CHAPTER V

DISCUSSION AND CONCLUSION

5.1 DISCUSSION

5.1.1 Interpretation of tin compounds

In preparation of sodium hydroxy stannate, zinc hydroxy stannate and hydroromarchite the X-ray diffraction patterns (figure 4-12 to 4-14) confirmed that the synthetic compounds were sodium stannate, zinc hydroxy stannate and hydroromachite, respectively.

Figure 4-15 to 4-18 were the spectrograms of sodium hydroxystannate and zinc hydroxystannate. Sodium hydroxystannate and zinc hydroxystannate showed O-H stretching at 3400-3600 cm^{-1}. and 3200-3300 cm^{-1}, respectively.

5.1.2 Fire-retardancy evaluation

5.1.2(a) Stannates system

The metal stannate compounds, zinc hydroxystannate (ZHS), zinc stannate (ZS) and hydroromarchite (HDR) were incorporated into the general purpose halogen-free polyurethane foams at the levels of 0.5%, 1.0%, 2.0%, 5.0% and 10% pbw. respectively. The relative effectiveness of these stannates additives on

the flammability of the foam was indicated in Table 4-2 to Table 4-5. The tin content at level of 0.5% pbw. to 5.0% pbw. of metal stannates could not increase LOI value. In general, there was little difference in their performance, although the ZHS appeared to be marginally supperior to the ZS and HDR at the higher loading studied. These observation was in agreement with the gennerally accepted fact that hydroxystannated system was more effective flame retardants, on the equal weight basis, than anhydrous stannated analogues. (At level 20% of ZHS ZS and HDR, LOI of ZHS was 23%, LOI of ZS was 20% and LOI of HDR was 20%.)

Whereas the chemical techniques to studies the mechanisms of flame retardants were resonably well established, small scale test methods which would provide meaningful data to predict their performance under conditions of actual use were still very much disputed. The mode of action of the hydroxystannate and the metastannate had also been investigated (Table 4-7).

To corroborate the solid state mode of action of metal stannate flame suppression, comparisons of the flammability of a flame retarded material, when burned in an oxygen atmosphere with its behavior when oxygen was used as the oxidant could yield clues as to whether the flame retardant acted in the solid or vapor phase.If a flame retardant acted as a gas phase inhibitor, its activity should be confined to combustion in an oxygen-
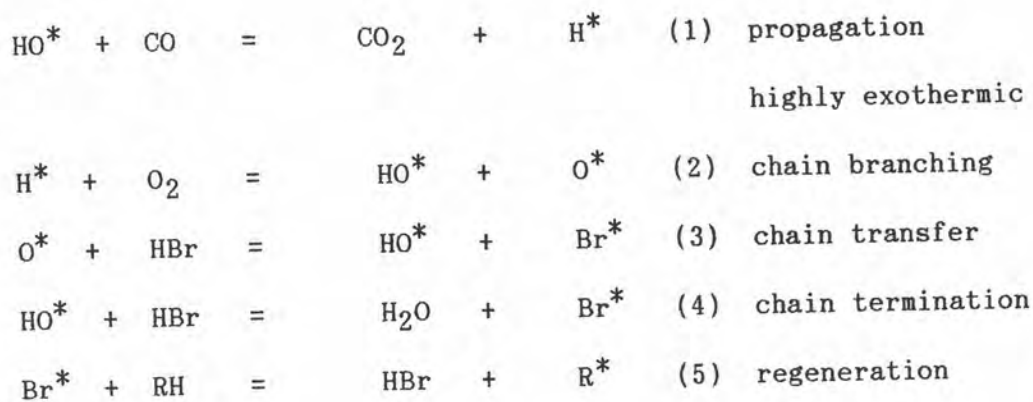
containing atmosphere and the activity of a solid state flame retardant should be uneffected by a change in oxidant since its activity was specific to pyrolysis reactions of the polymer. Table 4-12 showed differential scanning calorimetric result of PU containing ZSH and ZS. Increasing of melting temperature (T_m) with increased tin contents. It was possible that, H or O atom from ZHS and ZS occured bond formation with O and H atom of PU. Therefore, PU containing tin compounds used more energy to degrade. In oxygen, ZHS , ZS and HDR were also effective. Increasing the concentration of ZHS had effected on LOI (increase 5 units), but increasing the concentration of ZS and HDR had little effect on LOI (increase 2 units).

On combustion, both the flexible and the rigid polyurethane containing-metal stannate systems evolved carbon (as soot), carbon monoxide, carbon dioxide and stannic oxide (SnO_2). The CO and CO_2, were transparent gases. Metal oxides, such as SnO_2, could act as heterogenous oxidation catalysts for CO (2,3), and in the present situation, it was possible that the oxidation of carbon in the polymer could be assisted by a catalytic effect. At the initial burning temperature of the polyurethane (ca.200 ^{O}C), it was likely that a large amount of decomposition of the hydrate stannates and anhydrous stannate to SnO_2 and metal oxides will occur. But hydroxy stannate was decomposed at 180°C before PU and ZS decomposed. ZHS would decomposed and released Sn to reduced combustion. In addition,

the dehydation reaction of hydrate stannate may absorbed energy from the flame and cool the flame. For anhydrous stannate, its decomposition temperature was 570° C and the decomposition would occur after polyurethane had melt. Its function might occur at the same time of the decomposition of PU.

5.1.2 (b) Halogen system

During combustion of polyurethane, free radicals were formed by pyrolysis. It was a chemical that intervened in flame reactions in a more subtle and chemically interactive maner to bring about flame degradation. In chain reaction, the reactive propagation centers which contained high reactive free radicals such as O^*, H^*, Cl^*, HO^* and HOO^* could either were eliminated by involement in the chemical diversion reactions, or neutralized by colliding with surrounding wall that absorbed their exess energy . Bromine acted as acceptors of plastic material was caused therby. For continued combustion it was necessary to have sufficient oxygen as well as combustible gaseous compounds. The combustion would be slowed down or interrupted if free radical, which were evolved by pyrolysis, were blocked. It was presumed that the following reactions took place, when flame-retarded polyurethane containing organobromine compounds were used flame-retardants (18).

$$HO^* + CO = CO_2 + H^* \quad (1) \quad \text{propagation}$$

highly exothermic

$$H^* + O_2 = HO^* + O^* \quad (2) \quad \text{chain branching}$$

$$O^* + HBr = HO^* + Br^* \quad (3) \quad \text{chain transfer}$$

$$HO^* + HBr = H_2O + Br^* \quad (4) \quad \text{chain termination}$$

$$Br^* + RH = HBr + R^* \quad (5) \quad \text{regeneration}$$

The radical chain reaction was interruped when the highly reactive HO-radical, which occupied a key position within the combustion process, was replaced by the less reactive Br radical (reaction 4). The halogen containing organic compounds could also react as undecomposed molecules (6).

$$R-X \longrightarrow R^* + X^*$$

$$R'H \longrightarrow HX + R'^*$$

$$^*OH \longrightarrow H_2O + X^*$$
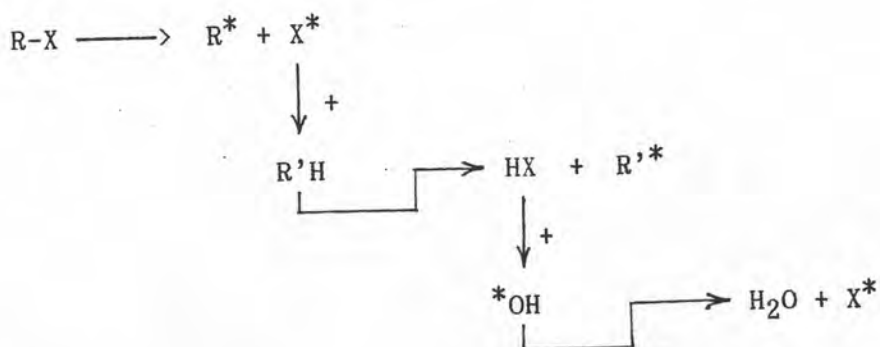
5.1.2(c) Halogen-tin synergistic system

Metal stannate served as synergist and strengthens the effect of organic halogen compounds, although it had little effect to retard flammability. LOI studied in Table 4-4 showed that, increasing concentration of DBDPE would increase flammability reduction. The synergistic of ZHS and ZS

were shown in table 4-4. When compared at the same level of DBDPE, increase in flammability reduction associated with increasing metal stannate content, 1.0% pbw. up to 5% pbw. It was possible that as a result of using tin stannate and organobromine compound (DBDPE), tin oxide and hydrobromic evolved from the decomposition of metal stannate and organobromide compound would react together and produced tin bromide and oxybromide which were gaseous at the ignition temperature. The strongly acidic tetrabromide was thought to function as a dehydration catalyst for materials as well as the flame quencher for flammable gases.

$$SnO_2 + 4 \ HBr \ \xrightarrow{\hspace{2cm}} \ SnBr_4 + 2 \ H_2O \hspace{2cm} (6)$$
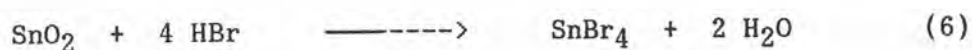
In addition, HBr was a heavy gas, actually smother a flame by an anti-oxygen effect. Hydrobromic acid was able to convert the highly reactive and chain-carrying hydroxyl radical in to the less reactive bromide radical (reaction 4). From result, it supposed that ZHS and ZS acted as synergistic additives in brominated polyurethane by accelerating the rate of loss of bromine from polyurethane. The efficiency of DBDPE related to the ease of dissociation of their C-X bonds. The rate at which the bromine was formed must also be such that a continuous source of radical trappers was available for as long as the temperature of the exposed region was above the ignition temperature of the volatiles. In DBDPE system, it seemed that the majority of additives was removed from the polymer during combustion (3).

In addition, reaction occuring in the solid phase could promote char formation by dehydration of alcohols. Smoke would also be formed as a result, which could contribute to deactivation of radicals by the wall effects.

In an attempt to futher establish how metal stannate function as additives, the effect of metal stannates on char formation unfilled polyurethane formulation and filled polyurethane formulation were examined by ICP analysis. Samples were burned and weight before and after decharring. As shown in Table 4-6 and 4-7 , it could see that the addition of ZHS, ZS and HDR, a vapor phase flame retardant, had little effected on char formation. The use of metal stannate alone increased little amount of char. These results confirmed that metal stannates acted as solid state char formers to reduced flammabilty.

The effect on the LOI on addition of decabromodiphenyl ether (DBDPE) and ammonium sulphate (AS)- containing foams to ZHS and ZS, at levels 1% and 5% pbw. was investigated. The data obtained, presented in Figure 4-5 and Figure 4-6, indicated that ZHS and ZS were effective flame-retardant synergists in these systems and that, an increase in the incorporation level of the tin additives leaded to a concomitant LOI elevation in each case.

Whereas, in foams containing DBDPE and AS, an increase in ZHS and ZS level from 1% pbw. to 5% pbw. only give rise to the modest LOI elevation, considerably larger increases in LOI were produced when the tin additive levels was increased in the 20% halogen-containing foams. These effects agreed with the hypothesis that high halogen : tin ratios were necessary for optimum flame retardants.

Further evidence for the vapor-phase mechanism for the condensed DBDPE and AS, and vapor phase and condense phase of ZHS and ZS containing DBDPE and AS had been obtained by employing ignition studied of polyurethanes containing ZHS and ZS plus DBDPE and AS. The data obtained in Table 4-6. On ignition, the DBDPE and AS containing-polyurethane sample weights lost over 63 % and 43 % of the original weight, confirming that bromine and ammonia must function in the condense phase. The ignition of ZHS and ZS plus DBDPE containing samples and the ignition of ZHS and ZS plus AS-containing samples were analysed by determined weight lost. Char formation indicated that the burned samples weight lost 64% and 55% pbw. respectively. The results were shown that bromine and ammonium sulphated acted as flame suppressant in vapor phase and tin acted as flame retardant in condense phase.

5.1.1 (d) <u>Ammonium sulphate system</u>

Ammonium sulphate was a flame retardant functioning by the formation of incombustible product such as ammonia, water and SO_3/SO_2 on heating. These gases would dilute the oxygen supply and reduce the rate of combustion. This in turn would decrease the temperature of the material, which might fall below the ignition temperature and caused self extinction. Table 4-8 showed the effect of ZHS and ZS at level 1% and 5% assynergistic compounds of ammonium sulphate additives. Similar to DBDPE, increasing in ammonium sulphate content would increase flammability reduction. LOI value increased from 1 unit up to 12 unit when using 1% pbw.ZHS and 3 unit to 21 unit when using 5% pbw. When using ZS as synergistic compound, LOI value increased 1-18 unit when using 1% pbw.ZS and 3-18 unit when using 5% pbw. The LOI results of ZHS when compared with ZS , showed little difference between the function of ZHS and ZS synergism systems. ZHS system was better than ZS system. Promoting endothermic reaction in the exposed regions reduced the temperature below that which would sustain ignition. Ammonium sulphate might sublimeat at temperatures around ignition temperature of it.

With the same level of ammonium sulphate content, flammability reduction increased as metal stannate content increased. Table 4-7 showed the results of char formation studied

of ZHS and ZS plus ammonium sulphate containing polyurethane. The weight of char residues indicated that the function of ammonium sulphate occured in vapor phase. The SO_3 gases from the decomposition of ammonium sulphate would react with water from the dehydration of ZHS to give H_2SO_4. The dehydrating agent, H_2SO_4, would promote char formation.

5.1.3 Mechanical property evaluation

Mechanical test showed that, metal stannate additives had little effect on stress at break, strain at break and 100% modulus (Table 4-8 and 4-9). Incorporation of the ZHS, ZS and HDR at level 0.5% pbw. to 10% pbw., decreased stress at break of polyurethane containing additives in the range of 1.441 -1.236 N/mm^2 for ZHS, 1.856-1-533 n/mm^2 for ZS and 1.400-1763 N/mm^2 respectively.

Strain at break of polyurethane containing fire retardants indicated that increasing the tin additives content would decrease strain at break decreasing. ZHS, ZS and HDR could decrease strain at break of polyurethane at level 0.276-0.250, 2.90-0.235 and 0.308-0.283 respectively.

Modulus of polyurethane containing ZHS, ZS and HDR was increased with tin content in the range of 3.951-4.826, 4.759-6.065 and 4.019-6.218 N/mm^2 respectively. It was shown that

stiffness of polyurethane would increase with increasing the amount of tin stannate content.

Filler size dimension had effective on flammability and mechanical properties of polyurethane. Modern technique for measuring small particles was the BET nitrogen absorption method. Significant elastomer reinforcement began when particles had surface area more than 50 m^2/g. Assuming sample spheres, this corresponded to the particle size of approximately 500 ^{o}A. In diameters, which was the same order of magnitude to or the distance between crosslink sites in the matrix elastomer. Apparently, when the particles became larger than the average end-to-end distance between crosslink, reinforcement declined due to polymer and particle adhesion failure when attached chains became highly extended, during deformation.

A great deal of attention had been paid to reactive sites on the filler and types of bond formed. Although most investors thinked that good bending was essential to reinforcement, two major ideas of though had appeared (Kraus, 1965). The first idea held that primary chemical bonds were essential to reinforcement, while the second idea held that secondary physical forces were sufficient. However, there were some person (Petterson and Kuri, 1961; Rowland et.al, 1965) discovered that the low strength physical force attached chains to filler surface quite firmly.

Important evidence existed that these particles were not randomly distributed throughout the polymer matrix. In deed, much evidence showed that a complex state of aggregation was important for reinforcement in fire retardants. Two levels of structure had been identified in reinforcing fillers beyond the primary particles aggregate of primary particles, which were bonded together rather strongly, and weakly bonded collections of these aggregates which were sometimes called agglomerates.

In rigid polyurethane, fire retardant content had little effect on mechanical properties. Decreasing stress at break and strain at break with increase tin stannate content, increasing modulus with increase tin contents. At level of 0.5-10 % pbw. tin content, strain at break was decreased from 1.264-1.361 N/mm^2, 1.856-1.533 pbw. and 1.375-1.763 pbw. respectively. Stress and strain at break of polyurethane were not changed with tin contents. Modulus was increased with tin content. At 0.5-10% pbw. tin content stress at break increased in the range of 1.028 -5.865 N/mm^2, 4.847-6.879 N/mm^2, 7.720-10.130 N/mm^2 respectively.

Table 4-10 showed mechanical properties of ZHS, ZS as synergistic compound of DBDPE. When ZHS, ZS and DBDPE were varied, they had little effect on modulus at level 2.744-4.579 N/mm^2.

Table 4-11 showed mechanical properties of ZHS, ZS as synergistic compound of AS. When ZHS, ZS and DBDPE were varied,

they had little effect on modulus at level 2.512-3.843 N/mm^2 except on 5% ZHS plus 10% AS (7.829 N/mm^2) and 20% AS (8.017 N/mm^2).

5.2 CONCLUSION

In this studied we found that tin stannates (ZHS,ZS and HDR) had little effect on flammability and mechanical properties of polyurethane. 10 % Hydroxy stannate (ZHS) was the best fire retardant and smoke suppressant. Synergistic effect of ZHS and ZS on flammability of PU containing DBDPE and AS were better than when they wrer using alone.