruded through a single screw extruder "Betol BM1820" using the conditions as reported previously.<sup>15</sup>

The test samples were prepared by the Windsor injection molding machine keeping the machine settings as communicated earlier.<sup>15</sup>

### Characterization

**DTA.** DTA measurements were carried out in an inert atmosphere on a Stanton Redcroft DTA-671, differential thermal analyzer, using alumina as a reference material. The samples (in powdered form) were first heated at the rate of  $10^\circ\text{C}/\text{min}$  to obtain the melting endotherm, sample was kept at  $200^\circ\text{C}$  for 5 min so as to eliminate the effect of previous thermal history. The crystallization exotherm was then obtained during the cooling cycle at a cooling rate of  $10^\circ\text{C}/\text{min}$ .

**XRD.** For XRD measurements, the sample in the powdered form was compressed into a small rectangular orifice in a glass holder of rotating stage of Phillips Norelco X-ray diffraction equipment with a recorder. Radial scans of intensity v. diffraction angle ( $2\theta$ ) were recorded in the range  $8-40^\circ$  of  $2\theta$  using Ni-filtered  $\text{Cu}\alpha$  radiation.

**Tensile Strength.** The load-elongation plot was directly obtained by the Instron (Model 1121) using dumbbell-shaped samples (ASTM D-638 type I). The gauge length was 60 mm, and the crosshead and the chart speed were fixed at 50 and 100 mm/min, respectively. From the load-elongation curves, stress-strain curves were computed, and the yield stress, yield strain, and the initial modulus were calculated.

**Impact Strength.** The notched izod-impact strength was determined as per the ASTM-D-256 standard by FIF Impact Testing Machine Model IT-0.42.

TABLE I  
Thermal Behavior of Halogenated Organoantimony Compounds Filled Polypropylene

Flame retardant formulation		Melting endotherm				Crystallization exotherm				Degree of super-cooling (°C)	ΔW (arbitrary units)	HDT <sup>a</sup> (°C)
Additive	Concentration (phr)	Code	T <sub>onset</sub> (°C)	T <sub>m</sub> (°C)	T <sub>offset</sub>	T <sub>i</sub>	T <sub>c</sub>	T <sub>p</sub>	T <sub>c</sub> - T <sub>p</sub>			
Ph <sub>3</sub> SbBr <sub>2</sub> mp 214-16°C	—	P <sub>0</sub>	148	168	176	138	137	129	8	39.0	22.0	108
	5	P <sub>1</sub>	142	161	168	136	133	127.5	5.5	33.5	20.0	103
	10	P <sub>2</sub>	138	162	169	134	132	127	5	34.0	19.8	103
	15	P <sub>3</sub>	136	162	172	134	131	126	5	35.0	19.3	100
	20	P <sub>4</sub>	139	162	175	134	132	125	7	37.0	18.9	99
Ph <sub>3</sub> Sb(tbp) <sub>2</sub> mp 240-42°C	5	P <sub>5</sub>	150	165	170	132	130	125	5	40.0	24.0	104
	10	P <sub>6</sub>	145	165	175	130	129	124	5	41.0	25.1	100
	15	P <sub>7</sub>	143	166	175	131	129	123	6	43.0	26.2	100
	20	P <sub>8</sub>	149	166	179	129	128	121	7	45.0	26.0	98
	Ph <sub>3</sub> Sb(tcp) <sub>2</sub> mp 225-227°C	5	P <sub>9</sub>	143	165	174	130	129.5	124	5.5	41.0	24.1
10		P <sub>10</sub>	148	166	170	130	129	123	6	43.0	25.3	102
15		P <sub>11</sub>	141	165	176	130.5	128	121	7	44.0	25.9	102
20		P <sub>12</sub>	150	165	170	128	127	120.5	6.5	44.5	26.2	100
Ph <sub>3</sub> Sb(pcp) <sub>2</sub> mp 236-239°C		5	P <sub>13</sub>	149	166	172	132	131	125	6	41.0	24.5
	10	P <sub>14</sub>	142	167	179	130	129	123.5	5.5	43.5	24.0	101
	15	P <sub>15</sub>	139	167	179	132	128	122.0	6	45.0	23.9	100
	20	P <sub>16</sub>	144	166	175	128	126	120.0	6	46.0	23.0	100

<sup>a</sup>Heat distortion temperature.

**Heat Distortion Temperature.** The heat distortion temperature was determined as per the ASTM D-648-72 standard on a heat distortion temperature unit manufactured by Toyo Seiki Seisaku-SHO Ltd., Japan. The maximum fiber stress applied at the center was 455 kPa.

**Scanning Electron Microscopy.** The fractured ends of the specimens, as obtained from the Instron tensile tests, were examined with the help of the Cambridge S4-10 scanning electron microscope.

## RESULTS AND DISCUSSION

### Differential Thermal Analysis

The blending of organoantimony compounds in polypropylene was found to lower the melting temperature of the filled polypropylene compared to that of unfilled polypropylene (Table I). The lowering in  $T_m$  was found to be influenced by the type of organo-antimony compound used. Thus, for example,  $\text{Ph}_3\text{SbBr}_2$ -depressed the  $T_m$  by 6–7°C, which is independent of additive concentration in the range studied (5–20 phr), while  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ ,  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ , and  $\text{Ph}_3\text{Sb}(\text{pcp})_2$  additives showed an insignificant decrease in the  $T_m$  (by 1–3°C only).

The depression in  $T_m$  of polypropylene may be attributed to the reduction in crystalline order, and also due to the diluent effect and plasticization of the crystalline regions as reported in the literature.<sup>18–22</sup> The larger depression in  $T_m$  of the polypropylene filled with  $\text{Ph}_3\text{SbBr}_2$  might have resulted from its diffusion in the polypropylene matrix, as the melting point of  $\text{Ph}_3\text{SbBr}_2$  (214–216°C) is quite close to the processing temperature (210°C). The crystalline regions can, therefore, be plasticized resulting in a decrease in  $T_m$  as reported by Chang et al.<sup>19</sup> However, the other flame-retardant additives appear to be of inert filler type, which hardly affect the  $T_m$ , but significantly decreases the  $T_{\text{onset}}$  (Table I), suggesting that these additives interact only with the less ordered or smaller crystallites.

The heat of fusion ( $\Delta H_f$ , calculated after normalizing for the weight of the additives) of the filled polypropylene also decreased in the presence of additives compared to the unfilled polypropylene (Table II), depending upon the loading, and the nature of the flame-retardant additive.

The present crystallinity of the polypropylene component in the filled system was calculated by the heat of fusion using the following formula:

$$W_c = \frac{\Delta H_f}{\Delta H_u} \times 100$$

where  $W_c$  is the percent crystallinity and  $\Delta H_f$  and  $\Delta H_u$  are the heats of fusion of the actual PP sample and the theoretical 100% crystalline isotactic sample, respectively. A value of 35 cal/g for  $\Delta H_u$  was chosen from the various values given in the literature,<sup>23–29</sup> as this was determined calorimetrically using polypropylene without any antioxidant.<sup>25</sup>

The percent crystallinity was found to decrease in the presence of additives, and this was dependent on the additive concentration and the type of FR additive (Table II). Thus, a small decrease in the % crystallinity was observed

TABLE II  
Crystallinity Contents of Organoantimony Compounds Filled Polypropylene

Sample	$\Delta H_f$ (from melting endotherm in DTA) (cal/g)	% Crystallinity by	
		DTA	XRD
P <sub>0</sub>	26.6	76.0	66.0
P <sub>1</sub>	24.1	68.8	58.0
P <sub>2</sub>	22.0	62.8	54.0
P <sub>3</sub>	20.0	57.2	50.0
P <sub>4</sub>	19.6	56.0	47.0
P <sub>5</sub>	23.5	67.2	59.0
P <sub>6</sub>	21.4	61.1	55.0
P <sub>7</sub>	18.6	53.0	48.0
P <sub>8</sub>	16.5	47.1	42.0
P <sub>9</sub>	23.5	67.1	60.0
P <sub>10</sub>	21.8	62.3	58.0
P <sub>11</sub>	18.9	54.0	49.0
P <sub>12</sub>	16.8	48.0	41.0
P <sub>13</sub>	22.5	64.3	56.0
P <sub>14</sub>	20.7	59.1	54.0
P <sub>15</sub>	17.8	50.9	50.0
P <sub>16</sub>	15.8	45.1	40.0

in Ph<sub>3</sub>SbBr<sub>2</sub>-filled polypropylene, which further decreases in the Ph<sub>3</sub>Sb(tbp)<sub>2</sub>-, Ph<sub>3</sub>Sb(tcp)<sub>2</sub>-, and Ph<sub>3</sub>Sb(pcp)<sub>2</sub>-filled systems.

A decrease in the crystallinity of filled PP may be accounted for by the fact that the crystallization of polypropylene during processing is hindered in the presence of FR additives as indicated from the decrease in the onset of crystallization temperature.

### Crystallization Exotherm

The crystallization exotherm is studied in terms of the following quantities (Fig. 1) as has been used by the previous workers.<sup>10,11</sup>

(a) The peak temperature  $T_p$  occurs at the intercept of the tangents at the two sides of the exotherm. It is a measure of the temperature where the bulk of polymer has crystallized.

(b) The initial temperature  $T_i$ , at which the curve first deviates from the base line, is a measure of the onset of crystallization.

(c) Constructed temperature  $T_c$  is obtained at the intercept of the tangents to the base line and the high temperature side of the exothermic peak. The quantity  $T_c - T_p$ , i.e., the difference between the constructed temperature and the peak temperature, is a measure of the overall rate of crystallization: the smaller the difference the greater the rate of crystallization.

The onset of crystallization  $T_i$  (138°C) of the unfilled polypropylene shifts to lower temperature (128–136°C) in organo-antimony compounds filled polypropylene with a minimum decrease in the Ph<sub>3</sub>SbBr<sub>2</sub>-filled polypropylene.

The addition of organoantimony compounds also lowers the crystallization peak temperature  $T_p$  to 120–127.5°C from 129°C, for unfilled polypropylene. The drop in  $T_p$  value is least in the Ph<sub>3</sub>SbBr<sub>2</sub>-filled polypropylene. An

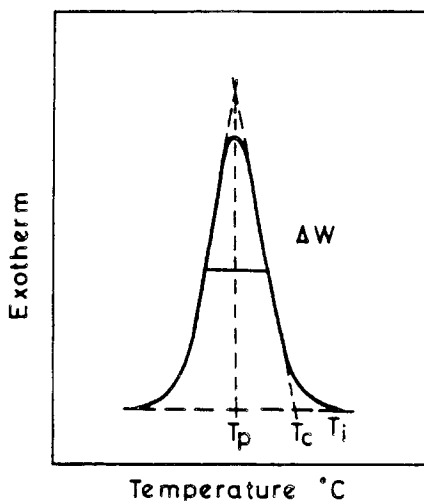


Fig. 1. Resolution of DTA exotherm for various crystallization parameters.

increase in the flame retardants concentration further lowers the  $T_p$  in all the PP samples (Table I).

The degree of supercooling ( $T_m - T_p$ ) of unfilled polypropylene ( $39.0^\circ\text{C}$ ) was also studied which decreases to  $33.5\text{--}37.0^\circ\text{C}$  in  $\text{Ph}_3\text{SbBr}_2$ -filled system, whereas, in other flame retardants filled polypropylene, it increases by  $1\text{--}7^\circ\text{C}$ , i.e., between  $40$  and  $46^\circ\text{C}$ . Here, it may be noted that the increase in  $T_p$  with a lowering in supercooling was observed by Beck and Ledbetter,<sup>10</sup> in the presence of nucleating agents, viz., aluminium dibenzoate, potassium benzoate, etc., in polypropylene.

The decrease in supercooling along with lowering in crystallite size in  $\text{Ph}_3\text{SbBr}_2$ -filled polypropylene is, therefore, suggestive of its nucleation effect, while the replacement of two bromine atoms in  $\text{Ph}_3\text{SbBr}_2$  with substituted phenol moieties results in the loss of its nucleating ability. This observation is in conformity with Beck's work,<sup>30</sup> who observed that the decreasing nucleating ability is associated with the increase in the number of phenol moieties in the nucleating agents, for polypropylene.

Thus, the cumulative influence is the faster rate of crystallization in the presence of these flame retardants with respect to the unfilled polypropylene, as inferred from the decrease in  $T_c - T_p$  value. The crystallization process tends to become slower with the increasing concentration of the flame-retardant additives in all the four additives studied. However, in all the systems the onset of crystallization is delayed in the presence of these FR additives, which is also supported by the decrease in the degree of crystallinity in the filled polypropylene.

### Wide Angle X-Ray Diffraction Studies

All the filled polypropylene samples showed four characteristics of diffraction peaks at  $2\theta$ ,  $14.5^\circ$ ,  $17^\circ$ ,  $18.5^\circ$ , and  $21.5^\circ$ , from 110, 040, 130, and the combination of (111, 131, and 041) planes, respectively, as observed by Natta and Corradini<sup>31</sup> for the unfilled polypropylene (Fig. 2) The occurrence of the diffraction peaks at the same  $2\theta$  indicates that unit cell dimensions of

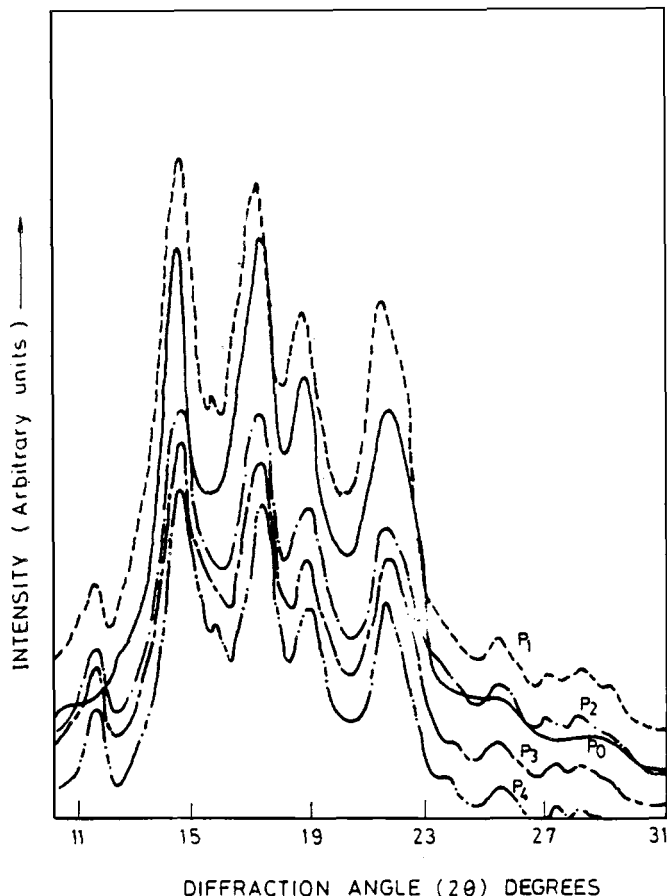


Fig. 2. X-ray diffractograms of  $\text{Ph}_3\text{SbBr}_2$ -filled polypropylene (—)  $P_0$ , unfilled PP; (---)  $P_1$ , (— · —)  $P_2$ , (— — —)  $P_3$ , (· · · ·)  $P_4$ , PP filled at 5, 10, 15, and 20 phr levels, respectively.

polypropylene are not disturbed in the presence of 5–20 phr of organoantimony compound fillers though the rate of crystallization is affected, as shown by the DTA studies.

Besides the characteristic diffraction peaks of unfilled polypropylene, some additional peaks are also observed in the filled PP samples. The  $\text{Ph}_3\text{SbBr}_2$ -filled polypropylene showed an additional peak at  $2\theta$ ,  $11.5^\circ$ , which was intensified at higher additive levels of 20 phr (Fig 2), while the  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ -filled polypropylene showed an additional peak in its diffraction pattern at  $2\theta$ ,  $12.5^\circ$  only at high additive levels (at and above 15 phr, Fig 3). The additional peaks as observed in  $\text{Ph}_3\text{SbBr}_2$ - and  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ -filled polypropylene are due to the presence of additives as confirmed from X-ray diffraction pattern of the neat  $\text{Ph}_3\text{SbBr}_2$  and  $\text{Ph}_3\text{Sb}(\text{tbp})_2$  compounds.

The percent crystallinity of the filled polypropylene sample was calculated by the method reported by Bell and Dumbleton<sup>32</sup> after neglecting the peaks due to additives.

The incorporation of these additives has decreased the percent crystallinity, which further decreases with the increase in the additive concentration (Table II). It can be seen from the data that the trend in % crystallinity obtained by XRD agrees well with that obtained by DTA, although the absolute values in

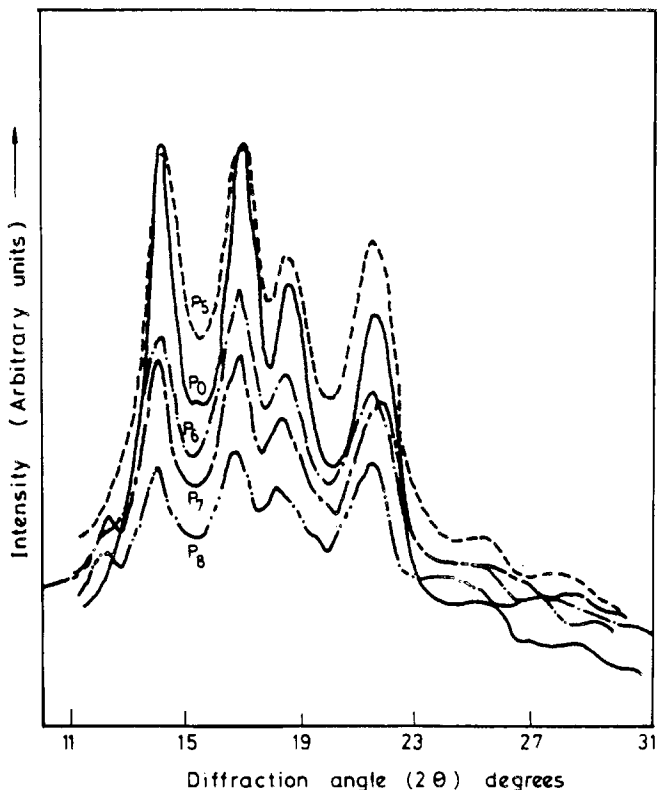


Fig. 3. X-ray diffractograms of  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ -filled polypropylene (—)  $P_0$ , unfilled PP; (---)  $P_5$ , (— · —)  $P_6$ , (— — —)  $P_7$ , (- · - · -)  $P_8$ , PP filled at 5, 10, 15, and 20 phr levels, respectively.

the two cases are different. This difference in the crystallinity value may be attributed to uncertainties in applying corrections for the background and amorphous contributions in the X-ray diffractograms as reported by Vonk,<sup>33</sup> Ke,<sup>34</sup> and Chang et al.,<sup>19</sup> who have also observed a difference in the percent crystallinity values obtained by XRD and DTA.

## MECHANICAL PROPERTIES OF ORGANOANTIMONY COMPOUNDS FILLED POLYPROPYLENE

### Tensile Behavior

The yield stress of the filled polypropylene decreased over the unfilled polypropylene irrespective of the nature of the flame-retardant filler (Fig. 4). However, the initial modulus and the yield strain are dependent on the chemical structure of the additive. In general, the  $\text{Ph}_3\text{SbBr}_2$  decreases the yield strain and increases the initial modulus, whereas, in other flame retardants, viz.,  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ ,  $\text{Ph}_3\text{Sb}(\text{tcp})_2$  and  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene, the trend reverses (Table III)

The increase in the additive concentration also effects the mechanical properties (Fig. 5) which can be summarized as follows:

(a) In  $\text{Ph}_3\text{SbBr}_2$ -filled polypropylene, the yield stress and yield strain decreases while initial modulus increases with the increase in loading.



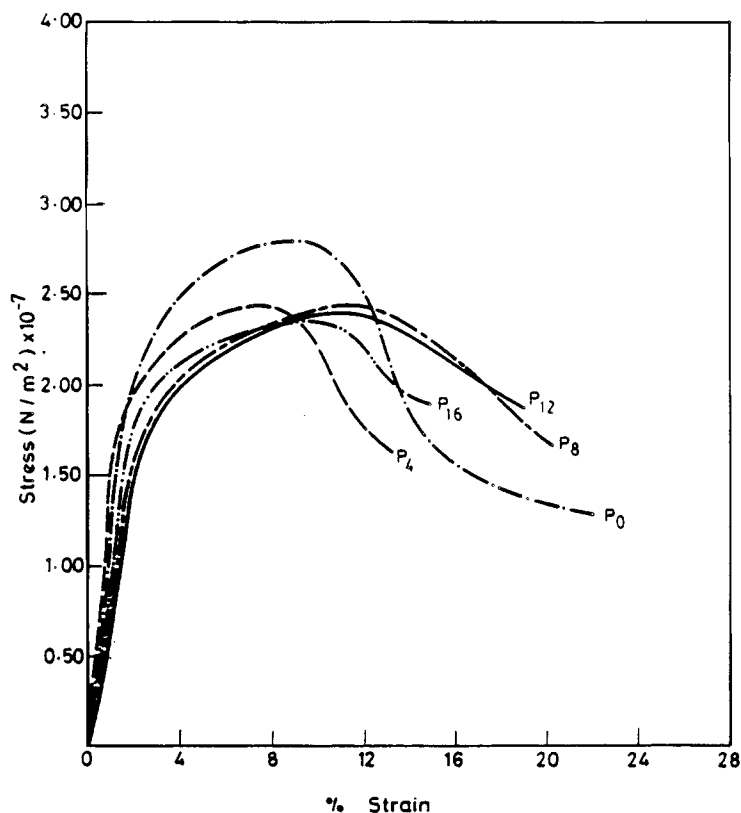


Fig. 4. Stress-strain curves of organoantimony compounds filled polypropylene (—)  $P_0$ , unfilled PP; (---)  $P_4$ , PP filled with 20 phr of  $\text{Ph}_3\text{SbBr}_2$ ; (— — —)  $P_8$ , PP with 20 phr  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ ; (—)  $P_{12}$ , with 20 phr of  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ ; (- · - · -)  $P_{16}$ , with 20 phr of  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ .

TABLE III  
Mechanical Properties of Organoantimony Compounds Filled Polypropylene

Sample code	Yield stress, $(\text{N}/\text{m}^2 \times 10^{-7})$	Yield strain (%)	Initial modulus $(\text{N}/\text{m}^2 \times 10^{-9})$	Impact strength (kg m/M)
$P_0$	2.82	9.13	0.99	5.16
$P_1$	2.71	8.33	1.10	4.81
$P_2$	2.60	8.10	1.15	4.78
$P_3$	2.53	7.35	1.21	4.60
$P_4$	2.46	7.06	1.27	4.43
$P_5$	2.71	10.53	0.84	5.51
$P_6$	2.60	10.79	0.82	5.75
$P_7$	2.53	11.28	0.79	6.26
$P_8$	2.46	11.30	0.80	6.50
$P_9$	2.70	10.48	0.86	5.53
$P_{10}$	2.62	10.85	0.82	5.92
$P_{11}$	2.50	11.05	0.82	6.24
$P_{12}$	2.41	11.00	0.79	6.65
$P_{13}$	2.66	10.62	0.83	5.57
$P_{14}$	2.55	10.51	0.83	5.81
$P_{15}$	2.46	10.35	0.87	6.20
$P_{16}$	2.35	10.10	0.90	6.21

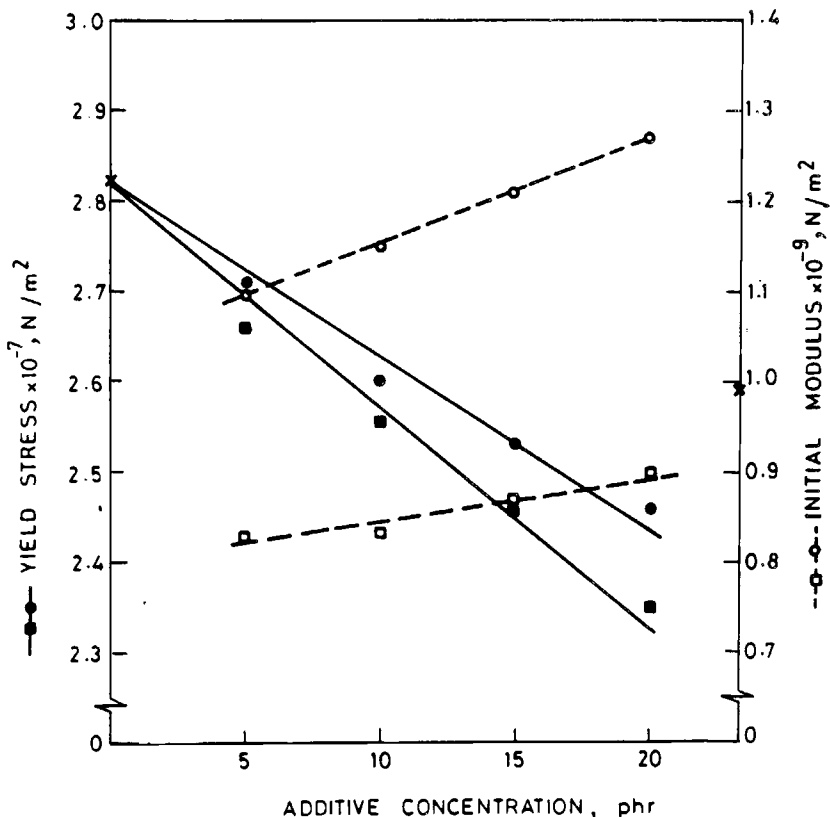


Fig. 5. Mechanical properties of organoantimony compounds filled polypropylene as a function of additive concentration: (X) unfilled, (O,●)  $\text{Ph}_3\text{SbBr}_2$ -filled PP; (□,■)  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled PP.

(b) In  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ - and  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ -filled systems, the increase in the additive concentration resulted in low yield stress and initial modulus values with increased percent yield strain. The  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene showed similar behavior to that of  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ -filled polypropylene except that the yield strain was slightly decreased at higher loading while initial modulus was increased (Table III).

The increase in percent yield strain and a decrease in the initial modulus as observed in polypropylene filled with  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ ,  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ , and  $\text{Ph}_3\text{Sb}(\text{pcp})_2$  may be attributed to the plasticizing action of those additives, as also evidenced by the decrease in the melt viscosity, reported earlier.<sup>14</sup>

A decrease in the yield stress in all the filled samples, irrespective of the flame retardants, may be attributed to low crystallinity values (Fig. 6) of the filled PP samples. However, the yield strain and the initial modulus of the filled polypropylene appear to be dependent on the structure of the additive. Thus, the  $\text{Ph}_3\text{SbBr}_2$ -filled polypropylene showed a decrease in the yield strain and increase in the initial modulus with a decrease in the crystallinity of virgin polypropylene, though the crystallinity of the composite material (PP +  $\text{Ph}_3\text{SbBr}_2$ ) is high due to the crystalline nature of  $\text{Ph}_3\text{SbBr}_2$ .

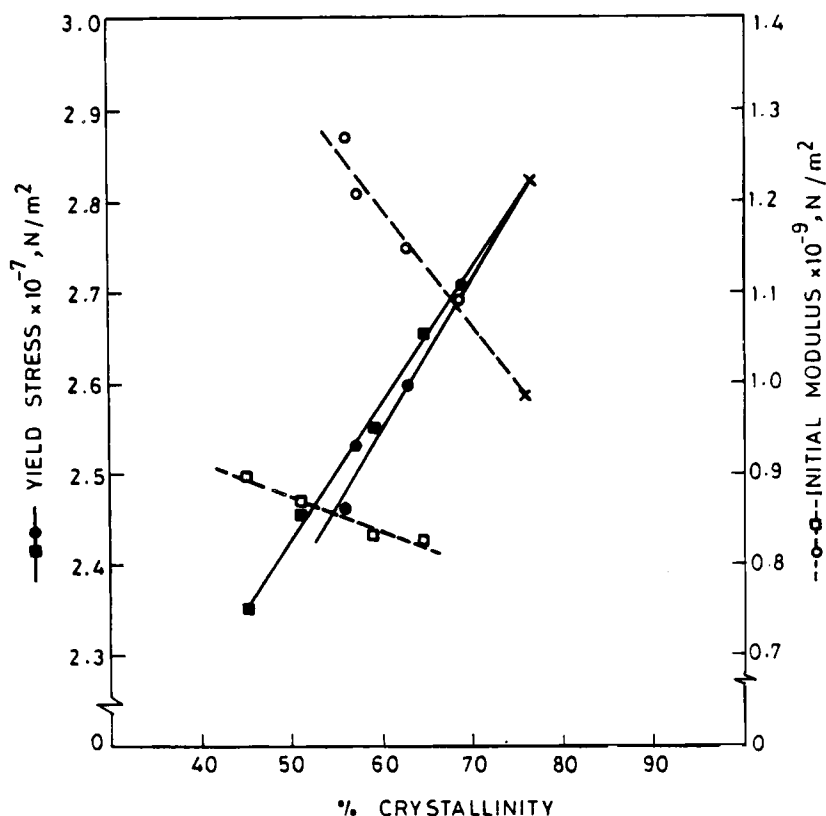


Fig. 6. Correlation of crystallinity (as obtained by DTA endotherm) with mechanical properties of organoantimony compounds filled polypropylene: (x) unfilled, (○,●)  $\text{Ph}_3\text{SbBr}_2$ -filled PP; (□, ■)  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled PP.

In  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ -,  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ -, and  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene, a decrease in crystallinity is associated with an increased yield strain and low initial modulus values.

The decrease in yield strength with a decrease in the crystallinity is also observed by Robertson and Paul<sup>35</sup> in polyolefin blends.

### Impact and Flexural Strength

The impact strength of the filled polypropylene samples was found to be dependent on the filler concentration, and the chemical structure of the organoantimony compounds,  $\text{Ph}_3\text{SbBr}_2$  decreased the impact strength of polypropylene which further dropped with increasing  $\text{Ph}_3\text{SbBr}_2$  concentration. In other flame retardants, viz.,  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ -,  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ -, and  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene, the impact strength increased over unfilled polypropylene, which further increases by increasing the additive concentration.

The flexural rigidity of those filled polypropylene systems was not much affected, as none of the samples like unfilled polypropylene could be broken at the maximum applied load of 31 kg.



(a)



(b)

Fig. 7. Scanning electron microphotographs of the tensile fractured surface of organoantimony compounds filled polypropylene: (a) unfilled PP,  $P_0$ ; (b and c) filled with  $\text{Ph}_3\text{SbBr}_2$  at 10 and 20 phr levels,  $P_1$  and  $P_4$ ; (d and e) filled with 10 and 20 phr of  $\text{Pd}_3\text{Sb}(\text{tbp})_2$ ,  $P_5$  and  $P_8$ ; (f and g) filled with 10 and 20 phr  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ ,  $P_9$  and  $P_{12}$ ; (h and i) with 10 and 20 phr of  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ ,  $P_{13}$  and  $P_{16}$ . [Degree of magnification indicated on Fig. 7(a) applies to all microphotographs in this set.]



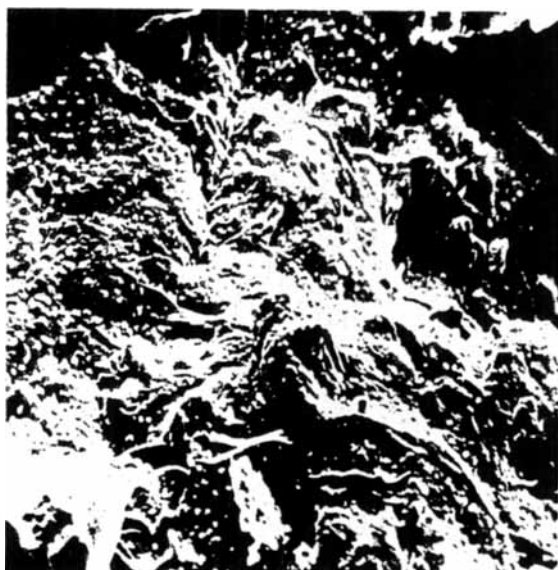
(c)



(d)

#### **Morphology of the Tensile Fractured Surface of Injection-Molded Specimens**

The scanning electron microphotographs of the tensile fractured polypropylene samples filled with organoantimony compounds are shown in Figure 7. The addition of  $\text{Ph}_3\text{SbBr}_2$  changed the fibrillar morphology of polypropylene into lobed structures. Here, the fracture is brittle and is due to interspherulitic



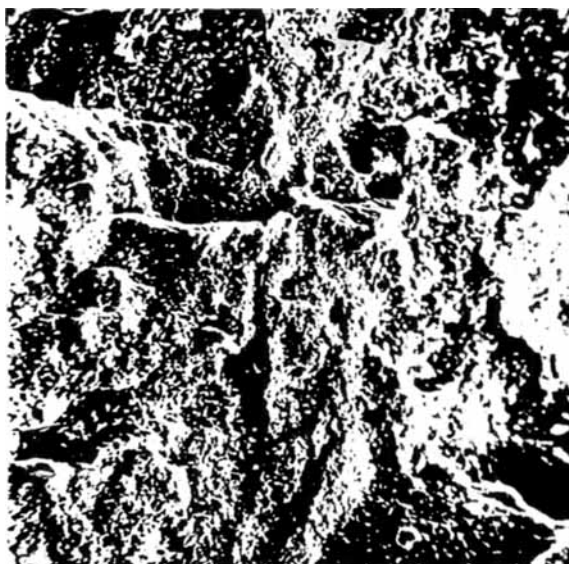
(e)



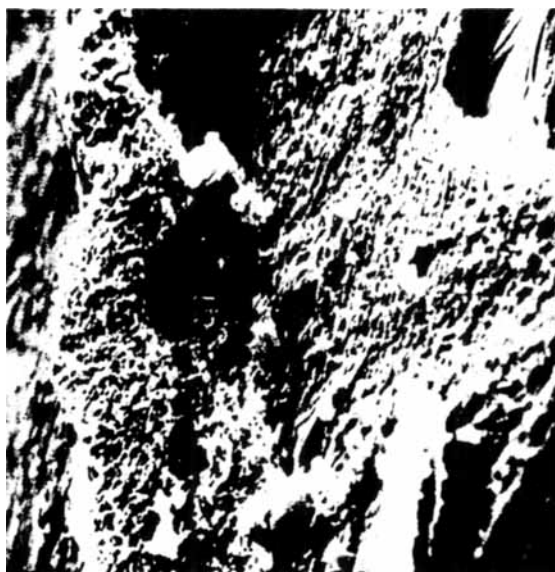
(f)

voids which are clearly seen around the lobe. The increase in  $\text{Ph}_3\text{SbBr}_2$  concentration has further weakened the spherulite boundaries; hence larger voids are seen around the lobe, which presumably results in poor yield strength and yield strain at higher additive loadings.

The  $\text{Ph}_3\text{Sb}(\text{tbp})_2$ - and  $\text{Ph}_3\text{Sb}(\text{tcp})_2$ -filled polypropylene show fibril morphology, indicating ductile failure occurring at the interspherulite boundaries,



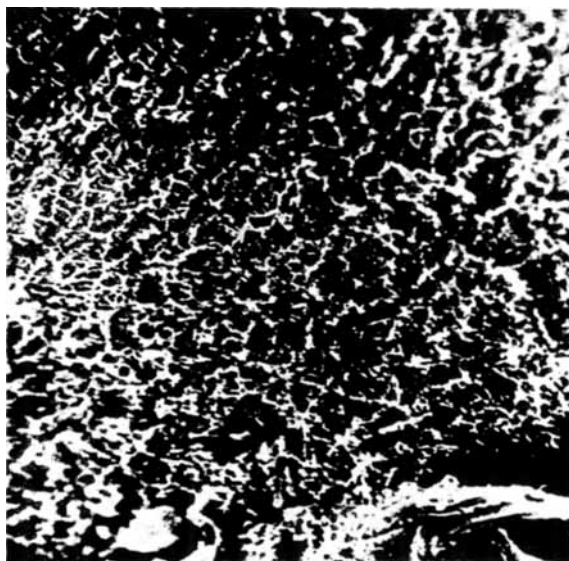
(g)



(h)

which seems to be responsible for higher yield strain and flexural rigidity of these samples.

In  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene samples, although the fibril structure is there, the fracture seems to be different from other filled polypropylene systems. Here, the fracture initiation appears to be due to the interspherulitic voids as well as due to the poor interaction of the flame-retardant particles



(i)

with the polymer matrix, hence under strain the polymer matrix detaches itself from the additive particles, thereby dislodging the particle, resulting in a network type structure with large number of small voids. This type of morphology appears to be responsible for a large drop in yield strength in the  $\text{Ph}_3\text{Sb}(\text{pcp})_2$ -filled polypropylene; however, the fibril structure still maintains its flexural rigidity.

#### Heat Distortion Temperature

Heat distortion temperature of the polypropylene decreases by the addition of organoantimony compounds (Table I). An increase in the flame retardants' concentration further decreases the heat distortion temperature, irrespective of the nature of the additive, which may be attributed to the lowering in melt viscosity in the presence of organoantimony compounds as reported elsewhere.<sup>14</sup>

#### SUMMARY AND CONCLUSIONS

The study clearly shows that  $\text{Ph}_3\text{SbBr}_2$  additive behaves differently in relation to its phenolic derivatives, in influencing the structural and mechanical properties of the filled polypropylene.

— $\text{Ph}_3\text{SbBr}_2$  was found to be a nucleating agent to a small extent, while other compounds appear to be nonnucleating in nature with respect to the crystallization of polypropylene.

—The blending of  $\text{Ph}_3\text{SbBr}_2$  in polypropylene resulted in a decrease in the crystallinity, crystallization peak temperature, degree of supercooling, and crystallite size, which is accompanied by a decrease in the yield stress, yield strain, and impact strength, but an increase in the initial modulus while other



flame-retardant-filled polypropylene samples showed a decrease in the crystallinity and  $T_p$ , and an increase in the degree of supercooling and crystallite size with a decrease in the yield stress, and initial modulus and increase in the yield strain and impact strength.

Heat distortion temperature of the filled polypropylene was also decreased in the presence of these additives irrespective of the chemical nature of the flame-retardant additives.

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