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Review

The Decomposition of Polyurethane and Fire Retardants: A Review

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Abstract: Polyurethane is used extensively in the furniture industry, primarily in beds and sofas. There is a significant volume of research pertaining to the flammability of polyurethane materials, but very little regarding smoke toxicity. Given toxic fire effluents are a primary cause of injury and fatalities, more work needs to be done to test the toxicity of polyurethane materials and the fire retardants they are coated/bound with. The aim of the review is to provide a comprehensive analysis of the decomposition of polyurethane and discuss the development and application of modern fire retardants and their effect on smoke toxicity. This work then provides discussion on the challenges faced when attempting to quantify the toxicity of the effluent produced during combustion. Future work should aim to reduce the toxicity and flammability of polyurethane simultaneously by; reducing the pyrolysis of the polymer, preventing the escape of volatile products, reducing radicals within the system and lowering the temperature of the system. Before this can be achieved, a better understanding of smoke toxicity and the ability to test materials is needed.

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1. Introduction

The fire toxicity and smoke production of polyurethane based materials is becoming an increasingly pressing issue for the polymer industry. Upon thermal decomposition, polyurethanes are known to break down, producing a number of toxicants in the process, including; CO, HCN and various other toxicants. It is the toxic fire effluents that are the leading cause of injury and fatality from building fires to date (1), thus making it imperative to simultaneously reduce both the toxicity and flammability of insulation materials to increase the safety of buildings. In order to do this, the chemistry of polyurethanes needs to be understood, and determination of the toxicity and flammability of the materials must be quantified.

Polyurethane is classified as a thermosetting polymeric material, composed via the reaction of a rigid polyol (R-OH) with a multifunctional isocyanate group (-R-N=C=O), to produce the urethane bond (-R-NH-C(O)O-), that is repeated throughout the material's structure (2). Alongside this, the polymer chain can interchange between hard and soft segments throughout, allowing control over the desired physical properties of the material. Longer flexible segments throughout the polymer chain (contained within the polyol), will give rise to a softer, more elastic material, whereas shorter chains will produce a much more rigid structure. Within the structure, there is also the potential for cross-linking. The higher the degree of cross-linking throughout the polymer chain, the more rigid the material becomes. The physical characteristics of the polyurethane can be tailored to fulfil desired requirements, due to the wide variety of polyols and isocyanates available. This, in addition to the excellent properties already possessed by the material (low density, low thermal conductivity, low processing cost), makes polyurethane a desirable material to use in a wide range of applications and industry.

The decomposition of polyurethane

The determination of a definitive set of decomposition products for PUR and PIR materials is a challenging task, due to the large number of possible structures the products can have. Confounding this, the added complication of the interaction of decomposition products makes understanding the decomposition process of these materials more difficult. However, despite these added complications, there have been a number of generalized mechanisms proposed for the thermal decomposition of polyurethane based materials. One such mechanism proposes that the decomposition of polyurethane occurs from 170 ˚C, with decomposition intensifying above 200 ˚C (3). During the decomposition, it is thought that the material not only evolves halogenated effluents from the additive flame retardants, but has the ability to produce original compounds used to make the urethane (isocyanates and polyols), as well as having the potential to give rise to olefins and amines (from subsequent secondary reactions) (4,5). Further studies also suggest that at temperatures below 300 ˚C, isocyanates and amines are released into the gas phase, leaving polyols as the main product in the condensed phase. Following this, between 300- 600 ˚C, the isocyanates begin to break down into low molecular weight fragments containing nitrogen, meanwhile the polyol begins to fragment into the gas phase, leaving the char residue in the condensed phase (6). Approaching temperatures of 800 ˚C, Nitrogen molecules within the gas phase begin to break down into HCN, CO and PAH's. The char also has the potential to pyrolyze to produce PAH's and other simple organic fragments. When in contact with air, these small organic species may be oxidized to form CO, CO_2 and water, along with NO_x species, however this is oxygen concentration dependent, and so the concentrations of species present will vary accordingly. Depending on the blowing agents, surfactants and fire retardants used, there may be a number of other species present, ranging from halogens and phosphorus, to sulphur and silicon. A summary of some of the studies into the process of thermal decomposition of polyurethane are shown in Table 1.

It can be seen from literature regarding the thermogravimetric (7) analysis of polyurethane based materials that the thermal decomposition usually occurs in two to three steps. The first step is a loss of mass at 200-350 ˚C, with the second following at 350-600 ˚C, and the third occurring briefly after the second, within the same temperature range. However, these stages are not only test condition dependent, but are also structurally dependent (structures of the polyol, isocyanate and final polymer vary widely), and so the temperatures of thermal degradation will vary accordingly. Despite the variation in temperature, the stages of degradation remain similar, and so can be generalized into two stages; the first stage is assigned to the breakdown of rigid segments within the polymer chain. This leads to the formation of isocyanates, CO_2 and olefins from the main chain. This stage is then followed by the degradation of the flexible segments within the chain, comprised of longer linear chains, which lower the decomposition temperature whilst increasing the rupture rate throughout the second stage (and in some cases, the third stage), due to their low bond energy. A brief list of the thermal disassociation temperatures for specific bonds can be seen in Table 2 (2). It may pose useful to first refer to the number of parameters with potential to effect the decomposition mechanisms of polyurethanes including; molecular structure, isocyanate to polyol ratio, catalytic presence and effects of cross-linking density, prior to looking into generalized mechanisms (8).

Table 1. Summary of studies into the combustion of different types of PU (2).

Reference	**Composition**	**Decomposition stages**	**Temperature of stages**	**Measurement conditions**
25	FPUF	2 stages	240–300 °C	TGA, N_2, 10 K min^{-1}
			350–420 °C	
25	FPUF	3 stages	300 °C	TGA, air, 10 K min^{-1}
			339 °C	
			550 °C	
26	FPUF	2 stages	200–300 °C	TGA, air, 176 K min^{-1}
			300–400 °C	
27	FPUF	3 stages	230–270 °C	TGA, N_2, 10 K min^{-1}

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			280–320 °C 340–440 °C	
28	FPUF	2 stages	190–308 °C 350–450 °C	TGA, N_2, 20 K min^{-1}
29	FPUF	2 stages	200–300 °C 300–400 °C	TGA, N_2, 10 K min^{-1}
30	FPUF	2 stages	300 °C 356 °C	TGA, N_2, 10 K min^{-1}
31	RPUF	2 stages	240–340 °C 350–520 °C	TGA, N_2, 10 K min^{-1}
32	RPUF	3 stages	220–350 °C 350–420 °C 450–600 °C	TGA, air, 10 K min^{-1}
33	RPUF	2 stages	200–400 °C 450–600 °C	TGA, air, 10 K min^{-1}
34	RPUF	3 stages	200–350 °C 350–550 °C 550–800 °C	TGA, air, 20 K min^{-1}
35	PUR-PIR	3 stages	230–280 °C 280–410 °C 420–550 °C	TGA, N_2, 20 K min^{-1}
36	PUR-PIR	2 stages	250–400 °C 400–650 °C	TGA, air, 10 K min^{-1}
37	PUR-PIR	2 stages	200–300 °C 400–510 °C	TGA, air, 5 K min^{-1}
38	PU particle	2 stages	250–340 °C 350–480 °C	TGA, N_2, 5 K min^{-1}
39	PU elastomers	1 stage	330–420 °C	TGA, N_2, 10 K min^{-1}
40	PU elastomers	3 stages	230–340 °C 350–370 °C 400–500 °C	TGA, N_2, 10 K min^{-1}
41	PU elastomers	2 stages	150–250 °C 335–400 °C	TGA, N_2, 10 K min^{-1}

Table 2. Thermal disassociation temperatures for specific bonds occurring in PUS.

Linkage	Onset of dissociation/ ˚C
arbodiimide	250–280
Isocyanurate	270–300
Aliphatic allophanate	85–105
Aromatic allophanate	100–120
Aliphatic biuret	100–110
Aromatic biuret	115–125

Aliphatic urea	140–180
Aromatic urea	160–200
Aliphatic urethane	160–180
Aromatic urethane	180–200
Disubstituted urea	235–250

Smoke production

Throughout the process of combustion, polyurethane produces a large quantity of smoke. The smoke originates from the thermal decomposition within the condensed phase, which then breaks through the carbon layer developed through char formation and begins developing into smoke particles within the gas phase. Once sufficient temperatures are reached, gas phase particles begin to migrate away from the sample, and therefore the heat source. As the gas particles rise away, their temperature slightly decreases, which in turn allows for the aggregation of gas particles. As the temperature cools, a phase change occurs where by which the gas phase particles become solid, seen in the reminiscence of the char from the polymer. The smoke produced contains a mixture of toxicants, including; HCN, isocyanates, NH_3, CO and NO_x, which are primarily produced within the first few minutes of the fire starting, followed by a high level of smoke production throughout the first 10 minutes of a fire with consistent smoke production occurring after, only stopping once one of; fuel, heat or oxygen levels have reached a low enough level for burning to cease. Although there are certain products of combustion that remain similar, the fragmentation that occurs is heavily reliant on the structural composition of the polymer chain and so the toxicity of the combustion products varies accordingly. This also suggests that the fire retardants that work based on chemical structure will need to be tailored to the individual structure of the polyurethane in question, rather than using a generalized structure to reduce toxicity. This is further explained in Section 3.

The key issues faced when looking at the toxicity of PU effluents is the production of isocyanates and hydrogen cyanide, which are released in the form of gaseous material upon depolymerization during burning. The isocyanate(s) produced are a highly toxic and have been found to possess adverse health effects on those exposed, as well as the potential carcinogenic and mutagenic effects attributed by potential additives within the foams structure (9). The main health effects exhibited are the irritation of mucous membranes, as well as chest tightness and breathing difficulties (10). In a fire situation, this has the potential to reduce the chances of escaping a fire if isocyanates are inhaled. Hydrogen cyanide also has known adverse health effects, including; tissue hypoxia, cellular asphyxia, organ failure and death (11). On exposure, body cells detect the oxygen deprivation in the surrounding area, stimulating hyperventilation, thus increasing the uptake of hydrogen cyanide. This leads to rapid unconsciousness, followed by a fall in respiration rate. At this point, a fire victim can be rescued, however they will be unable to conduct their own escape.

Due to the variety of additives available (blowing agents, surfactants, fire retardants), the combination of species present in smoke produced during decomposition can vary widely, from containing halogenated species to containing phosphorus, sulphur and silicon based products, all with adverse health effects of their own. Some additives however, enhance the thermal stability and reduce the volume of smoke produced by forming a char layer during combustion. Typically, once a char has been formed some of the fragments produced during combustion are kept in the condensed phase, thus resulting in less gas phase products being released. This almost always results in a decrease in fire toxicity. Certain groups, such as aromatics, are used specifically for this purpose. Certain fully aromatic liquid-crystalline polyesters and poly(ether amides) have been found to form excellent char layers upon degradation, whilst maintaining excellent thermal properties and in some cases, increasing thermal stability of the foam itself. Carbodiimide groups have a similar ability, as urethane foams containing some form of carbodiimide group were found to generate less smoke than typical urethane foams when exposed to fire (12).

2. Flammability reduction

Due to the flammable nature of polyurethane based materials, a wide variety of fire retardants have been designed and implemented in attempt to improve the fire safety of these materials. The main aims of a fire retardant are to work as a formulation fire to pass a regulation test. This may be to reduce ignitability, flame spread, peak heat release, total heat release and or some combination of the above. This must be achieved whilst maintaining the desired properties of the foam. In a few instances, such as mass transport industries (air, ship, train), the smoke toxicity is also regulated, as it is for construction in Japan and China.

The methods by which fire retardants work can be divided into three categories; Thermal shielding, Endothermic decomposition and radical quenching from the gas phase/ gas phase dilution.

Thermal shielding

Preventing flames from radiating into a polymer’s structure has proven to be an effective working method for fire retardants. Char forming and intumescent additives promote the formation of a thick barrier layer which protects the underlying polymer from thermal radiation, and prevents further decomposition. The char layer may also prevent oxygen from reaching the foam, and reduces the quantity of volatile fuel being emitted. Studies have proven that foams with enhanced charring additives, not only failed to ignite but also produced a lower yield of smoke and volatiles (HCN, HCl, NO2), with a general overall lower peak heat release rate (13). From this, it can be seen that there is much potential for further investigation of char forming additives and their effects on simultaneously reducing the flammability and toxicity of fire effluents.

Endothermic decomposition

A fire retardant that undergoes endothermic degradation has the capability to reduce the heat within a system, thus lowering the temperatures reached during the process of a fire. Aluminum hydroxide (ATH) is one such fire retardant that works via this process. The ATH begins this process at approximately 200 ˚C, where by the following reaction [1] occurs.

$$2Al(OH)_3 \xrightarrow[180 - 250\ ^{\circ}C]{\Delta} Al_2O_3 + 3H_2O \qquad [1]$$

$$Mg(OH)_2 \rightarrow MgO + H_2O \qquad [2]$$

These water molecules go on to dilute the free radicals responsible for flame propagation, interrupting the spread of the fire . However, for these type of fire retardants, a relatively high quantity needs to be present in order to produce a significant effect on the system, with the potential to have detrimental impacts on the physical and mechanical properties of the composite. Studies have shown the presence of ATH has a negligible effect on the combustion toxicity of ethylene-vinyl copolymer. Magnesium hydroxide (MDH) is another fire retardant classified under this branch. It works similarly to ATH, with the only difference being a slightly higher thermal release temperature for the water molecules (MDH has a water release temperature of 330 ˚C, which can be seen in equation [2]). Studies have also shown that ATH can reduce the production of volatile organic carbon when implemented into a PIR, however in doing so the ATH caused an increase in CO2 yield (14), however little is known regarding the effects of ATH and MDH on fire toxicity.

Gas phase quenching

Many halogenated flame retardants, such as Tris (1,3-dichloro-2-propyl) phosphate (TCPP) work via gas phase quenching. The selected retardants are typically phosphorus or halogen based, and have the ability to produce relatively stable free radicals in the gas phase. These radicals then replace the high energy free radicals produced within the system, particularly; H•, •OH and •O•, that are needed to sustain flaming, and slow (in some cases ceasing) burning throughout the material (15). Unfortunately, as these retardants interfere with flaming reactions, an increase in asphyxiate gasses (such as CO and HCN) is often observed, as well as an increase in other products of incomplete

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combustion released throughout decomposition of the polymer's fire retardant (16). Due to the potentially carcinogenic nature and environmental persistency of halogenated flame retardants (17), phosphorous based retardants are often the preferred choice of fire retardant.

3. Char forming additives

Previous studies on PIR foams found that the volume of nitrogen found in the char of thermally degraded polymers can be directly related to the volume of nitrogen present in the raw polymer, thus allowing the assumption to be made that increasing the volume of char formation will reduce the total amount of volatiles and hence, induce a fall in the concentration of N based gasses (HCN, NOx) produced during combustion. Leading from this, it is also reasonable to assume that the denser the char layer created, the better at inhibiting the diffusion of toxic gases away from the polymer structure, as well as its ability to protect the underlying polymer from further pyrolysis.

Metal based fire retardants and additives

As the advancement of fire retardants progressed, the interest in the application of transition metals for use as smoke suppressants flourished. Elements such as Mo, Ti, Mn, Zn and Fe were found to exhibit excellent smoke suppressant properties, and showed potential for fire retardant applications. Particular studies into the addition of ferrite into polymeric structures showed potential for the application of ferrites as char forming additives, as when tested, the char morphology of the ferrite treated PIR had become more compact than the untreated foams (18) (this is from the ferrous changing expansion degree in the char residue. APP also decomposes to produce polyphosphoric acid forming ion pyrophosphate). The smoke suppressive effects of ferrite were further studied in synergy with APP as a fire retardant. It was found that when used in conjunction with APP, ferrite exhibited excellent smoke reductive behaviors (both with and without the presence of flame). It also effectively decreased the total smoke release (TSR) heat release rate (HRR) and total heat release in cone calorimetric tests when compared to untreated foams.

The use of ferrocene as a fire retardant has recently become a popular topic of interest within the fire retardant community. When incorporated into PU foams, an increase in thermal stability and improved char residue can be observed, particularly when using ferrocene with poly-phosphate esters (19). To combat the potential volatility of ferrocene, researchers introduced the molecule into the backbone of the polymer, rather than as an additive, leading to a decrease in CO production, and a decrease in smoke production. This suggests that certain additives may work differently when incorporated into the polymer chain, rather than simple mixing into the material, leading to the possibility of more chemically modified PU chains with the fire retardant implemented within them. Perhaps certain undesirable qualities of previous additives could be minimized if the additive were applied into the polymer's backbone, as this modifies how the retardant works.

The structural composition of metal oxides provide an excellent basis for flame retardancy, with their structures (in particular the hydroxyl end groups and oxide anions) providing a hook for other chemical species to latch onto during combustion, withholding the release of certain gases. Research into the use of Molybdenum trioxide loaded graphene nano-sheet (MoO3-GNS) hybrids as flame retardants proved hopeful for use in polyurethane based materials. The MoO3-GNS hybrid revealed a significant increase in char yield when incorporated at 2.0 w.t% in PU, as well as obvious reductions in heat release rates, smoke densities and total heat release rates. The hybrid also exhibited improvements in both flame retardancy and smoke suppressive properties. When PU foams were treated with 0.1 wt% cuprous oxide, a 90% reduction in HCN generation was observed, along with a reduction in smoke release (20).

Zinc compounds

When used in synergy with ammonium pentaborate (APB) [$(NH_2)_2B_{10}O_{16} \bullet 8H_2O$], Zincronium oxide proved to be a promising contender in the development of fire retardants due to its known catalytic capabilities aiding isosynthesis. When incorporated at 5 to 20 w.t%, the polymers in question exhibited a reduction in peak heat release rate between 35 to 80%, with no reduction in effectiveness at high heat flux's (70 kWm^{-1}) (21). However, little research has been undertaken regarding toxicity and so uncertainty still remains as to how effective ZrO_2 based fire retardants could be. Alternatively, $ZnAl_2O_4$ and Zn_2SiO_4 were found to decrease both smoke density and the evolution of CO and HCN in non-flaming microscale tests of PIR-PUR foams (22). Significant decreases observed in HCN yield were thought to be a result of the combination of the nitrogen containing catalyst with NO_x, opposing the formation of HCN.

Amongst this, Zinc borate has exhibited excellent properties in regards to dense char formation, likely due to the action of boronic acid (23). At high temperatures, the retardant also releases water, aiding smoke suppression and a decrease in CO yield. Further studies have shown slight improvements in mass loss (24), reductions in total heat released (25), lowered CO and CO_2 as well as increased LOI. Interestingly, two studies showed confounding conclusions, with one proposing the lower CO yields were due to oxidation of CO to CO_2 via the catalytic ability of Zinc on CO, with another proposing decreased levels of pyrolysis and retention of carbon in the char leading to the lower CO levels observed.

Studies have also shown the use of Zinc borate in conjunction with oleic acid on a nanoscale (26). The Oleic acid was found to aid even dispersion of the zinc borate and prevent agglomeration throughout the material. Despite showing decreased mass loss and slight improvements in flammability, fire effluent toxicity reports are yet to be carried out, meaning the safety of this retardant is yet to be confirmed.

$ZnSn(OH)_6$ has also been found to significantly reduce both the smoke density and production of HCN and CO (27). With the ability to form hydrogen bonds between zinc hydroxystannate and phosphoric acid (produced from the degradation of APP used as a flame retardant in this study), combined with good char forming abilities allow for $ZnSn(OH)_6$ to be used in conjunction with APP as an excellent smoke suppressor and fire retardant (28).

Iron compounds

When studied in combination with phosphorus-containing flame retardants, $CuFe_2O_4$ and $NiFe_2O_4$, $ZnFe_2O_4$ exhibited superior abilities in decreasing smoke evolution, as well as inducing reductions in isocyanate concentrations (29). It is thought that this occurred due to two reactions occurring, combining to produce the result observed. Firstly, the reaction between $ZnFe_2O_4$ and the phosphonate flame retardant, whereby a larger quantity of phosphorus was retained in the solid material thus producing less smoke; followed by the reaction between $ZnFe_2O_4$ and the foam itself, as the metal salt facilitated the dehydrogenation of the polymer, promoting char formation and subsequently reducing the amount of pyrolysis products such as CO and HCN formed. It was further suggested that the $ZnFe_2O_4$ performed better than the other iron structures tested due to the presence of zinc acting as a stronger Lewis acid, thereby improving dehydrogenation and the quantity of char formed. Despite the complete mechanism not being understood, it is clear that both iron and zinc have properties which contribute to char formation, with the effects potentially being synergistic. It is essential to keep in mind the study based its findings on using a TCPP/ DMMP flame retardant, and so further study would be required to determine the full effects with less harmful phosphorus-containing flame retardants.

Iron powder used in conjunction with APP also proved to possess abilities to reduce smoke production, and decreasing heat evolved. Smooth, shiny dense char layers were formed when treated with Fe powder with APP, suggesting it has the ability to protect the underlying polymer, however no focus was directed towards toxicity or mechanical properties of the foams tested, suggesting further study would be required in order to establish toxicity and effectiveness of this potential fire retardant. The study also only used APP as a fire retardant as opposed to others such as TCPP or DMMP, and so it is hoped that Fe has the ability to work in synergy with any phosphorus containing fire retardants.

Phosphorus based materials

After recent studies into the adverse health effects of halogen based fire retardants (30), phosphorus based fire retardants have become a preferred choice. Despite their ability to increase char formation, phosphorus based systems have proven to increase smoke production, making their applications in fire retardants questionable, as there are many alternative additives with the ability to lower smoke production, at lower loading rates (many phosphorus based retardants require a fairly high loading, potentially affecting physical and mechanical properties of foams).

Research into the use of phosphorylated polyols as PUR/PIR co-monomers as well as reactive fire retardants has also been undertaken. Studies show that PU coatings developed with a phosphorylated polyol retardants exhibited a significant increase in the formation of char throughout combustion (31). Although it is practically more difficult to use reactive flame retardants, they have several advantages over additives, minimizing release into the environment, with little adverse effects on physical properties and reduced potential for detrimental health effects.

TCPP (tris (2-chloroethyl) phosphate) is a well-known phosphorous based fire retardant that is widely used throughout infrastructure. It has been shown to increase CO and HCN yield throughout several small scale test, including cone calorimetric testing, despite having the ability to reduce the heat release rate of materials. The use of TCPP alone is seemingly becoming outdated as the use of more developed fire retardants progress. TCPP incorporated with montmorillonite however, proved to be successful in reducing both the smoke production and heat release rate, as well as successfully reducing CO and HCN production yields throughout thermal decomposition (32).

Toluidine spirocyclic pentaerythritol bisphosphate (TSPB) is another phosphate based fire retardant in the market. However, significantly less research has been undertaken regarding the use of TSPB, particularly in the area of smoke and fire effluent toxicity. Irrespective of this, TSBP was found to provide stable char formation, with excellent retardant properties, both before and after water exposure (33).

10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives have also proven to be a popular choice of phosphate based fire retardant (34). When compared with tris(1-chloro-2-propyl) phosphate (TCPP), it was found that rigid polyurethane foam (RPUF) containing DOPO exhibited lower production of smoke, alongside lower toxicant production and increased dense char formation (which goes on to act as a strong barrier in the condensed phase) during combustion. It was also observed that RPUF with 2 wt% phosphorus achieved a reduction in peak heat release rate of 23 to 42%. This suggests that despite studies showing phosphate based additives to increase smoke production, DOPO has the ability to aid reductions in smoke production, and in some cases aiding significant reductions in decomposition products such as NCO and HCN (observed via the use of RPUF containing 6-(2-(4,6-diamino-1,3,5-triazin-2-yl)ethyl) dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DTE-DOPO)) (35).

Lignin has also shown abilities to aid reductions in mass loss and decrease HRR in PUR foams (36). Further studies proved Lignin modified with nitrogen and phosphorus enhanced charring and effectively protected underlying foam (37). This occurred due to a combination of the aromatic structure of the lignin integrating with the char, alongside the phosphorus promoting cross-linking, with the nitrogen producing ammonia, resulting in an expansion in the char.

Following this, investigations into the effects of modifying APP with polybenzoxazine revealed that modified FR (BMAPP) induced a reduction in LOI and enhanced char formation (38). Researchers proposed this was due to the presence of Si-O in the char residue. It should be noted that an increase in volatile aromatic products could occur at higher temperatures, and so toxicity levels would be expected to increase at higher temperatures.

Expandable graphite with APP

When used in conjunction with expandable graphite (EG), APP has been found to possess excellent char forming capabilities, with an added significant decrease in smoke production due to the use of APP. Studies show a 10% increase in improvement in the LOI of PU containing expandable graphite with APP (39). It has been proposed that the phosphoric acid aids the formation of a compact char layer when combined with EG. Although expandable graphite has shown increased LOI values when used alone, the results are not significant enough for singular use as a fire retardant, and so use of EG in synergy with other fire retardants is a much more viable option.

Expandable Graphite

Due to expandable graphite's (EG) ability to form a thick insulating char layer, the underlying polymeric structure is provided with a protective layer that reduces the availability of fuel to a fire, proving EG to hold excellent fire retardant applications. When used in synergy with [bis(2-hydroxyethyl)amino]-methyl-phosphonic acid dimethyl ester (BH), EG was shown to enhance char layer stability, alongside char layer density when compared to the use of EG alone (40). This was further reinforced by another study regarding the effects of EG with boron (41), showing an increase in LOI and a more stable, compact char being formed from the graphite. EG in combination with aluminum hypophosphite (AH) has also shown an increase in the insulating effects of the char, allowing for better prevention of pyrolysis of the underlying polymer than when using EG or AH alone (42).

Low melting glass

Literature shows low melting glass to be a proficient fire retardant in polymeric structures, however due to the generally high water solubility of low melting glasses it is questionable as to how applicable low melting glass is as a fire retardant in polyurethane based structures (as water is incompatible with isocyanates and polyols) (43). The effects on smoke toxicity in use of PU is yet to be investigated, however studies showed low melting point glass, containing a mixture of; P_2O_3, SO_3, ZnO, Al_2O_3, Li_2O, Na_2O and K_2O was found to improve both the fire retardancy and smoke suppression the polymers tested containing this material (44). Various other patents have also been documented to produce good fire retardant properties in materials similar to PU (45,46).

Calcium compounds

Both calcium carbonate and calcium hydroxide have been found to induce a reduction in HCN yield in a study of pyrolysis (47). Despite an increase in N_2 yields being observed, CaO has shown excellent conversion rates of HCN to N_2. HCN toxicity of materials is a leading problem to this day, opening windows of opportunity for calcium based compounds to be used in synergy with pre-existing fire retardants, allowing the properties of calcium based retardants to be fully explored and applied.

Copper compounds

Small scale testing has shown an 87% reduction in HCN concentration in PU foams containing cuprous oxide (Cu_2O), with a 70% reduction occurring in larger scale testing (48). It is believed that cuprous oxide acts as an oxidative catalyst, decomposing HCN to $N_{2,}$ H_2O and trace amounts of nitrogen oxide. Alternative studies have also shown Cu_2O to aid the formation of CO_2 from CO when used in conjunction with microencapsulated ammonium polyphosphate. This can be further explained via the use of redox equation [3]. Although this study did not focus on toxicity reductions, Cu2O has the potential to lead to further reductions in fire toxicity, due to its ability to reduce both CO and HCN formation (49).

$$\begin{gathered} Cu^{2+} + 2e^{-} \rightarrow Cu^{0} \\ Cu_2O + CO \rightarrow 2Cu + CO_2 \end{gathered} \tag*{[3]}$$

Silica based materials

Silicon based materials have also attracted attention for their fire retardant properties. Addition of silicon-based siloxane has proven to increase the char yields of PU foams (50). Although attention has been drawn to silicon based fire retardants, little has been published on their effectiveness. Silicon holds a large quantity of potential development as a fire retardant due to its ability to form a protective surface coating (composed of silicon dioxide) during combustion through a low rate of heat release. Some of the few studies published have reported an improvement in LOI and UL-94 performance in tests, at low levels of silicon in organic polymer systems. Addition levels as low as 1% were found to reduce heat release during combustion by 30% as a minimum, with up to 50% has being achieved at concentrations higher than 3% (51), however little research has been reported on the fire effluent toxicity of silicon based materials meaning their effects on toxicity are still yet to be fully investigated.

Borosilicate glass

The applications of borosilicate glass for fire retardancy is still in its infancy, with very little research into the effectiveness of this compound being available. Borosilicate glass is composed of a mixture of boronic oxide, silica and a metal oxide, and is known to have excellent chemical stability. A study into the use of borosilicate glass powder (50 to 100 phr) used in synergy with expandable graphite (EG) (100 phr), showed excellent basis for fire retardant properties for this material. Calcium borosilicate has also been investigated for use in fire retardancy, however little research is published for its applications within polyurethane based materials. Calcium borosilicate is often used in wire and cables to prevent shrinkage and cracking in fires, which could pose useful for PU materials (52). Upon thermal decomposition, PU materials are often seen to crack, allowing for flame spread deeper within the structure (this is a typical observation in most cone calorimetric tests of rigid PU foam structures). Calcium borosilicate could have potential applications in preventing PU materials from cracking upon decomposition, aiding the potential reduction of flame spread. If used in conjunction with other flame reducing, or smoke suppressing additives, calcium borosilicate could hold various potential applications in fire retardancy.

Melamine and melamine derivatives

The movement away from halogenated flame retardants sparked an interest into the use of melamine and other organic nitrogen based compounds in the application of fire retardants. With sublimation occurring at temperatures surplus of 200 ˚C, melamine has the ability to act as both a heat sink and a diluter of fuel gasses within and around the polymer. Their added ability to aid char formation and free radical scavenging behaviors make them a popular choice of fire retardant (53). Melamine based fire retardants have also been found to have smoke suppressive behaviors, with a reduction of heat release from 80 to 8 mm-2 in flexible PU treated with 60 wt%, and a 50% decrease in CO production, proving it to be an effective smoke suppressant (54).

Melamine cyanurate is a salt derivative of cyanuric acid and melamine, which is actively used as a fire retardant. Its ability to remain stable in temperatures around to 320 ˚C (compared to 200 ˚C for pure melamine) makes it an appealing choice for use as a fire retardant. Upon its breakdown, melamine is produced, which is expected to act as both a char forming enhancer, and a smoke suppressor. However, cyanuric acid is also produced, which could have potentially detrimental health effects to those exposed. The high concentration of nitrogen in melamine and its derivatives is a potential concern in regards to fire toxicity. It is known that melamine decomposes with the release of ammonia in several stages, but the nitrogen rich char also has potential to form HCN from gas phase nitrogen compounds in under-ventilated fires which must also be considered.

Zeolite structures

Zeolites are microporous materials with a very wide, diverse set of uses and applications. Their structures vary widely due to the interchangeable ratio of Si:Al within its structure, allowing for control over pore size and charge-balancing cation distribution (55). Their surface is covered with ion exchangeable groups, allowing for a wide range of chemistries to be imparted to the polymer. Despite their wide variation in applications, few studies have been conducted into the use of zeolites as fire retardants. However, they have shown enhanced char forming properties in a range of different polymer based materials, showing potential for applications in PIR/PUR based materials.

Due to the chemical nature of zeolites, they are often used as molecular sieves for industrial applications. As the chemical composition of a zeolite can be altered via exchangeable cations, the nature of the sieve also has the potential to be tailored to sieve out toxic species or smoke particles during combustion, assuming the structure of the zeolite can remain stable at temperatures reached during fires. The zeolite structures are thought to break down into SiO_2 and Al_2O_3, enhancing the char formation within the polymers. Lewis acid sites available within the zeolite structure also have the potential to promote charring by dehydrogenation (56). The hydrophilic nature of zeolites ensures that they have a significant degree of hydration at normal temperatures. In polymer processing this disadvantage can be avoided by heating to 100 ˚C and dehydrating, otherwise the water could be released into the molten polymer, or in the case of polyurethane, react with the isocyanates present.

Zeolite 4a has been subjected to testing of up to 560 ˚C in a study of fire retardant abilities. The zeolite was found to raise the LOI at additions of 1.5 wt%, and resulted in stable intumescent char formation, with degradation occurring around 550˚C with no observed expansion in the char (57). However, the material was not subjected to testing at higher temperatures, nor was the toxicity studied and so further testing would be required in order to establish the effects of the char on the toxicity of fire effluent produced to provide more relevance to real fire scenarios.

Following this, Zeolite 4a and 13x were further studied, showing significant reductions in mass loss at around 500 ˚C. Taking into consideration the relations between mass loss and toxicity, it proves these findings to be promising for fire retardant use (58). Further studies comparing the effects of zeolites as fire retardants with ZnO with MMT showed zeolites to be the most effective for reducing pHHR and had the fastest char layer formation out of all samples tested. The effectiveness of zeolites is thought to be linked to their high surface area, however in this study, no specific reference for the type of zeolite was given and so due to the large variety of zeolites available, it can not be said for certain which type of zeolite induces this effect (59). In another study of comparison, zeolites were studied amongst amorphous aluminosilicate material (kaolin) in order to determine if the ordered structure of the zeolite used was necessary to attain improvements in LOI testing (51). Although both the zeolite and the kaolin induced improvements in LOI testing, the materials treated with zeolites proved superior in every test, however there is varying evidence to suggest this superiority is due to the presence of the ordered structure, or the presence of exchangeable cations.

$AlPO_4$-5 has also been the subject of study, however this research focused heavily on mechanical properties as opposed to fire retardancy. Despite this, $AlPO_4$-5 was found to improve the tensile strength of the polymeric material, with conclusions suggesting applications for use as a fire retardant, however no follow up study could be found and so the effectiveness of the use of $AlPO_4$-5 as a fire retardant still remains unknown (60).

Zeolite additives in polymers have been shown to act via a number of different mechanisms. When used in synergy with APP and pentaerithitol (PER) additives, zeolites are able to catalyze the esterification reaction between APP and PER at temperatures between 250 to 400˚C. Temperatures surplus of 400 ˚C, the zeolite begins to break down into SiO_2 and Al_2O_3, whilst enhancing the cross linking and charring of the polymer (61). It is also thought that the Lewis acid sites present within the catalyst promote charring by dehydrogenation.

Montmorillonite clay

Montmorillonite (MMT) is a naturally occurring clay, commonly used in conjunction with other fire retardants. Its hydrophilic surface renders it incompatible with most polymers, hence organic modification is necessary prior to usage. Studies into the use of organo-modified MMT (OMMT) in conjunction with intumescent PLA showed that OMMT caused an improvement in fire properties exhibited by the intumescent PLA, including lowered flammability, increased char formation, improved LOI values, and reduced heat release rates of the material (62). MMT can be used in order to increase both the mechanical strength and thermal stability, evidenced by studies into the use of MMT composites to improve mechanical strength of PU foams (63), showing an obvious increase in both mechanical strength and thermal stability. MMT clays have also been found to cause a reduction in CO, HCl, HCN and NO_x production (64). MMT is often used in conjunction with other fire retardants, including phosphorus based materials. Zheng et al (65) reported an increase in char formation and improved thermal stability of PU foams treated with APP, combined with OMMT. A 5% dosage showed the slowest heat release, and the lowest total smoke production in the foams tested. Despite the many potential uses of MMT, obtaining even dispersions within foams has proven to be difficult when initially creating the flame retarded polymer.

4. Bio-inspired fire retardants

When searching for new ideas for fire retardant formulations, it is becoming increasingly common to seek inspiration from pre-existing chemical processes, such as those that occur in nature. A polydopamine (PDA) based nano-coated layer has recently been developed for potential fire retardant uses (66). When incorporated into PU foams, planar sub-layers of the nano-coating were found to evolve together with the secondary granular layers of the coating producing a dense, carbonaceous char layer on all foam surfaces. Samples treated with the PDA nano-coating showed significant reductions in flammability, with increasing reductions being observed with increased coating thickness, as well as full shape preservation and self-extinguishing properties being observed when exposed to a flame in torch burn test. However, no research regarding the effects on toxic fire effluent have been undertaken.

5. Summary

Much of the research carried out in this field has focused primarily on the flammability of materials, with toxicity reports occurring much less frequently. It is clear that more in-depth investigations and analysis into the toxicity of PU materials is needed, as opposed to the reliance on cone calorimetry or TGA data to provide a loose connection to toxicity. As previously stated, fire toxicity is the leading cause of injury and fatality in fires to date, so it is imperative that more focus be directed towards the issues of toxicity, instead of solely focusing on flammability issues.

Already, toxicity is a large problem faced by the polymer industry, particularly the polyurethane industry. Studies list fire retardants ability to reduce one toxic gas, while others show the same fire retardant significantly increasing another. Conducting a study into the fate of nitrogen would pose extremely useful for studies regarding toxicity, especially if toxic gas evolution and benign gas formation could be reliably predicted, as this could provide a quick, easy method to instigate the much needed control over toxicity.

It may pose useful to investigate the decomposition process of raw PIR/PUR foams without additives in order to establish a good foundation for developing the most effective additives for both fire retardancy and reductions in toxic fire effluents. With deeper understanding and knowledge of specific temperatures required for toxic gas formation, conjoined with known data for active temperatures for catalysts, potential lies for the targeting of specific gas formation to aid toxic fire effluent reductions. However, due to the range of toxic gases produced at different temperatures, designing a formulation to address each gas produced requires much work still.

Ideally, the perfect fire retardant would reduce both the toxicity and the flammability of polyurethane simultaneously by; reducing the pyrolysis of the polymer, preventing the escape of volatile products, reducing radicals within the system and lowering the temperature of the system. Although it is a difficult task to design a fire retardant that is capable of fulfilling these demands alone, the use of retardants in synergy to combine effects may be the way forward. However, due to the complex nature of polyurethane chemistry, there is much to be done in order to render PU based materials safe via the production of a formulation addressing all of the issues previously mentioned.

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