CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Acrylonitrile-Butadiene-Styrene Copolymer (ABS)

    - Flame retardant grade

    - ABS resin

    : Thai Petrochemical Industrial Co., Ltd.

2. 1,2-bis(tribromophenoxy)ethane (BTBPE)

    : Great Lakes Chem. Corp.

3. Zinc hydroxystannate (ZHS)

    : Alcan Chemical Ltd.

4. Zinc stannate (ZS)

    : Alcan Chemical Ltd.

5. Antimony trioxide (Sb_2O_3)

    : Dai-ichi Co., Ltd.

6. Chlorinated polyethylene (CPE)

    : Dow Chemical Ltd.

7. Zinc oxide (ZnO)

    : Koch-Light Laboratories Ltd.

8. Ammonium bromide (NH_4Br)

    : Mallinckrodt Chemical Works.

9. Ammonium chloride (NH_4Cl)

    : Merck

10. Tin (9.42%)

    : British Geological Survey Ltd.

11. Antimony tetroxide (Sb_2O_4)

    : Johnson & Matthey Co., Ltd.

3.2 Apparatus

1. Flammability testing ; Polymer Laboratories FTA module
   (ASTM D2863-91)
2. Two-Roll Mill ; Lab Tech Co., Ltd. Model LRM 150
3. Cutting machine ; Labtech Engineering , Model LRM 110
4. Injection molding machine ; Weltec Industrial Equipment Ltd, Model TTI-220/80
5. Universal testing machine ; LR 30K
6. Impact testing machine ; Zwick 1435
7. Scanning Electron ; Model JSM 35 CF
   Microscope (SEM)
8. Thermogravimetry and ; Netzsch STA 409 C
   differential thermal analyzer
9. Neutron Activation ; Canberra Industries, Model GR 2018,
   Analysis apparatus program MCA-S100

3.3   Preparation of ABS Compositions

An ABS composition was prepared using the ingredients listed in Table 3-2 to 3-5, in the following manner. A virgin ABS plastic polymer material, free of additives, was utilized as the base resin. An ABS formulation can be blended and injection molded at ambient temperature using the following procedure :

a) An ABS plastic was preheated on the two-roll mill for about 5 min. The temperature of the roll were maintained constant at 180 ^{o}C for the front roll and at 170 ^{o}C for the back roll, at which temperature it was in the molten state.

b) The halogenated flame retardant, 1,2-bis(tribromophenoxy)ethane, (BTBPE) and/or synergist flame retardant were added to the molten ABS and allowed to blend. The mass was rotated at 50-60 rpm.

c) After blending, it was homogenized for 10 min, the blended sheet was removed from the two-roll mill and cut into the small chips by the cutting machine.

d) The polymer chips were dried at 80 ^{o}C for 3 hr before injection molding with the following processing conditions :

Cycle time	: 35 seconds,	Injection time	: 1.4 seconds
Hold time	: 12 seconds,	Cooling time	: 12 seconds
Melt temperature	: 210 ^{o}C,	Mold temperature	: 40 ^{o}C
Injection pressure	: 450 psi hydraulic oil, 8000 psi on the plastic in the barrel		
Hold pressure	: 8000 psi in the barrel, 5000 psi mold-cavity pressure		

Test specimens were obtained for testing, according to Table 3-5.

BTBPE is a halogenated fire retardant for applications where thermal stability at high processing temperature is important. It is used for many thermoplastic and thermoset systems. It also has good UV light stability for light-stable applications [23]. Some properties of this compound are shown in Table 3-1

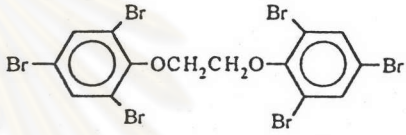Table 3-1   Properties of 1,2-bis(tribromophenoxy)ethane

Properties	BTBPE
Chemical formula	
Appearance	white crystalline powder
Bromine content	70.0 %
Melting range (^{o}C)	223-228
Specific gravity	2.6
Toxicity	Not a skin or eye irritant

Table 3-2   Halogenated fire retardant properties on ABS composition.

Composition	Halogenated fire retardant level (by weight)							
	control	15%	18%	20%	23%	25%	27%	30%
ABS resin	100	85	82	80	77	75	73	70
Fire retardant BTBPE [*]	-	15	18	20	23	25	27	30

[*] BTBPE = 1,2-bis(tribromophenoxy)ethane

Table 3-3   Synergist fire retardant properties on ABS composition.

Composition	Synergist fire retardant level (by weight)			
	2%	4%	5%	6%
ABS resin : Synergist fire retardant (ZHS) (ZS) (Sb_2O_3)	98:2	96:4	95:5	94:6

Table 3-4   Halogenated fire retardant together with synergist
fire retardant properties on ABS composition

Composition	ratio (part by weight)
ABS resin	100
Fire retardant	
18% BTBPE + 2% (ZHS, ZS, Sb_2O_3)	22.5 : 2.5
4% (ZHS, ZS, Sb_2O_3)	23.1 : 5.1
6% (ZHS, ZS, Sb_2O_3)	23.7 : 7.9
20% BTBPE + 2% (ZHS, ZS, Sb_2O_3)	25.6 : 2.6
4% (ZHS, ZS, Sb_2O_3)	26.3 : 5.3
6% (ZHS, ZS, Sb_2O_3)	27.0 : 8.1
23% BTBPE + 2% (ZHS, ZS, Sb_2O_3)	30.7 : 2.7
4% (ZHS, ZS, Sb_2O_3)	31.5 : 5.5
6% (ZHS, ZS, Sb_2O_3)	32.4 : 8.5

Table 3-5   Fire retardant properties with chlorinated polyethylene on ABS composition

Composition	ratio (part per weight)
ABS resin	100
Fire retardant	
18% BTBPE + 4% (ZHS, ZS, Sb_2O_3) + 3% CPE	24.0 : 5.3 : 4.0
5% CPE	24.7 : 5.5 : 6.8
20% BTBPE + 4% (ZHS, ZS, Sb_2O_3) + 3% CPE	27.4 : 5.5 : 4.1
5% CPE	28.2 : 5.6 : 7.0
20% BTBPE + 6% (ZHS, ZS, Sb_2O_3) + 3% CPE	28.2 : 8.5 : 4.2
5% CPE	29.0 : 8.7 : 7.2

Chlorinated polyethylene (CPE) is added to most commercial ignition-resistant ABS formulations to improve processibility, impact properties and to help reduce flammability and dripping from burning ABS as measured by the UL 94 test [24]. The properties of CPE are shown below :

Chlorine content   :   36 %
Specific gravity   :   1.16
Molecular weight   :   about 80,000

3.4 Test Method

Various properties of ABS compositions were tested using the condition listed in Table 3-6.

Table 3-6   Conditions for testing ABS compositions

Properties	Unit	Test method	Specimen	Condition
Flammability : Limiting Oxygen Index : UL-94	% V-0, V-1, V-2	D-2863 UL-94	1/8"x 1/4"x2.5" 5"x 1/16"x 0.5"	Mixture of O_2 and N_2 V test
Tensile strength	kgf/cm^2	D-638	ASTM Type I 3.0 mm Thickness	speed : 5mm/min
Izod impact strength	kgf-cm/cm^2	D-256	1/8"x 1/2"x 2.5"	Notched bar
Heat Distortion Temperature	^{o}C	D-648	1/4"x 1/2"x 5"	18.6 kg/cm
Melt Flow Index	g/10 min	D-1238	5 g	220 ^{o}C x 10 Kg
Rockwell Hardness	R Scale	D-785	ASTM type 1	R Scale

3.4.1 Fire Properties Test of ABS

Fire retardancy was measured as Limiting Oxygen Index (LOI), which is a method for the determination of the relative flammability of polymeric materials. This test conformed to ASTM D2863-91[25]. A material in the form of thin strips of approximate dimensions 100 x 7 x 3 mm is clamped vertically and ignited at the top, so that it burns in a candle-like manner in an upward flowing mixture of oxygen and nitrogen. The oxygen concentration of the gas is then adjusted until the minimum level for sustained burning is reached. In this

study, LOI values were determined by using 10 samples in a Polymer Laboratories FTA Apparatus. The Polymer FTA model LOI Apparatus is shown in Figure 3-1. The fire performance data obtained in this study are summarised in Table 4-1 to 4-8

Figure 3-1   LOI apparatus

Another method for flammability testing is UL-94 standard [26]. UL-94 contains test procedures for both horizontally and vertically positioned solid plastic test specimens in the form of rods. There are two methods ;

HB test : The test specimen is clamped with its longitudinal axis horizontal and a Bunsen burner flame is applied to its free end for 30 sec, the burning rate of the test specimen should not exceed a maximum

value dependent on its thickness or that the specimen extinguishes itself after removal of the flame.

V test : There is double Bunsen burner flame in the vertical dimension and lists the criteria for each V classification as Table 3-7

Table 3-7   UL-94 vertical burn test

Rating [*]	V-O	V-1	V-2
Max individual burn time	≤ 10	≤ 30	≤ 30
Total of 5 specimens	≤ 50	≤ 250	≤ 250
Glow time after second ignition	≤ 30	≤ 60	≤ 60
Ignites cotton	No	No	Yes

[*] Rating criteria are reported in seconds.

If only one specimen from a set of five specimens does not comply with the requirements, another set of five specimens is to be tested.
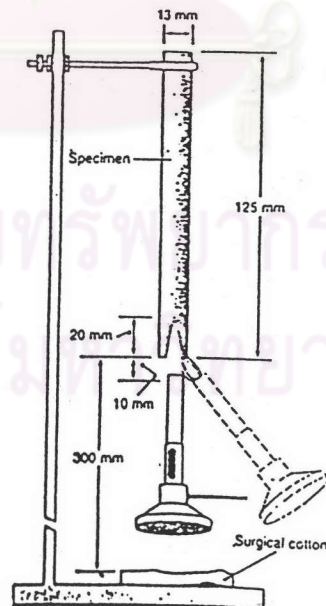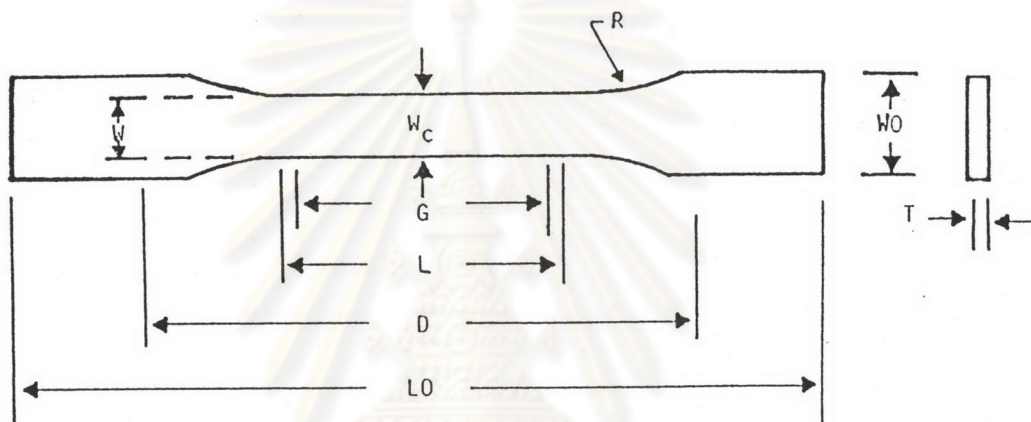

Figure 3-2   UL-94 vertical burn test

3.4.2 Mechnical Properties Testing [27].

Mechnical properties of the thermoplastic were measured by following the ASTM test methods as follows :

ASTM D638 : Standard test method for tensile properties.

The test specimens (type I) dimension is shown in Figure 3-3

W : 13 mm	W_o : 19 mm	G : 50 mm	R : 76 mm
L: 57 mm	L_o : 165 mm	D : 115 mm	

Figure 3-2   Schematic of tensile test specimen (type I)

The tensile testing conditions were as follows :

Temperature :	23.0	°C
Relative humidity :	50.0	%
Distance between grips :	115	mm
Gage length :	50	mm

ASTM D256 :   Standard test method for impact resistance.

The test specimens dimension for Cantilever Beam

(Izod Type) test is shown in Figure 3-4
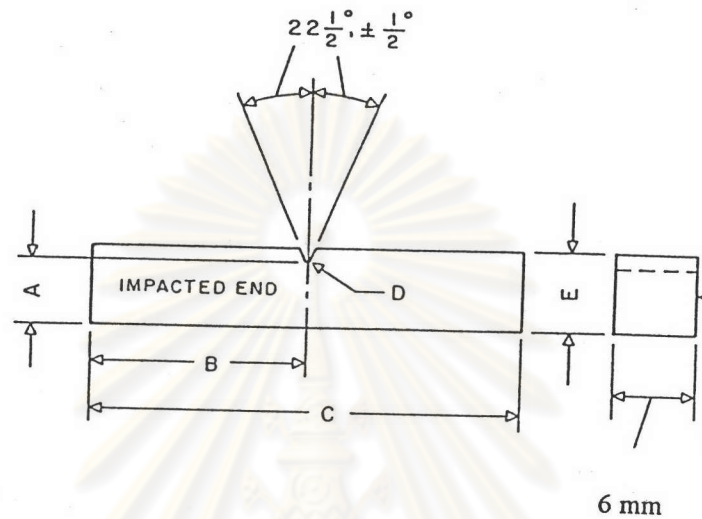
Unit : mm

A :   10.16 ± 0.05   D :   0.25 ± 0.05

B :   32.00 max., 31.50 min.   E :   12.70 ± 0.15

C :   63.50 max., 63.30 min.

Figure 3-4   Schematic of Izod type test specimen.

The machine parameters and testing conditions of the impact test are listed below :

Temperature :	23.0	°C
Relative humidity :	50	%
Depth of specimen :	10.16	mm
Pendulum capacity :	11.0	J

ASTM D648 : The test method for heat distortion temperature.

At least three test specimens were used for the test. The specimen were tested under the conditions in Table 3-5 at 23 ± 2 °C and 50 ± 5 % relative humidity for not less than 40 h prior to testing.

ASTM D785 : Standard test method for Rockwell hardness

The condition of specimens was in accordance with Table 3-6. The surface of each specimen was flat and parallel over a sufficient area to permit the presser foot to contact the specimen.

For each of the properties measured, at least three samples were tested to obtain a reliable average and standard deviation.

3.5 Mechanistic Studies

The elemental analysis of residues can be achieved by NAA, whereas burning characteristics can be generally examined by thermogravimetric analysis. These techniques can indicate the mode of action of the additive : solid phase or gas phase retardation.

3.5.1 Quantitative Analysis of Elemental by NAA

Activation analysis is commonly considered a method of analysis for chemical elements in trace quantities. A radioactive nuclide is formed when an element is bombarded by neutrons or charged particles such as electrons and protons.

In a nuclear reactor, stationary conditions are established when the number of neutrons released in a given volume is about equal to the number of

neutrons which participate in new fission acts. Neutrons from a nuclear reactor are composed of thermal and fast neutrons. Thermal neutrons are neutrons with an energy of about 0.025 eV.

The interactions between thermal neutrons and most of the nuclides through the (n,γ) reaction produce radioisotopes which can be identified by their characteristic decay rates and energies of the emitted radiations. The amount of radioisotope produced can be calculated from the well-known activation equations :

$$A = A_o e^{-\lambda t} \qquad (3.1)$$

$$A_o = A e^{\lambda t} \qquad (3.2)$$

from

$$\lambda = 0.693/ t_{1/2} \qquad (3.3)$$

$$A_o = A e^{0.693T/ t_{1/2}} \qquad (3.4)$$

where :

A = Activity at anytime of irradiation

A_o = Activity at irradiation time to be zero

λ = Decay constant of product nuclide

T = Decay time

$t_{1/2}$ = Half-life of product nuclide

Theoretical, it is possible to calculate the amount of the element present in a sample by comparing the count rate of a standard with that of the sample. One can determine the amount of each element in the sample by the following equation :

$$\% EX = \frac{C_{ex}}{C_{std}} \times \frac{W_{std}}{W_{ex}} \times \%STD \qquad (3.5)$$

where :

%EX = % Element in sample

%STD = % Element in standard

C_{ex} =   Count rate of sample

C_{std} =   Count rate of standard

W_{ex} =   Weight of sample

W_{std} =   Weight of standard

In this study, NAA was used for Zn, Sn, Br, Cl and Sb analyses in the char of ABS. After preparation of the sample and standard, the sample was weighed (about 0.05-0.07 g) into a polyethylene vial and the vial was sealed by heat. The standard and sample were loaded with neutron radiation and the amount of radioisotope produced calculated by equations 3.4 and 3.5. The results are summerized in Table 4-9.

Irradiation times, decay times, counting times and energies of the emitted radiations are shown in the Table 3-8

Table 3-8   Nuclear properties of elements and conditions used for analysis

Elements	Isotopes	Half-life	Irradiation time	Cooling time	Energy (keV)	Counting time
Zn	^{65}Zn	243.8 d	10 h	10 d	115.5	120 s
Sn	^{125}Sn	9.5 m	5 m	-	332.0	200 s
Sb	^{122}Sb	2.72 d	30 m	30 m	564.0	100 s
Br	^{82}Br	1.47 d	20 m	10 m	776.6	100 s
Cl	^{38}Cl	37.2 m	5 m	-	2167.0	300 s

3.5.2 Thermal Analysis

Thermal analysis has been used extensively to study in detail the various individual stages occuring during the breakdown of polymer under the action of heat, and can provide useful information regarding the mode of action and effectiveness of flame retardant additives.

For this study, simultaneous thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) provided a useful way to investigate the thermal degradation and combustion processes which occured within the burning polymer.

Two main processes may be observed; initial degradation wherein the readily combustible material is burnt to yield a char; and char oxidation in which the char produced from the initial combustion is then burnt off. Furthermore, the weight of the residue remaining after combustion can indicate the presence or formation of non-combustible material.

The effect of additive on the burning characteristics of the polymeric materials may be inferred by comparison between the additive-free, and the with-additive plots. Changes in the plot profile of the initial degradation step would indicate that the fire retardant properties arise from a condensed phase reaction, i.e. polymer breakdown had been modified. If however, the initial degradation profile is unchanged, a vapour phase fire retardant mechanism is implied. A change in the char oxidation profile often indicates the formation of a more stable component within the char.

In this study, the samples, weighing about 50 mg, were analyzed on a NETZSCH STA409 instrument. The heating rate was 20 $^{\circ}$C/min from ambient temperature to 1000 $^{\circ}$C. The atmosphere was air, with a flow rate of 100 cm^3/min. The results are summerized in Table 4-10 and plotted in Figure B.20 to B.30 in Appendix B.