CHAPTER 5

DISCUSSION

5.1 Flame retardancy evolution

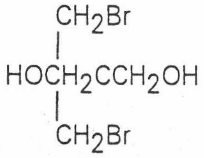
5.1.1 Polyurethane foams with tin compounds.

The LOI of the untreated and treated foams were measured to obtain an indication of the flame retardancy of these materials as shown in table 4-1 to 4-3. While Smoke evolution data are presented in table 4-1, 4-2, 4-4 and figure 4-1 to 4-14 by which sample tested in the NBS smoke chamber gave a high LOI value.

The untreated foam had an LOI of 20.5 which was increased to 23.6 when treated with the commercial phosphorous flame retardant, dimethoxymethyl phosphate(DMMP). These results indicated that DMMP was the most effective flame retardant. Unfortunately, DMMP double the smoke production of the foam, thus DMMP is not an effective fire retardant.

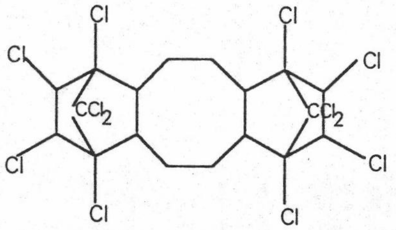
Of the tin treated foams, only those treated with dibutyltin diacetate, DBTA, exhibited in increase in LOI value more than 1% . The LOI value of DBTA treated foam was 22.7, which this flame retardancy was not as good as that given by the commercial DMMP. Furthermore, the DBTA treated foam produced a similar amount of smoke generated by DMMP treated foam. DBTO containing foams produced a reduction in smoke density but a reduction in flame retardancy was also observed. Other tin compound used in this experiment is similar to flame retardant efficiency of that imparted by DBTO. The results obtained clearly showed that the inclusion of tin compounds produced little or no further improvements to the fire retardancy of the polyurethane.

For the four halogenated fire retardants used in this study, C70 and DBNPG are both aliphatic compounds with contain 70% chlorine, and 61% bromine, respectively.

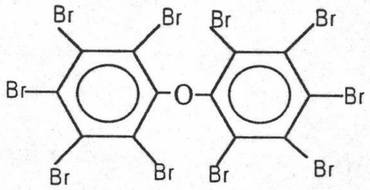


$\mathrm{HOCH_2\overset{CH_2Br}{\underset{CH_2Br}{C}}CH_2OH}$: Dibromoneopentylglycol (DBNPG)

Dechlorane is an alicyclic compound which contains 65 % chlorine while DBDPO is aromatic and contains 83 % bromine.



Dechlorane Plus (DECH)



Decabromodiphenyl oxide(DBDPO)

The LOI data of these additives were shown in table 4-2. Dechlorane was not an effective flame retardant in this polymeric system, whereas the other three additives all raised the LOI by over 2.0 units. However, all of them increased the smoke production of the burning foam. This was especially for the two brominated derivatives. According to the results, C70 was the most effective halogenated additive for this particular polyurethane.

From these results, the effect of halogenated organic fire retardants, C70 and DBDPO, in combination with tin or DMMP additive were studied. The flame retardancy of polyurethane treated with DMMP was enhanced about 2 to 3 units when used with halogen source but DMMP was still not an actually good fire retardant because of its toxicity and smoke evolution.

The tin compounds, DBTA, DBTO, DBTM and ZHS in combination with C70 and DBDPO imparted relatively high LOI value (>23 unit). Besides these LOI values were higher than those of polyurethane containing only the halogenated additive.

Hence tin additives had synergistic effect to halogen in polyurethane. The smoke data presented that all of tin compounds produced significant reductions in smoke evolution. Particularly, DBTM/C70 imparted the lowest Dmc/g values to the foam, 47.8 while the additive free foam has Dmc/g about 34.7.

The results clearly indicated the tin compounds, in combination with halogen source, were flame retardant and smoke suppressant additives for polyurethane foams. Although their flame retardancies were not as good as DMMP, but their lower smoke production could make them into viable alternatives to DMMP. It is particularly fortunate that C70 worked well with the tin compound because this material was the cheapest of the four halogenated additives used in this study.

On the basis of these results, the further studies focused on the effects of tin/C70 and tin/DBDPO additives as flame retardant at different addition levels.

5.1.2 Polyurethane foam with tin and chlorinated paraffin wax 70 compounds

From table 4-5, it can be seen that DBTA at a loading of 7 g, DBTO at 3 g and 7 g, and ZHS at 7 g, in combination with C70, with LOI value more than 24.0 unit, were the most effective flame retardants. In addition, the resulting foams burnt with considerably less smoke approaching 40 % for the higher loadings than did the DMMP/C70 treated foam. DBTM also gave good improvements in flame retardancy, although not as high as those combinations mentioned above. However, the smoke reduction of DBTM treated polyurethane was superior to DBTA, DBTO or ZHS treated foams. Unfortunately, the foams containing 1 g and 3 g DBTM tended to be of a poorer quality than foams containing the other tin additives used in this study so it was not recommended for further study.

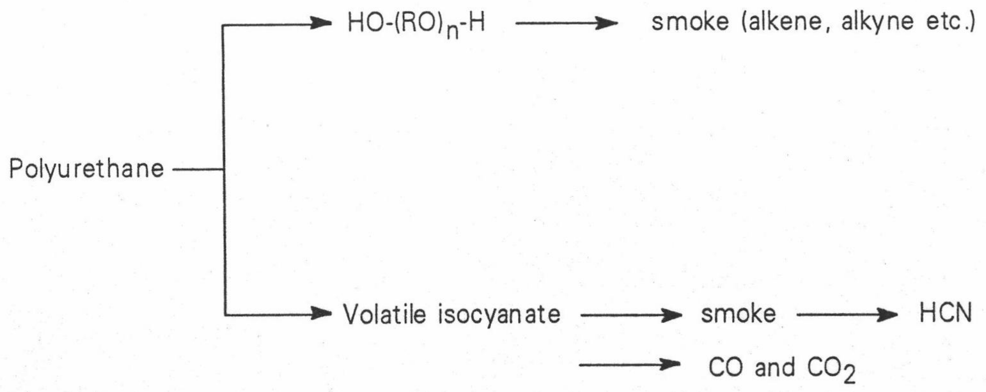
In general, a reduction in addition level of the tin compound resulted in a decrease in LOI and an increase in Dmc/g. DBTA was the only additive for which a lowest addition level gave a reduction in smoke emission (figure 4-6). Indeed, the presence of C70 with 1g DBTA produced a significant reduction, Dmc/g = 41.6. Thus, DBTA at the loading of 1 g and 3 g in combination with 10 g of C70 was more suitable binary system than at 7 g loading.

5.1.3 Polyurethane foam with tin and decabromodiphenyl oxide compounds.

The results in table 4-6 obtained for the tin/ DBDPO containing foams, with regards to flame retardancy, were quite similar to those for the tin/C70 analogous with the latter being slightly more effective. The amount of smoke emission was a significant difference of the two halogenated system. The organotin/DBDPO formulations were considerably more smoky than with inorganic tin/DBDPO, whose Dmc/g values were analogous to those given by the tin/C70 polymers. Once again, a decrease in addition level of the tin additive produced a decrease in LOI and an increase in Dmc/g, and once again DBTA was the exception to this role in that a decrease in amount additive gave a reduction in smoke evolved (figure 4-10).

5.2 Mechanistic studies

The effect of the tin additives on the thermal degradation of the polyurethanes in air was investigated using simultaneous TG/DIG/DTA. The data were presented in table 4-7 and 4-8, and figure 4-15 to 4-28. The additive-free foam (figure 4-15) losted about 45 % of its weight during the initial decomposition stage occurred in the temperature range 225-350 ^{o}C. This decomposition was largely due to the loss of volatile isocynate[12]. All the resulting char was subsequently oxidised to generate CO and CO_2 in the temperature range about 470 to 590^{o}C, in a highly exothermic process as indicated by large broad peaks in the corresponding DTA traces. The reaction may be commonly explained below.



The presence of DMMP (figure 4-15) had little effect on the combustion profile of the foam although the flame retardancy was improved and the smoke production altered. While the foam containing C70 underwent initial degradation at the lower temperature than that observed for the base foam. This mode of reaction was gas-phase retardation. In general, halogenated derivatives worked on gas-phase retardation. If these compounds decomposed at slightly lower temperature than that of untreated polymer, they mostly were the good effective retardants for this polymer. However, the flame-retardant compounds must be sufficiently stable thermally under mechanical work for practical application [14-16]. Dechlorane Plus, aliphatic chlorinated compound, had high decomposed temperature, about 350°C. Thus, it could not produce HCl above the ignition temperature of the foam so it was not a good flame retardant for this system. Since the ignition temperature of the other halogenated compounds in this study was not too high, these additives generated HCl below the ignition temperature of base foam and were a effective flame retardant. In the case of the DMMP/C70 foams (figure 4-18), The DMMP in combination with C70 additive altered the decomposition profile such that a distinct three-step initial breakdown was observed, with the first step occurring at a much lower temperature, and the third step at a significantly higher temperature than that of the corresponding single step for base polymer. In addition, it increased the amount of non-combustible fraction. It would appear that the phosphorus/chloride combination promoted a different reaction pathway, which led to the formation of this non-combustible deposit.

TGA curve of zinc hydroxystannate/C70 foams was shown in figure 4-21. When compared to TGA curve of base polymer, TGA curve of 7 g ZHS/C70 treated foam showed that the presence of ZHS altered both the initial and oxidative decomposition stages of the foam 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 (5-1).

$$ZnSn(OH)_6 \longrightarrow ZnSnO_3 + 3\,H_2O \qquad (5\text{-}1)$$

The DTA curve indicated that this first step was endothermic reaction. Then, a secondary process occurred at higher temperature as presented in equation (5-2).

$$2\,ZnSnO_3 \longrightarrow Zn_2SnO_4 + SnO_2 \qquad (5\text{-}2)$$

In the latter step, $ZnSnO_3$, product from first step, might promote the volatilisation of chlorine, possibly in form of metallic chlorides or oxychloride [8-10]. These occurred non-flammable products diffused in flame zone and leaded to a reduction in the supply of combustible volatiles to the flame zone for vapour phase action, behave as flame inhibitors in a similar manner to the analogous antimony halide species. Mechanisms of those systems might be similar to that of Sb_2O_3/halogenated system. The expected mechanism was shown below.

$$ZnSn(OH)_6 \longrightarrow ZnSnO_3 + 3\,H_2O \qquad (5\text{-}3)$$

$$ZnSnO_3 + 2\,RCl \longrightarrow SnOCl_2 + Zn(OR)_2 \qquad (5\text{-}4)$$

$$2\,SnOCl_2 \longrightarrow SnCl_4 + SnO_2 \qquad (5\text{-}5)$$

Gas flame retardant action of $SnCl_4$ might explain in same route of Sb_2O_3 action.

$$SnCl_4 + H\cdot \longrightarrow HCl + SnCl_3 \qquad (5\text{-}6)$$

$$SnCl_3 + H\cdot \longrightarrow HCl + SnCl_2 \qquad (5\text{-}7)$$

$$SnCl_2 + H\cdot \longrightarrow HCl + SnCl \qquad (5\text{-}8)$$

$$SnCl + H\cdot \longrightarrow HCl + Sn \qquad (5\text{-}9)$$

$$Sn + OH\cdot \longrightarrow SnOH\cdot \qquad (5\text{-}10)$$

$$SnOH\cdot + H\cdot \longrightarrow SnO + H_2 \qquad (5\text{-}11)$$

The occurred $SnCl_4$ attacked H· and OH· 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 and retarding the combustion.

Furthermore, the formation of tin halide and / or oxychloride 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 increase the amount of char formation particularly in 7 g ZHS addition. Hence it was possibly that 7g ZHS with 10 g of C70 exhibited mainly in a solid phase retardation.

According to smoke data, the observed smoke-suppressant effects in this system might arise from char promotion, reducing flammable volatiles to the flame zone, and gas phase oxidation of the soot and aromatic tars produced during foam burning because of the effectiveness of SnO_2 as catalyst in oxidation of carbon monoxide[25,26].

Interestingly, level of ZHS addition affected to combustion profile of the foam. An increase in the amount of tin additives leaded to a decrease in the weight loss during initial pyrolysis, and at the highest loading a more stable fraction was presented. Indeed, the char burn-off profile for the 1 g and 3 g additions was slightly similar to that of the C70 containing foam, whereas for 7g addition was extremely altered. Hence, the extent of Sn:Cl ratio in the polymer formulation mostly influenced to action mode of flame retardant.

With the ZS/C70 foams (figure 4-22), an increase in the tin additive level resulted in a decrease in the weight loss during initial pyrolysis as well, but the energy released by this process was unaffected. The effect of ZS in oxidation stage was similar to that of ZHS since ZHS decomposed to ZS as demonstated in equation (4-1). All three ZS/C70 containing foams showed a significant increase in the amount of non-combustible material, which was present after pyrolysis. So, its mechanism should be mainly a solid phase retardation as well.

For the DBTA/C70 and DBTO/C70 treated foams, The initial degradation profiles of both foams were significantly altered. DBTO itself produced SnO_2 at temperature range 160-280°C[27]

$$Bu_2SnO \text{ ------> } SnO_2 + BuOBu \qquad (5\text{-}12)$$

Whereas DBTA decomposed and gave SnO_2 at approximately 150°C. Both compounds increased in the amount of non-flammable material foam thus, their mechanisms are possibly as same as those of ZHS and ZS.

In case of foam containing DBDPO and tin compounds, DBDPO in the foam (figure 4-17) caused an increase in the weight loss during initial combustion, thus producing HBr, and a decrease in the amount of char formed. DMMP in combination with DBDPO decrease the weight loss during initial combustion and further increased the non-flammable fraction.

The ZHS and ZS greatly reduced the initial weight loss and increased the degradation temperature, thus demonstrating that ZHS and ZS stabilised the polymer. Furthermore, these systems caused the formation of a more stable char, coupled with the presence of a significant amount of non-combustible material so these compounds may act mostly in solid phase retardation.

The two organotin additives, DBTA and DBTO (figure 5-23 and 5-24) clearly altered the degradation pattern of the foam. An increase in the amount of organotin used, resulted in a decrease in the number of char-burnt off. DBTA foams produced very little non-combustible aterial, whereas DBTO foams gave amounts comparable to those given by the inorganic additives.

Mechanism of DBDPO was similar to that of C70. Since bond strength of C-Br weaker than that of C-Cl, DBDPO worked on both solid- and gas-phase retardations. In the first step, DBDPO produced easily HBr which acted as acceptor, converting the highly reactive and chain-carrying hydroxyl radical to the less reactive bromine radical as equation (5-13) to (5-17).

$$O\cdot + HBr \rightleftharpoons HO\cdot + Br\cdot \qquad (5\text{-}13)$$

$$HO\cdot + HBr \rightleftharpoons H_2O + Br\cdot \qquad (5\text{-}14)$$

$$Br\cdot + RH \rightleftharpoons HBr + R\cdot \qquad (5\text{-}15)$$

$$Br\cdot + Br\cdot \rightleftharpoons Br_2 \qquad (5\text{-}16)$$

$$Br\cdot + R\cdot \rightleftharpoons RBr \qquad (5\text{-}17)$$

Thus mechanism of DBTA in combination with DBDPO possibly act mainly in gas-phase retardation in which the tin oxide (SnO_2) and HBr evolved from the decomposition of tin compound and DBDPO respectively might react together and generated tin bromide and oxybromide to reduce H· and OH· radical in vapour phase. On the other hand, mechanisms of DBTO, ZHS or ZS in combination with DBDPO possibly should be solid phase retardation since these compounds increased char formation. However, the expected mechanisms which were described above should be confirmed for the further study.