CHAPTER IV

RESULT AND DISCUSSION

Flame Retardancy Evaluation

In this study, the flammability is expressed on percentage limiting oxygen index (%LOI). Each value performed an average LOI value, which was obtained from 5 individual LOI values of each sample.

The flame retardancy of zinc stannate and zinc hydroxystannate on polypropylene were obtained by comparing to antimony trioxide at loading volume 2.5-10.0% by weight of based polypropylene. Limiting oxygen index results for the prepared composition were listed in table 4-1. The relationship between the flammability and content of flame retardant were shown in fig.4-1.

Table 4-1 Effect of ZS, ZHS and Sb_2O_3 on the flammability of polypropylene.

Flame retardant	**%LOI**		
	ZS	**ZHS**	**Sb_2O_3**
No additive	17.2	17.2	17.2
2.5% additive	17.8	17.8	17.8
5.0% additive	18.4	18.7	17.8
7.5% additive	18.5	19.2	17.9
10.0% additive	18.4	19.7	17.6

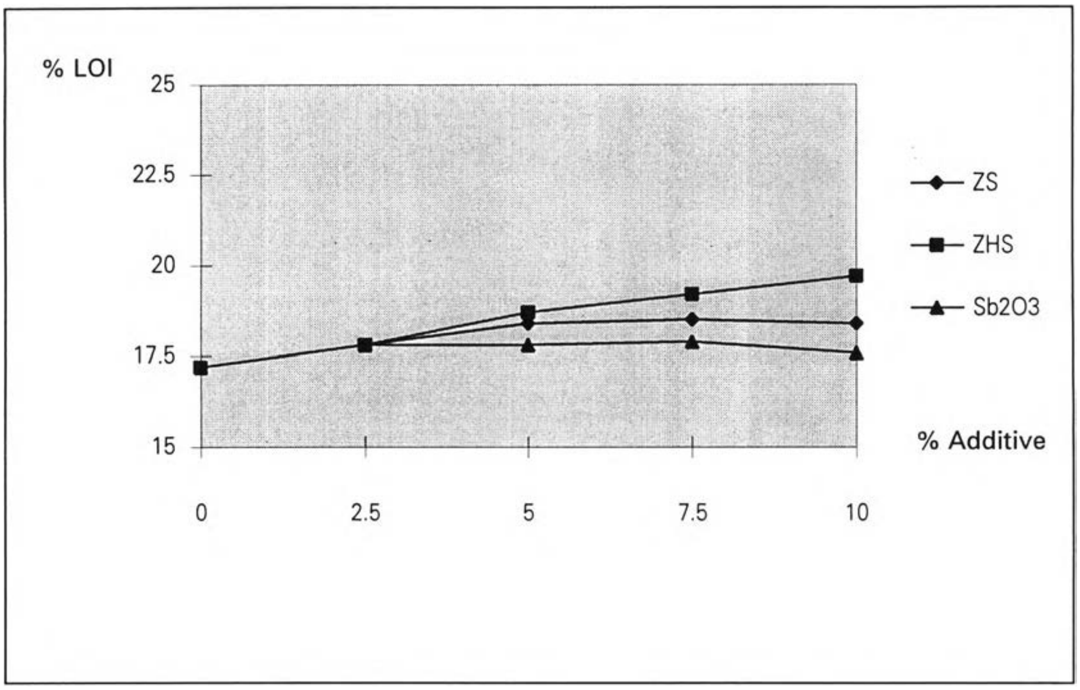

Figure 4-1 Relationship between the flammability and flame retardant content of polypropylene containing ZS, ZHS and Sb_2O_3 as flame retardant.

The flammability of flame-retarding polypropylene contained decabromodiphenyl oxide and alumina trihydrate as flame retardant were shown in table 4-2 and 4-3. The relationship between LOI and flame retardant concentration of DBDPO and ATH , were shown in figure 4-2 and 4-3.

Table 4-2 Effect of DBDPO as flame retardant in polypropylene.

Flame Retardant	**% LOI**	**Δ%LOI**
no additive	17.2	-
5% DBDPO	19.2	2.0
10% DBDPO	20.3	3.1
20% DBDPO	21.4	4.2
30% DBDPO	22.3	5.1

Table 4-3 Effect of ATH as flame retardant in polypropylene.

Flame Retardant	**%LOI**	**Δ%LOI**
no additive	17.2	-
10% ATH	18.8	1.6
20% ATH	19.2	2.0
30% ATH	19.8	2.6
40% ATH	20.8	3.6
50% ATH	21.5	4.3

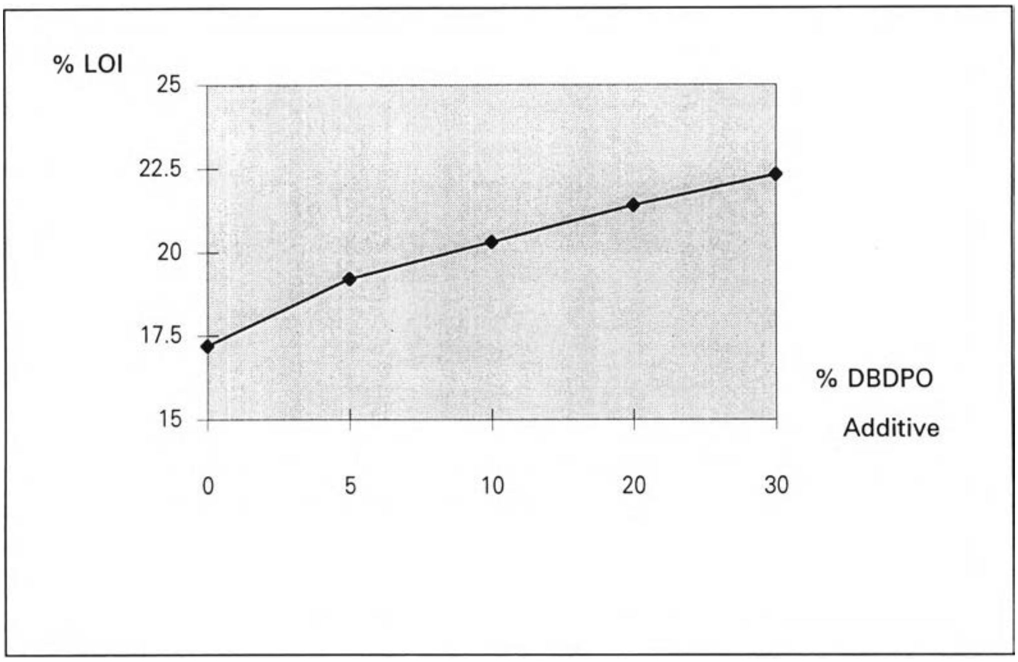

Figure 4-2 Relationship between the flammability and DBDPO content of flame-retarding polypropylene.

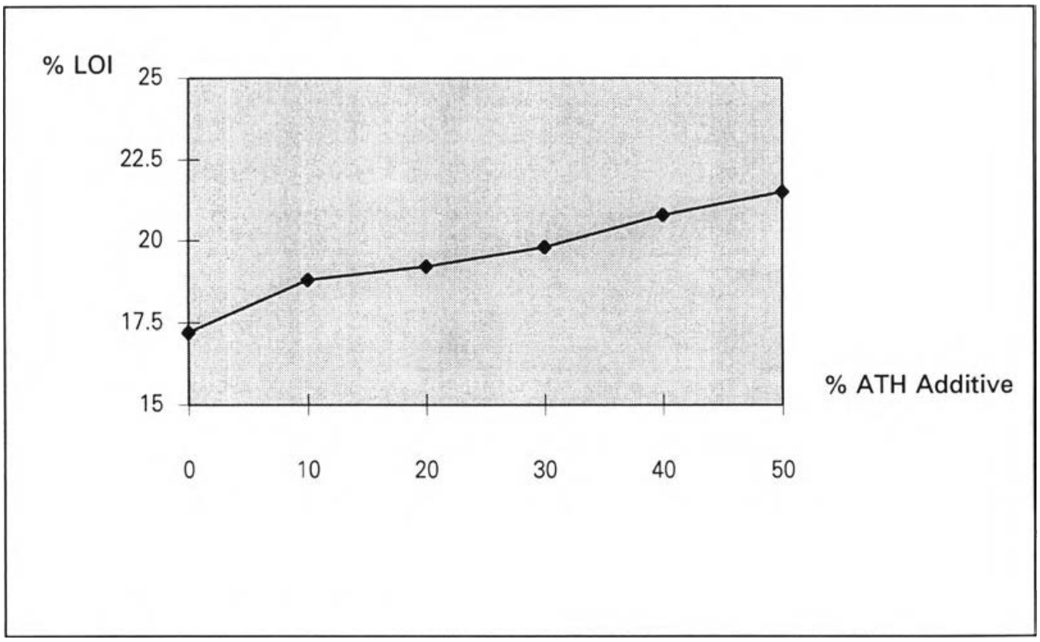

Figure 4-3 Relationship between the flammability and ATH content of flame-retarding polypropylene.

The synergistic effect of decabromodiphenyl oxide with zinc stannate and zinc hydroxystannate on the flammability of polypropylene was compared to antimony trioxide by varying % content of DBDPO from 5,10,20, and 30% , respectively.

The LOI data in the result of brominated polypropylene containing ZS are listed in table 4-4. The relationship between the flammability and DBDPO content of polypropylene containing ZS as flame retardant at 2.5, 5.0 and 7.5% level loading, were shown in figure 4-4.

The significant synergism effect of decabromodiphenyl oxide with zinc hydroxystannate on the flammability of polypropylene, were shown in table 4-5. The relationship between the flammability and DBDPO content of ZHS flame-retardant polypropylene at 2.5, 5.0 and 7.5% ZHS level loading, were shown in figure 4-5.

The combination of decabromodiphenyl oxide with antimony trioxide at level 2.5, 5.0 and 7.5%, shown the synergism effect of polypropylene containing DBDPO at level 5, 10, 20, and 30%, respectively.(table 4-6) The synergistic relationship between the flammability and DBDPO content, was clearly observed on figure 4-6.

The figure 4-7 was the comparison of the efficiency of zinc stannate, zinc hydroxystannate and antimony trioxide as flame retardant in polypropylene at 5% content which synergisted with decabromodiphenyl oxide at the level of 5%, 10%, 20% and 30% , respectively.

Table 4-4 Synergistic effect of DBDPO with ZS on the flammability of polypropylene.

Flame Retardant	%LOI	Δ%LOI
no additive	17.2	-
PP.flame (TPI)	26.2	9.0
2.5% ZS + 5% DBDPO	19.9	2.7
10% DBDPO	21.3	4.1
20% DBDPO	22.1	4.9
30% DBDPO	23.4	6.2
5.0% ZS + 5% DBDPO	20.2	3.0
10% DBDPO	20.8	3.6
20% DBDPO	21.3	4.1
30% DBDPO	22.0	4.8
7.5% ZS + 5% DBDPO	20.0	2.8
10% DBDPO	20.4	3.2
20% DBDPO	21.4	4.2
30% DBDPO	22.2	5.0

Table 4-5 Synergistic effect of DBDPO with ZHS on the flammability of polypropylene

Flame Retardant	%LOI	Δ%LOI
no additive	17.2	-
PP.flame (TPI)	26.2	9.0
2.5% ZHS + 5% DBDPO	19.8	2.6
10% DBDPO	21.8	3.6
20% DBDPO	23.1	5.9
30% DBDPO	24.0	6.8
5.0% ZHS + 5% DBDPO	20.2	3.0
10% DBDPO	22.3	5.1
20% DBDPO	23.2	6.0
30% DBDPO	24.5	7.3
7.5% ZHS + 5% DBDPO	20.2	3.0
10% DBDPO	22.1	4.9
20% DBDPO	23.4	6.2
30% DBDPO	24.7	7.5

Table 4-6 Synergistic effect of DBDPO with Sb_2O_3 on the flammability of polypropylene

Flame Retardant	%LOI	Δ%LOI
no additive	17.2	-
PP.flame (TPI)	26.2	9.0
2.5% Sb_2O_3 + 5% DBDPO	22.5	5.3
10% DBDPO	23.7	6.5
20% DBDPO	24.7	7.5
30% DBDPO	25.5	8.3
5.0% Sb_2O_3 + 5% DBDPO	22.6	5.4
10% DBDPO	23.6	6.4
20% DBDPO	24.4	7.2
30% DBDPO	25.5	8.3
7.5% Sb_2O_3 + 5% DBDPO	22.5	5.3
10% DBDPO	23.4	6.2
20% DBDPO	23.7	6.5
30% DBDPO	24.0	6.8

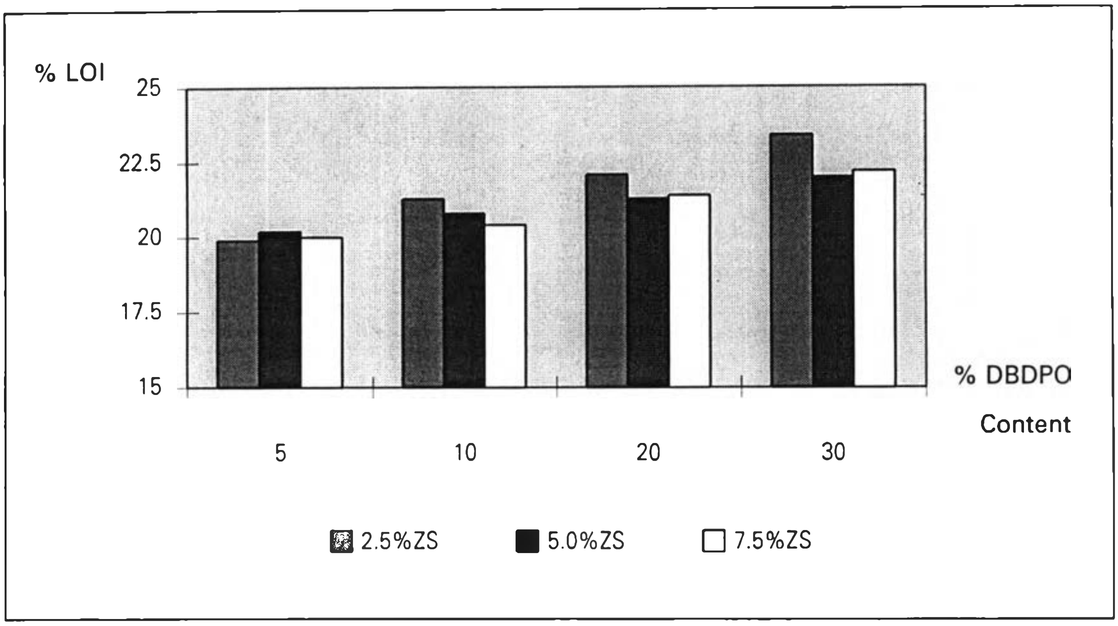

Figure 4-4 Synergistic relationship between the flammability and DBDPO content of polypropylene containing 2.5, 5.0 and 7.5% ZS.

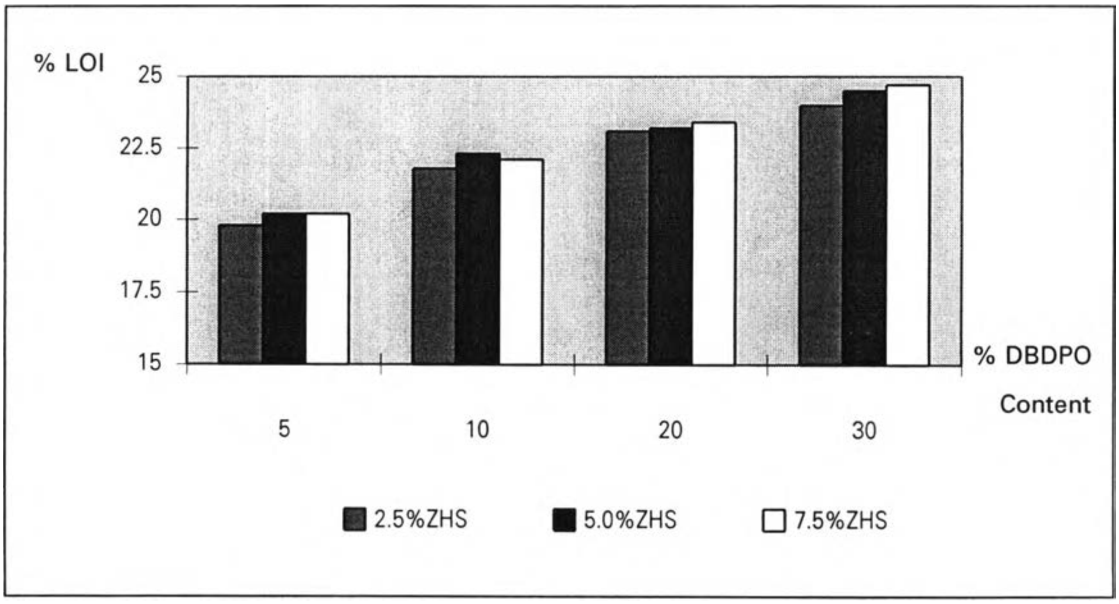

Figure 4-5 Synergistic relationship between the flammability and DBDPO content of polypropylene containing 2.5, 5.0 and 7.5% ZHS.

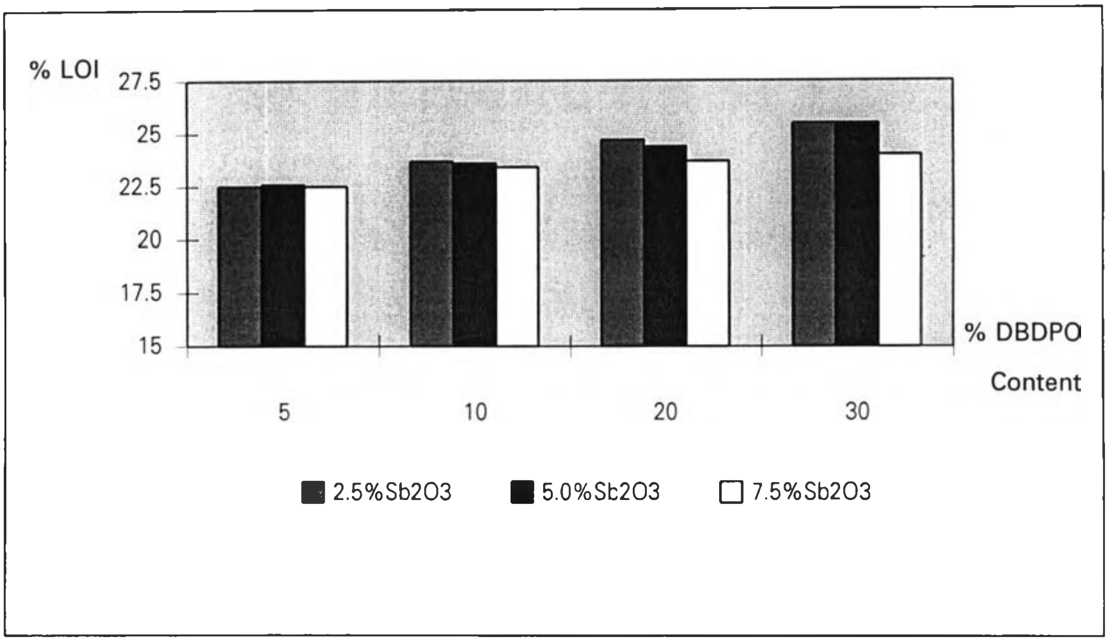

Figure 4-6 Synergistic relationship between the flammability and DBDPO content of polypropylene containing 2.5, 5.0 and 7.5% Sb_2O_3.

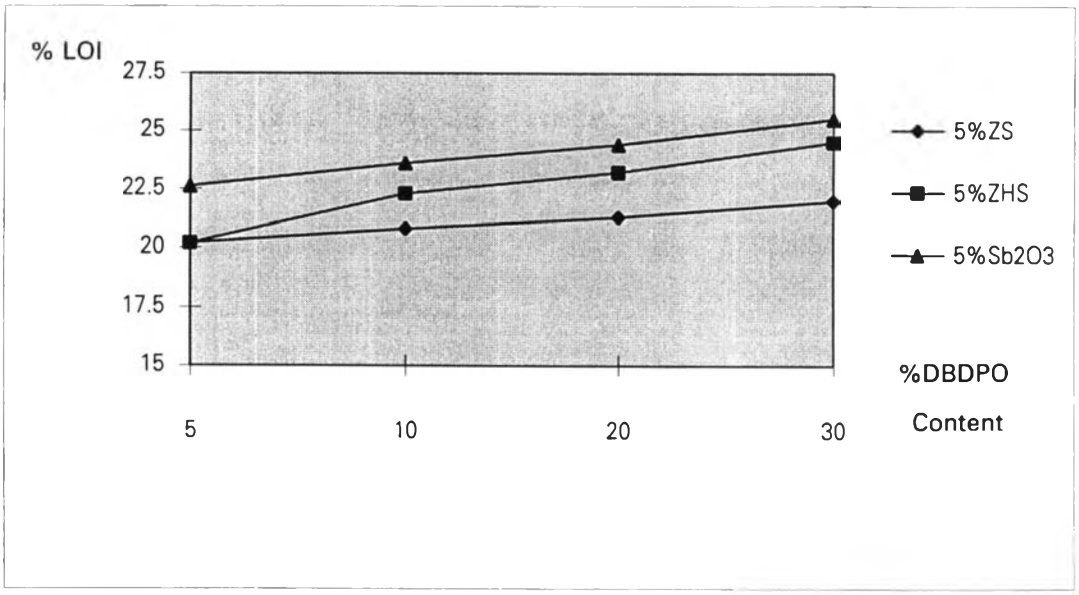

Figure 4-7 Synergistic effect of DBDPO on the flammability of polypropylene containing 5% ZS, ZHS and Sb_2O_3.

From figure 4-1, it could be seen that zinc stannate, zinc hydroxy stannate and antimony trioxide had no significantly effect on the flammability of polypropylene. However, their observation was in agreement with the generally accepted fact that hydroxystannate system was more effective flame retardants, on the equal content, than zinc stannate and antimony trioxide. Whereas the limiting oxygen index of polypropylene when treated with decabromodiphenyl oxide, was increased from 17.2 to 22.3 with increasing % content of flame retardant from 0-30% as shown in figure 4-2.

The observed data from table 4-3 and figure 4-3 indicated that the effectiveness of alumina trihydrate as flame retardant is less than decabromodiphenyl oxide.

A further improvement in flame-retardant efficiency of zinc stannate, zinc hydroxystannate and antimony trioxide are observed when synergisted with decabromodiphenyl oxide. The results from table 4-4 to table 4-6 presented that the flame retardancy of polypropylene treated with ZS was enhanced about 2-6 units when used with brominated compound at the various level contents. Whereas LOI value of polypropylene treated with ZHS was increased about 2-8 units when combined with brominated compound at 5% - 30% level content. Besides, these LOI values were higher than those of polypropylene containing only the brominated additive or inorganic tin additive. The results clearly indicated that inorganic tin compounds had synergism effect to brominated compound in polypropylene, were quite similar to the synergistic of antimony trioxide and brominated compound.

The flame retardancy evaluation (LOI comparison) performed that zinc stannate considered to be less effective as compare with antimony trioxide in any content of brominated compound at level of 5% in polypropylene. However, the flame retardancy of zinc hydroxystannate system were considerably effective as good as antimony trioxide system in any content of decabromodiphenyl oxide. The data were presented in figure 4-7.

From table 4-4 to table 4-6, the LOI value of commercial flame-retarding polypropylene was 26.2 which this flame retardancy was not more significantly effective than these of polypropylene containing 7.5% ZHS and 30% DBDPO (24.7). In the observation of the smoke production of the burning plastics , it could be seen that both of tin compounds produced significant reductions in smoke evolution by comparing to antimony trioxide in the flame-retarded combination with DBDPO compound.

Hence, the zinc hydroxystannate have been shown to impart properties to brominated polypropylene, in terms of flammability, and the improvements in performance of smoke suppressant were clearly to those exhibited by the commercially available antimony trioxide.

4.1 Mechanical Properties Measurement

The physical properties of the finished product were measured according to ASTM D 638-58T . An average of five specimens was considered as representative value. The physical properties results of flame-retarding polypropylene were tabulated in table 4-7, 4-8, and 4-9. The relationship between decabromodiphenyl oxide content and tensile strength of polypropylene containing ZS , ZHS and Sb_2O_3 as flame retardant were shown in figure 4-8, 4-9 and 4-10, respectively.

The relationship between decabromodiphenyl oxide content and modulus of elasticity of polypropylene containing ZS , ZHS and Sb_2O_3 at % loading 2.5%, 5.0% and 7.5% as flame retardant, were shown in figure 4-11, 4-12 and 4-13 , respectively.

The effect of decabromodiphenyl oxide content on the impact strength of ZS , ZHS and Sb_2O_3 flame-retarding polypropylene, were shown in figure 4-14, 4-15 and 4-16, respectively.

Table 4-7 Mechanical properties of polypropylene containing ZS and DBDPO.

Flame Retardant	Tensile Strength (PSI)	Modulus of Elasticity (10^5 PSI)	Impact Strength (kJ/m^2)
No additive	5315	1.047	210.83
PP. flame (TPI)	4310	1.090	210.91
2.5 % ZS + 5 % DBDPO	4574	1.186	210.51
10 % DBDPO	4519	1.255	210.25
20 % DBDPO	4149	1.307	210.00
30 % DBDPO	3951	1.393	209.87
5.0 % ZS + 5 % DBDPO	4645	1.235	209.48
10 % DBDPO	4470	1.331	209.64
20% DBDPO	4154	1.188	209.67
30 % DBDPO	3815	1.351	210.18
7.5 % ZS + 5 % DBDPO	4600	1.242	210.26
10 % DBDPO	4444	1.317	210.14
20 % DBDPO	4176	1.378	210.23
30 % DBDPO	3909	1.328	210.15

Table 4-8 Mechanical properties of polypropylene containing ZHS and DBDPO.

Flame Retardant	**Tensile Strength (PSI)**	**Modulus of Elasticity (10^5 PSI)**	**Impact Strength (kJ/m^2)**
No additive	5315	1.047	210.83
PP. flame (TPI)	4310	1.090	210.91
2.5 % ZHS +5 % DBDPO	4550	1.171	210.37
10 % DBDPO	4299	1.263	210.44
20 % DBDPO	3974	1.301	210.27
30 % DBDPO	3655	1.405	210.19
5.0 % ZHS +5 % DBDPO	4609	1.230	210.11
10 % DBDPO	4435	1.306	210.67
20% DBDPO	4150	1.302	210.83
30 % DBDPO	3882	1.232	210.64
7.5 % ZHS +5 % DBDPO	4498	1.218	210.55
10 % DBDPO	4443	1.274	210.52
20 % DBDPO	4085	1.276	210.49
30 % DBDPO	3743	1.374	210.53

Table 4-9 Mechanical properties of polypropylene containing Sb_2O_3 and DBDPO.

Flame Retardant	Tensile Strength (PSI)	Modulus of Elasticity (10^5 PSI)	Impact Strength (kJ/m^2)
No additive	5315	1.047	210.83
PP. flame (TPI)	4310	1.090	210.91
2.5 % Sb_2O_3+5 % DBDPO	4905	1.222	210.30
10% DBDPO	4768	1.309	210.40
20% DBDPO	4381	1.387	210.44
30 % DBDPO	4007	1.465	210.44
5.0 % Sb_2O_3+5 % DBDPO	4917	1.271	210.51
10 % DBDPO	4412	1.375	210.45
20% DBDPO	4272	1.379	210.52
30 % DBDPO	4144	1.282	210.44
7.5 % Sb_2O_3+5 % DBDPO	4926	1.217	210.26
10 % DBDPO	4714	1.154	210.48
20 % DBDPO	4317	1.335	210.26
30 % DBDPO	4006	1.188	210.14

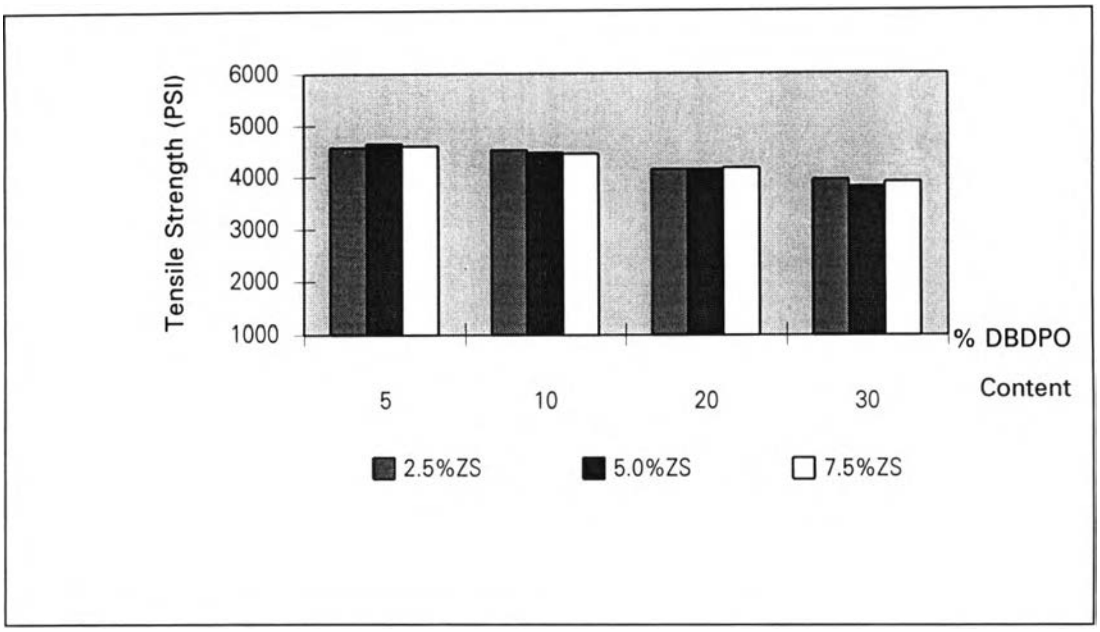

Figure 4-8 Effect of ZS and DBDPO content on tensile strength of polypropylene

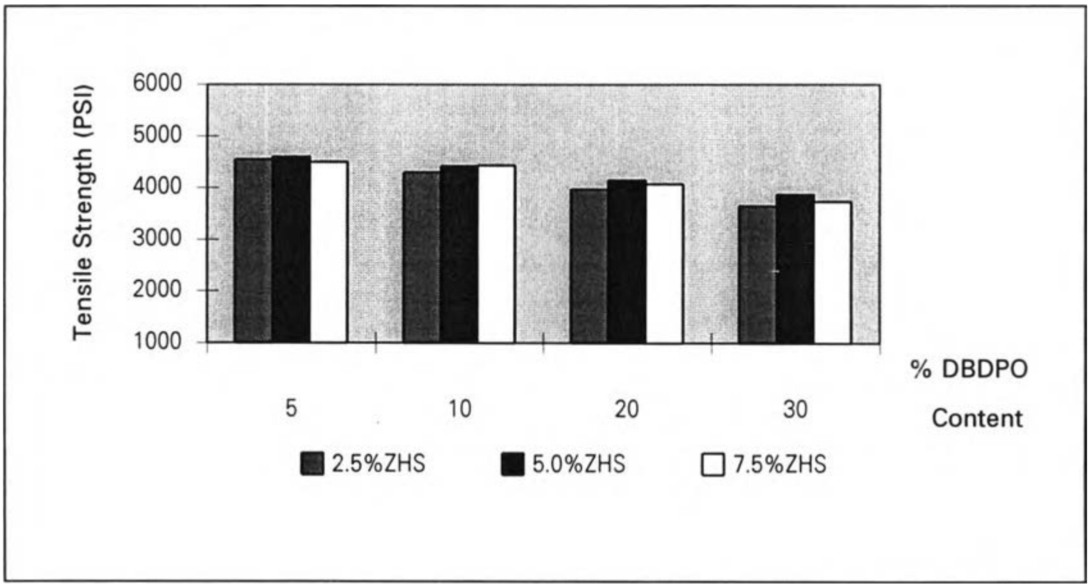

Figure 4-9 Effect of ZHS and DBDPO content on tensile strength of polypropylene

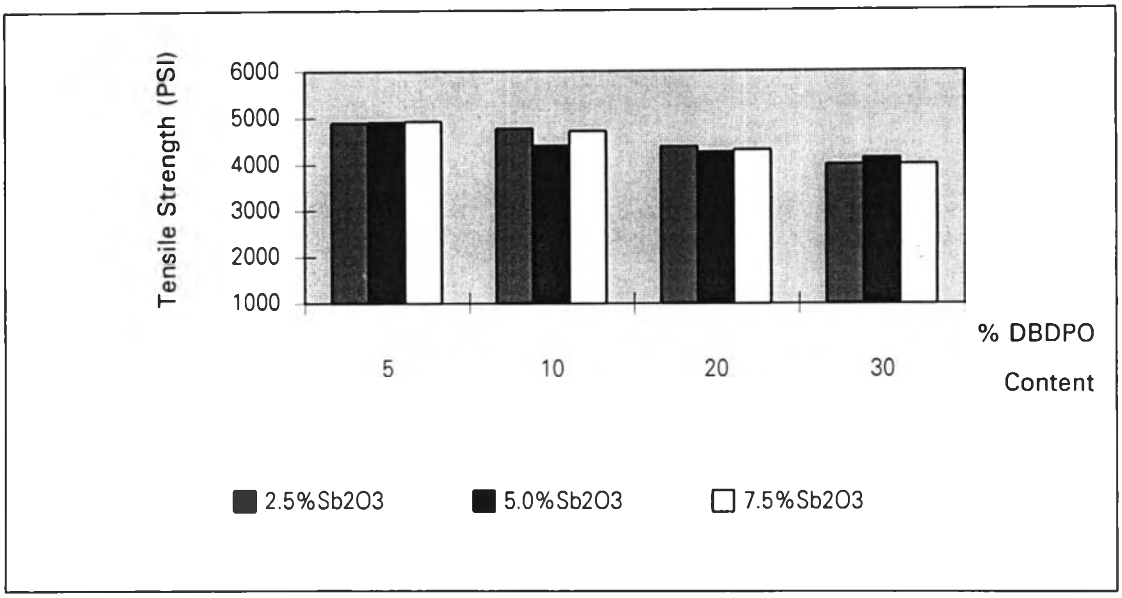

Figure 4-10 Effect of Sb_2O_3 and DBDPO content on tensile strength of polypropylene

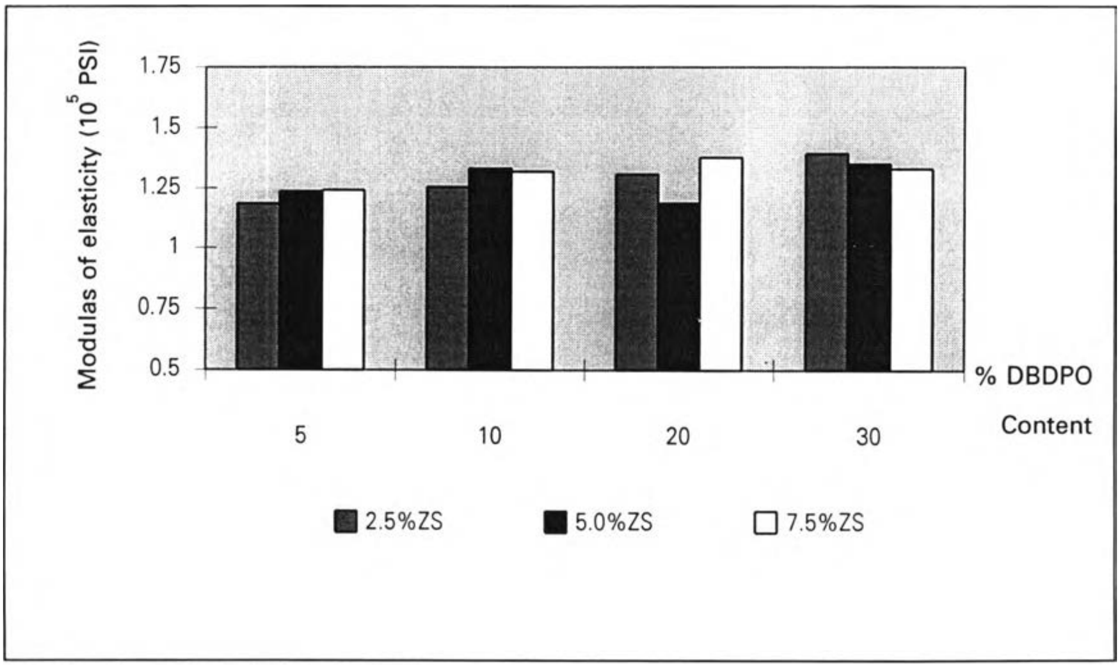

Figure 4-11 Effect of ZS and DBDPO content on modulus of elasticity of polypropylene

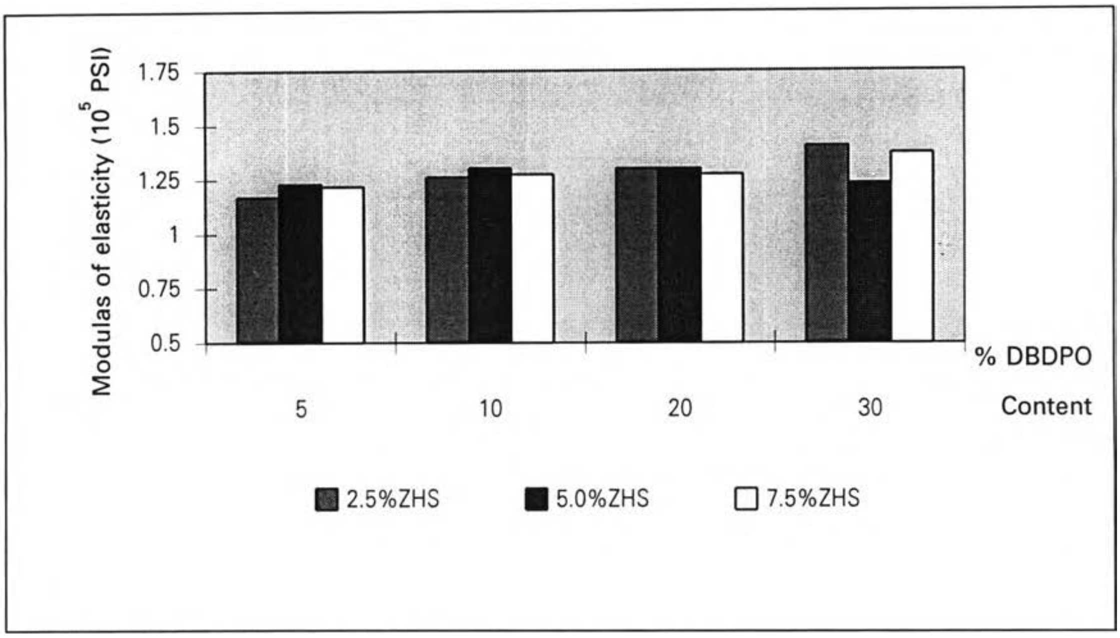

Figure 4-12 Effect of ZHS and DBDPO content on modulus of elasticity of polypropylene

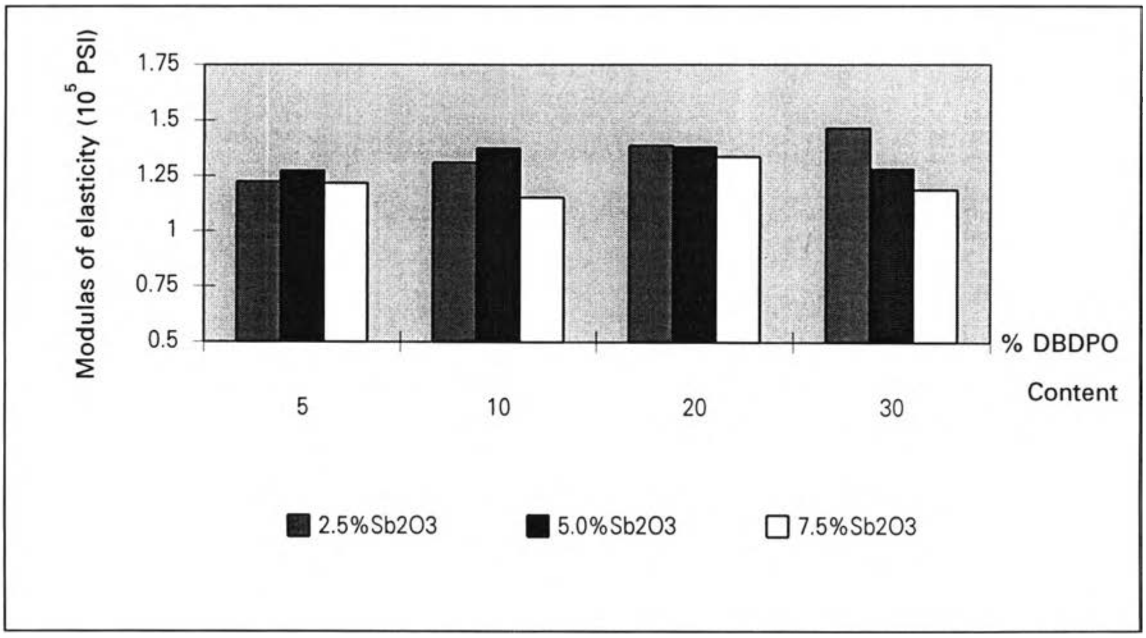

Figure 4-13 Effect of Sb_2O_3 and DBDPO content on modulus of elasticity of polypropylene

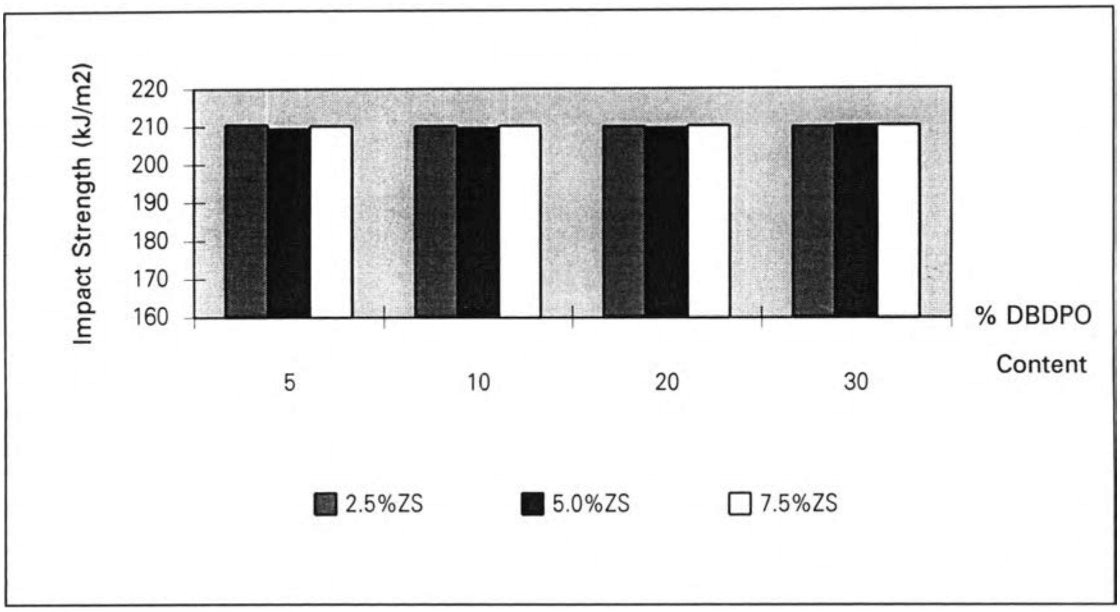

Figure 4-14 Effect of ZS and DBDPO content on impact strength of polypropylene

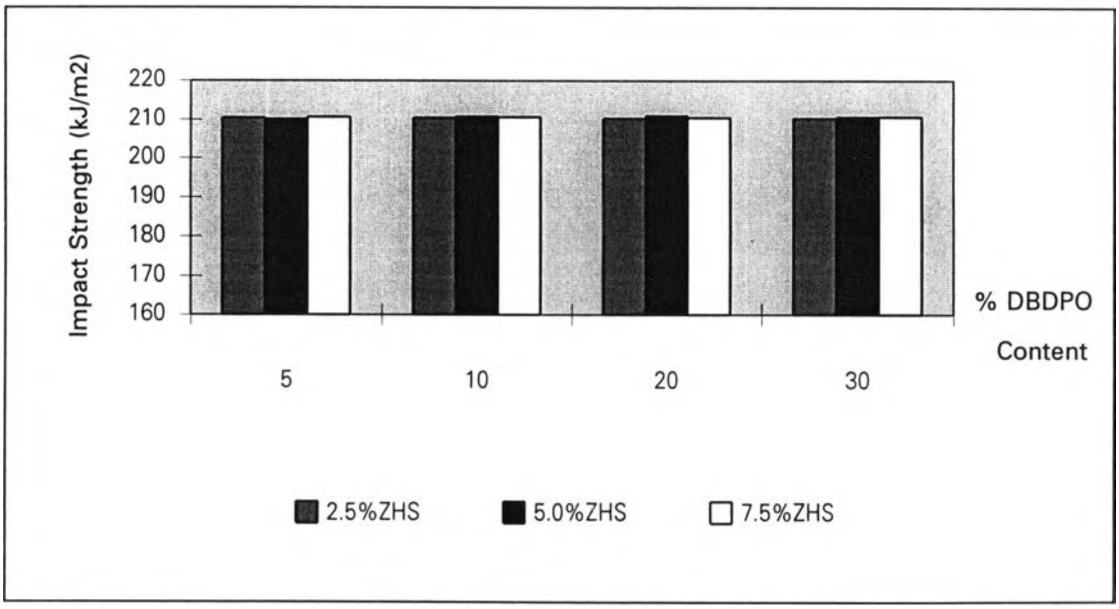

Figure 4-15 Effect of ZHS and DBDPO content on impact strength of polypropylene

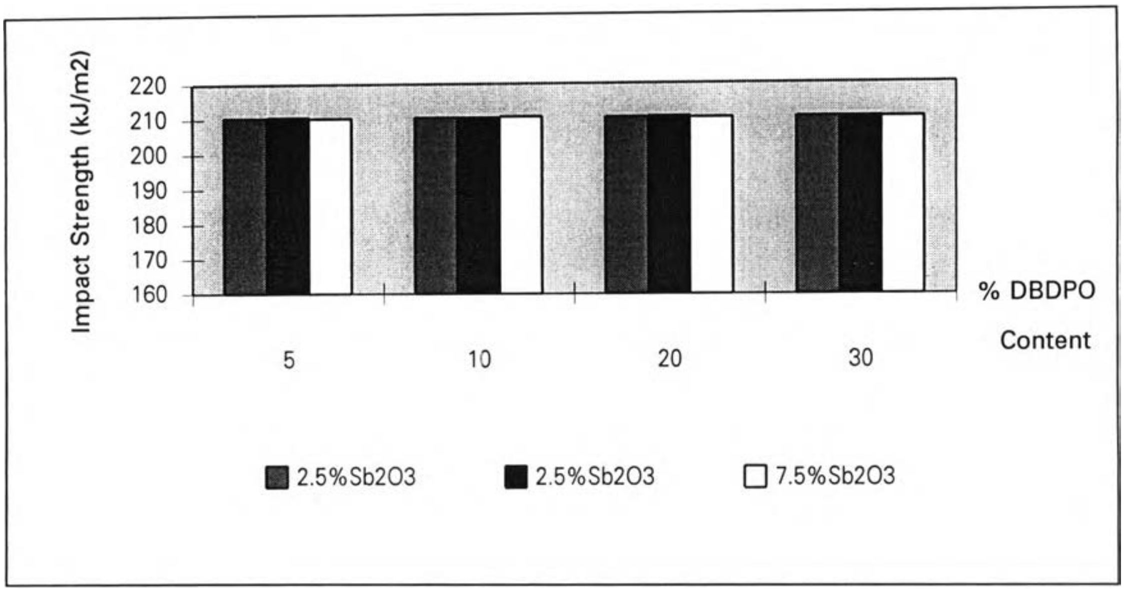

Figure 4-16 Effect of Sb_2O_3 and DBDPO content on impact strength of polypropylene

It would be of academic interest to show the effect of ZS, ZHS and Sb_2O_3 on the physical properties of plastics, especially since the brominated compound is the major compound of the flame retardant mixtures. Therefore, any consideration of changes in physical properties must included the entire combination.

The data obtained from table 4-7, 4-8 and 4-9 showed that the changes in physical properties were depended on the characteristics of the brominated compound but the impact strength was exceptionally.

From figure 4-8 to figure 4-13, it could be seen that the loading content of brominated compound trend to reduced tensile strength while raising the modulus of elasticity of flame-retarding polypropylene containing ZS, ZHS and Sb_2O_3 at level 2.5%, 5.0% and 7.5%, respectively.

The zinc stannate, zinc hydroxystannate and antimony trioxide which combined with decabromodiphenyl oxide flame retardant had a little effect on impact strength as shown in figure 4-14 to figure 4-16.

4.2 Mechanistic Studies.

4.2.1 Elemental Analysis.

The study on the mode of action of ZS and ZHS as flame retardant in the brominated polypropylene was carried out by elemental analysis using neutron activation analysis. The elemental analysis of the residue involatile carbonaceous char formed when the resins were completely burnt were shown in figure A-1 to figure A-12 and summarized on table 4-10. The relevant data were present in table A-1 to table A-4.

Table 4-10 Residual char yields and extents of elemental volatilization from brominated polypropylene samples during combustion in air.

Sample	Char Yields (%)	Elemental Volatilization (%)				Primary Phase of Action
		Br	Sn	Zn	Sb	
10%DBDPO	1.02	N.D.*	N.D.	N.D.	N.D.	-
10%DBDPO: 5% ZHS	4.13	85.00	86.92	62.63	-	condensed+vapor
10%DBDPO: 5 % ZS	4.62	87.59	95.70	56.45	-	condensed+vapor
10%DBDPO: 5% Sb_2O_3	1.10	99.58	-	-	93.29	vapor

*N.D. = Not Determined.

Table 4-10 showed that the yield of involatile carbonaceous char, formed when brominated polypropylene was completely burnt, was more than 4 times when 5% of zinc stannate or zinc hydroxystannate were added to the plastic. This observation was consistent with condensed phase retardation.

Elemental analysis of the residue suggested that in the case of zinc stannate and zinc hydroxystannate, only partial fraction of the zinc was volatilized, A very significant proportion of both zinc and tin were volatilized from the zinc stannate and zinc hydroxystannate-containing polypropylene which could be indicative of vapor phase action. Antimony trioxide, which was undergone almost complete volatilization in the polymer, showed little char enhancing behavior and operated primarily in the vapor phase.[17]

Hence, this investigation suggested that inorganic tin-based flame retardants operated in both the condensed and vapor phases.

4.2.2 Thermal Analysis

Further mechanistic information could be deduced from thermoanalytical measurements. The effects of zinc stannate and zinc hydroxystannate on the thermal degradation of the brominated polypropylene in air has been investigated using simultaneous thermogravimetry(TG) and derivative thermogravimetry (DTG). The relevant data were presented in table 4-11 and were plotted in figure A-13 to A-20.

Table 4-11 Thermal analysis of brominated polypropylene samples in air.

Brominated Additive	Additive	Initial Degradation		Char Oxidation		Residue at 600 °C (%)
		wt.loss(%)	DTG_{max} (°C)	wt.loss(%)	DTG_{max}(°C)	
10% DBDPO	None	12.80	-	1.74	-	0.35
		85.11	418.2			
10% DBDPO	5 phr ZS	8.03	303.9	5.80	501.2	3.46
		82.71	424.5			
10% DBDPO	5 phr ZHS	7.29	262.3	7.50	505.0	2.51
		82.70	432.6			
10% DBDPO	5 phrSb_2O_3	20.46	332.0	3.88	495.1	0.49
		75.17	406.5			
20% DBDPO	None	12.03	277.8	3.24	-	0.99
		83.74	417.2			
20% DBDPO	5 phr ZS	7.60	-	7.24	481.0	2.73
		82.43	404.5			
20% DBDPO	5 phr ZHS	7.45	259.0	9.18	491.5	1.69
		81.68	405.6			
20% DBDPO	5 phrSb_2O_3	22.45	336.9	2.91	480.1	0.89
		73.75	407.7			

Simultaneously TG studies of zinc hydroxystannate in the previous reports [17], indicated that dehydration of this compound occurs during the temperature range of 190-285 °C, which was corresponding to the loss of 3 moles of water:

$$ZnSn(OH)_6 \longrightarrow ZnSnO_3 + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This thermal dehydration was indicated that the first step was endothermic reaction. Then, a secondary process occurred at higher temperature as presented in equation (2)

$$2ZnSnO_3 \longrightarrow Zn_2SnO_4 + SnO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The polypropylene containing brominated additives alone underwent initial degradation over the temperature range *ca* 230-450°C in two major steps, with the losses of *ca* 12% of their initial weight in the first major step. A further major step represented a weight loss of about 80% of the initial sample weight.

When compared to TGA curve of brominated polypropylene, TGA curve of 5% ZHS treated polypropylene showed that the presence of ZHS altered both the initial and oxidative decomposition of the polymer. The weight loss at the lower temperature step was decreased (from *ca.* 12 to 7), and further the non-flammable fraction was increased. Interestingly, level of DBDPO addition affected to combustion profile of the polymer. An increase in the amount of DBDPO additive leaded to a decrease in the weight loss during initial decomposition at the lower temperature step, and at the higher loading a more stable fraction was presented.

The ZHS greatly reduced the initial weight loss, thus decomposition of ZHS stabilized the polymer, coupled with the presence of a significant amount of non-combustible material. Hence, its mechanism should be condensed phase retardation as well. According to smoke data, the observed smoke-suppressant effects in this system might arise from char promotion, reducing flammable volatiled into the flame zone.

Furthermore, the amount of char burnt off in the oxidation step was significantly increased in the ZHS/DBDPO system compared to that in the base polymer which implied the extensive volatilization of tin and zinc occurred in this system, This was being in agreement with the result from the combustion experiments discussed earlier. Hence, it appeared that ZHS might be act not only in condensed phase but also in vapor phase.

The investigation of ZS/DBDPO containing polypropylene in weight loss of the initial and oxidation decomposition was similar to that of ZHS/DBDPO system.

In contrast to these observation, a 5% addition of Sb_2O_3 to the polymer caused an increase in the weight loss during initial combustion at the lower temperature step. And it was interesting to note that there was small amount of residue left at 600°C in the Sb_2O_3-containing polypropylene degradation which indicated the extensive volatilization of antimony in this system, and this was in agreement with the generally accepted observation that antimony additives operated primarily in the vapor phase retardation.

From TGA data described above, the expected mechanism of ZS and ZHS / brominated system was shown below.

$ZnSn(OH)_6 \longrightarrow ZnSnO_3 + 3H_2O$ ....(3)

$ZnSnO_3 + 2RBr \longrightarrow SnOBr_2 + Zn(OR)_2$ ....(4)

$2SnOBr_2 \longrightarrow SnBr_4 + SnO_2$ ....(5)

Gas flame retardant action of $SnBr_4$ might explained in the same route of Sb_2O_3 action.

$SnBr_4 + H\bullet \longrightarrow HBr + SnBr_3$ ....(6)

$SnBr_3 + H\bullet \longrightarrow HBr + SnBr_2$ ....(7)

$SnBr_2 + H\bullet \longrightarrow HBr + SnBr$ ....(8)

$SnBr + H\bullet \longrightarrow HBr + Sn$ ....(9)

$Sn + OH\bullet \longrightarrow SnOH\bullet$ ....(10)

$SnOH\bullet + H\bullet \longrightarrow SnO + H_2$ ....(11)

The occurred $SnCl_4$ attacked $H\bullet$ and $OH\bullet$ radicals so that the concentration of the latter species were reduced, thus resulting in the formation of CO_2, H_2 , H_2O and solid carbon to retard the combustion.

Mechanism of the tin compounds in combination with DBDPO compound possibly acted both condensed and gas phase retardation in which the tin oxide (SnO_2) and HBr, evolved from the decomposition of tin compounds and DBDPO, respectively, might reacted together and generated tin bromide and oxybromide.