CHAPTER IV
RESULTS AND DISCUSSION

4.1 Flame Retardancy Evolution and Mechanical Testing.

4.1.1 ABS with Bromine Compound.

In the present work, 1,2-bis(tribromophenoxy)ethane (BTBPE) was used as fire retardant for ABS. The LOI measurements with the variation of BTBPE 15-30 wt% are shown in Table 4-1

Table 4-1 The LOI data for ABS containing bromine compound

Composition	LOI	LOI [a]
No additive	17.9	-
15% BTBPE	20.4	2.5
18% BTBPE	20.6	2.7
20% BTBPE	20.9	3.0
23% BTBPE	22.2	4.3
25% BTBPE	22.6	4.7
27% BTBPE	24.3	6.4
30% BTBPE	28.2	10.3
Commercial ABS	26.7	-

a : Each LOI value was compared with that of the sample with no additive.

The results obtained clearly showed that LOI value increased with increasing amounts of bromine compound. The ABS resin had an LOI of 17.9, when blended with BTBPE, 15-30 wt%, the LOI value increased from 20.4 to 28.2. These results indicate that BTBPE is an effective flame retardant for ABS. Figure 4-1 shows LOI curves for this system.

4.1.2 ABS with Tin Compounds and/or Antimony Trioxide

For the synergist fire retardant, ZHS, ZS and Sb_2O_3 were used in this study at 2, 4 and 6 wt%. The LOI data of these additives are shown in Table 4-2

Table 4-2 The LOI data for ABS containing synergist fire retardants

Composition	LOI		
	ZHS	ZS	Sb_2O_3
No additive	17.9	17.9	17.9
2% additive	18.0	17.9	18.9
4% additive	18.1	18.1	19.1
6% additive	18.2	18.2	19.4

ZHS, ZS and Sb_2O_3, when used alone, had little effect on the flammability on ABS. Of these data, ABS containing antimony trioxide (Sb_2O_3) exhibited higher LOI values than tin compounds. Figure 4-2 shows the relationship between LOI value and synergist fire retardant level.

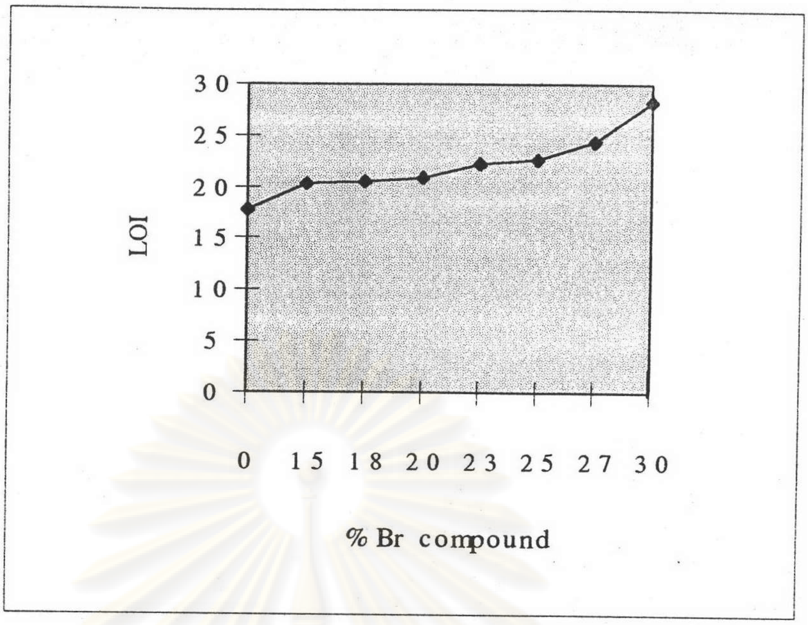


Figure 4-1 Fire retardancy of bromine compound in ABS

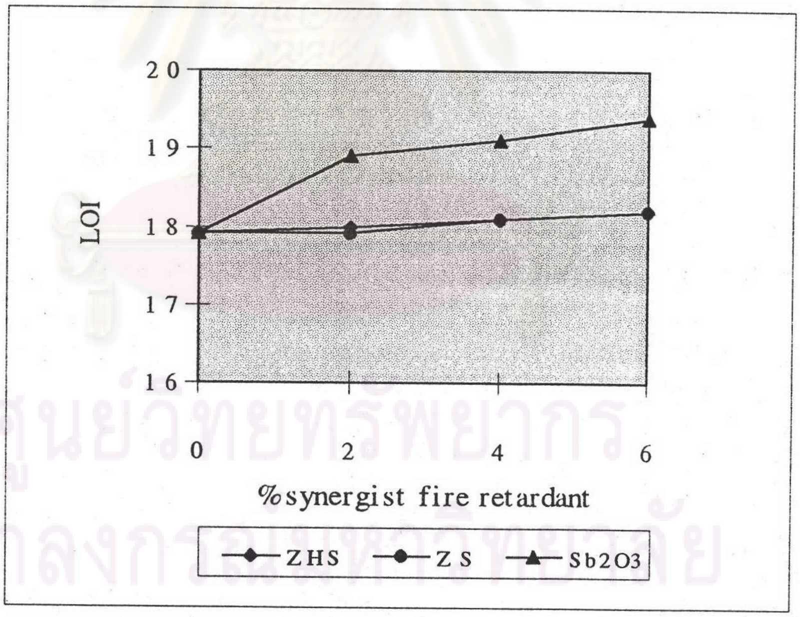


Figure 4-2 Relationship between flammability and synergist fire retardant level for ABS

4.1.3 Mechanical Properties of ABS Containing Bromine Compound or Synergist fire retardant

To select the suitable percentage of bromine compound and synergist fire retardant for the binary system, both measurement of LOI values and investigation the properties of ABS composition are needed. The value of tensile strength and impact strength of ABS containing bromine compound are shown in Table 4-3 and plotted in Figure 4-3 to 4-4.

Table 4-3 The effect of bromine compound content on tensile strength and impact strength

Composition	Tensile strength (kgf/cm^2)	S.D [a]	Impact strength (kgf-cm/cm^2)	S.D
No additive	564.9	3.6	14.7	0.100
15% BTBPE	544.3	2.7	11.7	0.000
18% BTBPE	535.6	2.9	11.5	0.100
20% BTBPE	527.3	0.1	11.3	0.217
23% BTBPE	502.1	3.1	9.8	0.246
25% BTBPE	499.9	3.8	9.5	0.100
27% BTBPE	484.3	1.8	9.1	0.316
30% BTBPE	475.2	2.5	8.6	0.361
Commercial ABS	480.8	2.1	9.5	0.152

b : standard deviation

From Table 4-3, it can be seen that tensile strength of ABS containing the bromine compound decreases when the fire retardant content increases. Similar results for impact strength were found.

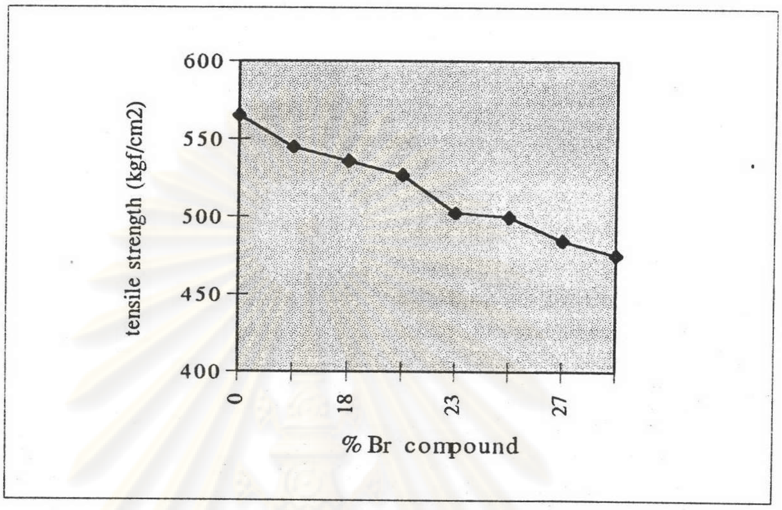


Figure 4-3 Tensile strength of ABS containing the bromine compound

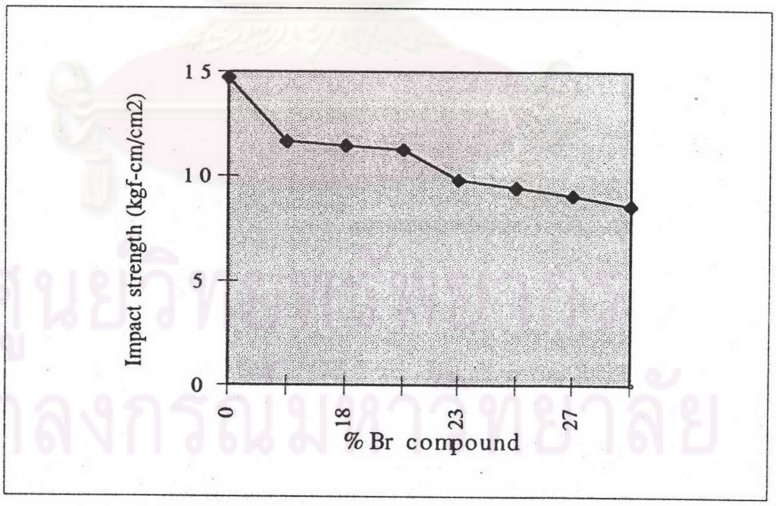


Figure 4-4 Impact strength of ABS containing the bromine compound

For synergism (tin compounds and antimony trioxide), the data for tensile strength and impact strength are shown in Table 4-4 to 4-5 and plotted in Figure 4-5 to 4-6.

Table 4-4 The effect of synergist fire retardant content on tensile strength

Composition	Tensile strength (kgf/cm^2)		
	ZHS	ZS	Sb_2O_3
No additive	564.9	564.9	564.9
2% additive	552.5	555.9	564.0
4% additive	539.6	534.4	552.9
5% additive	530.4	529.7	546.7
6% additive	525.7	528.3	539.4

Table 4-5 The effect of synergist fire retardant content on impact strength

Composition	Impact strength (kgf-cm/cm^2)		
	ZHS	ZS	Sb_2O_3
No additive	14.7	14.7	14.7
2% additive	12.0	12.5	10.8
4% additive	11.2	11.5	9.4
5% additive	10.7	10.7	9.1
6% additive	10.2	10.4	8.5

The results in Table 4-4 and 4-5 obtained for ABS containing tin compounds and antimony trioxide, with regards to tensile strength and impact strength, are quite similar to those for the bromine compound. An addition of the synergist fire retardant produced a decrease in tensile and impact strength.

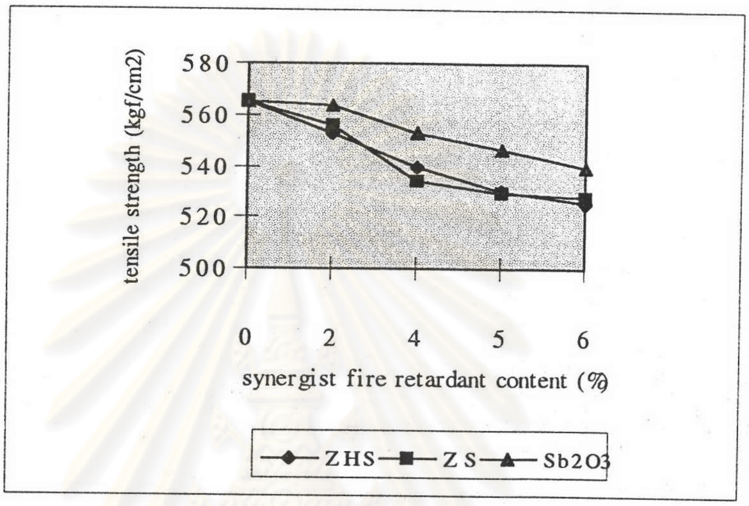


Figure 4-5 Relationship between the tensile strength values and synergist fire retardant level of ABS

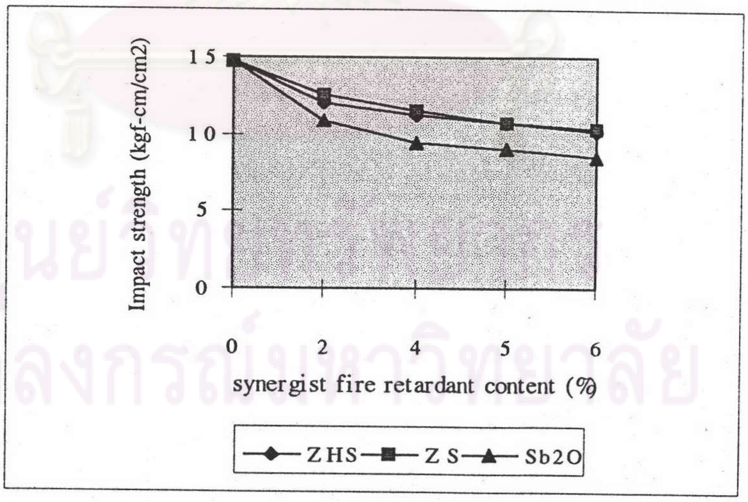


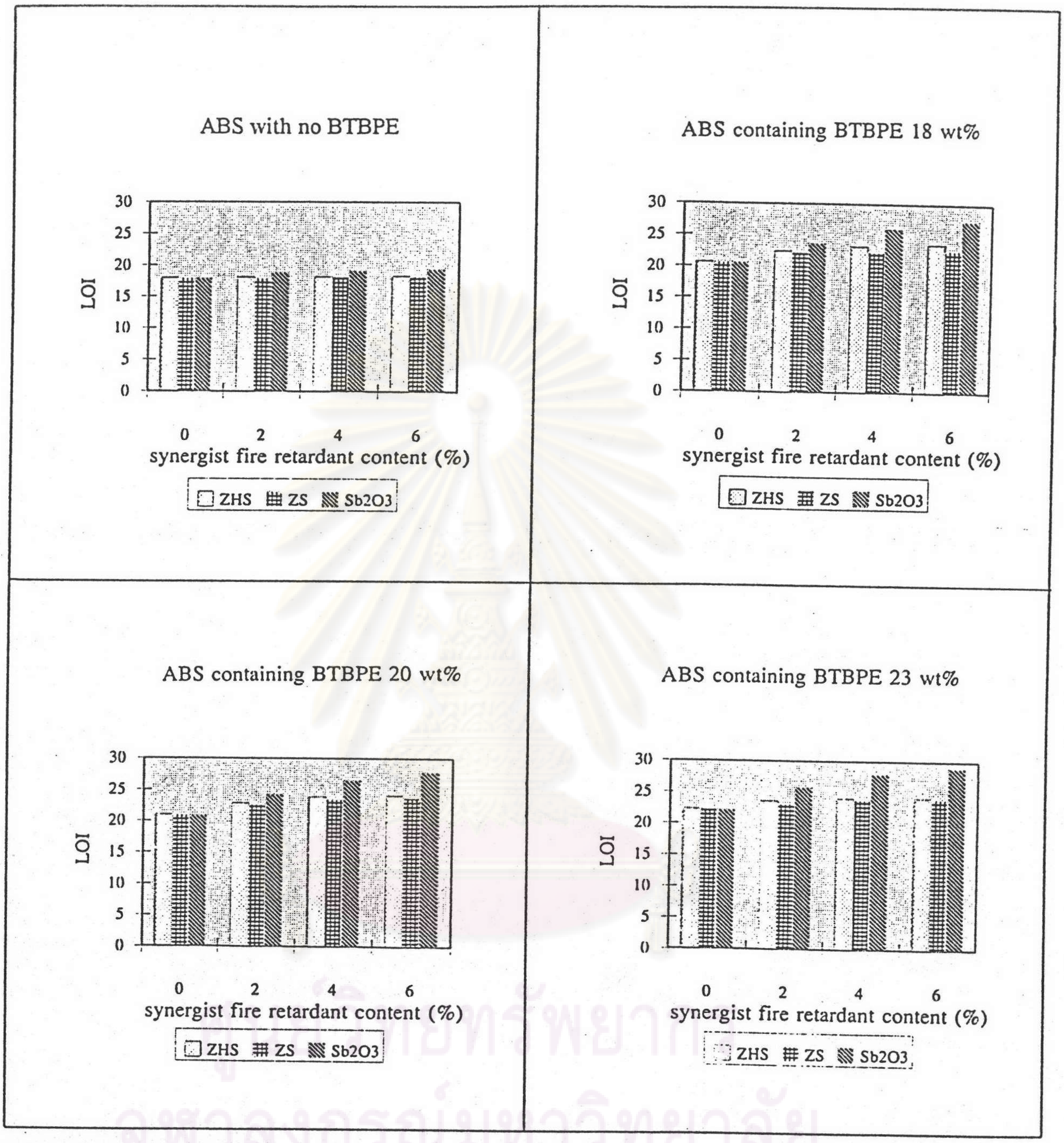
Figure 4-6 The impact strength values and synergist fire retardant level of ABS

4.1.4 ABS with Tin and Bromine Compounds

From the LOI data in Table 4-1 to 4-2 and mechanical properties data in Table 4-3 to 4-5, commercial ABS had an LOI of 26.7, tensile strength of 480.8 kgf/cm^2 and impact strength of 9.5 kgf-cm/cm^2. Addition of fire retardants produced an increased LOI value, but decreased mechanical properties. Thus, to obtain results as good as commercial ABS, it would be neccessary to vary the percent of the bromine compound in the range 18-23 wt% in combination with tin 2-6 wt% (compared with antimony trioxide) for the binary system. The results are demonstrated in Table 4-6 and the graphs are shown in Figure 4-7.

Table 4-6 The LOI data for ABS containing tin and halogenated additives.

Composition	LOI			
	0% BTBPE	18% BTBPE	20% BTBPE	23% BTBPE
No additive	17.9	20.6	20.9	22.2
2% ZHS	18.0	22.4	22.8	23.5
ZS	17.9	22.2	22.6	23.1
Sb_2O_3	18.9	23.7	24.2	25.8
4% ZHS	18.1	23.2	23.8	24.0
ZS	18.1	22.4	23.5	23.9
Sb_2O_3	19.1	26.1	26.5	27.9
6% ZHS	18.2	23.6	24.0	24.1
ZS	18.2	22.7	23.9	24.0
Sb_2O_3	19.4	27.4	27.8	29.0



ABS with no BTBPE

ABS containing BTBPE 18 wt%

ABS containing BTBPE 20 wt%

ABS containing BTBPE 23 wt%

Figure 4-7 Effect of tin in combination with halogenated fire retardant on flammability of ABS, compared with antimony trioxide.

LOI values of tin compounds, ZHS and ZS in combination with halogenated fire retardant were higher than those of ABS containing only the halogenated additive, but lower than ABS containing Sb_2O_3 as a synergist fire retardant.

4.1.5 The Effect of CPE on Flammability of ABS

To improve the LOI values (>24 unit) and inhibit the drip of burning material in order to obtain V-0 rating in the UL-94 test, it should be using CPE in combination with tin and halogenated additives.

From the results in Table 4-6, the suitable system for adding CPE to obtain LOI values more than 24 units were bromine compound at 20% in combination with tin at 4 and 6% and bromine compound at 18% in combination with tin at 4%. In addition, antimony trioxide additive was compared. The data are shown in Table 4-7.

Table 4-7 The effect of CPE on LOI values of ABS containing halogenated fire retardant and tin compounds, or Sb_2O_3 additives

Fire Retardant	0% CPE	3% CPE	5% CPE
18% BTBPE + 4% ZHS	23.2	23.5	23.8
4% ZS	22.4	22.8	23.2
4% Sb_2O_3	26.1	26.4	27.8
20% BTBPE + 4% ZHS	23.8	24.1	24.4
4% ZS	23.5	23.6	24.0
4% Sb_2O_3	26.5	27.8	28.3
20% BTBPE + 6% ZHS	24.0	24.3	25.0
6% ZS	23.7	23.9	24.8
6% Sb_2O_3	27.8	28.0	29.4

From Table 4-7, it can be seen that ZHS and ZS at a loading of 4% in combination with CPE at 5% and BTBPE at 20% by weight gave an LOI value more than 24.0, similar to the ABS containing ZHS and ZS 6% in combination with BTBPE 20% and CPE at 3 or 5% by weight.

4.1.6 The Properties of ABS Containing Tin Compared with Commercial ABS

To confirmed that the ZHS and ZS can be used in ABS (flammability grade), UL-94 test and mechanical properties were compared with commercial ABS. Table 4-8 shows these data.

Table 4-8 Property testing of ABS containing ZHS and ZS compared with commercial ABS

PROPERTIES		TESTING VALUES *						
		STD	ZHS1	ZHS2	ZHS3	ZS 1	ZS 2	ZS 3
LOI		26.7	24.4	24.3	25.0	24.0	23.9	24.8
Tensile Strength (kgf/cm^2)		485.9	508.8	493.9	500.6	505.8	504.0	492.3
	SD	0.7	4.3	3.1	2.9	3.9	2.7	7.9
Izod Impact (kgf-cm/cm^2)		9.47	10.25	9.80	10.03	10.69	9.57	10.12
	SD	0.1	0.4	0.1	0.3	0.2	0.1	0.1
Hardness (R-Scale)		94.4	96.2	98.6	96.6	96.7	99.3	97.4
	SD	0.12	0.17	0.17	0.05	0.09	0.22	0.06
HDT (°C)		75	74	74	74	74	74	74
	SD	2.8	0.8	0.2	0.1	0.4	2.0	0.4
MFI (g/10 min)		71	64	65	67	59	63	63
	SD	0.03	0.04	0.03	0.01	0.03	0.02	0.02
Specifig Gravity		1.19	1.22	1.24	1.24	1.22	1.23	1.23
	SD	0.003	0.001	0.002	0.001	0.002	0.002	0.004
Flammability (UL-94)		V-0	V-0	V-0	V-0	V-1	V-2	V-0

* STD = commercial ABS

ZHS1 = ABS with 20% BTBPE, 4% ZHS and 5% CPE

ZHS2 = ABS with 20% BTBPE, 6% ZHS and 3% CPE

ZHS3 = ABS with 20% BTBPE, 6% ZHS and 5% CPE

ZS1 = ABS with 20% BTBPE, 4% ZS and 5% CPE

ZS2 = ABS with 20% BTBPE, 6% ZS and 3% CPE
ZS3 = ABS with 20% BTBPE, 6% ZS and 5% CPE

From Table 4-8, ABS containing all ZHS systems gave a V-0 rating for the UL-94 test. While ZS systems, only ZS3 (ABS containing BTBPE 20% in combination with ZS 6% and CPE 5%) gave a V-0 rating. In the mechanical tests such as tensile strength, impact strength, hardness, HDT, MFI and specific gravity, ABS containing all tin systems showed similar behavior to commercial ABS.

From these results and the observation of burning of ABS compositions, the effect of halogenated fire retardant, BTBPE, in combination with tin or Sb_2O_3 additives were studied. The results clearly indicated that the tin compounds, ZHS and ZS, in combination with a halogen source, were flame retardant and smoke suppressant additives for ABS, according to the Figure 4-8 to 4-10. Although their flame retardancy were not as good as Sb_2O_3, their lower smoke production could make their use in ABS viable.

Figure 4-8 The burning of ABS resin

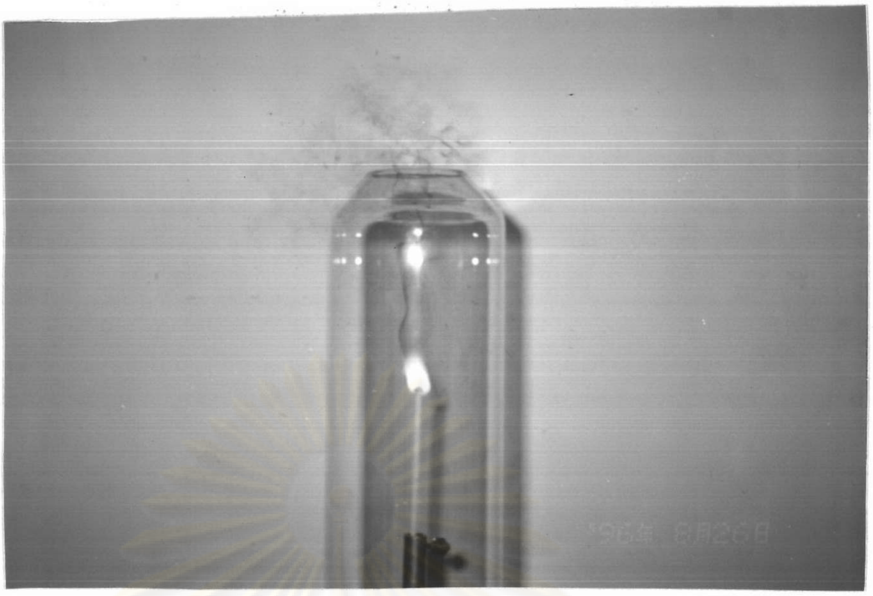


Figure 4-9 The burning of ABS containing tin additives (ZHS)

Figure 4-10 The burning of ABS containing Sb_2O_3 additive

4.2 Determination of the Dispersion of Fire Retardant Particles of ABS Blends

The dispersion and morphology of flame retardants in ABS are the most important factors in determining toughness, rheology and the overall performance properties of ignition-resistant ABS.

For scanning electron microscopy, samples were prepared by cutting a small (1 cm) rectangular specimen out of a two-roll mill. The thin section were examined and photographed in a JSM35 CF-SEM at 20 kV. Photomicrographs were provided at x2000 magnification. The results are shown in Figure 4-11 to 4-19.

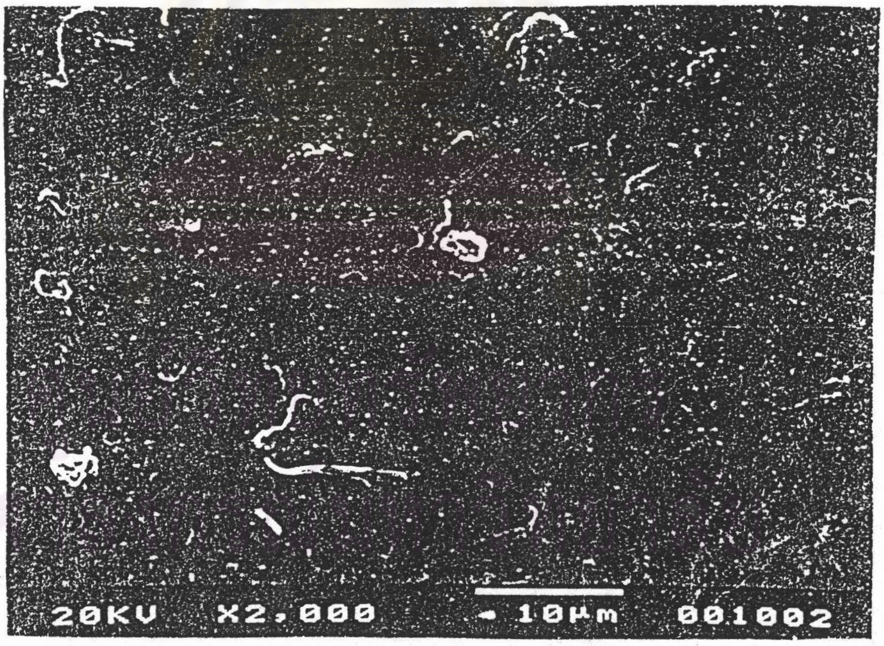


Figure 4-11 Scanning Electron Micrograph of ABS resin

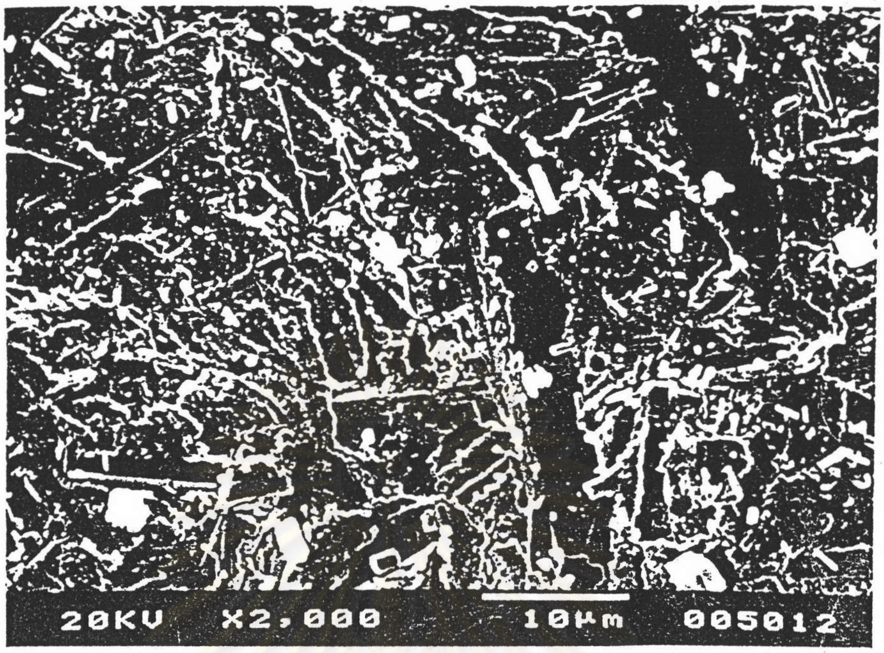


Figure 4-12 Scanning Electron Micrograph of ABS with BTBPE

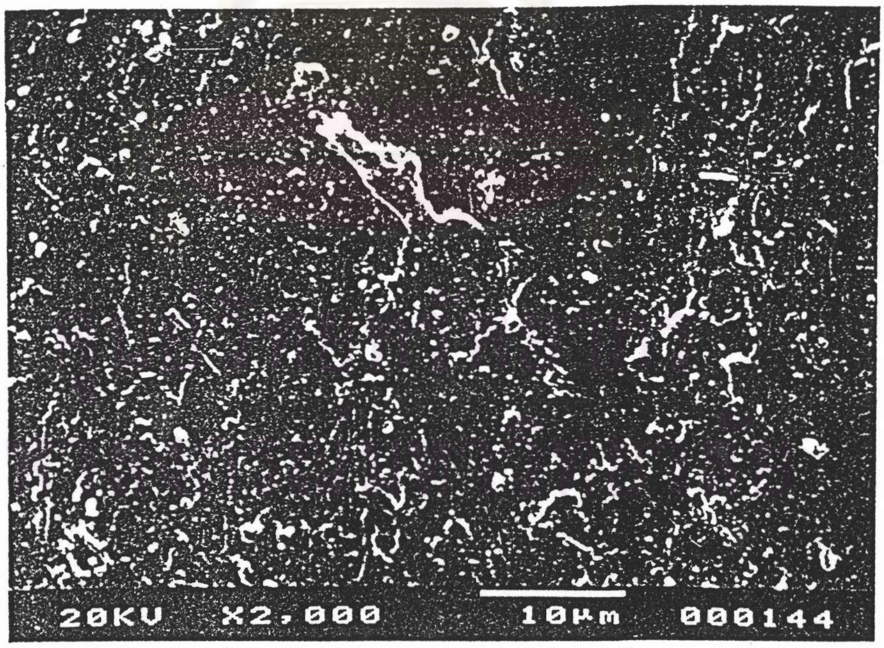


Figure 4-13 Scanning Electron Micrograph of ABS with Sb_2O_3

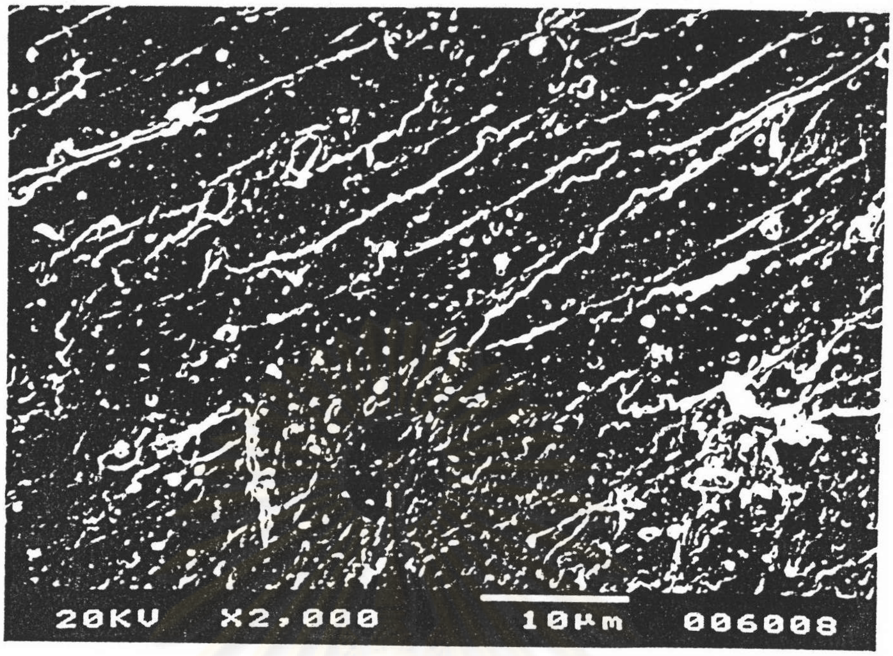


Figure 4-14 Scanning Electron Micrograph of ABS with ZHS

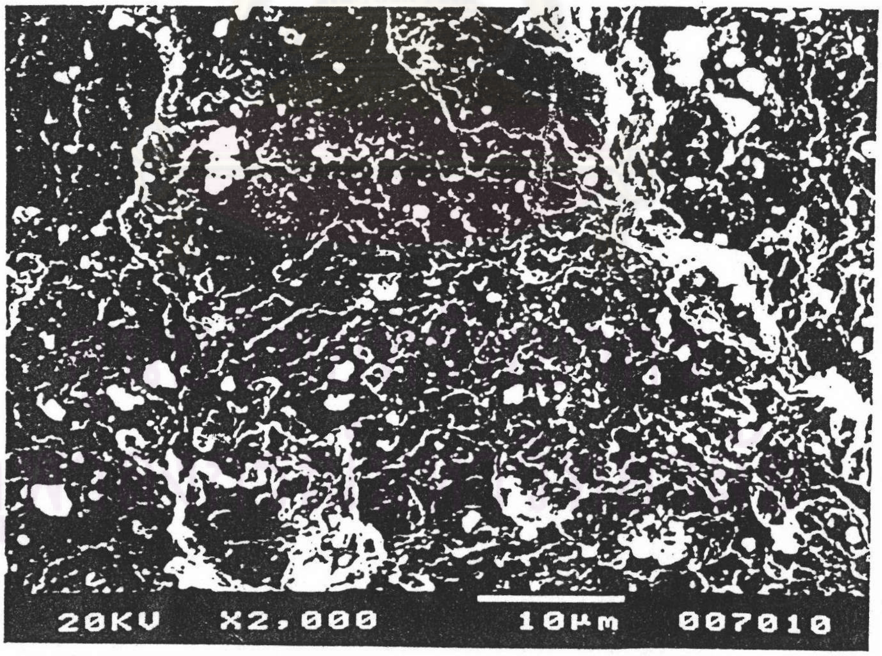


Figure 4-15 Scanning Electron Micrograph of ABS with ZS

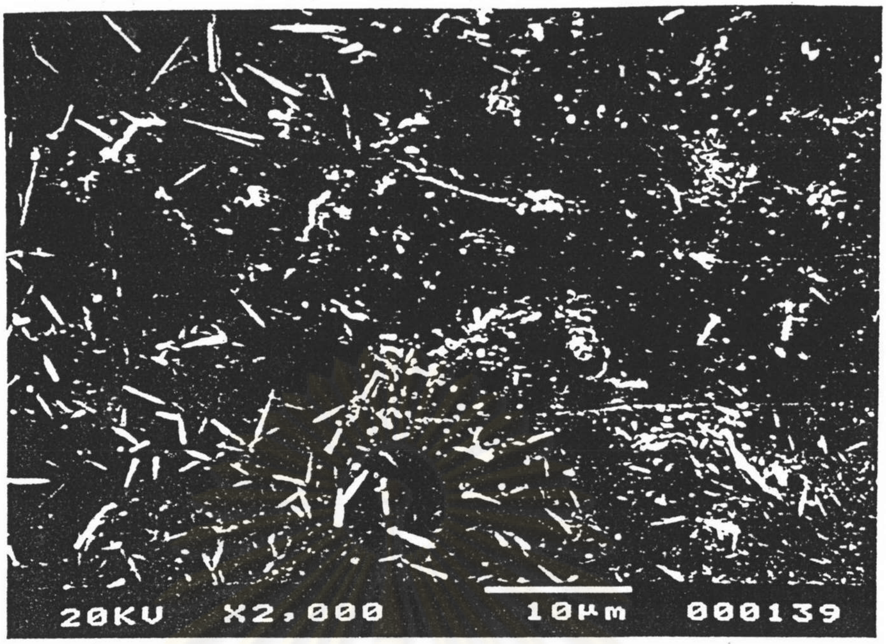


Figure 4-16 Scanning Electron Micrograph of commercial ABS.

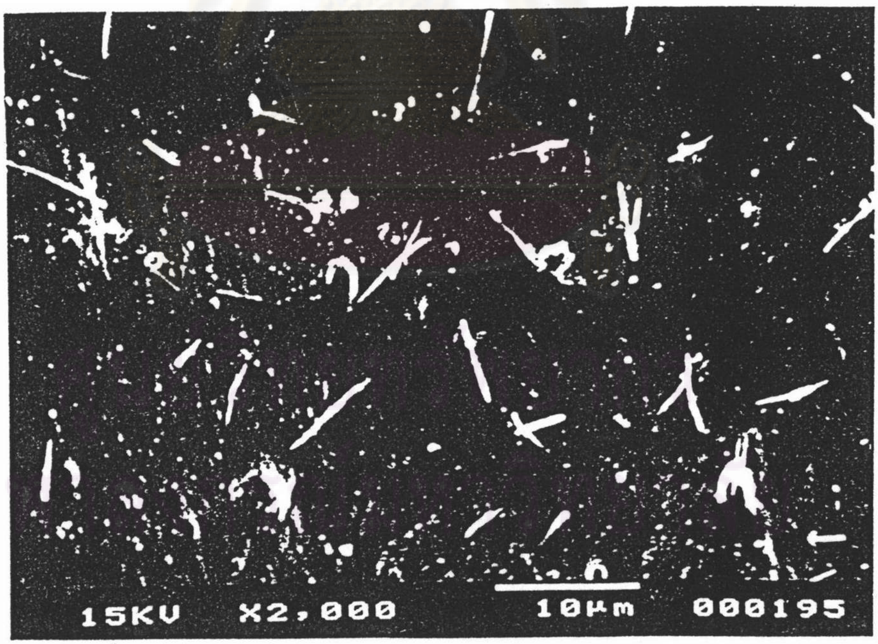


Figure 4-17 Scanning Electron Micrograph of ABS with BTBPE, Sb_2O_3 and CPE

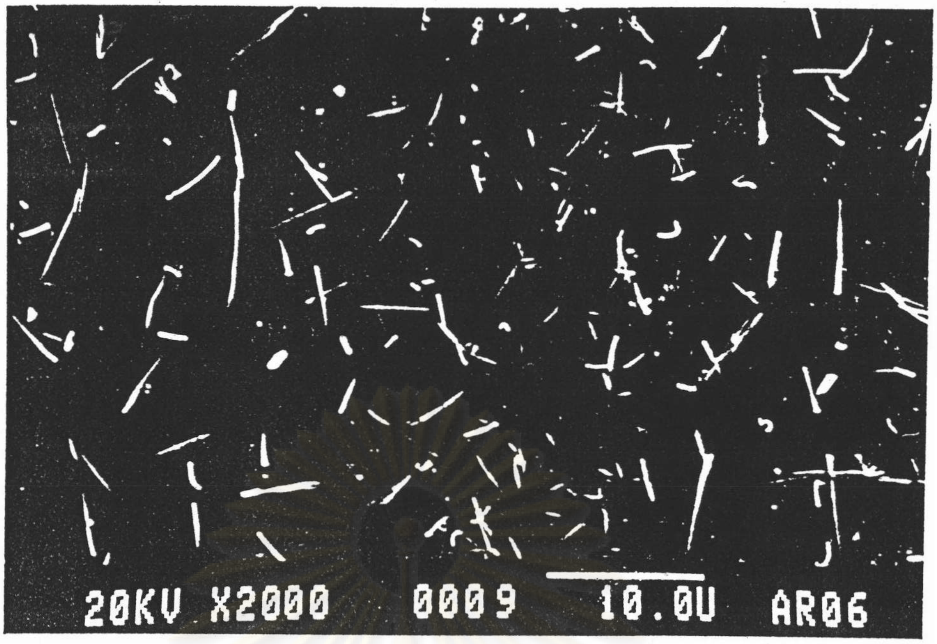


Figure 4-18 Scanning Electron Micrograph of ABS with BTBPE, ZHS and CPE

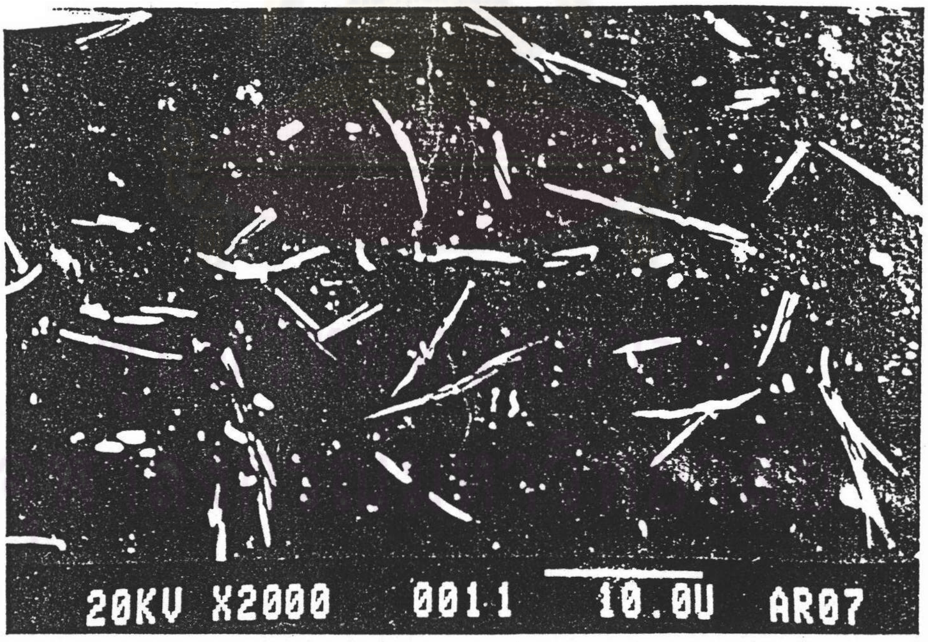


Figure 4-19 Scanning Electron Micrograph of ABS with BTBPE, ZS and CPE

From Figure 4-10 to 4-18, photographs of ABS blend containing fire retardants indicated the blend was rather homogenious, compared with commercial ABS.

4.3 Mechanistic Studies

4.3.1 Elemental Analyses

An insight into the mode of action of ZHS and ZS in the ABS containing the bromine compound is provided by simple combustion experiments carried out in air. Table 4-9 showed that the effect of ZHS, ZS or Sb_2O_3 on the yield of involatile carbonaceous char, formed when ABS compositions are burned to completion, is more than seven times when 4% additions of either zinc hydroxystannate or zinc stannate is made to the plastic, and more than ten times when in combination with 3% CPE, this observation being consistent with condensed phase behaviour.

The elements of residues were determined by neutron activation analysis. The details of all data and calculations are shown in Appendix B. Elemental analysis suggested that, in the case of ZHS and ZS, only a small fraction of the zinc is volatilised, which may be indicative of condensed phase action. Interestingly, the extent of bromine and chlorine loss is significant indicating vapour phase action.

Antimony trioxide, which undergoes almost complete volatilisation in the polymer, showed little char enhancing behaviour and operates primarily in the gas phase. The apparent ability of zinc hydroxystannate and zinc stannate to act in

Table 4-9 Residual char yields and extents of element volatilisation from ABS samples during combustion in air

Sample	char yield %	Elemental Volatilisation (%)					Primary Phase of action
		Sn	Zn	Br	Cl	Sb	
NO FR.	1.52	-	-	-	-	-	-
18% BTBPE + 4% Sb_2O_3	6.64	-	-	98.86	-	73.83	Vapor
18% BTBPE + 4% Sb_2O_3+ 3%CPE	11.47	-	-	96.78	98.51	75.68	Vapor
18% BTBPE + 4% ZHS	10.61	85.88	61.82	89.02	-	-	Condensed + Vapor
18% BTBPE + 4% ZHS + 3% CPE	16.68	74.07	52.78	81.21	97.84	-	Condensed + Vapor
18% BTBPE + 4% ZS	9.90	90.84	64.71	91.45	-	-	Condensed + Vapor
18% BTBPE + 4% ZS + 3% CPE	16.27	89.47	54.76	84.65	97.13	-	Condensed + Vapor

both the condensed and vapour phase may account for its overall flame retardant superiority to the other inorganic additives.

Further mechanistic information can be deduced from thermoanalytical measurements.

4.3.2 Thermal Analyses

The effects of ZHS and ZS additives on the thermal degradation of ABS in air were investigated using simultaneous TG/DTG/DSC, and the relevant data are presented in Table 4-10 and Figure B.20 to B.30 in Appendix B.

The untreated resin (Figure B.20) lost about 94% of its weight during the initial decomposition stage in the temperature range 350-490 °C.All the resulting char was subsequently oxidised to generate CO and CO_2 in the temperature range about 580 to 650 °C, in a highly exothermic process as indicated by large broad peaks in the corresponding DSC traces.

The presence of ZHS, ZS or Sb_2O_3 (Figure B.21, B.22 and B.23), when used alone, had little effect on the combustion profile of the resin. BTBPE underwent initial degradation at the lower temperature than that observed for the resin. This mode of reaction was gas-phase retardation. In general, halogenated derivatives worked on gas-phase retardation. If these compounds decomposed at a slightly lower temperature than that of the untreated polymer, they tended to be good retardants for the polymer. However, the flame-retardant compounds must be sufficiently stable thermally under mechanical work for practical application [10]. In the case of BTBPE/Sb_2O_3 resin (Figure B.27), the BTBPE in combination with Sb_2O_3 additive altered the decomposition profile such that a distinct two-step

Table 4-10 Thermal gravimetry analysis data for ABS sample

Sample	Initial Degradation $^{+}$		Char Oxidation $^{++}$	
	Weight Loss (%)	DTG Max (°C)	Weight Loss (%)	DTG Max (°C)
1. NO FR	93.66	416.1	5.61	594.1
2. 4% ZHS	89.41	417.4	7.80	604.5
3. 4% ZS	89.23	416.6	6.63	595.5
4. 4% Sb_2O_3	90.95	415.7	6.95	559.6
5. 18% BTBPE	24.58 62.55	360.3 414.3	12.36	547.9
6. 18% BTBPE + 4% ZHS	74.44	383.7	22.86	601.2
7. 18% BTBPE + 4% ZS	76.72	393.2	18.53	603.2
8. 18% BTBPE + 4% Sb_2O_3	18.67 68.83	349.4 410.5	10.89	608.0
9. 18% BTBPE + 4% ZHS + 3% CPE	72.71	371.0 417.5	23.91	644.0
10. 18% BTBPE + 4% ZS + 3% CPE	76.29	391.5 412.4	22.08	661.0
11. 18% BTBPE + 4% Sb_2O_3 + 3% CPE	19.40 67.47	333.3 431.9	10.41	634.6

$^{+}$ Temperature range : c. 200 - 500

$^{++}$ Temperature range : c. 500 - 900 initial breakdown was observed, with the first step occuring at a much lower temperature, and the second step at a slightly lower temperature than that of the corresponding single step for base polymer. It would appear that the bromine/Sb_2O_3 combination promoted the formation of these volatile combustible products.

The TGA curve of zinc hydroxystannate/BTBPE resins is shown in Figure B.25. When compared to the TGA curve of base polymer, the TGA curve of ZHS/BTBPE treated ABS showed that the presence of ZHS altered both the initial and oxidative decomposition stages of the ABS breakdown. This occurred reaction may be explained in a same route of ZHS in which its initial decomposition step occurred at low temperature possibly due to dehydration of the ZHS additive as presented in equation (4-1) [10].

$$ZnSn(OH)_6 \longrightarrow ZnSnO_3 + 3\ H_2O \qquad (4\text{-}1)$$

The DSC curve indicated that this step was endothemic. Then, a process occured at higher temperature as presented in equation (4-2).

$$2\ ZnSnO_3 \longrightarrow Zn_2SnO_4 + SnO_2 \qquad (4\text{-}2)$$

In the latter step, $ZnSnO_3$, product from first step, might promote the volatilisation of bromine, possibly in the form of metallic bromides or oxybromide [27]. These non-flammable products diffused into the flame zone and coused a reduction in the supply of combustible volatiles to the flame zone for vapor phase action. They behave as flame inhibitors in a similar manner to the analogous antimony halide species. The mechanisms of those systems might be similar to that of Sb_2O_3/halogenated system. The expected mechanism is shown below, equations (4-3) to (4-5).

$$ZnSn(OH)_6 \longrightarrow ZnSnO_3 + 3\ H_2O \qquad (4\text{-}3)$$

$$ZnSnO_3 + 2\ RBr \longrightarrow SnOBr_2 + Zn(OR)_2 \qquad (4\text{-}4)$$

$$2\ SnOBr_2 \longrightarrow SnBr_4 + SnO_2 \qquad (4\text{-}5)$$

Gas flame retardant action of $SnBr_4$ might be explain in same way as of Sb_2O_3 action.

$$SnBr_4 + H^{\cdot} \longrightarrow HBr + SnBr_3 \qquad (4\text{-}6)$$

$$SnBr_3 + H^{\cdot} \longrightarrow HBr + SnBr_2 \qquad (4\text{-}7)$$

$$SnBr_2 + H^{\cdot} \longrightarrow HBr + SnBr \qquad (4\text{-}8)$$

$$SnBr + H^{\cdot} \longrightarrow HBr + Sn \qquad (4\text{-}9)$$

$$Sn + OH^{\cdot} \longrightarrow SnOH^{\cdot} \qquad (4\text{-}10)$$

$$SnOH^{\cdot} + H^{\cdot} \longrightarrow SnO + H_2 \qquad (4\text{-}11)$$

The $SnBr_4$ attacked $H^{\cdot}$ and $OH^{\cdot}$ radicals so the concentration of the latter species were reduced, thus resulting in the formation of CO_2, H_2, H_2O and solid carbon, thus retarding combustion. Furthermore, the formation of tin halide and/or oxybromide may catalyse the formation of cross-links within the polymer and lead to an increase in char. For the results of this study, the presence of ZHS markly increased the amount of char formation (Table 4-9). Hence it was possible that ZHS/BTBPE exhibited both a condensed and vapor phase retardation. With the ZS/BTBPE resins (Figure B.26), the effect of ZS in the oxidation stage was similar to that of ZHS since ZHS decomposed to ZS [equation (4-1)].

The ZHS and ZS greatly reduced the initial weight loss, thus demonstrating that ZHS and ZS stabilised the polymer, but decreased the degradation temperature so that there may be production of a significant amount of volatile combustible materials. These compounds may act both in the condensed phase and vapor phase retardation.

In the first step the mechanism BTBPE produced HBr which acted as an acceptor, converting the highly reactive and chain carrying hydroxyl radical to the less reactive bromine radical [equation (4-12) to (4-16)].

$$O^{\cdot} + HBr \rightleftharpoons HO^{\cdot} + Br^{\cdot} \qquad (4\text{-}12)$$

$$HO^{\cdot} + HBr \rightleftharpoons H_2O + Br^{\cdot} \qquad (4\text{-}13)$$

$$Br^{\cdot} + RH \rightleftharpoons HBr + R^{\cdot} \qquad (4\text{-}14)$$

$$Br^{\cdot} + Br^{\cdot} \rightleftharpoons Br_2 \qquad (4\text{-}15)$$

$$Br^{\cdot} + R^{\cdot} \rightleftharpoons RBr \qquad (4\text{-}16)$$

Thus, the mechanism of BTBPE in combination with ZHS or ZS might me to generate tin bromide and oxybromide to reduce $H^{\cdot}$ and $OH^{\cdot}$ radical in the vapor phase. However, the expected mechanism which is described above should be confirmed by further study.