

# Antimony Polymers. III. Flame Retardant Behavior of Chloroprene and Natural Rubber Vulcanizates with Antimony Polymer

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**ABSTRACT:** The antimony-containing polymer of bisphenol-A (BPA) and triphenyl antimony dinitrate was used as a flame retardant (FR) for chloroprene rubber (CR) and natural rubber (NR). The flame retardancy of this additive was monitored by the limiting oxygen index (LOI) measurements of the rubber vulcanizates and compared with that for antimony trioxide used as a FR additive. The thermogravimetric analysis (TGA) of the vulcanizates has also been studied. A structure flammability relationship has been established. The effect of this FR additive on physical properties of the vulcanizates undergoing heat aging and solvent leaching has also been evaluated. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 927–935, 1998

**Key words:** flame retardant; antimony polymer; limiting oxygen index (LOI); structure flammability relationship

## INTRODUCTION

Antimony oxide is one of the most important and widely used flame retardant additives in combination with organohalogen compounds.<sup>1,2</sup> The combined system of antimony oxide and halogen compound is always more effective than either of the components. The antimony compounds inhibit the flame mainly through the vapor phase mechanism by the formation of volatile antimony halides and oxyhalides. There are a number of suggested modes of action of antimony-halogen synergism: 1)  $SbX_3$  is itself believed to be an effective free radical trap or chain breaker in the gas phase of burning process, just as HX is, 2) the trivalent antimony facilitates the generation of halogen radicals, which interfere with the normal free radical mechanism of flame propagation, 3) the for-

mation of  $SbOX$  and/or  $SbX_3$  simply delays the rate of escape of the halogen from the flame and thus increases the probability of their reaction with propagating species, 4) the formation of volatile  $SbX_3$  could act as a flame extinguisher by blanketing the flame and cutting off the air supply, and 5) condensed liquid or solid  $SbX_3$  particles could probably reduce the energy of the flame by the "wall" or surface effect.<sup>1,3,4</sup> Although there are a number of reports<sup>5–7</sup> where  $Sb_2O_3$  alone has been found to be a suitable effective flame retardant without the need of halogens, the flame retardancy was probably due to simple physical dilution of the flammable substrate and formation of an impermeable glassy layer or coating on the burning surface at ignition temperature.<sup>8</sup> Besides  $Sb_2O_3$ , some organoantimony compounds have been used as flame retardant additives to polymers.<sup>8</sup>

It has been observed that polymeric flame retardant additives are more effective and preferable to conventional small molecular additives because macromolecular additives are better resis-

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tant to solvent extraction, migration, leaching, volatile loss, and so on and also more compatible with the polymer system.<sup>9,10</sup> Again, the amount of conventional low molecular weight additives required to be incorporated for effective flame retardancy of a material is relatively higher, and consequently the physical and mechanical properties of such filled polymers are adversely affected. Thus a number of phosphorus,<sup>11,12</sup> halogens,<sup>13</sup> and nitrogen<sup>9,14</sup>-containing polymers have been developed as polymeric flame retardant additives. But so far there is no report on antimony polymers as flame retardant additives.<sup>15</sup>

In the present article we report for the first time an antimony polymer as a flame retardant additive for CR and NR vulcanizates. An attempt has been made to correlate the ratio of antimony to chlorine content of the rubber vulcanizates with their flame retardancy. The TG analysis of the vulcanizates was carried out to examine how the flame retardant additives affect their decomposition behavior. The effect of this fire retardant on physical properties of the vulcanizates undergoing heat aging and solvent leaching has also been reported.

## EXPERIMENTAL

### Materials

An antimony polymer of bisphenol-A (BPA) and triphenyl antimony dinitrate was synthesized as reported recently.<sup>16</sup> Toluene (S.D. Fine Chem.) was purified, following the usual procedure.<sup>17</sup> Sb<sub>2</sub>O<sub>3</sub> (S.D. Fine Chem.) was used as received. NR (RMA-3), PVC, CINR (Chlororub-20), and CR (WRT) were procured from a local market and used as the base polymer. ZnO (LOBA Chemie), sulfur (LOBA Chemie), stearic acid (S.D. Fine Chem.), CBS (ICI, India), MgO (LOBA Chemie), and NA 22 (Aldrich, USA) were used as received.

### Preparation of the Rubber Vulcanizates Containing Antimony Polymer

Vulcanizate samples were prepared by a two-roll laboratory rubber mixing mill (6" × 6" size), by a conventional rubber compounding procedure. The friction ratio between the rolls used was 1 : 1.09. The gum stocks and filled stocks were compounded at 50 ± 2°C for 15 min and at 60 ± 5°C for 25 min, respectively. Appropriate amounts of

rubber, antimony polymer, and other ingredients were mixed and the sheets of the blends were prepared in the mill, which were vulcanized at 150°C under a pressure of 40 ± 2 kg/cm<sup>2</sup> for the respective optimum cure time (*t*<sub>90</sub>), as obtained by rheometric (Monsanto R-100) studied in a laboratory hot press (Carver Laboratory Press, Model 2627, USA).

### Flame Retardancy Test

A flame retardancy test of the vulcanizate samples was carried out by a limiting oxygen index (LOI) test as per the ASTM D 2863-77 procedure. The test samples were burned in an FTA flammability tester (S.C. Dey, Calcutta) under a nitrogen–oxygen environment. The minimum concentration of oxygen in the nitrogen–oxygen gas environment just sufficient to sustain the flame for 30 s was used for calculating LOI values using the formula

$$\text{LOI} = \frac{\text{volume of oxygen}}{\text{volume of nitrogen} + \text{volume of oxygen}} \times 100$$

The LOI values obtained by this test are the average of three tests for each sample. The variance ( $\sigma^2$ ) of the values is ±0.1.

### TG Analysis

Thermogravimetric analysis (TGA) of the filled vulcanizates of NR and CR was made with a Stanton Redcroff STA-625 thermal analyzer in air at a heating rate 10°C/min.

### Physical Test Methods for Rubber Vulcanizates

To determine the physical properties at least three specimens per test were evaluated for such properties and the mean value was reported.

Tensile strength, modulus at 200% and 300%, strain, and elongation at break were carried out according to the ASTM D 412-51 T procedure using dumbbell-shaped specimens at room temperature by a tensile tester (K. M. Industry, Model 1.3D). The hardness of the vulcanizates was measured by a Shore-A type durometer, model SHR-MARK-III as per the ASTM D 676-59 T standard procedure.

**Table I Mechanical Properties of the Gum Vulcanizates**

Composition of the Rubber Vulcanizates (phr)	T.S. (kg/cm <sup>2</sup> )	Modulus 200% (kg/cm <sup>2</sup> )	Modulus 300% (kg/cm <sup>2</sup> )	EB (%)	Hardness Shore A
NR (100)	150.9	9.46	12.34	906	35
NR/AP (100/5)	159.4	9.86	13.04	915	36
NR/Sb <sub>2</sub> O <sub>3</sub> (100/1.25)	142.8	8.38	11.11	850	37
NR/Sb <sub>2</sub> O <sub>3</sub> (100/5)	140.6	7.16	10.75	800	37.5
CR (100)	115.21	13.06	15.54	780	49
CR/AP (100/5)	125.30	13.53	15.87	790	48
CR/Sb <sub>2</sub> O <sub>3</sub> (100/1.25)	112.24	12.82	14.81	750	50
CR/Sb <sub>2</sub> O <sub>3</sub> (100/5)	108.68	12.05	14.01	745	51

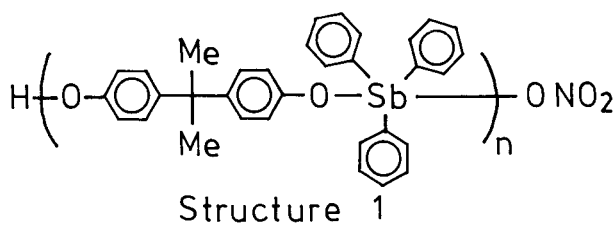
Base formulations (phr): stearic acid: 2, ZnO: 5, sulfur: 2.5, and CBS (*N*-cyclohexylbenzthiazyl sulfenamide): 1.

### Aging and Leaching Tests

Samples were immersed in water for 3 days and toluene for 24 h at 30°C. The heat aging test was carried out at 100°C for 3 days in an electrically heated air circulating oven as per the ASTM D 573 standard procedure.

## RESULTS AND DISCUSSION

The structure of the antimony polymer synthesized by the reaction between bisphenol A and triphenyl antimony dinitrate may be shown as follows.<sup>16</sup>



### Mechanical Properties

Mechanical properties and hardness for both gum and filled vulcanizates of NR and CR with antimony polymers and antimony oxide are presented in Tables I and II. For gum formulation no carbon black or oil were given. The tensile strength, 200% modulus, 300% modulus, and elongation at break of the rubber blends with antimony polymer are higher than the original rubbers. With the addition of antimony trioxide also these mechanical properties do not decrease both for gum and filled

vulcanizates. The increment of the above physical properties of rubber vulcanizates by the addition of the antimony polymer may be due to its better compatibility with rubbers, enhancement of polymer–filler interaction, or it may help in proper curing of the vulcanizates as supported by a higher extent of cure in rheometric study. The major drawbacks of the conventional FR additives such as Sb<sub>2</sub>O<sub>3</sub> are their migration and leaching in contact with solvents and even in air during service. The small molecular additives like Sb<sub>2</sub>O<sub>3</sub> are generally not compatible with the polymer system and under stress this may even initiate cracks or aid in crack propagation. The antimony polymer, on the other hand, has better resistance to leaching and migration due to its polymeric nature and better compatibility with the base rubber systems. This is reflected on the better retention properties of rubber vulcanizates with antimony polymer compared to virgin specimens (Table III). The results are considerably better in the case of heat aging at 100°C for 72 h both for NR and CR with antimony polymer. It appears that the phenolic endgroups of the antimony polymer (Structure 1) act as an antioxidant for both NR and CR rubbers. From this laboratory the antioxidant properties of two other plant products used as FR additives were also found.<sup>9,10</sup>

### Flame Retardancy

The flame retardancy of various rubber vulcanizates containing antimony as antimony polymer and/or oxide has been shown in Figures 1–4. The limiting oxygen index (LOI) of the vulcanizates first increases and finally remains almost con-

**Table II Mechanical Properties of the Filled Rubber Vulcanizates**

Composition of the Rubber Vulcanizates (phr)	T.S. (kg/cm <sup>2</sup> )	Modulus 200% (kg/cm <sup>2</sup> )	Modulus 300% (kg/cm <sup>2</sup> )	EB (%)	Hardness Shore A
NR (100)	222.0	41.5	71.9	650	54
NR/AP (100/5)	224.2	43.5	80.0	650	56
NR/Sb <sub>2</sub> O <sub>3</sub> (100/1.25)	219.9	42.1	73.03	650	55
NR/Sb <sub>2</sub> O <sub>3</sub> (100/5)	220.1	41.6	76.49	647	56
CR (100)	150.0	39.1	74.70	410	60
CR/AP (100/5)	160.4	41.4	76.41	430	63
CR/Sb <sub>2</sub> O <sub>3</sub> (100/1.25)	148.4	40.3	72.8	410	59
CR/Sb <sub>2</sub> O <sub>3</sub> (100/5)	147.6	38.9	75.1	412	60

Base formulations (phr): stearic acid: 2, ZnO: 5, HAF [high abrasion furnace (N 330)]: 40, P. oil: 5.0, sulfur: 2.5, and CBS: 1.

stant with the antimony content in the CR vulcanizates (Fig. 1), but for NR samples there is no effect up to 20 phr of antimony polymer. The simi-

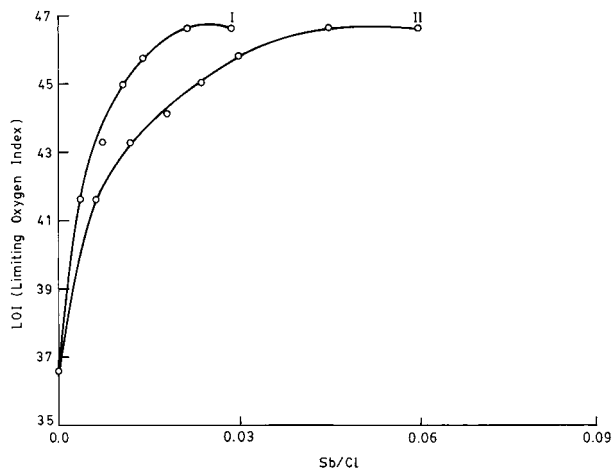
lar trend is observed in the case of Sb<sub>2</sub>O<sub>3</sub> up to 10 phr in the above two cases. Figures 1–4 show the relation between Sb/Cl atomic ratio versus LOI

**Table III Effect of Leaching and Heat Aging on the Mechanical Properties of the Filled Rubber Vulcanizates**

Composition of Rubber Vulcanizates (phr)	Sample Treatment <sup>a</sup>	% Retention of Properties after Treatment				
		T.S.	Mod. 200%	Mod. 300%	EB	Hardness
NR (100)	LW	98.9	97.5	100.0	98.2	99.0
	LT	87.7	84.6	86.2	89.2	93.0
	HA	72.5	70.1	67.6	68.9	110.4
NR/AP (100/5)	LW	99.0	100.0	100.0	99.4	100.0
	LT	93.3	95.0	96.2	95.6	94.5
	HA	80.1	79.6	78.4	79.0	112.5
NR/Sb <sub>2</sub> O <sub>3</sub> (100/1.25)	LW	96.0	96.3	98.2	95.0	98.2
	LT	85.5	87.2	90.2	88.7	91.2
	HA	72.2	71.2	73.0	70.4	115.3
NR/Sb <sub>2</sub> O <sub>3</sub> (100/5)	LW	95.0	96.0	97.0	94.3	96.7
	LT	84.5	83.2	85.3	87.4	90.6
	HA	71.9	70.6	67.9	69.4	116.4
CR (100)	LW	98.5	96.4	96.2	97.1	98.2
	LT	92.5	93.6	93.2	94.4	90.3
	HA	77.5	76.4	75.8	74.3	72.9
CR/AP (100/5)	LW	100.0	99.2	98.9	99.3	118.9
	LT	99.3	99.6	98.8	99.1	98.7
	HA	89.6	88.9	91.4	90.8	110.2
CR/Sb <sub>2</sub> O <sub>3</sub> (100/1.25)	LW	99.2	95.7	95.2	96.7	98.1
	LT	91.1	90.6	90.4	91.2	89.6
	HA	75.4	74.3	74.2	70.6	119.1
CR/Sb <sub>2</sub> O <sub>3</sub> (100/5)	LW	98.1	93.2	92.8	94.8	95.6
	LT	90.2	89.3	88.9	87.8	90.1
	HA	72.1	70.1	68.9	70.2	120.4

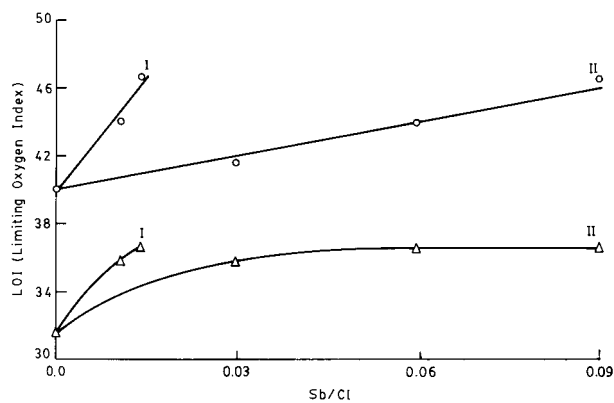
Base formulations and properties of the samples before these treatments are shown in Table II.

<sup>a</sup> LW = Leaching with water for 3 days at 30°C; LT = leaching with toluene for 24 h at 30°C; HA = heat ageing for 72 h at 100°C.

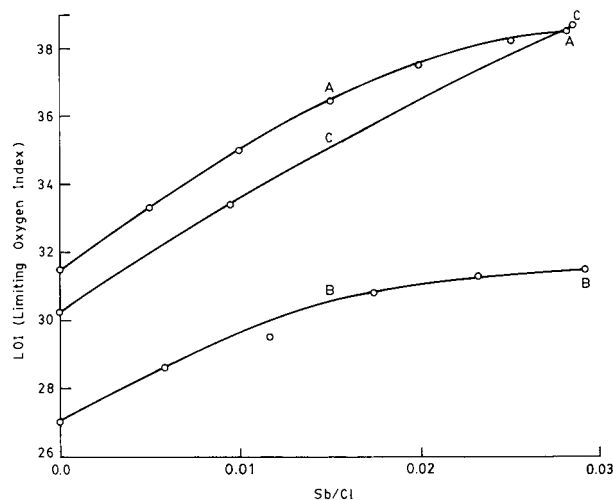


**Figure 1** Variation of LOI value with the Sb/Cl atomic ratio in pure CR rubber vulcanizates (I = Sb as antimony polymer and II = Sb as antimony oxide) using the recipe (phr): Stearic acid: 1.0, MgO: 4.0, NA22: 0.8, and ZnO: 5.0.

values of various rubber specimens containing antimony in the form of either antimony polymer or  $\text{Sb}_2\text{O}_3$ . It is found that the LOI values for CR vulcanizates almost reach a saturation value in both the cases within our instrumental sensitivity. But the antimony polymer, as an FR additive, is about twice as effective as the  $\text{Sb}_2\text{O}_3$ . Similar results were obtained in case of phosphorus flame retardant additives.<sup>9</sup> The greater effectiveness of polymeric FR additives may be due to lower sta-

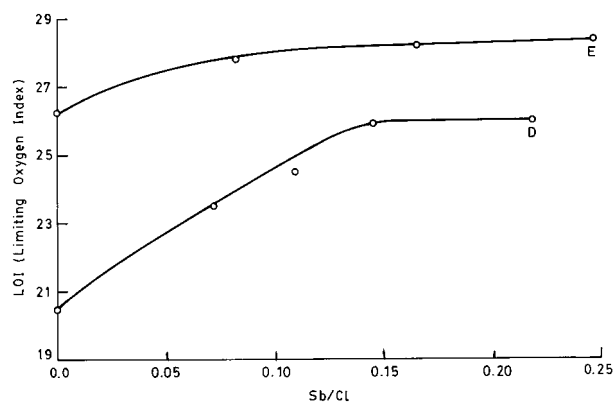


**Figure 2** Variation of LOI value with the Sb/Cl atomic ratio in CR/CINR/PVC (50/25/25) blend and CR/NR/PVC (50/16.64/33.34) blend (I = Sb as antimony polymer, II = Sb as antimony oxide,  $\circ$  for CR/CINR/PVC blends and  $\Delta$  for CR/NR/PVC blends) using the recipe (phr): Stearic acid: 1.0, MgO: 4.0, NA22: 0.8, and ZnO: 5.0.



**Figure 3** Variation of LOI value with Sb/Cl atomic ratio in PVC and polyester compounds (A = PVC 100/DOP 20, B = PVC 100/DOP 40. These curves were constructed utilizing the data of Ref. 20. C = polyester/25% chlorine. This curve was constructed utilizing the data of Ref. 22.)

bility of the C—O bond of Sb—O—C in the antimony polymer (C—O bond strength = 334 kJ/mol) than that of the Sb—O bond of Sb—O—Sb in  $\text{Sb}_2\text{O}_3$  (Sb—O bond strength = 420 kJ/mol). This is consistent with the halogen flame retardant additives (compounds as well as polymers) where the flame retardant effectiveness of halogens decreases as their stability increases. Thus bromine compounds or polymers are more



**Figure 4** Variation of LOI value with Sb/Cl atomic ratio in chlorinated polypropylene compounds (D = chlorinated polypropylene, Cl = 16.7% and E = easily dehydrogenated chlorinated polypropylene, Cl = 7.6%. This figure was constituted utilizing the data of Ref. 24.

effective as fire retardants than corresponding chlorine additive.

It is reported<sup>18,21-23</sup> that the flame retardancy of a chlorine containing polymer varies with the chlorine concentration in the system. For example, the LOI value also increases with the chlorine content of PVC with different doses of DOP.<sup>21</sup> But in case of chlorinated polypropylene (CPP),<sup>24</sup> the reverse is true (Fig. 4) which is due to different chemical reactivity of chlorine present in chlorinated polypropylene. The flame retardancy of chlorine containing polymers can be effectively improved by the addition of antimony in the form of either antimony oxide or antimony polymer, and the LOI value increases with increasing antimony concentration in the system keeping chlorine concentration constant (Figs. 1 and 2). The LOI values of the chlorinated polymers not only depend on the Sb/Cl atomic ratio but also on the initial concentration of chlorine and the availability of chlorine in the polymer. Hence there is no universal relation of LOI with the Sb/Cl atomic ratio for different chlorinated polymers. This is also true for small molecular chlorinated flame retardant additives in nonchlorinated polymers.<sup>22</sup> Even with the same polymer, or different polymer formulations having same initial chlorine concentration, the flame retardancy will vary.

#### Role of the Sb/Cl Atomic Ratio in Flame Retardancy

In order to examine the effect of the Sb/Cl atomic ratio on the flame retardancy of different chlorine containing polymers as well as different polymer compositions with varying doses of antimony in the form of either  $Sb_2O_3$  or antimony polymer, studies have been made with pure CR, CR/ClNR/PVC blends, and CR/NR/PVC blends. The LOI value increases in all the above cases with increasing antimony doses. But for pure CR and the CR/NR/PVC blend specimens a saturation level is obtained after a particular dose of antimony in each case (Figs. 1 and 2). A similar observation was reported in PVC earlier.<sup>21</sup> The data presented by Avento and Touval<sup>21</sup> have been utilized to construct the curve of Figure 3 in this article to show that the saturation level of fire retardancy is obtained at the Sb/Cl atomic ratio of about 0.03. Table IV presents the saturation level of the flame retardancy in various polymers and blends with the antimony-chlorine system. In the present article also the saturation level of CR is obtained at the Sb/Cl atomic ratio at about 0.03 for antimony

polymer and 0.06 for antimony oxide (Fig. 1). In the CR/NR/PVC blend specimens, the LOI value increases continuously (Fig. 2), which is similar to that in case of polyester with 25% of chlorine (Fig. 3). In these cases also the effectiveness of polymeric antimony as fire retardant is much higher than that of  $Sb_2O_3$ .

The limiting value of LOI in case of the CR rubber vulcanizates was found through addition of both  $Sb_2O_3$  and antimony polymer as stated before. A similar type of the limiting LOI value was reported in case of polychloroprene foam where the addition of 35% mixture containing  $(NH_4)_2SO_4$  or melamine-aldehyde condensation product into the polychloroprene foam did not increase the flame resistance.<sup>20</sup> In the case of chlorinated polypropylene<sup>24</sup> the antimony halogen synergism reaches a saturation level at a Sb/Cl atomic ratio of about 0.22 for 16.7% chlorine and 0.25 for 6.7% chlorine (Fig. 4), although the author reported<sup>24</sup> it to be about 0.5.

Attempts have been made to improve the fire retardancy of NR by adding antimony oxide or antimony polymer. No detectable enhancement of LOI was observed even by adding up to 20 phr antimony polymer or 30 phr antimony oxide along with 30 phr CR. The nonburning rating NB for NR was made through the addition of 25 phr  $Sb_2O_3$  and 50 phr chlorowax70 with 50% reduction of tensile strength and 73% reduction of tear strength.<sup>19</sup> This high flammability of NR may be due to its chemical nature and constituents. NR was reported<sup>20</sup> to form flammable volatile products at 300°C and is completely volatilized at about 350–360°C. So when the pilot flame (temperature  $\sim 640^\circ C$ ) is brought to the surface of the NR specimen, the polymer is volatilized and autoignition occurs. Similar results are also found in the case of NBR. The low LOI value of NBR may be due to the presence of butadiene moiety, which degrades to form volatile flammable products although the acrylonitrile (AN) moiety may impart flame retardancy through char formation. NBR with very high AN content may show higher fire retardancy.

#### Prospect of $Sb_2O_3$ Alone as Flame Retardant

Despite a few examples which suggest that  $Sb_2O_3$  alone can act as an effective flame retardant without addition of halogen,<sup>5-7</sup> it is not possible in this article to show the flame retardancy of  $Sb_2O_3$  alone in NR and NBR vulcanizates even by adding

**Table IV The Saturation Level of Fire Retardancy in Various Polymers and Blends with Antimony–Chlorine Systems**

Polymers/ Blends	Chlorine		Saturated Level Sb/Cl Ratio		Reference
	Nature	%	for Sb <sub>2</sub> O <sub>3</sub>	for Sb-polymer	
PVC/DOP <sup>a</sup> (20)	Secondary	47.3	0.03	—	21
PVC/DOP (40)	Secondary	40.6	0.03	—	21
CR	Tertiary	40.0	0.06	0.03	this work
CPP	Primary	16.7	0.22	—	24
CPP	Tertiary	6.7	0.25	—	24
CR/NR/PVC	Secondary & Tertiary	40.0 (overall)	0.09	0.03	this work

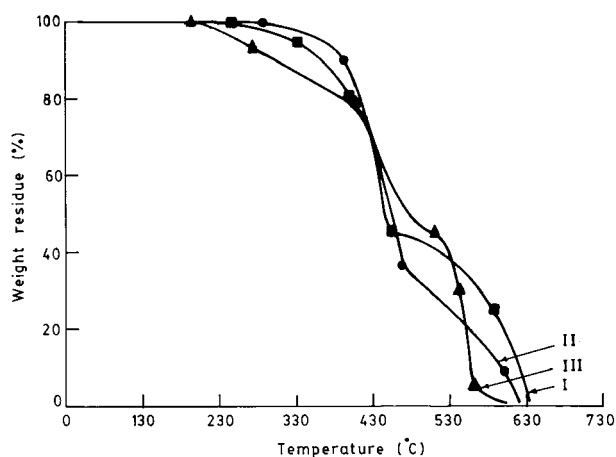
<sup>a</sup> DOP = Dioctyl phthalate.

up to 10 and 20 phr of Sb<sub>2</sub>O<sub>3</sub>, and 20 and 15 phr of antimony polymer, respectively, without adding halogen. Our observations are supported by the results of Pitts, Scott, and Powell<sup>23</sup> in the case of flexible urethane foam even by adding up to 60 phr Sb<sub>2</sub>O<sub>3</sub>. Similar results were also found in case of polypropylene, where addition of 20 phr Sb<sub>2</sub>O<sub>3</sub> causes no effect.<sup>24</sup> The flame retardancy of Sb<sub>2</sub>O<sub>3</sub> in absence of halogen is mostly found in case of polymers containing higher amount of oxygen such as sorbitol based polyether<sup>6</sup> and polyester glass laminates.<sup>7</sup> No explanation for such observations was offered by these workers.

#### Thermal Analysis for Flame Retardancy Evaluation

The flame retardancy of the CR and NR vulcanizates with antimony in the form of antimony polymer and Sb<sub>2</sub>O<sub>3</sub> was also tested from thermogravimetric analysis (TGA) (Figs. 5 and 6). The initial decomposition temperature (IDT) and 50% decomposition temperature (DT<sub>50</sub>) are presented in Table V. The results have been checked independently by isothermally heating the samples in a muffle furnace at appropriate temperature and the loss in weight in each case was found almost identical with those obtained by TGA. Addition of FR additive to polymers reduces the initial decomposition temperature of the vulcanizates. The antimony polymer in NR vulcanizates reduced the IDT by 65°C, whereas equivalent amount of antimony as antimony oxide (1.25 phr) only lowered by 5°C. Even by adding four times of antimony as antimony oxide (5 phr) the reduction is less than half (30°C) of the antimony polymer. So though the LOI of the NR vulcanizates has not been raised by adding only antimony in the form of

either antimony polymer or oxide, the IDT has been reduced very effectively by adding antimony polymer. This may be due to higher effectiveness of antimony in antimony polymer. In case of CR vulcanizates, the reduction of IDT is more in case of 5 phr of antimony oxide. This is due to the fact that the determining factor of lowering the IDT is the Sb/Cl ratio and as the antimony amount increases the IDT value decreases. Similar observation was reported<sup>25</sup> in case of nylon 6 polymer, where IDT lowered by 50°C by addition of hexabromobiphenyl FR additive. The efficiency of the flame retardant additives would be high if the decomposition of the substrates is much faster than that of original one. The FR will inhibit the flame by the vapor phase mechanism through the

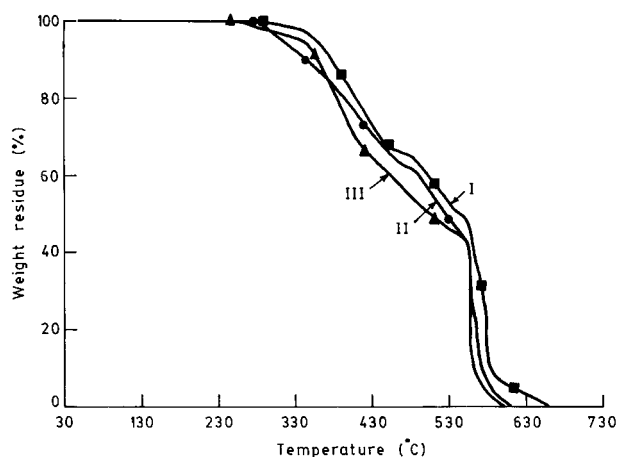


**Figure 5** TG thermogram for NR vulcanizates (I = original NR, II = NR with 5 phr antimony polymer, III = NR with 5 phr antimony oxide) using the recipe (phr): stearic acid: 2.0, ZnO: 5.0, HAF (N330): 40.0, P. oil: 5.0, sulfur: 2.5 and CBS: 1.0

formation of nonflammable volatile gases, or by the condensed phase mechanism where there is high amount of carbonaceous product. In these cases the flame retardancy may be through the vapor phase mechanism as the amount of char was not increased in any case with addition of FR additive (Figs. 4 and 5).

## CONCLUSIONS

1. Antimony oxide,  $\text{Sb}_2\text{O}_3$ , is found to provide fire retardancy to polymers when used in combination with halogen compounds, in polymers, and in some special cases it was reported to be effective even in the absence of halogen.
2. Fire retardancy of the antimony–halogen systems depends on the Sb/halogen (in this case Sb/Cl) atomic ratio, but it does not solely depend on it. The nature of the polymer, the nature of antimony compound, the nature of halogen, and the presence of other additives in polymers influence the fire retardancy of the system.
3. The LOI of polymer systems increases with the Sb/Cl atomic ratio and attains almost a constant value. However, in the case of CR/NR/PVC blends and polyester with 25% chlorine the LOI continuously increases with the increase of Sb/Cl atomic ratio.
4. The antimony polymer is almost twice as ef-



**Figure 6** TG thermogram for CR vulcanizates (I = original CR, II = CR with 5 phr antimony polymer, III = CR with 5 phr antimony oxide) using the recipe (phr): stearic acid: 1.0, MgO: 4.0, NA22: 0.8, HAF(N330): 40.0, P. oil: 5.0 and ZnO: 5.0)

**Table V** Decomposition Temperatures of NR and CR Filled Vulcanizates with Antimony Polymer/ $\text{Sb}_2\text{O}_3$

Compositions of Rubber Vulcanizates <sup>a</sup> (phr)	IDT, °C	DT <sub>50</sub> , °C
NR (100)	280	440
NR/AP (100/5)	215	445
NR/ $\text{Sb}_2\text{O}_3$ (100/1.25)	275	460
NR/ $\text{Sb}_2\text{O}_3$ (100/5)	250	455
CR (100)	290	540
CR/AP (100/5)	280	530
CR/ $\text{Sb}_2\text{O}_3$ (100/1.25)	275	540
CR/ $\text{Sb}_2\text{O}_3$ (100/5)	250	500

<sup>a</sup> Base formulations (phr): stearic acid: 2, ZnO: 5, HAF (N330): 40, P. oil: 5, sulfur: 2.5, and CBS: 1.

fective a fire retardant, as  $\text{Sb}_2\text{O}_3$ . This may be due to the lower stability of the Sb—O—C bond present in the former than that of the Sb—O—Sb bond in the latter.

5. The antimony polymer is more compatible with other polymers than  $\text{Sb}_2\text{O}_3$ , which is reflected in their mechanical properties.
6. The antimony polymer is found to exhibit antioxidant property to rubbers possibly due to the presence of phenolic moiety in its structure.

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