Thermal Volatilisation Analysis of a TDI-based Flexible Polyurethane Foam containing Ammonium Polyphosphate.

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ABSTRACT

In this paper, we report a comprehensive study on a TDI-based foam containing 13% ammonium polyphosphate (APP) in order to examine the effect that this conventional fire retardant [17,18] has on the thermal and thermo-oxidative degradation behaviour of the polyurethane foam. The results from the TVA, ~~TGA~~ and ~~DSC~~TGA analysis show that the APP foam undergoes a significantly different degradation mechanism to the standard foam that we have reported previously. The ~~DSC and~~ TGA results revealed the presence of a two stage degradation process under a non-oxidative environment. The TVA results, on the other hand, revealed that degradation of the APP foam in fact occurs in four overlapping steps compared to the two-step process which occurs for the standard foam. The additional degradation steps observed for the APP foam are proposed to correspond to degradation of the fire retardant. Evolution of volatile material was also observed to occur at a lower temperature for the APP foam and it is proposed that the primary degradation of the urethane linkages *via* a depolycondensation reaction is acid-catalysed by the acidic hydroxyl groups which arise from degradation of APP. The sub-ambient differential distillation trace revealed that the nature and distribution of the volatiles evolved from the APP foam was profoundly different to the standard foam, which confirms that the secondary degradation is also altered in the presence of APP.

KEYWORDS:

Polyurethane foam; TDI; evolved gas analysis, mechanism

INTRODUCTION

Polyurethanes are one of the most versatile classes of polymers which now find vast use in modern society in applications as diverse as wound care and building insulation [1]. A major drawback of these materials, however, is their ease of flammability and the toxic nature of the gases which are evolved. Polyurethane foams, in particular, are widely used in upholstery and home furnishings and, as a result, are often major contributors to fires. At present there are effective fire retardant formulations available, however, many of these are now regarded as environmentally unacceptable. There is, therefore, the need to develop new formulations for use in polyurethane foams. The behaviour of a polymer in a fire is closely associated with its degradation behaviour and, as a result, much research has been conducted to study the thermal stability and degradation of polyurethane materials. Given the chemical and morphological complexity of polyurethanes, it is no surprise that the thermal degradation of polyurethane is equally complex; it depends on the structure of the material, making it strongly dependent on the type of polyol or polyisocyanate from which it is synthesised. The presence of additives, such as fire retardants, can also significantly affect the degradation processes which occur.

Whilst there have been a number of studies published on the thermal degradation chemistry of polyurethane materials [2-15], the literature concerning the degradation of foams is limited. Knowledge on the processes which occur during the degradation of toluene diisocyanate (TDI) based foams is more limited still as most studies have been conducted on methylene diphenyl diisocyanate (MDI) based materials. This is despite the fact that TDI is the isocyanate of choice for the majority of flexible foam formulations in the UK and North America. In our previous paper [16], we reported thermal degradation behaviour of a polyurethane foam, synthesised from TDI and a polyether polyol. The thermal degradation behaviour of this material was evaluated by a combination of thermogravimetric analysis (TGA) and thermal volatilisation analysis (TVA). The results demonstrated that the thermal degradation is a complex process which consists of competing mechanisms which yield an array of degradation products. The TVA results revealed that the degradation occurs in two steps, with the initial step corresponding to degradation of the urethane

linkages by two competing mechanisms. The first mechanism, proposed to be the predominant mechanism, involves simple depolymerisation of the urethane bond to yield TDI and polyol. A second, competing mechanism was proposed which involves dissociation of the urethane linkages to yield DAT, CO_2 and alkene-terminated polyol chains. The second degradation step has been shown to involve degradation of the polyol which was regenerated in the first degradation step. This was proposed to occur by random radical chain scission of the polyol to yield propene, formaldehyde, acetaldehyde, C_3H_6O isomers and high molar mass polyol chain fragments of various structures. Isothermal TVA studies revealed that this occurs as low as 250°C under vacuum but does not become significant until temperatures greater than 300°C.

In this paper, we report a comprehensive study on a TDI-based foam containing 13% ammonium polyphosphate (APP) in order to examine the effect that this conventional fire retardant [17,18] has on the thermal and thermo-oxidative degradation behaviour of the polyurethane foam. Again the overall degradation behaviour was examined by means of TGA, DSC and TVA studies. A small scale mini-crib fire test was also performed on the APP foam to examine the fire behaviour of the polyurethane foam and the effect which the fire retardant has on the flammability of the foam.

It has been established by Camino *et al*., [19] by means of TVA, that the thermal degradation of APP occurs in three steps between 200°C and 400°C. In the first step, which begins near 230°C, ammonia is eliminated from the -ONH_4 groups creating acidic hydroxyl groups which subsequently condense to form a crosslinked structure known as an ultraphosphate. The second step involves thermal degradation of the ultraphosphate to yield a highly cross-linked polyphosphoric acid, ammonia, water and phosphate fragments. Finally, above 370°C the polyphosphoric acid decomposes to yield phosphate fragments which will accumulate in the cold-ring fraction during TVA.

Grassie and Mendoza studied the effect of APP on the thermal degradation of a polyurethane based on MDI and PEGs of low molecular weights [20]. TVA results revealed that APP has a profound effect on the thermal degradation with significantly different products observed in the presence of the fire retardant. Volatile products observed included CO_2, ammonia, 1,4-dioxane, water, and aromatic amines including aniline and *N*-ethylaniline. In addition, a

cold-ring fraction comprising 25% of the original sample was obtained which was shown to contain phosphorus and amines, although definitive identification of the species present was not possible. A large quantity of residue was also obtained which suggests that cross-linked structures have formed during the degradation, with analysis of this residue showing the presence of amines. It appears, therefore, that the presence of APP promoted the production of amine compounds during the degradation of the polyurethane. The presence of both MDI and the secondary amine *N*-ethylaniline suggested that degradation of the urethane linkage occured by both a depolycondensation reaction and by a four-membered ring transition state mechanism, respectively. The depolycondensation reaction of the urethane is acid-catalysed by the acidic hydroxyl groups which arise from degradation of APP to form ultraphosphate.

In the presence of the acidic hydroxyl groups the regenerated PEG undergoes an acid-catalysed dehydration reaction to form 1,4-dioxane and water [21]. It is also possible that an alcoholysis reaction of the polyphosphate could occur to produce esters, resulting in a network of cross-linked polyether and polyphosphate chains. This network would then degrade yielding phosphate fragments, phosphoric acid and an alkene, which subsequently liberates acetaldehyde. Alkenes and acetaldehyde were not observed as degradation products suggesting that either this reaction does not occur or that once formed the phosphate esters volatilise and accumulate in the cold-ring before any further degradation can take place. The presence of acid groups during the degradation alters the route in which the secondary products are formed. In the pure polyurethane, thermal degradation yielded a residue rich in polycarbodiimide, however this was not observed in the presence of APP. It was proposed that carbodiimide may have formed but subsequently reacts with other degradation products. Alternatively, instead of reacting to form carbodiimide the isocyanate groups could have reacted with water or acidic hydroxyl groups on the phosphate.

The effect of APP on polyurethanes prepared from MDI and high molecular weight PEGs was also studied [22] and it was observed that APP alters the degradation of these polyurethanes in a similar way as for those containing low molecular weight PEGs. The main difference was the presence of acetaldehyde and ethene which were proposed to have been formed from degradation of the urethane linkage *via* a six-membered ring transition state.

Duquesne *et al*. [23,24] also observed that the thermal degradation of polyurethane begins at a lower temperature in the presence of APP, due to acid catalysis of the depolycondensation

reaction, and that a large quantity of residue is obtained. TGA studies under air and nitrogen revealed that the presence of oxygen leads to the formation of a carbonaceous char which is stable in the temperature range 350-530°C. ^{13}C and ^{31}P NMR analysis of the chars, in combination with FTIR spectroscopy, reveals that APP reacts with polyurethane and forms a phosphocarbonaceous char containing P-O-C bridges.

It is thus believed that the mode of action of APP in polyurethanes is associated primarily with condensed-phase processes and is similar to its activity in cellulosic materials, involving degradation to yield phosphoric acids which promote the formation of an insulating char. This explains the presence of large quantities of residue obtained when APP is present. This could occur by the reaction of the polyurethane with the degradation products of APP or the ultraphosphate could form a glass-like coating on the polymer thereby protecting it from heat and inhibiting the diffusion of combustible gases.

EXPERIMENTAL
Materials
Flexible polyurethane foam was prepared in the University of Strathclyde following a patented flexible foam formulation. [25] The isocyanate employed was TDI from Sigma-~~Aldriej~~Aldrich (with an isocyanate index of 108) and the polyol was Alcupol F-5611 from Repsol (a trifunctional polyether polyol of molar mass 3000 g mol^{-1} and hydroxyl index 56 mg KOH g^{-1}). Typically, the isocyanate was incorporated at a level of 46 parts per hundred polyol (pph).   Water (3 pph) was employed as the blowing agent and the catalysts employed were dimethylethanolamine (DMEA, Sigma-Aldrich 0.3 pph), triethylenediamine (Dabco 33LV, Air Products, 0.3 pph) and stannous octoate (Kosmos 29, Goldschmidt Chemical, 0.8 pph).   A silicone-based surfactant (L620LV, GE Silicones, 1 pph) was also employed. Ammonium polyphosphate (APP FR CROS 484, Budenheim, 20 pph) was dispersed into the polyol before the addition of the isocyanate.   It should be noted that the levels of surfactant and catalyst present are sufficiently low to assume that these do not participate in or affect the degradation reactions which occur.

Thermogravimetric Analysis (TGA)
All TGA experiments were carried out using a Perkin Elmer TGA7 thermogravimetric analyzer with 3-5 mg cylindrical foam samples being analysed. The system was initially heated to 50°C and held isothermally for five minutes. Following this, the sample was heated

at a rate of 10°C min^{-1} from 50°C to 800°C under a flow of 30 ml min^{-1} of helium. The mass loss as a function of temperature was monitored and from this the first derivative of the mass loss curve was calculated as a function of temperature. The temperature at which the onset of degradation occurs has been determined from the TGA curves and will be reported herein as the temperature at which the material has lost 5% of its original weight.

Thermal Volatilisation Analysis (TVA)

 All TVA analyses were carried out using a TVA line which was built in-house, based upon the apparatus and techniques described by McNeill *et al.* [26] and described in our earlier paper [1]. All dynamic TVA runs were conducted under vacuum using 25 mg samples, with the samples heated from ambient temperature to 550ºC at a rate of 10ºC min^{-1}. For the isothermal TVA experiments 50 mg samples were heated to the chosen temperature (250, 300, 350 or 400°C) at a rate of 10ºC min^{-1} and held isothermally for 30 minutes. ~~A 1-300 amu Hiden single quadrapole RGA mass spectrometer sampled a continuous product stream during both the degradation and differential distillation runs. Sub~~

The TVA apparatus consists primarily of a glass sample chamber connected to a primary liquid nitrogen cooled sub-ambient trap and a series of secondary liquid nitrogen cooled cold traps. The entire system is pumped to a vacuum of ~1x10^{-4} Torr by the use of a two-stage rotary pump and an oil diffusion pumping system. As the sample is heated at a linear rate, using a programmable tube furnace, low volatility products (e.g. oligomers) condense at the water jacket cooled 'cold ring' placed directly above the sample tube or the liquid nitrogen cooled primary trap. In contrast, more volatile degradation species with lower boiling points are collected in a primary liquid nitrogen cooled sub-ambient trap, maintained at a temperature of –196 ºC. These 'condensable' fractions are volatile at room temperature but involatile at liquid nitrogen temperatures, hence collect within the primary sub-ambient trap. Linear response Pirani gauges, positioned at both the entrance and exit of the primary sub-ambient trap, enables the evolution of both condensable and non-condensable volatiles to be continuously monitored as a function of pressure versus temperature. However, the volatile products collected in the cold ring fraction are not detected by Pirani gauges as they condense prior to exiting the degradation tube. Subsequent sub-ambient differential distillation of the collected volatiles was carried out by heating the primary sub-ambient trap from -196°C to ambient temperature. –A 1-300 amu Hiden single quadrapole RGA mass spectrometer samples a continuous product stream during both the degradation and sub-ambient

distillation runs. This is particularly useful for the identification of non-condensable degradation products such as carbon monoxide and methane and condensable degradation products collected from the sub-ambient distillation procedure.

Volatiles from the sub-ambient distillation are separated into four major fractions for subsequent IR and GC-MS analysis. All FTIR analysis of the collected TVA products is carried out using a Perkin Elmer Spectrum 100 FTIR Spectrometer used in transmission mode. High boiling 'cold-ring' fractions are cast from chloroform solution onto NaCl disks for analysis. Low-boiling volatiles are analyzed in the gas phase using gas phase cells with NaCl windows. All GC-MS analyses of the collected TVA products is carried out using a Finnigan ThermoQuest capillary column trace GC and Finnigan Polaris Quadrapole Mass Spectrometer. Cold-ring fractions and high molar mass products are dissolved in spectroscopy grade chloroform and subsequently analysed.

Mini-Crib Fire Test

The 'mini-crib' fire test performed in this investigation has been designed at Strathclyde as a small-scale test based on the British Standard 5852 crib-5 test which is used to test the flammability of upholstered seating when exposed to a flaming ignition source [27]. For the 'mini-crib' foam samples were cut into squares with dimensions 10 x 10 x 2 cm which were then stored in a desiccator for at least a week at 40°C to ensure the samples had similar moisture contents before the fire test was performed.

Two 12 x 12 cm squares of wire gauze were joined together at one edge and their mass recorded. Two 10 x 10 cm squares of foam were then pinned together using upholstery pins to form a "chair" and placed onto the wire gauze. The mass of the foam and gauze was then recorded and a piece of cotton wool pinned onto the foam chair. This assembly was then positioned on top of metal back and base plates positioned on a wooden block. An illustration of this assembly is shown in Figure 1. To start the test 0.5 g of propan-2-ol was poured onto the cotton wool and lit. The foam was then left to burn and once the fire had extinguished the assembly was weighed and the mass loss of the foam during the fire calculated.
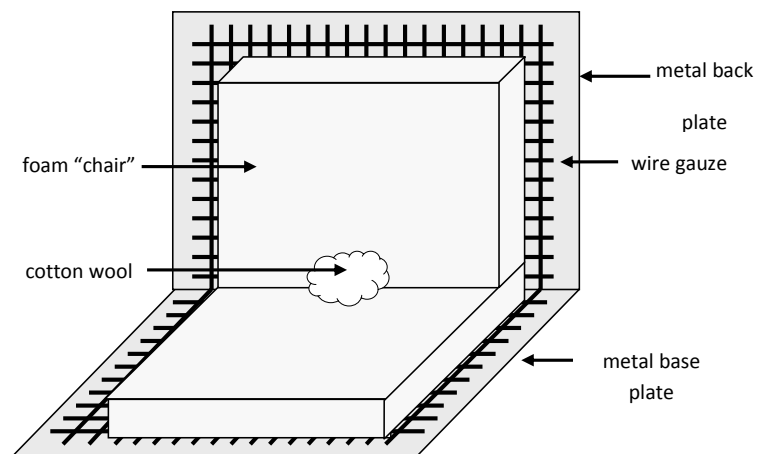
Figure 1: Set-up for the mini-crib fire test

RESULTS AND DISCUSSION

TGA

The TGA and DTG curves for the standard and APP foams analysed in air are presented in Figure 2 with the temperatures at which significant mass loss occurs and the maximum temperatures of the DTG peaks displayed in Table 1. A two-step degradation process is observed for the APP foam, however, there are differences observed in the thermo-oxidative behaviour compared to that of the standard foam. Significant mass loss is evident at similar temperatures for both foams and the initial mass loss step for the APP occurs with a maximum rate of mass loss at the same temperature as for the standard foam. This suggests that the temperature at which the first degradation step of the polyurethane occurs is not significantly altered in the presence of APP under an oxidative environment. The APP foam, however, exhibits less mass loss in this first step than the standard foam which suggests that the mechanisms of degradation may be altered by the fire retardant.
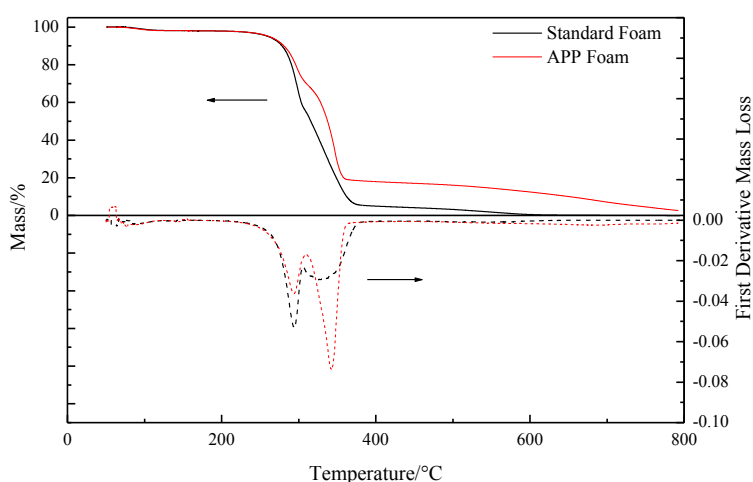

Figure 2: TGA (solid lines) and DTG (dashed lines) results for the standard and APP foam analysed in air

Type of Foam	Atmosphere	Onset of Significant Mass Loss /°C	Peak 1 Maximum /°C	Peak 2 Maximum /°C
Standard	Air	260	294	330
APP	Air	261	294	343
Standard	Helium	260	289	370
APP	Helium	268	295	365

Table 1: Onset temperatures and peak maxima for the standard and APP foams analysed in air and helium

The maximum rate of mass loss for the second step occurs at a higher temperature in the APP foam which suggests that the fire retardant is altering the secondary degradation mechanisms of the polyurethane foam. Finally, it can be observed from Figure 2 that the APP foam has a residue of approximately 20% remaining at 360°C before a slow continual mass loss occurs until 800°C resulting in a final residue of 3%. The standard foam, on the other hand, has significantly less residue remaining after the second mass loss step (approximately 6%) and has a negligible residue remaining at the end of the analysis. An increase in the level of char is expected as a proportion of the APP will remain in the solid-phase even at 800°C. The TGA of APP on its own under air shows that a residue of approximately 4% remains at 800°C, which equates to 0.5% of the 3% residue observed for the foam which contains 13.35% APP. This confirms that the observed increase in char yield for the APP foam is a result of the fire retardant promoting char formation, as has been reported in the literature [17,18].

Presented in Figure 3 are the TGA and DTG curves for the standard and APP foams analysed in helium. The temperatures at which significant mass loss occurs and the maximum temperatures of the DTG peaks are displayed in Table 1.
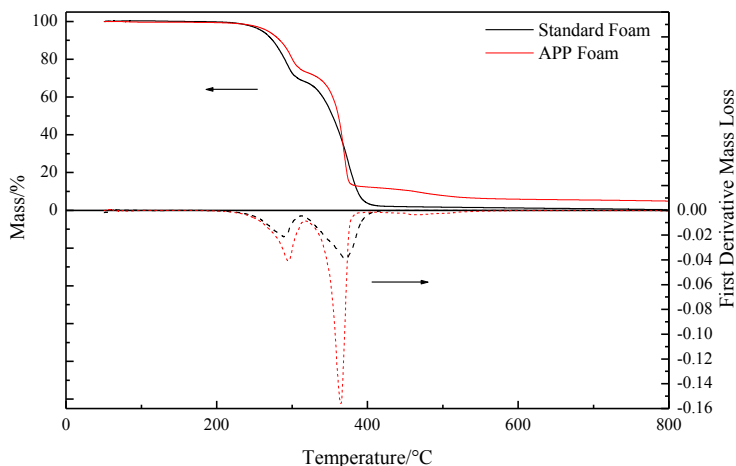
Figure 3: TGA (solid lines) and DTG (dashed lines) results for the standard and APP foams analysed in He

Once again it can be observed that the APP foam shows differences in its thermal degradation behaviour compared to that of the standard foam. A higher onset of significant mass loss is observed for the APP foam and the initial mass loss step occurs with a maximum rate of mass loss at higher temperatures. This suggests that the primary degradation step of the polyurethane foam may be altered in the presence of the fire retardant. The second degradation step, on the other hand, occurs with a maximum rate of mass loss at a lower temperature than for the standard foam. This suggests that the secondary degradation processes are accelerated in the presence of APP or are different to those which occur for the standard foam. Finally, it can be observed from Figure 3 that the foam has a residue of approximately 13% remaining at 380°C before a slow continual mass loss occurs until 800°C resulting in a final residue of 5%. This is in contrast to the standard foam which has significantly less residue remaining after the second mass loss step (approximately 3%) and has a negligible residue remaining at the end of the analysis. The TGA of APP on its own under helium shows that again a residue of approximately 4% remains at 800°C, which equates to 0.5% of the 5% residue observed for the foam. Again this indicates that APP promotes the formation of char in this polyurethane foam.

The TGA results reveal that the char yields obtained from the APP foam differ significantly between the oxidative and inert environments. At the lower temperatures under air the quantity of char is larger than under nitrogen. This is in correlation with the results of

Duquesne *et al.* who reported that the presence of oxygen during the degradation of an APP-containing polyurethane leads to the formation of a carbonaceous char which is stable in the temperature range 350-530°C [23,24].

Dynamic TVA Degradation Profile

The TVA degradation profiles for the standard and APP foams showing the rate of volatiles evolution as a function of furnace temperature are presented in Figure 4. The sample temperatures for the major events which occur during the degradation of these foams are presented in Table 2.
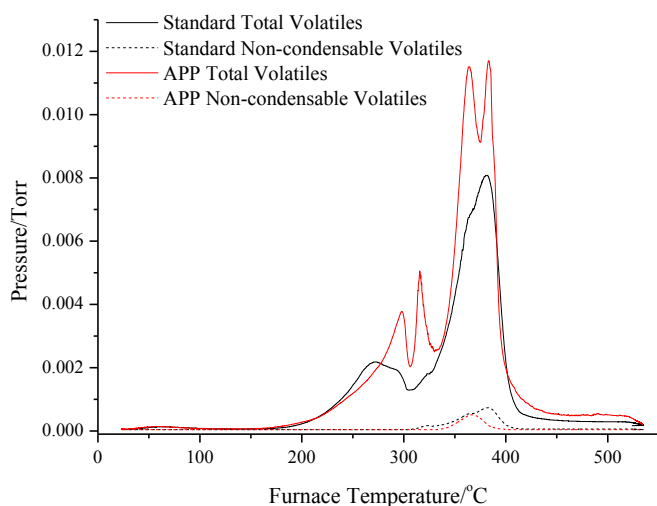

Figure 4: TVA degradation profiles for the standard and APP foams

Foam	Onset of Volatiles Evolution (°C)	Peak 1 Max. rate of volatiles evolution (°C)	Peak 2 Max. rate of volatiles evolution (°C)	Peak 3 Max. rate of volatiles evolution (°C)	Peak 4 Max. rate of volatiles evolution (°C)	End of volatiles evolution (°C)
Standard	~145	241	351	-	-	~400
APP	~135	268	285	334	352	~410

Table 2: Sample temperatures for the key events occurring during the degradation of the standard and APP foams

It can be clearly observed from Figure 4 that the APP foam exhibits a significantly different degradation profile to that of the standard foam. Evolution of volatile material occurs at a lower temperature for the APP foam which could be a result of degradation of the fire

retardant commencing, or it could indicate that the fire retardant lowers the temperature at which the polyurethane begins to degrade. Grassie and Mendoza [20] and Duquesne *et al.* [24] proposed that the depolycondensation reaction of the urethane linkages is acid-catalysed by the acidic hydroxyl groups which arise from degradation of APP to form ultraphosphate. It could, therefore, be the case that the evolution of volatile material occurs at a lower temperature as a result of the degradation of the urethane linkages being catalysed by the acidic species produced as the fire retardant degrades.

It can be observed from Figure 4 that the volatile degradation products are evolved from the APP foam in four steps, each of which corresponds to a different degradation process. The first two degradation steps with maximum rates of volatiles evolution at 268°C and 285°C are likely to correspond to degradation of the urethane linkages within the foam, primarily by an acid-catalysed depolycondensation reaction, and degradation of the APP to form the ultraphosphate followed by degradation of this compound to yield polyphosphoric acid [28]. The third degradation process, which exhibits a maximum rate of volatiles evolution at 334°C, occurs with evolution of a low level of non-condensable volatiles. These volatiles were identified by online MS as primarily methane and CO, with traces of hydrogen also present. This third step can, therefore, be attributed to degradation of the polyol component of the foam as these non-condensable volatiles result from degradation reactions of the polyol. This occurs at a lower temperature than that of the standard foam which suggests that the degradation mechanisms which are operating are altered in the presence of APP. Finally, the fourth degradation step can be proposed to be due to the final degradation step of the APP in which the polyphosphoric acid decomposes to yield phosphate fragments [28].

It is interesting to note that the TVA profile revealed the presence of four stages of volatiles evolution, whereas the TGA results only showed a two-step mass loss profile. It can be observed from the TVA profile that the first two steps are not completely resolved from each other, nor are the third and fourth steps, which indicates that the degradation steps for the APP foam are overlapping. Volatilisation of the degradation products is facilitated under vacuum; therefore, the presence of four overlapping steps is more evident in the TVA curves. During the TGA experiments, on the other hand, the degradation steps overlap to such an extent that only two mass loss steps are observed. This observation highlights the value of the TVA technique and the need to employ complementary analysis techniques when studying the degradation of polymers.

A significant residue remained at the base of the TVA tube following the analysis of the analysis of the APP foam; this was not observed during the degradation of the standard foam and suggests that APP promotes the charring reactions within the foam. Due to complications with removing the residue from the sample tube no further analysis was conducted on this material.

Cold-ring Fraction Analysis

During the analysis of the APP foam a significant yellow liquid cold-ring fraction was collected. The FTIR spectrum for this cold-ring fraction showed peaks similar to those for the cold-ring fraction collected from the standard foam [16]. The GC-MS chromatogram also showed similar results to that of the standard foam with TDI being identified, as well as a series of high molar mass polyol chain fragments which arise from degradation of the polyol component of the foam. The presence of TDI in the cold-ring fraction confirms that the degradation mechanism of the urethane bonds within the polyurethane foam is not significantly affected by the APP. The depolymerisation reaction is, therefore, proposed to be the predominant reaction which occurs.

Condensable Fraction: Sub-ambient Differential Distillation and Characterisation

The condensable fraction collected from the APP foam was separated by sub-ambient differential distillation into three fractions which were subsequently analysed by FTIR spectroscopy and GC-MS. The sub-ambient differential distillation trace for the standard and APP foams are presented Figure 5 with the identifications for each of the peaks in the sub-ambient differential distillation trace presented in Table 3.
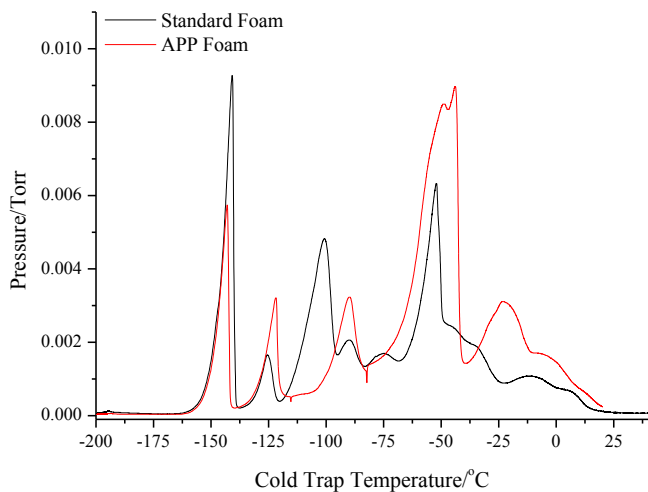
Figure 5: Sub-ambient differential distillation traces for the condensable fractions collected from the standard and APP foams

Peak	Standard Foam	APP Foam
1	Propene and CO_2	Propene and CO_2
2	Formaldehyde	Ammonia
3	Acetaldehyde	No peak 3 present for this foam
4	C_3H_6O compounds	Propanal
5	Higher molar mass polyol fragments	No peak 5 present for this foam
6	Water and higher molar mass polyol fragments	Water and higher molar mass polyol fragments
7	Higher molar mass polyol fragments	Higher molar mass polyol fragments including 2,5-dimethyl-1,4-dioxane

Table 3: Identifications for the peaks in the sub-ambient differential distillation traces of the standard and APP foams

It can be observed that the APP foam shows significant differences in both the nature and level of the degradation products evolved compared to the standard foam. Formaldehyde and acetaldehyde, which are two key degradation products evolved from the standard foam, are absent in the APP foam. Instead, ammonia and propanal are evolved and much larger

quantities of water and higher molar mass species are observed. Both the ammonia and the water are products of the degradation of the APP [28].

A complex mixture of higher molar mass compounds was evolved from -40°C onwards; these are likely to consist of polyol fragments and phosphate fragments which arise from degradation of the APP. The GC-MS chromatogram for the final fraction collected from the APP revealed the presence of an additional compound not present in the standard foam. The compound was identified as 2,5-dimethyl-1,4-dioxane.

The fundamental differences which are observed in the sub-ambient differential distillation trace for the APP foam compared to the standard foam suggest that different degradation mechanisms are occurring for this foam.

Isothermal TVA Degradation Profile

In order to gain further information regarding the overlapping degradation processes observed during the degradation of the APP foam, isothermal TVA experiments were conducted at 250, 300, 350 and 400°C.

Presented in Figure 6 are the TVA curves for the isothermal degradation studies for the APP foam. The TVA profile at 250°C shows the presence a broad peak corresponding to the evolution of a low level of volatile material at this temperature. These volatiles are most likely degradation products associated with the degradation of the urethane linkages and polyol component of the foam; however, the volatiles may also be associated with first degradation step of the APP fire retardant, *i.e.* degradation of the APP to form an ultraphosphate. If this was the case then ammonia and water would be observed. By 300°C the first two degradation steps are complete and the third step begins to occur during the isothermal hold. As was the case for the analysis of the standard foam, there were no significant non-condensable volatiles detected by 300°C which indicates that the degradation reactions of the polyol which yield CO, methane and hydrogen are not significant at lower temperatures.
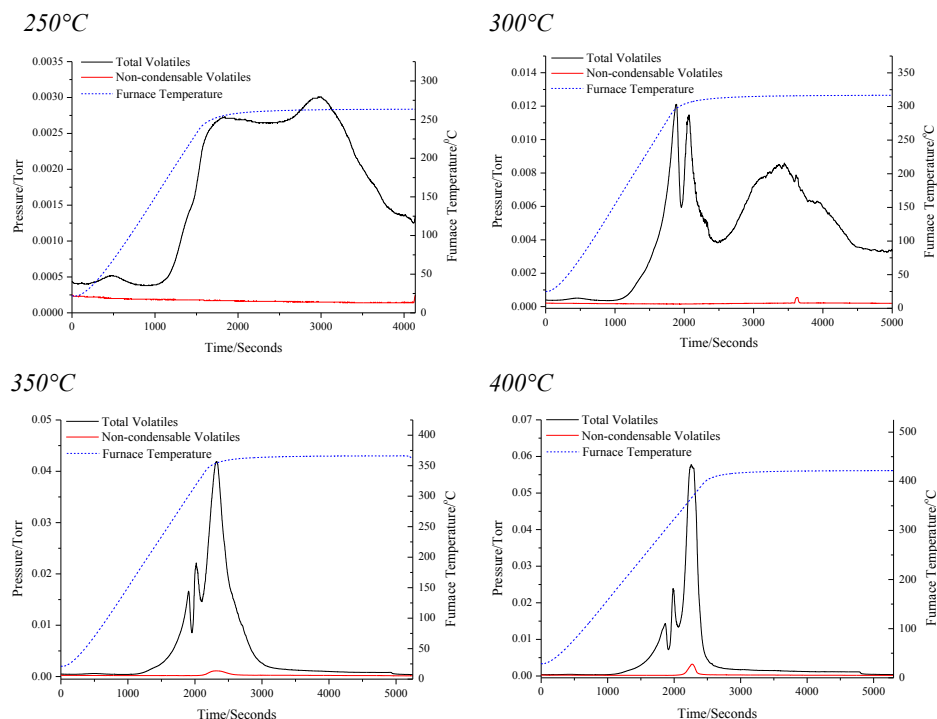
250°C

300°C

350°C

400°C

Figure 6: Isothermal TVA curves for the APP foam at 250, 300, 350 and 400°C

By 350°C the third peak is essentially complete and a peak corresponding to the evolution of non-condensable volatiles (methane, carbon monoxide and traces of hydrogen) is now observed. This indicates that at temperatures between 300°C and 350°C the degradation reactions of the polyol which yield non-condensable material have become significant. The TVA profile at 400°C shows little difference to that at 350°C. It is interesting to note that in the dynamic TVA experiment in which the sample was heated to 550°C there were two overlapping peaks observed between 300°C and 400°C, whilst in the isothermal runs there was only one peak observed. This suggests that in the isothermal experiments, where larger sample sizes are employed, the two peaks completely overlap and appear as one single peak. This is most likely a result of the greater thermal lag effects which will be encountered through use of significantly larger samples of foam.

Cold-ring Fraction Analysis

At 250°C a small amount of cold-ring fraction was recovered, however, the FTIR and GC-MS spectra of this fraction were weak and showed few peaks of interest. By 300°C the cold-

ring fraction was more significant, with the FTIR and GC-MS spectra revealing the presence of TDI and polyol-based degradation products. This indicates that at 300°C degradation of the polyol component of the foam to yield high molar mass fragments has become significant. Similar spectra were obtained for the cold-ring fractions collected at 350°C and 400°C.

Residue Analysis

During the isothermal degradation of the APP foam a clear liquid chloroform-soluble residue was recovered from the base of the TVA tube following the degradations at 250°C and 300°C. There was no liquid residue remaining at 350°C or 400°C which indicates that the polyol had degraded completely by 350°C. This is in contrast to the results for the standard foam which showed that a liquid residue was still present at 350°C. The absence of a liquid residue at 350°C for the APP foam could be due to degradation of the polyol being accelerated in the presence of the fire retardant or it could be the case that the APP causes the foam to char at lower temperatures and the remaining polyol gets incorporated into the char structure at 350°C. In either case these results, once again, highlight that the APP foam shows differences in its degradation compared to the standard foam.

The FTIR and ^{1}H NMR spectra of the residues collected from the APP foam were almost identical to those obtained from the standard foam and those of the neat polyol, demonstrating that the residues consist primarily of regenerated polyol. The FTIR spectrum of the residue at 250°C showed an additional small peak not observed in the polyol spectrum at 1731 cm^{-1}, which indicates the presence of residual urethane linkages within the residue. This carbonyl peak was less significant in the FTIR spectrum of the residue at 300°C, which indicates that further degradation of the urethane linkages has occurred by this temperature.

Condensable Fraction: Sub-ambient Differential Distillation and Characterisation

The condensable fractions collected during the isothermal TVA experiments were separated by sub-ambient differential distillation into four fractions which were then analysed by online MS, FTIR spectroscopy and GC-MS. Presented in Figure 7 are the differential distillation traces which show the volatile degradation products which are evolved at each of the temperatures employed.
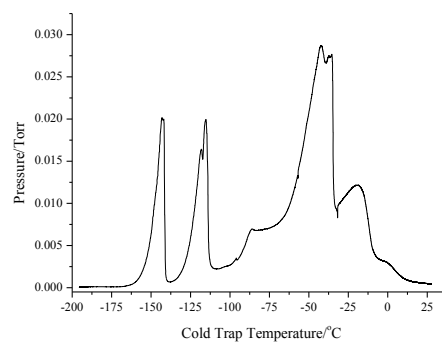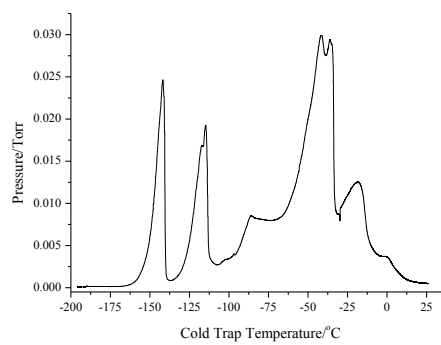
250°C
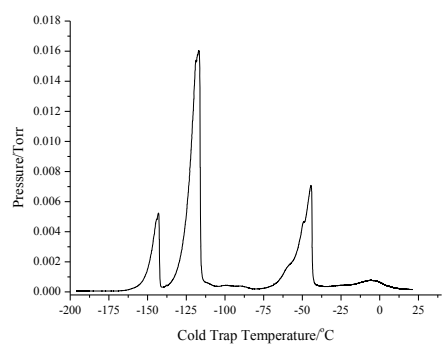
300°C
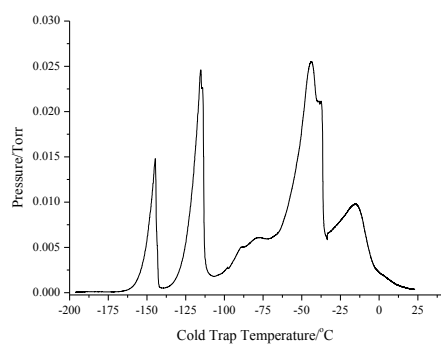
350°C

400°C

Figure 7: Differential distillation traces for the isothermal TVA studies on the APP foam

The temperature ranges of the fractions collected and the identity of each of the products within the fractions are presented in Table 4.

Fraction range	Degradation Temperature 250°C	300-400°C
-196°C to -140°C	Carbon dioxide	Propene, carbon dioxide
-140°C to -60°C	Ammonia	Ammonia, propanal
-60° to -40°C	Water and high molar mass polyol fragments	Water and high molar polyol fragments
-40°C to 25°C	High molar mass polyol fragments	High molar mass polyol fragments

Table 4: Sub-ambient differential distillations fractions collected from the isothermal TVA studies

It can be observed from Figure 7 that as the degradation temperature is increased greater quantities of condensable volatiles are evolved, and the product distribution is altered. At 250°C three major peaks are observed which correspond to carbon dioxide, ammonia and water. Low levels of higher molar mass species are also observed at this temperature. As was the case for the standard foam, the presence of carbon dioxide and TDI confirms that there are two competing degradation mechanisms occurring for the urethane linkages within the APP foam. The presence of ammonia and water at this temperature indicates that the fire retardant has begun to degrade to form ultraphosphate at 250°C.

By 300°C the trace is more complex, with propene, propanal and larger quantities of high molar mass polyol fragments now being observed which is indicative of significant polyol degradation occurring. There are no new products observed above 300°C, however, the level of some products does change, with the propene/ carbon dioxide and propanal peaks increasing in size as further degradation of the polyol occurs.

Fire Tests

Presented in Figure 8 are pictures taken 30 seconds into the mini-crib fire tests of the standard and APP foams, respectively.

After 30 seconds – standard

After 30 seconds - APP

Figure 8: Images from the mini-crib fire test of the standard foam (upper) APP foam (lower)

It can be observed from Figure 8 that once ignited the standard foam burned readily and did not self-extinguish the flame. This result is expected as non-fire retarded flexible polyurethane foams are reported to be easily ignited in air and burn rapidly once ignited. [11] The calculated mass loss for the non-retarded foam once the foam had burnt out was 86.4%. The APP foam, on the other hand, burned much more slowly than the standard foam and self-extinguished the flame before the entire foam was consumed. It could be seen that a section of the APP foam which has a layer of protective black char on the surface remained at the end of the test. The calculated mass loss from the APP foam was 44.5%, almost half that of the standard foam.

The results from the fire tests, therefore, confirm that APP reduces the flammability of the foam through the formation of a protective char which leads to significantly smaller quantities of the material being consumed.

PROPOSED MECHANISMS OF DEGRADATION AND CONCLUSIONS

The results from the ~~TVA,~~ TGA and ~~DSC analysis~~TVA analyses show that the APP foam undergoes a significantly different degradation mechanism to the standard foam. The ~~DSC and~~ TGA results revealed the presence of a two stage degradation process under a non-oxidative environment. The TVA results, on the other hand, revealed that degradation of the APP foam in fact occurs in four overlapping steps compared to the two-step process which occurs for the standard foam. The additional degradation steps observed for the APP foam are proposed to correspond to degradation of the fire retardant.

Evolution of volatile material was also observed to occur at a lower temperature for the APP foam and it is proposed that degradation of the urethane linkages *via* a depolycondensation reaction is acid-catalysed by the acidic hydroxyl groups which arise from degradation of APP, as shown Figure 9. This is in correlation with the work of Grassie and Mendoza which showed that APP caused the depolymerisation reaction for an MDI-based polyurethane to be acid-catalysed [20,22].

The sub-ambient differential distillation trace revealed that the nature and distribution of the volatiles evolved from the APP foam was profoundly different to the standard foam, which confirms that the secondary degradation processes are altered in the presence of APP. It is possible that acid-catalysed degradation of the regenerated polyol could occur as was observed by Grassie and Mendoza [20-22]. This would result in the formation of 2,5-dimethyl-1,4-dioxane, water and an alkene-terminated polyol chain as shown in Figure 10. Acid hydrolysis of the alkene-terminated polyol chain would then yield propanal.
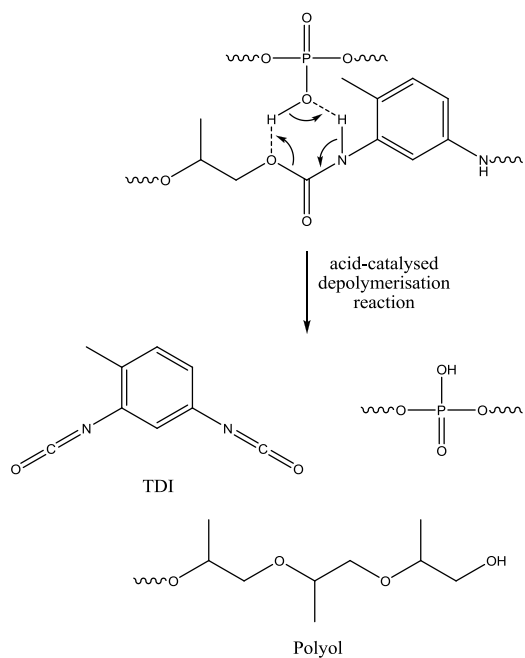
Figure 9: Acid-catalysed degradation of the urethane linkages
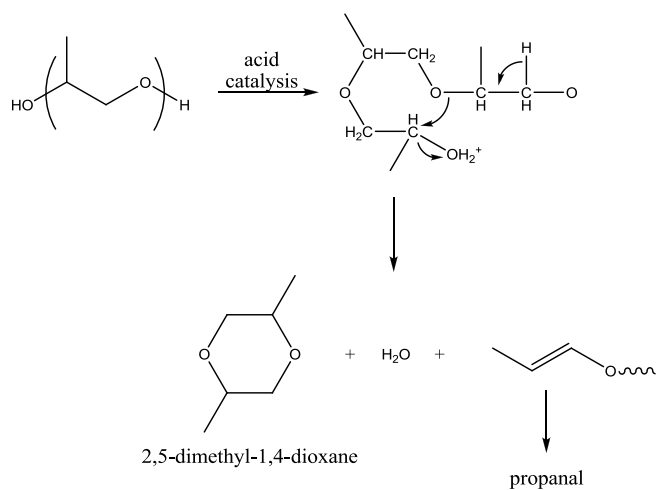

Figure 10: Acid-catalysed degradation of the polyol component

Grassie and Mendoza also proposed that a phosphorylation reaction could occur between the ultraphosphate and the polyol which would lead to phosphorus esters. Degradation of this

network would then occur yielding phosphoric acid and an alkene terminated chain, as shown in Figure 11. This would once again generate propanal by acid hydrolysis.

Both of the mechanisms shown in Figures 10 and 11 are plausible and explain the absence of acetaldehyde and formaldehyde and the presence of 2,5-dimethyl-1,4-dioxane and large quantities of propanal. The presence of acidic species during the degradation of the foam is believed to promote char formation and this is evident from the results of the mini-crib fire tests.
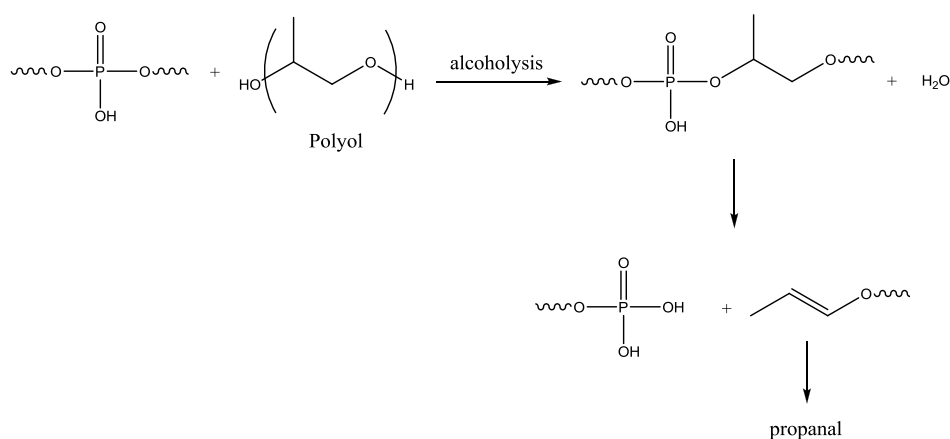

Figure 11: Phosphorylation of the polyol and subsequent degradation of the phosphorus esters

The results from the isothermal TVA studies provide further information regarding the degradation processes occurring within the APP foam. The presence of a polyol-based residue at 250°C and 300°C and TDI within the cold-ring fractions confirms that degradation of the urethane linkages within the APP foam occurs *via* a depolymerisation reaction. As was the case for the standard foam, CO_2 was identified as a degradation product at 250°C which indicates that the urethane linkages in the APP foam also degrade by dissociation *via* the six-membered ring or four-membered ring transition states discussed in our earlier paper [1].

In addition to CO_2, water and ammonia were evolved from the APP foam in significant quantities at 250°C. This confirms that the APP fire retardant begins to degrade at this temperature to yield an ultraphosphate, with water and ammonia as the volatile degradation products. By 300°C the polyol is proposed to be undergoing significant degradation, with propene and propanal being observed as additional degradation products. At temperatures

above 300°C no new degradation products were evolved, however, the levels of the volatile degradation products increases as the polyol undergoes further degradation.

In contrast to the standard foam, there were no liquid residues recovered from the APP foam at 350°C and 400°C. This suggests that degradation of the polyol in the presence of APP, which is proposed to occur *via* an acid-catalysed mechanism, is complete at lower temperatures than the random radical chain scission mechanism which occurs in the standard foam. It could also be the case, however, that APP causes the foam to char at lower temperatures and, as a result, any remaining polyol becomes incorporated into the char structure.

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