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Heat Release of Polyurethanes Containing Potential Flame Retardants based on Boron and Phosphorus Chemistries

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Abstract:

Using a polyurethane of methylene diphenyl isocyanate and 1,3-propane diol, several new non-halogenated aromatic boron and phosphorus flame retardants were evaluated for heat release reduction potential using the pyrolysis combustion flow calorimeter (PCFC). The polyurethanes were prepared in the presence of the potential flame retardants via solvent mixing and copolymerization methods, and were then analyzed via spectroscopic methods to determine if the flame retardant was still present in the final product. PCFC testing on the resulting products showed that the flame retardant molecule can have different effects on heat release depending upon how it is mixed into the polyurethane. Some materials showed strong effects on heat release reduction when reacted into the polyurethane during copolymerization, while others were more effective at heat release reduction when simply solvent blending into the polyurethane. The results from this screening study show that flame retardant chemical structure and its environment in the polymer (covalently bonded vs. noncovalent interactions) greatly affects flammability behavior. From the combined data, aromatic boronates were found to be very effective at reducing heat release and inhibiting melt flow during thermal decomposition, as were some aromatic phosphonic acid terephtalic acid and terephthalate derivatives.

Introduction:

Flexible polyurethane foam remains the largest fuel load that could potentially lead to a flashover event (total loss of property and/or life) in the US.[1] There are regulations in place which require the use of flame retardants to lower the fire risk associated with flexible polyurethane foam,[2,3,4] but some of the commercially available flame retardants are being deselected due to persistence, bioaccumulation, and toxicity (PBT) issues.[5,6] While some new flame retardants are becoming available which can meet existing regulations, the flammability tests themselves are in a state of flux, with arguments in place to have the tests focus on cigarette ignition, small flame ignition, and/or heat release.[7,8] Flame retardants, due to the complexity of fire physics and material flammability, must be optimized for a specific product in a specific test, and so when the flammability test is a "moving target" it becomes difficult for the flame retardant chemist to develop new chemistry. However, if one considers what makes polyurethane foam flammable, then one may have a "target" to begin developing new flame retardant chemistry. Such a target should address the polyurethane flammability problem while simultaneously addressing PBT issues. This is a problem with two inputs that need to be discussed separately before describing the approach in this paper which is focused on understanding and developing new flame retardant chemistries.

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The first of the two inputs is the flammability of polyurethane foam. When flexible polyurethane foam ignites and burns, it will drip and flow thus forming a fuel pool fire event.[9] This formation of a pool fire, plus the high heat release of polyurethane, can rapidly lead to a flashover event. Therefore, to truly lower the flammability of polyurethane foam, the flame retardant must lower the heat release of the polyurethane *and* slow or prevent dripping/liquefaction of the foam during thermal decomposition. So when screening for new flame retardant chemistry at the small scale, lowered heat release should be one result to look for, and additional char formation along with inhibition of flow under thermal decomposition conditions should be another. Small scale heat release testing can be achieved via pyrolysis combustion flow calorimetry (ASTM D7309), which has been shown to be a proven technique for flame retardant material development and screening.[10,11,12,13] The technique does have some limitations,[14,15] but provided those limitations are considered, the data generated by PCFC is still quite powerful in advancing new flame retardant chemistry. Addressing inhibition of liquefaction of a polymer is not easy to measure at small scale, and sometimes there is no substitute for actual vertical flame spread tests. However, studying increases in char yields and char residue structure from the PCFC test may be useful in determining the effectiveness of the flame retardant towards inhibition of foam liquefaction during burning. Admittedly, visual char studies can be qualitative (and subjective) in nature, but it is a place to start and should not just be dismissed out of hand, especially if the char structure generated by the flame retardant (FR) polyurethane is notably different than that of the non-FR polyurethane. In this case, looking for a lack of flow structure in the chars would suggest that the new flame retardant is inhibiting polyurethane liquefaction.

The second of the two inputs is the environmental impact of the flame retardant. There is convincing evidence that over time, some flame retardants will migrate out of polyurethane foam and become a PBT problem.[16,17] This also presents a fire safety problem in that the foam over time may lose its protection if enough of the flame retardant leaves the product. So the flame retardant chemist must now consider developing new flame retardants which either react into the polyurethane itself (cannot leave the polymer throughout its life cycle), or are polymeric in structure. Polymeric structures are preferred in that if they do get into the environment, they cannot easily bioaccumulate or become toxic should they be persistent. Environmental consideration must be included in new flame retardant design, but actual testing of chemical environmental impact can be expensive, and perhaps too expensive during early FR development. Predictive models for molecule toxicity exist as well, but these models have costs associated with them as well. At a minimum, determining if the FR covalently reacts into the polymer serves as useful screening criteria for ensuring low PBT profiles. If the FR cannot leave the polymer due to its covalent bonds with the main polymer chain, then it is less likely get into the environment to cause ecological damage. Therefore use of spectroscopic techniques that help show the FR is reacted into the polyurethane would be a good method to infer the environmental impact of the new FR.

In this paper, we report on the use of PCFC to study how new phosphonate and boronate flame retardants synthesized previously[18] affect heat release in a polyurethane. A polyurethane based upon methylene diphenyl isocyanate and 1,3-propane diol was used as a system to quantify heat release reduction potential of these potential flame retardant chemistries which may be useful to address flexible polyurethane foam flammability. Flame retardants were incorporated into a polyurethane at 10 mol% through direct reaction with polyurethane monomers during polymerization, or via solvent blending with the polyurethane after the monomers had been polymerized in a separate flask. With the use of the PCFC, the effectiveness of the flame retardant chemistry in lowering heat release was studied. The best performing flame retardants were further studied with thermogravimetric analysis-Fourier Transform Infrared Spectroscopy (FTIR) to see if the mechanism of heat release reduction could be determined. The chars collected from PCFC testing were evaluated in a visual qualitative manner to see if any of the flame retardants had a positive effect on char formation and/or flow inhibition. Additionally, measurements were conducted to determine how these chemistries do/do not react into the polyurethane to screen for potential environmental impact. This was done through nuclear magnetic resonance (NMR) measurements of the polyurethanes formed to determine if the flame retardant was incorporated into the final structure or not. The results of this study should give insight into which new boron and phosphorus chemistry has potential to solve the polyurethane foam flammability problem and deliver new FR chemicals with greatly improved environmental profiles provided those new flame retardants are reacted into the polyurethane matrix.

Experimental Procedures:

General Procedures and Chemicals:

^{1}H and ^{13}C spectra were recorded at 300 MHz and 75 MHz respectively and referenced to the solvent ($CDCl_3$: 7.27 ppm and 77.0 ppm; DMSO-d_6: 2.49 ppm and 39.5 ppm). ^{31}P NMR spectra were measured at 121 MHz, all in DMSO-d_6, and referenced to H_3PO_4 solution in DMSO-d_6 (0.0 ppm). The referencing was accomplished by measuring and calibrating the signal of the standard, followed by subsequent use of the Spectrum Reference (SR) feature of the NMR instrument, to standardize the rest of the spectra. ^{11}B NMR spectra were measured at 96 MHz, all in DMSO-d_6, and referenced to H_3BO_3 solution in DMSO-d_6 (0.0 ppm), again using the SR function. Elemental analysis was provided by Atlantic Microlab, Norcross, GA.

N-methylpyrrolidone, 1,3-propanediol and methylene diphenyl diisocyanate (MDI) were purchased from Acros Organics. Dibutyltin dilaurate was purchased from TCI America. The preparation of phosphonoterephthalic acid (**MPA**),[19,20] 2,5-diphosphonoterephthalic acid (**DPA**),[20] dimethyl 2,5-bis(dimethylphosphono)terephthalate (**DPME**),[20] boronoterephthalic acid (**MBA**),[18] diboronoterephthalic acid (**DBA**)[18] and dimethyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate (**DBB**)[18] was accomplished following previously published synthetic protocols. 1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (**MP**) and 1,4-dihydroxy-2,5-bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (**DP**) have been reported recently,[21,22] but we have included their preparation and isolation in the current manuscript, as the separation and purification protocol has been modified. 2*H*-5,5-Dimethyl[1,3,2]dioxaphosphorinane-2-oxide (**DDPO**) has also been reported in the literature,[23,24] but the protocol was modified, and its preparation is described.

Synthesized Flame Retardants:

In this effort we also used several synthetic flame retardants prepared in our laboratories which had shown effectiveness in reducing heat release when solvent blended with a thermoplastic polyurethane.[18] Their chemical structures with acronyms are shown in Figure 1, and some additional details about the compounds are included in Table 1.

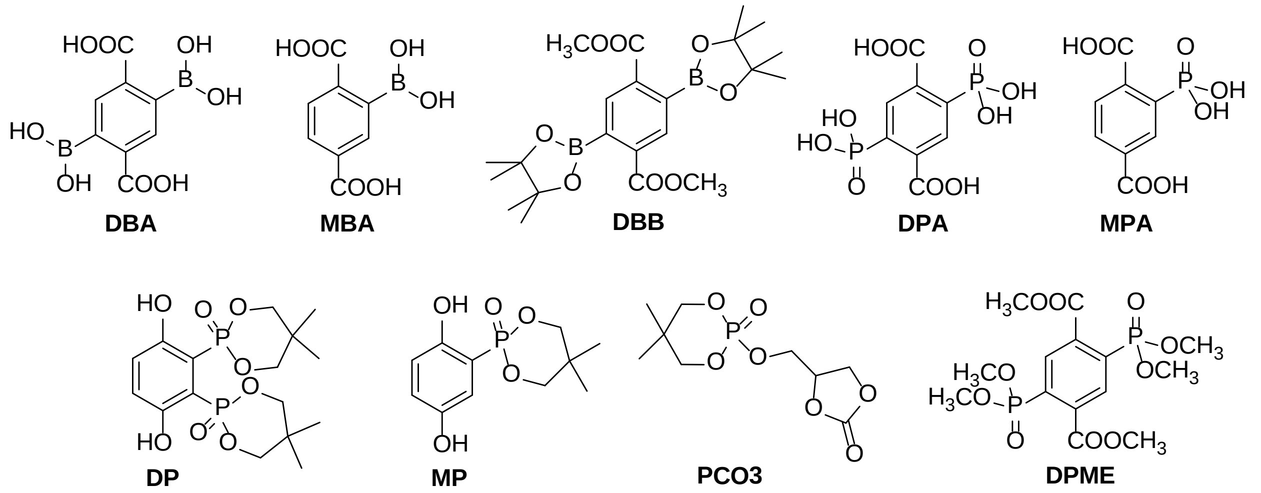

DBA MBA DBB DPA MPA
DP MP PCO3 DPME

Figure 1. Synthesized Flame Retardants

Table 1: New Synthesized Flame Retardants

Flame Retardant Name	Flame Retardant Acronym	Reactive (R) or Non-Reactive (NR)	Flame Retardant Chemistry Type
Diboronoterephthalic acid	DBA	R	Boron
Monoboronoterephthalic acid	MBA	R	Boron
Dimethyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate	DBB	NR?	Boron
2,5-Diphosphonoterephthalic acid	DPA	R	Phosphorus
Monophosphonoterephthalic acid	MPA	R	Phosphorus
1,4-Dihydroxy-2,5-bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene	DP	R	Phosphorus
1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene	MP	R	Phosphorus
5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yloxy)methyl-1,3-dioxolan-2-one	PCO3	R	Phosphorus
Dimethyl 2,5-bis (dimethylphosphono)terephthalate	DPME	NR?	Phosphorus

2*H*-5,5-Dimethyl[1,3,2]dioxaphosphorinane-2-oxide (DDPO). A mixture of 2,2-dimethyl-1,3-propanediol (62.4 g, 0.600 mol) and diethylphosphite (82.9 g, 0.600 mol, 77.3 mL) was stirred at 190 °C and atmospheric pressure, allowing for the continuous distillation of the ethanol formed during the reaction. Volatiles were removed under reduced pressure, followed by vacuum fractional distillation (0.05 mm Hg). The fraction distilling at 118 – 123 °C was collected, and NMR showed it to be pure for further use. Colorless oil, which solidifies upon standing. Yield: 34.9 g (38%). Mp 55 °C (Lit.[24] 58 °C). ^{1}H NMR (CDCl$_3$) δ 0.87 (s, 3H), 1.20 (s, 3H), 3.86 – 4.06 (m, 4H), 6.85 (d, J = 676.3 Hz, 1H).

1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (MP) and 1,4-dihydroxy-2,5-bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (DP). A solution of *p*-benzoquinone (2.00 g, 18.50 mmol), toluene (20 mL), and acetic acid (0.1128 g, 1.90 mmol) was added dropwise over a period of 20 min to a stirred solution of 2*H*-5,5-dimethyl[1,3,2]dioxaphosphorinane-2-oxide (**DDPO**, 2.84 g, 18.90 mmol) in toluene (30 mL). The mixture was stirred at 110 °C for 18 h. The solvents were removed under reduced pressure and acetone was added to the residue. The mixture was vacuum filtered and the filtrate was evaporated to dryness under reduced pressure. The resultant solid was washed with ether and separated on a silica gel column (methylene chloride).

1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (MP): Yield: 3.40 g (65%). Mp 184 – 187 °C (Lit.[4] 185 – 189 °C). ^{1}H NMR (DMSO-d_6) δ 0.90 (s, 3H), 1.26 (s, 3H), 3.93 – 4.06 (m, 4H), 6.75 (t, J = 7.7 Hz, 1H), 6.84 (dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, 1H), 6.91 (dd, J_1 = 15.6 Hz, J_2 = 2.9 Hz, 1H), 9.07 (s, 1H), 9.62 (s, 1H). ^{31}P NMR (DMSO-d_6) δ 12.1 (s, 1P).

1,4-dihydroxy-2,5-bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (DP). Yield: 0.53 g (7%). Mp 258 – 260 °C (Lit.[4] 260 °C). ^{1}H NMR (DMSO-d_6) δ 0.60 (s, 3H), 1.16 (s, 3H), 3.50 (d, J = 11.0 Hz, 2H), 3.70 (dd, J_1 = 23.0 Hz, J_2 = 11.3 Hz, 2H), 7.06 (t, J = 3.6 Hz, 2H), 9.85 (s, 2H). ^{31}P NMR (DMSO-d_6) δ 8.6 (s, 2P).

(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphan-2-yloxy)methyl-1,3-dioxolan-2-one (PCO3). 2-Chloro-5,5-dimethyl[1,3,2]dioxaphosphorinane-2-oxide[25] (**CDDPO**, 2.00 g, 10.80 mmol), pyridine (0.87 g, 10.80 mmol) and glycerol carbonate (0.92 mL, 10.80 mmol) were dissolved in a mixture of THF (5 mL) and chloroform (15 mL). The resultant solution refluxed for 18 h in inert atmosphere. Evaporation of the solvent left an oily residue, which was extracted with methylene chloride. The organic layer was dried (MgSO$_4$) and the solvent removed under reduced pressure. The resulting white solid was further purified by recrystallization from toluene. Yield: 2.31 g (80%). Mp 122 ˚C - 125 ˚C. ^{1}H NMR (CDCl$_3$) δ 0.91 (s, 3H), 1.29 (s, 3H), 3.88 – 4.01 (m, 2H), 4.13 (dt, J_1 = 8.9 Hz, J_2 = 2.3 Hz, 2H), 4.26 (ddd, J_1 = 11.9 Hz, J_2 = 6.1 Hz, J_3 = 2.6 Hz, 1H), 4.37 (ddd, J_1 = 11.9 Hz, J_2 = 6.1 Hz, J_3 = 2.6 Hz, 1H), 4.50 (dd, J_1 = 8.8 Hz, J_2 = 5.2 Hz, 1H), 4.60 (t, J = 8.7 Hz, 1H) 4.96 (m, 1H). ^{13}C NMR (CDCl$_3$) δ 20.0 (d, J = 0.7 Hz), 21.6, 32.1 (d, J = 6.0 Hz), 65.6, 65.7 (d, J = 5.0 Hz), 74.2 (d, J = 7.8 Hz), 78.1 (d, J = 6.7 Hz), 78.6 (d, J = 6.8 Hz), 154.6. ^{31}P NMR (DMSO-d_6) δ - 8.3 (s, 1P). Anal. Calcd. for $C_9H_{15}O_7P$: C, 40.61; H, 5.68. Found: C, 40.82; H, 5.68.

Polyurethane Synthesis:[26]

The samples tested in this paper were prepared in two different ways. The first was an *in-situ* polymerization where the polyurethane was synthesized with the flame retardant present with the polyurethane monomers. This gives the potential for the flame retardant to react into polymer backbone if it has functional groups that allow reaction with the isocyanate or the diol from the polyurethane monomers. Due to the synthetic process used, if the flame retardant cannot react into the polymer, or has a low propensity to do so, it will wash out of the final product during polymer precipitation and washing and therefore should have little effect on heat release as it would not be present for flame retardant effects. These samples are referred to as "Prep" in the tables and sections below. So for example, a sample named "Prep PU + DBB" would be a compound that used the *in-situ* procedure, and had 10mol% of the DBB flame retardant present in the sample. It should be pointed out that all of the potential flame retardants tested in this paper are soluble in methanol except for two. DBA is not soluble in methanol, but is soluble in water, so it would have been washed out in the "Prep" workup. DBB is not soluble in water, but is poorly soluble in cold methanol and is soluble in hot methanol. Discussion on the DBB molecule in the Prep and Blend samples is discussed in the Results section of this paper.

The second process used to prepare polyurethane + flame retardant samples was a simple solvent blending process. In this case, the polyurethane is synthesized first in the absence of flame retardant, and then while this polyurethane is in solution, the flame retardant additive is introduced into the flask, stirred for some time, and the solvent removed; no precipitation and washing of the final solid occurs. For these samples, the flame retardant should will be present, thus confirming the effect of a non-reactive flame retardant on heat release reduction in a polyurethane. These samples are referred to as "Blend" samples in the tables and sections below. A sample named "Blend PU + MP" would be a compound that used solvent blending procedure in this paragraph, and had 10mol% of 1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (MP) present in the sample.

These two sample preparation procedures are important in that they help confirm how the flame retardant works to reduce heat release and PU liquefaction as a function of synthetic process, and, they confirm if the flame retardant additive can react into the polyurethane or not. The latter point is quite important for the discovery of chemistry that enables new flame retardants with better environmental profile.

Preparation of "Prep" Polyurethane / Flame Retardant Samples:

An oven-dried, three neck flasks were fitted with a drying tube and continuously purged with a stream of nitrogen. The reactants/reagents were introduced at ambient temperature, and in the following order: N-methylpyrrolidone (solvent, 20 mL per 10 mmol of MDI), 1,3-propanediol (1 eq.), the flame retardant (0.1 eq., does not apply to the control sample), dibutyltin dilaurate (0.1 eq.), and finally methylene diphenyl diisocyanate (MDI, 1 eq.). The mixture was stirred at room temperature for a period of 5 – 10 min, and then immersed into an oil bath at 120 °C. Stirring was continued for 24 h at the same temperature. The resultant mixture was cooled and added dropwise and upon vigorous stirring to 500 mL of methanol, at ambient temperature. The precipitate was vacuum filtered (sintered-glass filter funnel, grade F), washed successively with ~ 200 mL of deionized water, followed by 200 mL of methanol. The solid was air-dried to yield a powder, whose color showed variation, depending on the employed flame retardant.

Preparation of "Blend" Polyurethane / Flame Retardant Samples:

A sample of polyurethane (typically in the range of 100 – 200 mg) was dissolved in about 1 mL of DMF. The flame retardant (10 mol %) was dissolved in about 0.5 mL of DMF. The two solutions were mixed and kept for about 1 h. The solvent was then removed under reduced pressure and at 60 – 70 °C. All samples were vacuum dried, to ensure complete removal of volatiles.

Heat Release Testing

All samples prepared in this paper were measured for heat release using pyrolysis combustion flow calorimetry (PCFC). Testing was performed via ASTM D7309-07, Method A (pyrolysis under nitrogen) with a heating rate of 1 °C/sec and heating of the sample from 175 °C to 800 °C. As per the ASTM method, all samples were tested in triplicate.

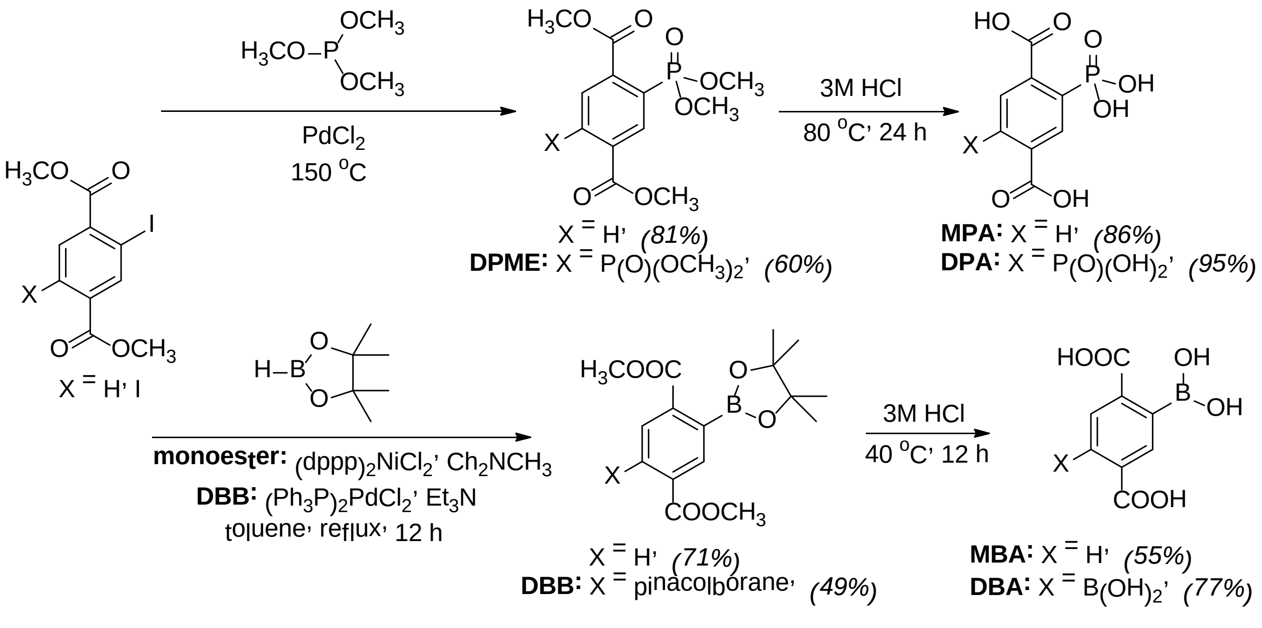
Thermal analysis

Thermogravimetric analyses (TGA) were carried out using a TGA Q5000 from TA Instruments at 60 °C/min in a nitrogen flow (25 mL/min) in order to be at the same heating rate as in the PCFC fire testing. Gases released during the degradation of the material were analyzed using a thermo gravimetric analysis (TGA Q5000, TA Instrument) connected to a Fourier transformed infrared (FTIR) spectrometer (ThermoScientific) Nicolet iS10. The IR spectra were recorded between 400 cm^{-1} and 4000 cm^{-1} (spectra recorded every 11 s). For each experiment, samples of 15mg material (powder) were positioned in alumina pans. All the analyses have been carried out in nitrogen flow (100 mL/min).

Results and Discussion:

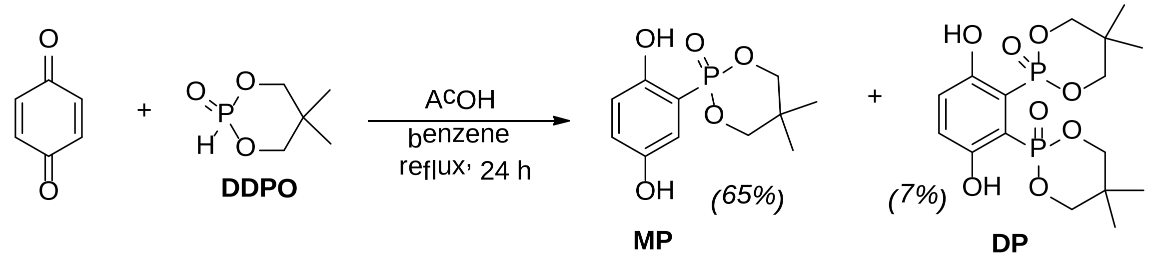
A. Synthesis. Part of the investigation was focused on new, potential reactive flame retardants, most of them reported in recent publications. Thus, we reported the synthesis and characterization of **MBA**, **DBA** and **DBB**,[18] using transition metal-catalyzed coupling reactions, followed by acid hydrolysis of the resultant pinacolboronic esters (Scheme 1). Separately, we have reported the preparation of **MPA**[19,20], **DPA**[20] and **DPME**[20], also based on transition metal-catalyzed coupling reactions, followed by acidic hydrolysis (Scheme 1).

Scheme 1



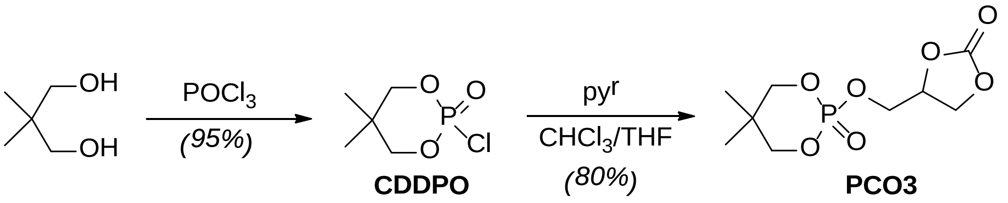
The synthesis and isolation of **MP** and **DP** was accomplished following a modified literature protocol,[21,22] utilizing *p*-benzoquinone, in reaction with 2*H*-5,5-dimethyl[1,3,2]dioxaphosphorinane-2-oxide (**DDPO**),[23,24] in the presence of acetic acid (Scheme 2). Although the structure with a single phosphonate ester is the major product, some quantity of the diphosphonate ester is generated as a bi-product. Structural studies of Döring *et al.* have unambiguously demonstrated that the bi-product has the structure shown in Scheme 2.[21]

Scheme 2



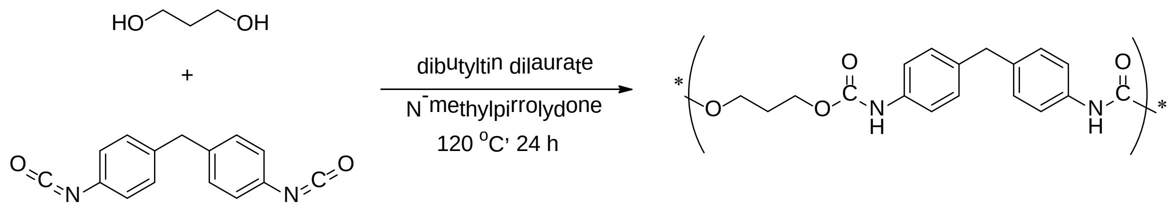
Compound **PCO3** was prepared using conditions typical for the preparation of phosphate esters, starting with 2-chloro-5,5-dimethyl[1,3,2]dioxaphosphorinane-2-oxide (**CDDPO**)[25] in reaction with glycerol carbonate, in the presence of pyridine base (Scheme 3).

Scheme 3



All commercial and newly prepared FR were used in the preparation of polyurethane samples with potential inclusion of the FR. Polyurethane was generated following the chemistry outlined in Scheme 4, with MDI and 1,3-propanediol as the principal monomers.[26]

Scheme 4



B. NMR studies. All of the "Prep" samples were characterized using ^{1}H NMR spectroscopy to determine if the flame retardant was incorporated into the structure or not. For the newly prepared, potential FR structures, ^{1}H NMR measurements showed no detectable incorporation of the FR at the 10 mol% level. In some cases, such as that of the 2,5-diphosphonoterephthalic acid, significant broadening of the N – H hydrogen signal was observed, which could be interpreted as resulting from the presence of acidic groups (and consequent hydrogen bonding), introduced by the incorporation of the FR into the PU.

Two factors have to be taken into account, however, when ^{1}H NMR results are used: 1) NMR has relatively low sensitivity and a small percentage incorporated FR may not be easily observable, and 2) Peaks for the FR, especially in the case of the newly generated compounds, are mostly in regions where the PU chain itself has prominent signals, the latter likely obscuring any information from the FR. We undertook therefore a series of ^{31}P and ^{11}B NMR measurements, whichever relevant for the particular sample. The results from those are summarized in Table 2 and Table 3.

Table 2. ^{31}P and ^{11}B NMR data on PU samples prepared using 10 mol% of FR. All results from measurements on a 300 MHz Bruker NMR instrument. ^{31}P signals referenced to H_3PO_4 dissolved in DMSO-d_6 (0.0 ppm). ^{11}B signals referenced to H_3BO_3 dissolved in DMSO-d_6 (0.0 ppm). Chemical shifts in *ppm*.

Compound	**^{31}P NMR signals of pure FR**	**^{31}P NMR signals of PU samples prepared with 10 mol% FR**
MPA	10.8 (sharp)	5.6 (broad, very weak), 8.24 (broad, very weak)
DPA	8.5 (sharp)	0.6 (broad), 6.8 (sharp), 7.3 (broad)
DPME	14.9 (sharp)	4.0 (broad), 6.5 (broad), 17.2 (sharp)
MP	12.1 (sharp)	10.3 (sharp), 11.7 (broad)
DP	8.6 (sharp)	-13.0 (sharp), 7.4 (broad), 9.0 (sharp), 13.5 – 14.9 (multiplet), 20.6 (doublet)
PCO3	-8.3 (sharp)	-7.9 (very weak), -4.4 (broad, very weak), -0.8 (sharp, very weak)

Table 3. ^{11}B NMR data on boron-containing flame retardants (FR) and the PU samples prepared using 10 mol% of FR. All results from measurements on a 300 MHz Bruker NMR instrument (96 MHz operating frequency for ^{11}B). ^{11}B signals referenced to H_3BO_3 dissolved in DMSO-d_6 (0.0 ppm). Chemical shifts in *ppm*.

Compound	**^{11}B NMR signals of pure FR**	**^{11}B NMR signals of PU samples prepared with 10 mol% FR**
MBA	9.2 (broad)	Weak broad peak detected
DBA	9.9 (broad)	Weak broad peak detected
DBB	35.9 (broad)	Weak broad peak detected

As can be seen from the data in Table 2, all studied samples showed some degree of incorporation of the FR, as evidenced by the presence and detection of a ^{31}P signal in every case. The newly prepared, potential FR also showed incorporation into the PU structure. In some cases, particularly MPA and PCO3 the final spectra had low signal-to-noise ratio, indicating relatively low percentage of phosphorous in the samples, i.e. low degree of inclusion of the FR. Table 2 also provides ^{31}P data on the starting FR, and comparison clearly shows a difference (often significant) in the NMR shifts and pattern between the starting FR and the resultant PU sample with the FR included. This may be due to other reactions between polyurethane monomers and the flame retardants, including transesterification of the 1,3-propane diol with the phosphonate esters rather than with carboxylic ester groups. ^{11}B NMR data collected was inconclusive about the degree of flame retardant incorporation other than to indicate that ^{11}B was detected, albeit weakly. This simply suggests that the boron compounds were incorporated into the structure, but it is not clear how much was incorporated. Since ^{11}B is never a strong signal source in NMR, other testing may be needed to confirm the degree of flame retardant incorporation.

C. Heat Release Results:

Before discussing the PCFC results, it is important to discuss polyurethane thermal decomposition chemistry and how that appears in the PCFC test in the absence of flame retardants. Polyurethane decomposition chemistry has been extensively studied to date,[9] and the mechanism is known to be a two-step decomposition. Figure 2 presents the TG and DTG curves obtained for the pure PU. It evidences that the degradation occurs in two main steps and the total char yield reaches 9% at 800°C. The temperature at which the degradation rate is maximum for the two steps are respectively 335°C and 470°C and the weight loss of each degradation step is 35% and 53%.

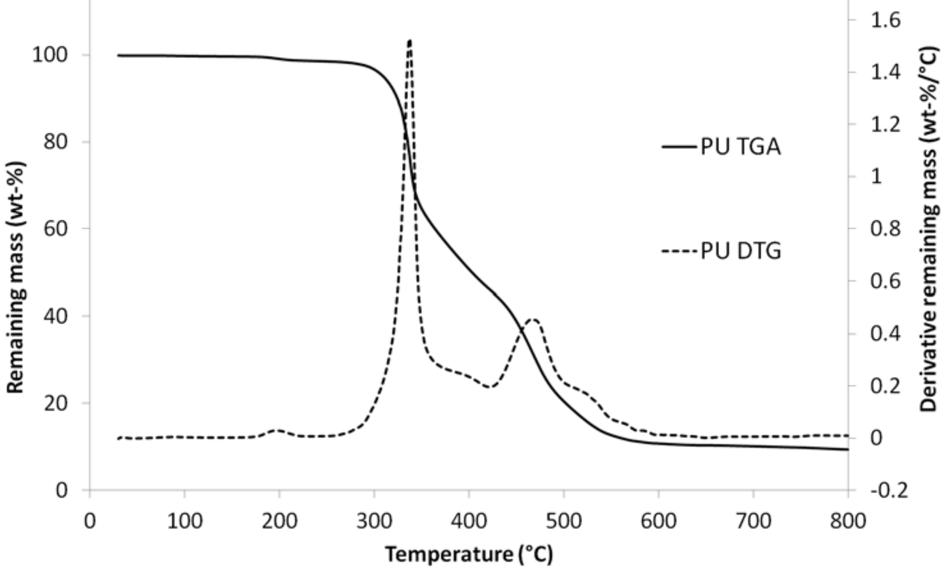


Figure 2: TG and DTG curve of pure PU in nitrogen flow

The gases evolved during the degradation of the PU are analyzed by FTIR to evaluate the main gases evolved during the thermal degradation. Figure 3a) shows the FTIR spectra of the gases released at the two DTG_{max}. During the first step the gases are composed of carbon dioxide (with absorptions bands at 2360, 2320 and 670 cm-1), N=C=O containing species (band at 2350 cm^{-1}) coming from the depolymerization of the PU, and some polyols characterizing by the bending vibrations of $C\text{-}H_{aliphatic}$, C–O–C or C–O–H and O-H at respectively 2940 cm^{-1}, 1045 cm^{-1} and 3500 cm^{-1}. During the second step of the degradation, aromatic compounds (with absorption at 3030 cm^{-1}), amino and carbonyl containing species with absorption band at respectively 1515 cm^{-1} and 1740 cm^{-1}.

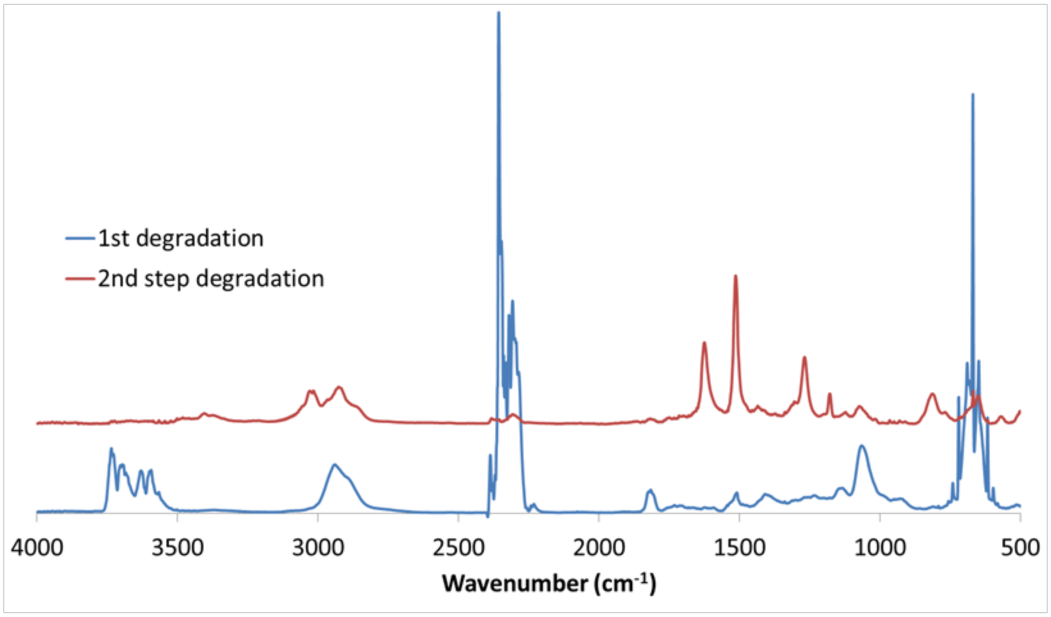


Figure 3: FTIR spectra of the gases released during the two steps of the thermal degradation of pure PU

During the two steps of degradation, several gases are evolved and can be ignited. In the PCFC test, a two-step heat release curve will be observed corresponding to the two peaks of flammable mass loss in the TGA.[9,18] Therefore, any flame retardants that change this two-step heat release curve in the PCFC can be inferred to be having an effect on the decomposition chemistry of the polyurethane. To focus our work, we first studied materials by PCFC to look for strong performance in reducing heat release, and then those best performing chemistries were studied further via TGA-FTIR to determine mechanism.

The primary use of PCFC in this paper is for focusing on the heat release reduction provided by the flame retardant, both from a reduction of heat release in the two peaks of HRR in normal polyurethane decomposition, and from a reduction in total heat release (total mass/fuel consumed). By studying the peak HRR and Total HR measurements, along with char structures obtained from the PCFC measurement, FR additives which lower heat release and inhibit melt flow/liquefaction would be good candidate materials to study further in full scale tests.

Before discussing the PU + FR systems, it is important to briefly discuss the control sample which contained no flame retardants since that is the system by which all others in this paper will be compared. The PU control sample (Scheme 4) shows a classic two peak HRR curve due to its two steps degradation and the char clearly shows sign of flow since the original sample placed into the PCFC was a fine brown powder.

Boron Containing Flame Retardant + PU Samples

Heat release data for Prep and Blend PU samples containing synthetized boron based materials with potential flame retardancy benefits are shown in Table 4 below. The diboronic acid (DBA) shows a mild effect on heat release reduction in the Prep and Blend forms (Table 4) with some minor differences noted between Prep and Blend samples (Figure 4). Both samples show some improved char structure but not inhibit melting and flowing during burning. The monoboronic acid (MBA) (Figure 4 right) shows similar behavior when compared to DBA (Figure 4 left). MBA is a bit more effective at total HR reduction when reacted into the polyurethane (Prep), but not as effective when blended into the polyurethane (Blend). Final chars show that this flame retardant helps form glassy chars that have some foamed structure, but no inhibition of melting and flowing during decomposition.

In theory, the diboronate (DBB) should be a non-reactive flame retardant as all of its chemical groups are bound up with ester functionality and should not be available for reaction. Specifically, previous studies on boron compounds have shown that boronic acids help promote char formation and flame retardant effects; boronates have no effect.[18,27] When studying the data for this material, we see one result that supports this hypothesis, and another which does not. For the Blend sample, DBB has no effect on HRR curve shape (Figure 5), nor on final chars formed in that the final char appears similar to that of the PU control (Figure 6, right). Instead it makes flammability slightly worse as it is effectively burned off since it is not chemically bound to the polymer (Table 4). However, in the prep sample, we see a very different effect. HRR curve shape (Figure 5) is completely changed, with the two main peaks of polyurethane decomposition being suppressed and a new peak of HRR around 350 °C forming instead. Total HR is greatly reduced and char yields are increased. Further, the final char for this sample (Figure 6, left) is a black shiny powder, suggesting that DBB inhibits melt flow during decomposition of the polyurethane. DBB has low solubility in cold methanol, and since it would not be washed out in the typical “Prep” synthesis, some additional consideration of the results is in order. If DBB was unchanged in chemical structure during both “Prep” and “Blend” experiments, the heat release results would be the same for both samples; little to no reduction in heat release. This is not what was observed. DBB, when added to PU monomers, does change the HRR curve shape and total heat release. Further, it changes the decomposition chemistry as outlined in the TGA results below. Therefore we can correctly infer that DBB is not in its original structure in the “Prep” sample and something is different. Most likely is that the 1,3-propane diol has trans-esterified with the carboxylic methyl esters, incorporating boron into the final structure of the polyurethane. While spectral data confirming this reaction is not available, it seems highly unlikely that DBB just left in the Prep sample and not washed out would account for the heat release and polymer decomposition changes observed for this sample. Therefore we believe that DBB has reacted into the PU backbone, but we admit to not knowing the exact chemical structure of that reacted species.

Table 4. HRR data for PU + Synthesized Boron FR

	Char Yield	HRR Peak(s)	HRR Peak Temps	Total HR	Total HR
Sample	(wt%)	Value (W/g)	(°C)	(kJ/g)	% Reduction
PU Control	8.87	267, 162	326, 437	21.8	0.0
PU Control	9.22	275, 158	328, 441	22.2	0.0
PU Control	8.39	207, 144	331, 439	21.9	0.0
PU Prep with DBA	14.95	8, 191, 92	191, 320, 432	19.9	9.4
PU Prep with DBA	15.38	8, 232, 87	192, 319, 432	19.4	11.7
PU Prep with DBA	15.39	6, 260, 82	194, 321, 434	19.8	9.9
PU Blend with DBA	12.90	14, 130, 113	184, 325, 453	20.1	8.5
PU Blend with DBA	13.16	14, 142, 110	187, 322, 451	19.8	9.9
PU Blend with DBA	12.98	13, 125, 102	186, 316, 452	19.9	9.4
PU Prep with MBA	16.38	7, 226, 97, 102	197, 316, 339, 434	19.0	13.5
PU Prep with MBA	16.54	8, 217, 107	196, 315, 433	19.2	12.6
PU Prep with MBA	16.32	8, 226, 99	196, 316, 435	19.3	12.2
PU Blend with MBA	13.22	17, 220, 130	201, 310, 461	21.4	2.6
PU Blend with MBA	13.00	17, 228, 156	198, 309, 457	20.7	5.8
PU Blend with MBA	12.94	17, 215, 144	199, 307, 459	21.0	4.4
PU Prep with DBB	26.61	13, 145, 56	206, 351, 405	17.4	20.8
PU Prep with DBB	26.66	14, 144, 57	208, 350, 405	17.3	21.3
PU Prep with DBB	26.41	13, 182, 76	208, 351, 402	17.4	20.8
PU Blend with DBB	9.83	7, 225, 114	192, 321, 454	22.0	-0.1
PU Blend with DBB	10.01	7, 256, 110	194, 318, 456	21.7	1.2
PU Blend with DBB	9.57	6, 210, 112	193, 324, 454	22.0	-0.1

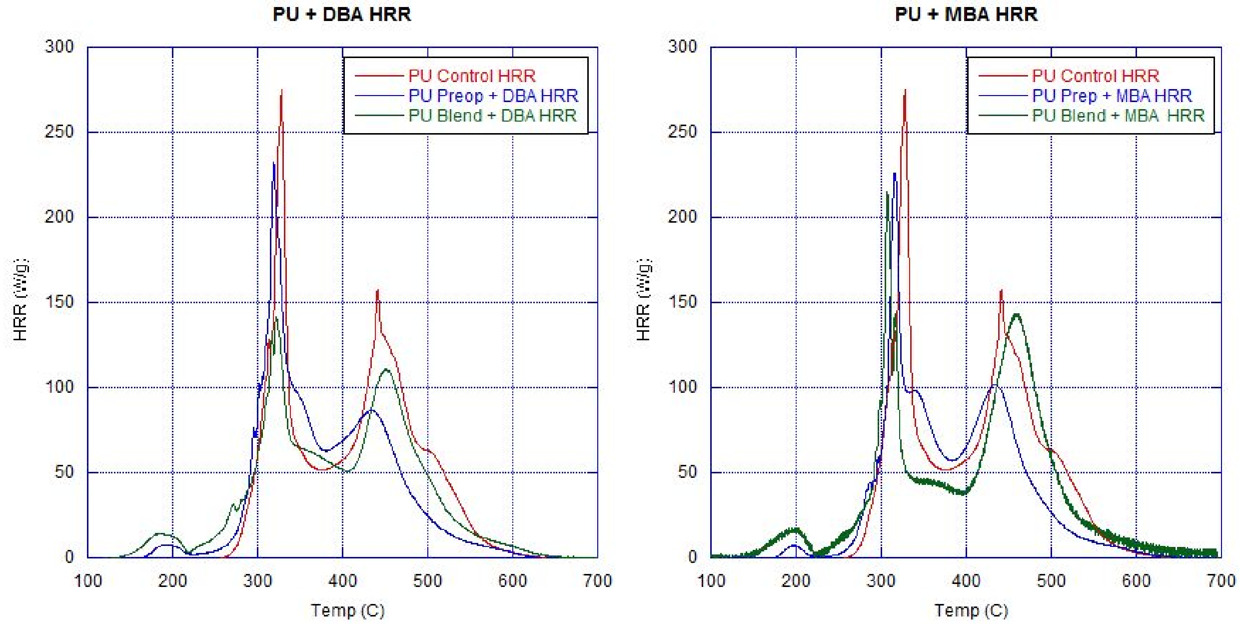


Figure 4. HRR plots for PU + DBA (left) and Blend PU + MBA (right)

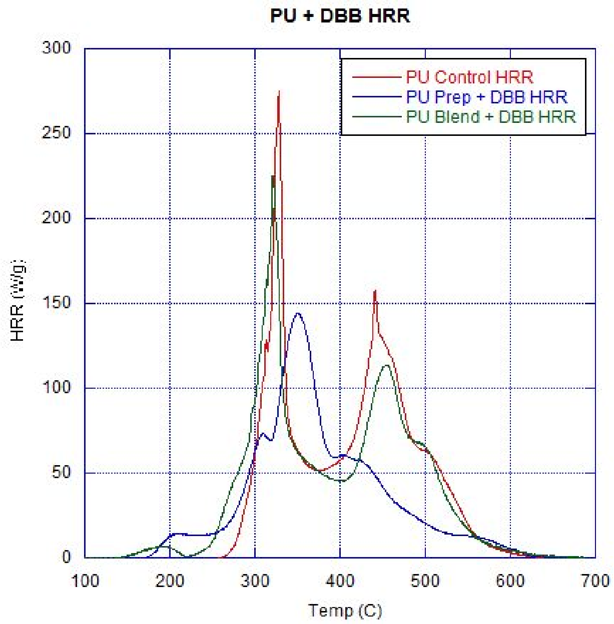


Figure 5. HRR plots for PU + DBB (left)

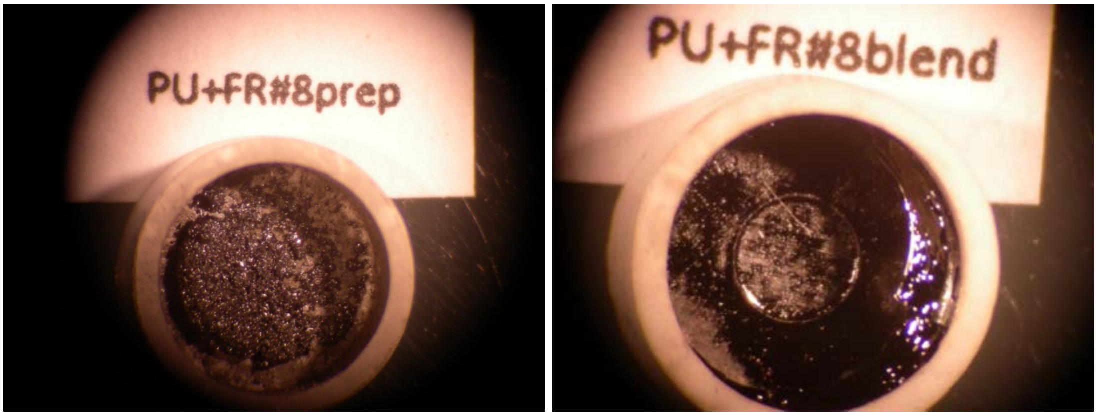


Figure 6. Chars for Prep PU + DBB (left) and Blend PU + DBB (right)

This impressive result led us to study how this flame retardant behaved via TGA-FTIR. At first, thermal stability of PU+10%DBB blend and prep are investigated. Figure 7a) and b) presents respectively the TGA and DTG of PU+10%DBB. TGA experiments highlight that the mode of incorporation of the DBB has a real influence on the thermal stability of the formulations. DTG curve presented in Figure 7b) evidences that when the DBB is incorporated by prep the thermal degradation occurs in one main step whereas as for the pure PU it occurs in two main steps for PU+10%DBB prep. Both samples, regardless of how the DBB was incorporated, begin to degrade at 200°C. For the prep sample, DBB increases significantly the char yield: 23% for PU+10%DBB prep against 9% for pure PU as well as for the blend sample. In this case, DBB decreases therefore the amount of combustible gases released during the thermal degradation of the material.

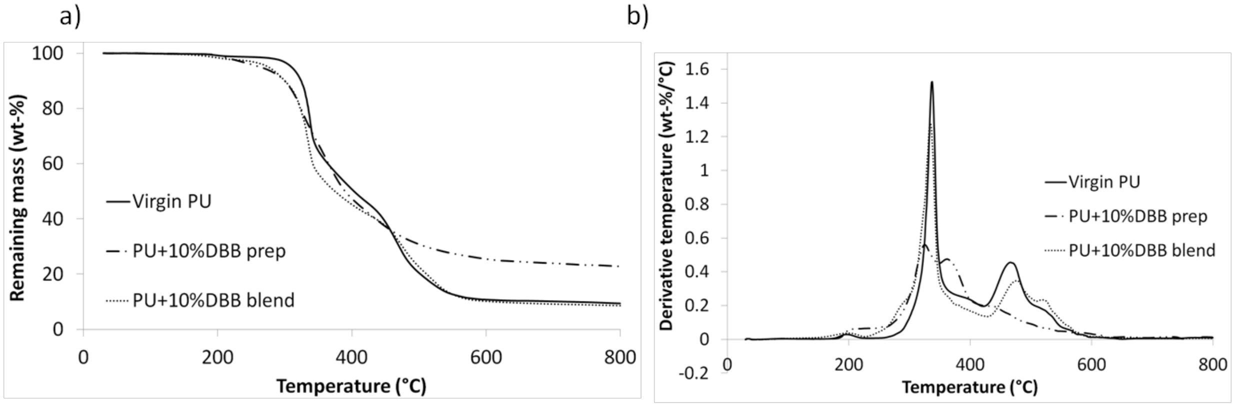


Figure 7: a) TGA of PU, PU+10%DBB prep and PU+10%DBB blend and b) DTG curve of PU, PU+10%DBB prep and PU+10%DBB blend

The TGA data alone, along with the PCFC data, suggest a char formation mechanism where the flammable PU decomposition products are being carbonized. TGA/FTIR was then employed to understand the influence of the DBB (and its mode of incorporation) of the nature of the gases emitted during their thermal degradation in order to explain their fire performance.

During TGA/FTIR experiments, spectral data are repeatedly collected in the form of interferograms and then processed to build up a Gram Schmidt reconstruction, each point of which corresponds to the total IR absorbance of the evolved components in the range of 4000-500 cm^{-1}, the Gram Schmidt plot is thus the result of averaging all FTIR peak intensities over the entire spectral range[28]. The Gram Schmidt graph is plotted in Figure 8 and demonstrates two things: (i) For PU and PU+10%DBB blends two gases population are released explaining the two peak of HRR during PCFC test. (ii) when 10% of DBB in incorporated by prep in PU matrix, only one main population of gas is evolved.

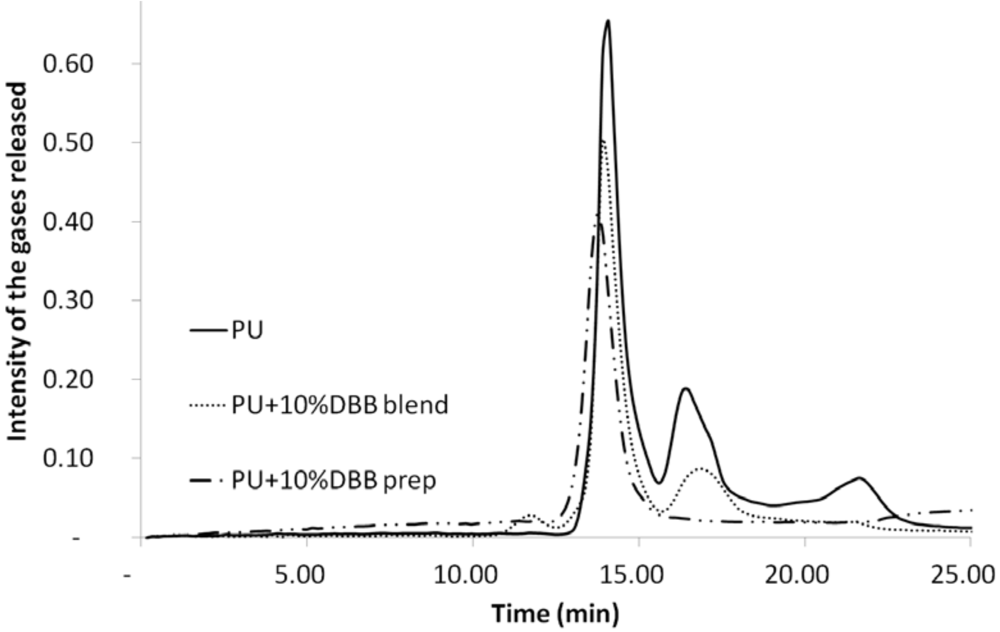


Figure 8: Gram Schmidt graph of PU, PU+10%DBB blend and PU+10%DBB prep during TGA experiment

This suggests that the DBB modifies the thermal degradation pathway when it is introduced by prep in the PU matrix. This can be observed via FTIR mapping of the gases released during the TGA experiment as presented in Figure 9. For PU+10%DBB and pure PU there is no significant modification of the gases released and the same peak appears for the two materials on the diagram. However, the 3D diagram of PU+10%DBB prep is in agreement with the Gram Schmidt graph and shows that during the second step of the degradation of PU, no significant peak around 1510 cm^{-1} corresponding to N-H band vibration and at 3050 cm^{-1} characterizing aromatic compound are detected.

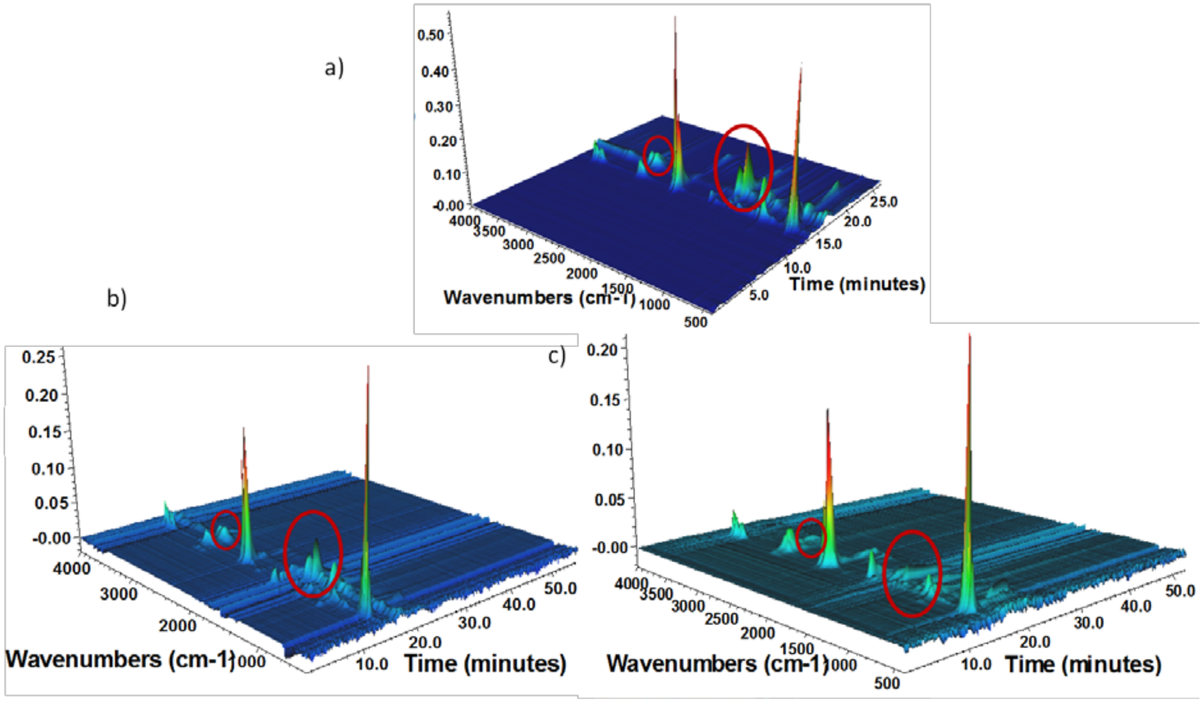


Figure 9: 3D diagram corresponding to gases released during the TGA experiment from 30°C to 800°C

Based upon these results, DBB has no effect on the chemical decomposition of the polyurethane when in "blend" preparation as the main gases for the PU control and the PU Blend + 10%DBB are mostly the same. This lack of influence on the thermal decomposition chemistry explains the low fire retardant property of PU+10%DBB blend.

However, for "prep" form, the DBB increases significantly the char yield of the PU matrix and limits the released of amino and aromatic compounds characterizing the second step of degradation of PU. It therefore decreases the evolving of combustible gases explaining, at least partially, the good fire retardant properties of PU+10%DBB prep and the modification of the HRR curve shape obtained in PCFC fire testing. While TGA/FTIR cannot directly infer the chemical structures that are forming in the char, the decrease of amino and aromatic compounds suggests that the boronate is reacting with the ureathane groups in such a way that when the bonds thermally break, it serves as a crosslinking chemical group which keeps these chemical groups bound into the condensed phase, rather than volatilized. More specifically, the boronate is likely complexing with the free electron pair on the NH of the urea group, which forms a stable octet for boron as an initial chemical complex. As thermal decomposition occurs, B-N bonds are likely forming (along with a variety of thermally stable B-O-C, B-O-B, and B-O-N bonds) and these thermally stable species carbonize further into thermally stable char, thus increasing char yield and decreasing heat release.[27]

Phosphorus Containing Flame Retardant + PU Samples

A total of six new synthesized phosphorus flame retardants were mixed with the polyurethane and studied for their effect on heat release and polyurethane heat release patterns. The results are summarized in Table 5.

The diphosophonate carboxylic acid (DPA) shows very different effects in Prep and Blend forms. When mixed in during polymerization (Prep), there is no change to the heat release rate curve shape (Figure 10, left), but all of the HRR peak values are reduced, and there is a notable reduction to total HR. ^{31}P NMR indicates that the flame retardant is present in the sample, but the degree of incorporation is not clear. The final char (Figure 11, left) is noteworthy as well, with a fine powder being obtained at the end of the experiment, suggesting this flame retardant does inhibit melting and flow. When DPA is blended into the polyurethane, the 1st peak of HRR is shifted to a lower temperature and 2nd peak of HRR is now almost completely absent (Figure 10, left). The final char for the blend sample (Figure 11, right) is somewhat powdery, but also somewhat foamed in structure. In either case, prep or blend, DPA does inhibit some melt flow in polyurethanes and does lower heat release.

The Monophosphonate dicarboxylic acid (MPA) does not show the same heat release behavior as the disubstituted molecule. In prep form, the total HR reduction is minimal and the HRR curve shape (Figure 10, right) is mostly unchanged. This may suggest that the MPA was not fully incorporated into the polyurethane during synthesis. NMR data (Table 2) shows weak and broad peaks, which may support this conclusion. In blend form, MPA is more effective in reducing total HR, and it shows three major peaks of HRR being observed from 250 °C to 450 °C. For both prep and blend samples, the final chars show signs of melting and flow.

The disubstituted phosphonate (DP) is equally effective in reducing total heat release in both Prep and Blend samples, but it shows different effects on HRR curves (Figure 12, left). NMR data (Table 2) does indicate that the compound is present, but in multiple forms/interactions with the polyurethane matrix as indicated by the large number of detected ^{31}P NMR peaks. The difference in HRR is likely due to the how the phosphorus is bound/coordinated by the polyurethane structure, which unfortunately cannot be discerned at this time. The final chars indicated that DP does not inhibit melting and flow of the polyurethane during thermal decomposition. The monophosphonate (MP) shows some similar trends to the DP molecule discussed above (Figure 12, right). The final chars for this sample were similar to that of the DP molecule; additional char formed, but no inhibition of melt flow.

The phosphate carbonate (PCO3) is a potentially reactive flame retardant in that the polyol portion of the polyurethane used in this paper could react with the carbonate to incorporate the molecule into the polymer. NMR data however (Table 2) shows very weak peaks, suggesting that only a small amount of the PCO3 was incorporated into the polymer structure meaning that the carbonate is not as reactive as believed. In Prep form, this potential flame retardant greatly reduces the 1st peak of HRR (Figure 13) but total HR is mostly unchanged. For the Blend sample, PCO3 gives a more complex HRR curve, but the HRR and total HR reductions are minimal. Finally, chars show the effects of flow, indicating that PCO3 does not inhibit melt flow in the polyurethane during decomposition. This data indicates clearly that PCO3 has low effective flame retardant potential for polyurethane.

The diphosphonate methyl ester (DPME) was originally expected to be a non-reactive flame retardant for polyurethane, but its activity in the polyurethane in Prep form suggests otherwise. NMR data (Table 2) shows that the molecule is incorporated, but there is more than one ^{31}P NMR peak present, perhaps suggesting that the methyl esters on the carboxylic acids and phosphonate groups have reacted with the polyols. HRR curve shapes are very similar to that of DPA (Compare Figure 13 to Figure 10) in both Prep and Blend forms. Additionally, the amount of heat release reduction and char yields are similar as well. The chars formed for DPME show an inhibition of melt and flow, much like those seen for DPA (Figure 14). DPME may be more effective per mol% of phosphorus than DPA and therefore should be studied further for its mechanism of flame retardancy.

Table 5. HRR data for PU + New Synthesized Phosphorus FR

Sample	Char Yield (wt%)	HRR Peak(s) Value (W/g)	HRR Peak Temps (°C)	Total HR (kJ/g)	Total HR % Reduction
PU Control	8.87	267, 162	326, 437	21.8	0.0
PU Control	9.22	275, 158	328, 441	22.2	0.0
PU Control	8.39	207, 144	331, 439	21.9	0.0
PU Prep with DPA	29.00	11, 181, 79	243, 338, 411	16.5	24.9
PU Prep with DPA	29.22	12, 182, 76	241, 339, 414	16.4	25.4
PU Prep with DPA	28.90	8, 175, 85	242, 338, 409	15.7	28.5
PU Blend with DPA	25.75	142	297	15.6	29.0
PU Blend with DPA	25.93	147	297	15.0	31.7
PU Blend with DPA	25.63	152	297	15.8	28.1
PU Prep with MPA	12.69	9, 124, 149, 144	205, 294, 315, 445	21.0	4.4
PU Prep with MPA	13.00	8, 92, 135, 148	204, 289, 312, 443	20.8	5.3
PU Prep with MPA	13.89	8, 151, 142	206, 311, 445	20.5	6.7
PU Blend with MPA	20.30	103, 106, 115	280, 322, 400	19.1	13.1
PU Blend with MPA	20.37	93, 113, 114	278, 321, 400	18.4	16.2
PU Blend with MPA	19.39	16, 88, 106, 110	205, 281, 323, 398	17.9	18.5
PU Prep with DP	14.81	169, 120	329, 418	20.0	9.0
PU Prep with DP	15.71	153, 119, 120	328, 354, 421	19.8	9.9
PU Prep with DP	15.17	159, 117, 121	329, 352, 420	20.0	9.0
PU Blend with DP	15.06	252	300	19.9	9.4
PU Blend with DP	15.84	255	308	19.6	10.8
PU Blend with DP	14.93	239	309	19.8	9.9
PU Prep with MP	17.66	191, 106, 97	301, 345, 420	19.5	11.2
PU Prep with MP	17.67	171, 107, 97	307, 343, 417	19.6	10.8
PU Prep with MP	17.39	205, 157, 99, 91	303, 320, 345, 415	19.4	11.7
PU Blend with MP	12.94	247, 148, 145	336, 371, 393	19.7	10.3
PU Blend with MP	12.75	304, 150	337, 394	20.4	7.1
PU Blend with MP	12.48	269, 149, 149	335, 372, 395	20.5	6.7
PU Prep with PCO3	11.09	105, 78, 138, 127	313, 351, 432, 447	21.5	2.1
PU Prep with PCO3	11.33	115, 138	302, 440	20.5	6.7
PU Prep with PCO3	11.96	95, 106, 76, 164	300, 314, 348, 436	20.6	6.2
PU Blend with PCO3	11.47	268, 137, 120	330, 362, 402	20.6	6.2
PU Blend with PCO3	11.21	262, 130, 131	331, 364, 403	20.3	7.6
PU Blend with PCO3	11.02	278, 215, 134, 129	330, 341, 362, 403	19.9	9.4
PU Prep with DPME	27.52	12, 190, 98	222, 343, 405	17.4	20.8
PU Prep with DPME	27.87	12, 193, 97	226, 342, 404	17.6	19.9
PU Prep with DPME	27.94	12, 189, 100	224, 342, 403	17.5	20.3
PU Blend with DPME	27.56	190	296	15.7	28.5
PU Blend with DPME	27.26	157, 182	279, 297	15.9	27.6
PU Blend with DPME	27.31	188	297	15.6	29.0

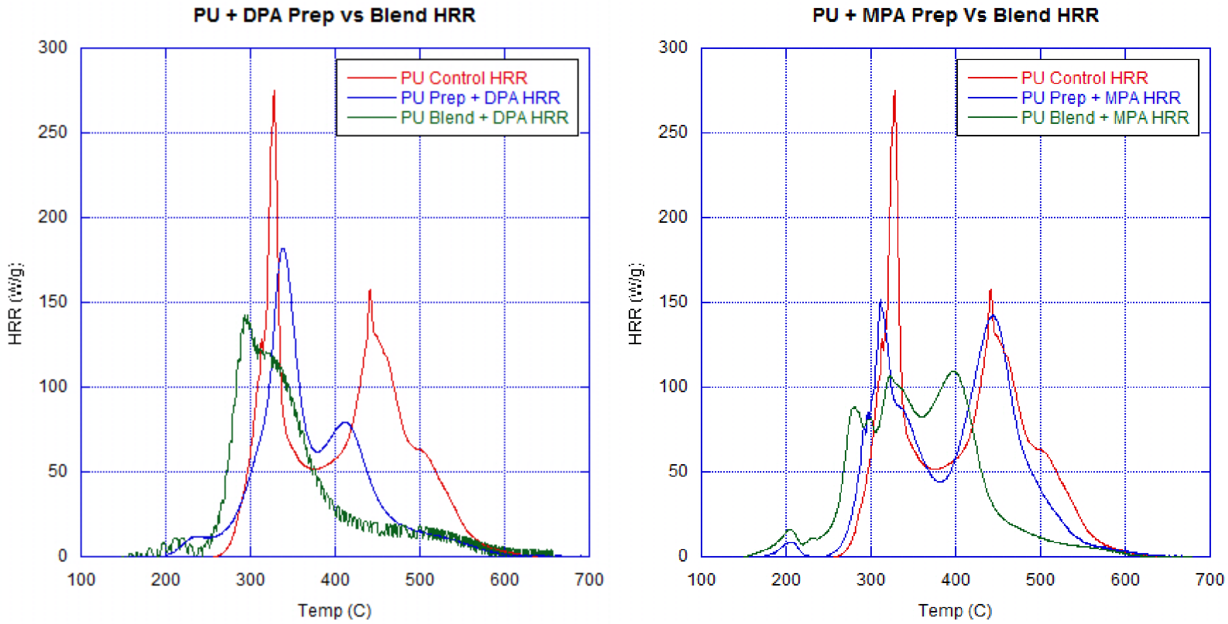


Figure 10. HRR plots for PU + DPA (left) and PU + MPA (right)

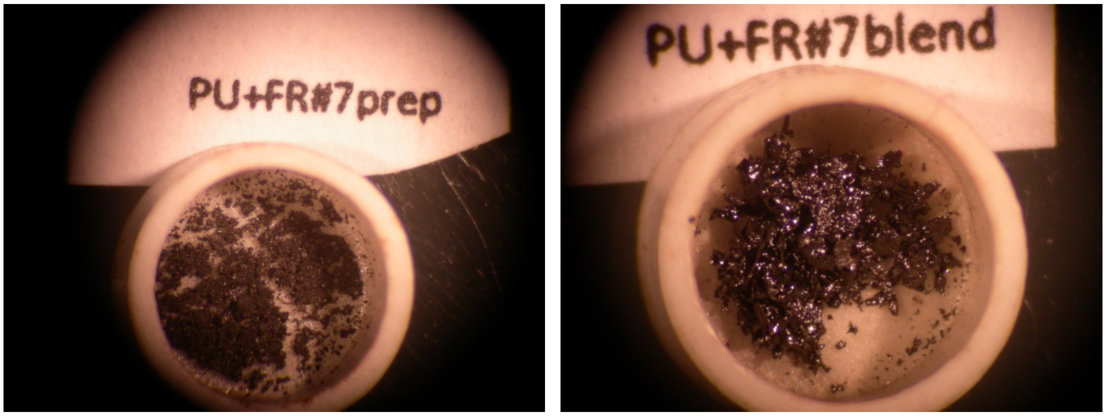


Figure 11. Chars for Prep PU + DPA (left) and Blend PU + DPA (right)

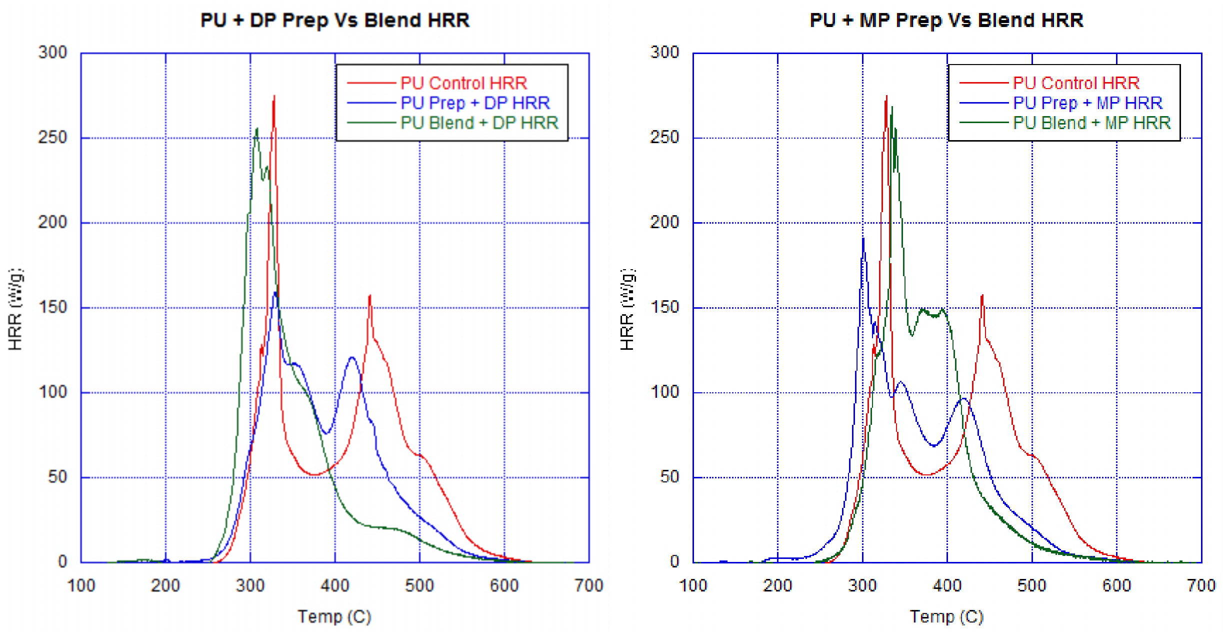


Figure 12. HRR plots for PU + DP (left) and PU + MP (right)

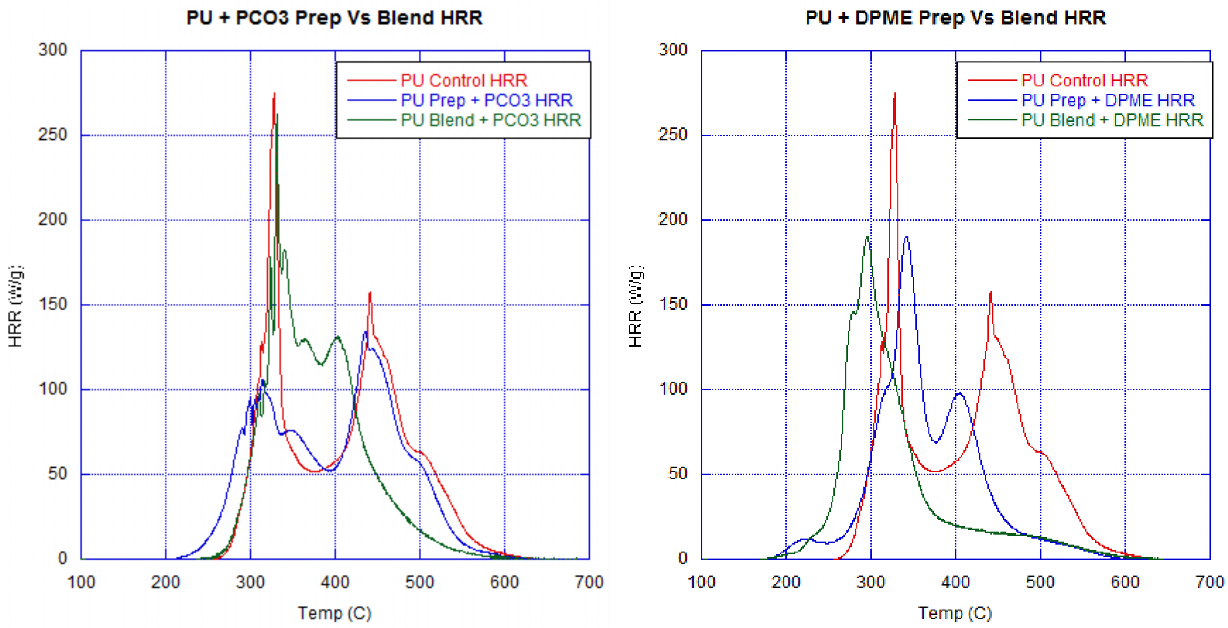


Figure 13. HRR plots for Prep PU + PCO3 (left) and PU + DPME (right)

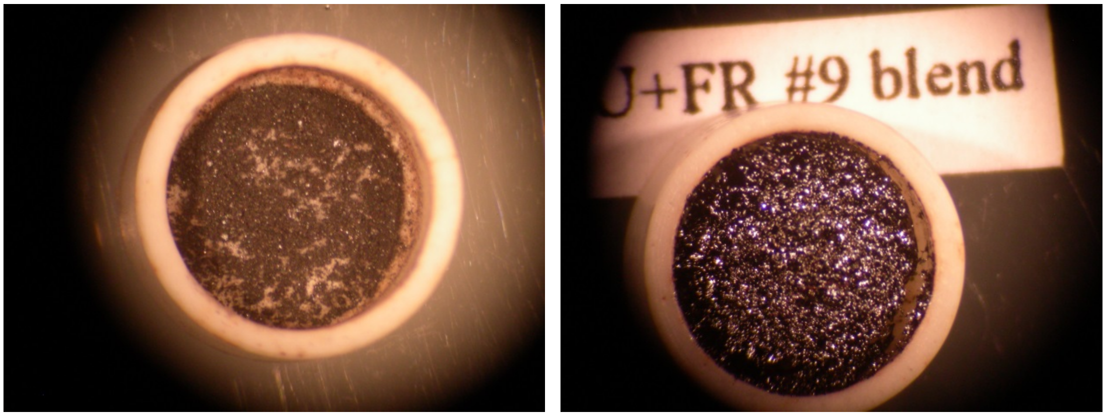


Figure 14. Chars for Prep PU + DPME (left) and Blend PU + DPME (right)

In order to propose a mode of action of DPA flame retardant, the same TGA/FTIR analysis as for DBB are carried out. Figure 15a) and b) respectively show TGA and DTG curves of PU and PU+10%DPA. Concerning PU+10%DPA blend material, the degradation occurs in three main steps at respectively 210°C, 295°C and 331°C and DPA increases the char yield of the PU at 800°C (remaining mass 23%). For PU+10%DPA prep, the thermal degradation occurs in two steps at 335°C and 415°C. The residue of PU+10%DPA prep reaches 29% at 800°C. This study points out two main things: (i) in both cases DPA increases the char yield of PU decreasing therefore the amount of combustible gases and (ii) when incorporated by blend, it modifies the thermal degradation pathway of the PU.

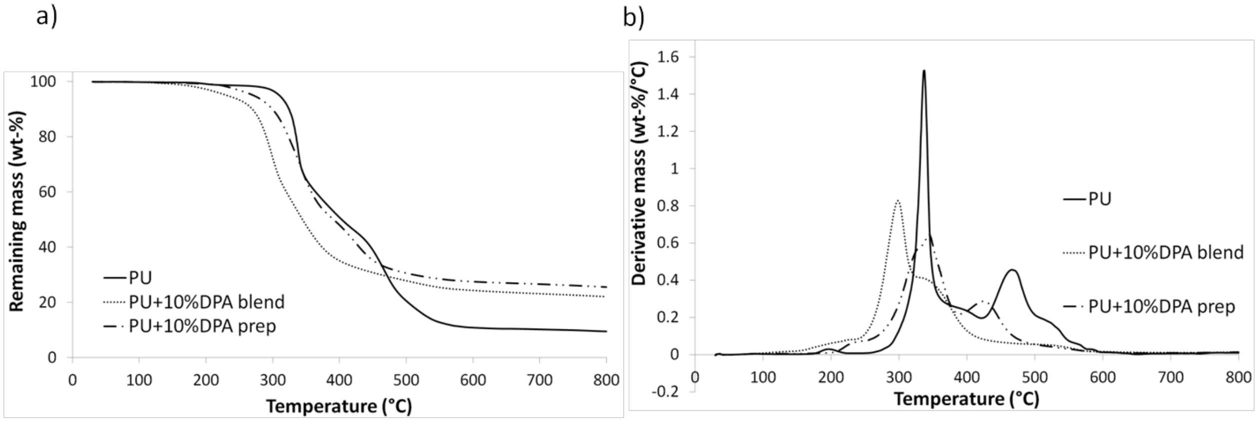


Figure 15: a) TGA and b) DTG curve of PU+10%DPAblend and PU+10%DPA prep

Once again, the gases released are analyzed by FTIR in order to propose a mode of action of DPA in the PU matrix. Figure 16 shows the Gram Schmidt graph of PU, PU+10%DPA blend and prep forms. Concerning blend preparation, it highlights that when DPA is incorporated by blend the gases are evolved sooner and at lower temperature. This is in agreement with TGA analysis since PU+10%DPA blend degrades at a lower temperature than pure PU. Moreover, there is no peak at 16 min corresponding to the gases released during the second step of the PU degradation. This lack of 2nd gas release partially explains the shape of the PCFC curve for this material (only one HRR peak).

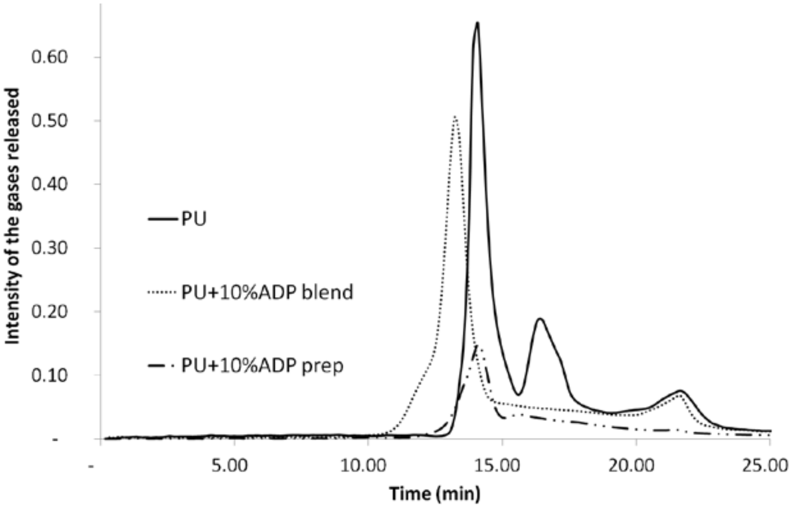


Figure 16: Gram Schmidt graph of PU, PU+10%DPA blend and PU+10%DPA prep

Moreover, in the PCFC curve, there is a significant decrease of the first HRR peak compared with that of pure PU (about 30%). The nature of the gas released in the range 150°C-330°C are analyzed by FTIR (Figure 17). For PU+10%DPA blend, at 220°C, the gases are composed of carbon dioxide (absorption band at 2360, 2320 and 670 cm^{-1}), carbonyl containing species (absorption band at 1710 cm^{-1}). The polyols are released at 295°C characterizing by the bending vibrations of $C\text{-}H_{aliphatic}$, C–O–C or C–O–H and O-H at respectively 2940 cm^{-1}, 1045 cm^{-1} and 3500 cm^{-1}. However, the band at 2350cm -1 is significantly decreased when DPA is incorporated in PU matrix suggesting that this flame retardant limits the evolution of N=C=O containing species coming from the depolymerization of the PU. We can therefore reasonably suppose that when the DPA is incorporated by blend in PU matrix its FR mode of action consists of (i) the release of potentially less combustible gases at lower temperature than pure PU, (ii) limiting the depolymerization step of the PU (characterized by the delayed evolving of isocyanate species) and (iii) all thermal decomposition in the PU+10%DPA mostly ceases above 450°C. So in blend form, it is very likely the phosphorus groups in DPA are catalyzing char formation reactions between C-O groups and the phosphonic acid, although the limited evolution of isocyanate also suggests that some P-N and P-O-C groups may be forming to enhance the thermal stability of the char to lead to quick carbonization and ceasing of mass loss.[4,29]

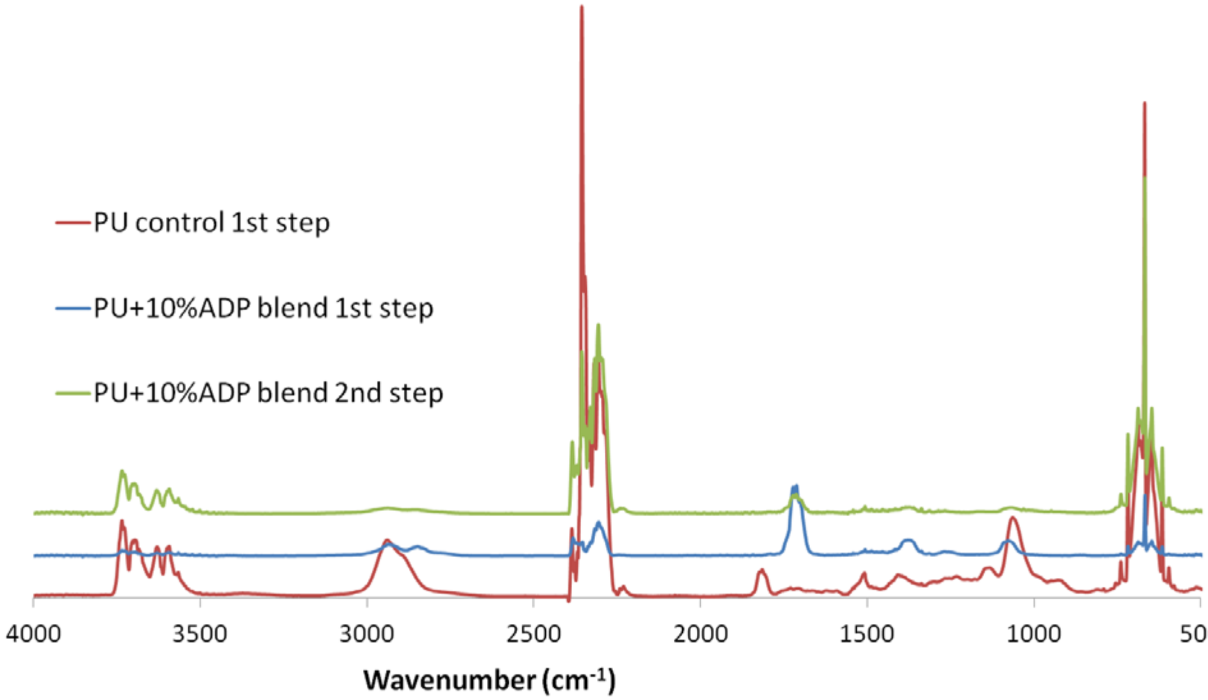


Figure 17: FTIR gases of PU at 335°C, PU+10%DPA blend at 220°C (1st step) and at 295°C (2nd step)

Concerning PU+10%DPA prep, Gram Schmidt graph highlights the presence of two peaks as for pure PU and the shape of the HRR curve is thus similar. However, a significant decrease of the HRR is obtained. FTIR spectra of PU and PU+10%DPA prep are presented in Figure 18 and evidence that the band corresponding to isocyanate species (2360 cm^{-1}) disappears. It points thus out that DPA modifies the thermal degradation pathway of pure PU (as for the blend form).

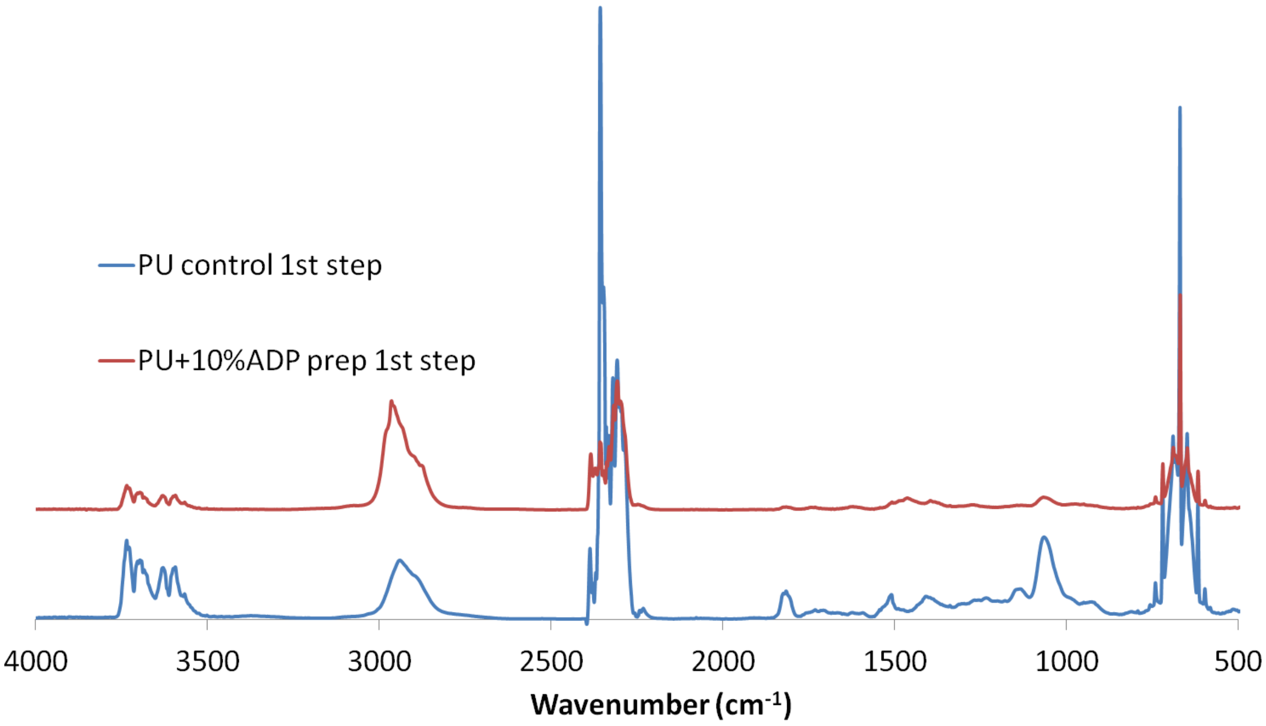


Figure 18: FTIR spectrum of PU and PU+10%DPA at 335°C

During the second step of degradation there is no modification of the nature of the gas release with and without DPA (Figure 19)

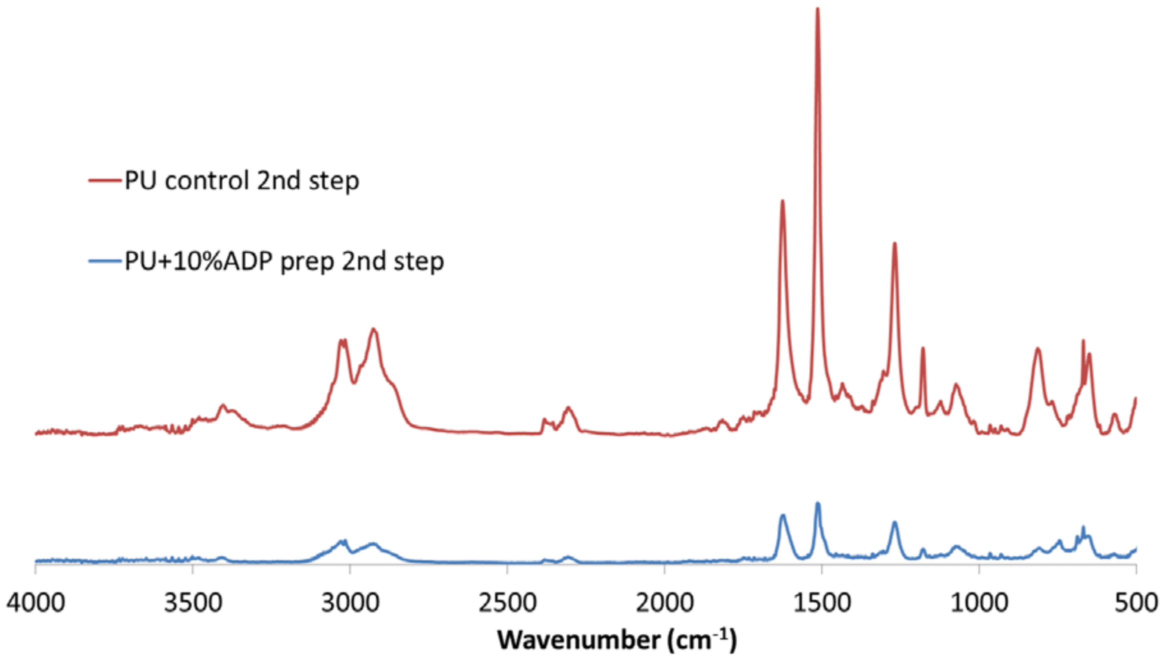


Figure 19: FTIR spectrum of PU at 470°C and PU+10%DPA prep at 410°C

The results show that the mechanism of DPA in PU is complex. When chemically incorporated into the polymer structure (Prep), there is a change in thermal decomposition chemistry where the release of just N=C=O species is inhibited. This suggests that the phosphorus is reacting with the urethane groups during thermal decomposition which lowers initial HRR, but also sets up more thermally stable species for further heat release reduction. When DPA is in blend form though, the chemical decomposition pathway changes greatly rather than just inhibition of particular chemical release. DPA in blend form appears to prevent the 2nd step of decomposition in the PU matrix, thus leading to a one peak HRR curve.

Conclusions:

With the use of the PCFC and spectroscopy techniques, data has been presented on how potential flame retardants affect the heat release of a polyurethane and if the flame retardants have potential to react with the polyurethane during manufacture. Using those two criteria, we have attempted to screen for performance and can show that some of the flame retardants have great potential, but there are some unknowns.

The unknowns from the results in this paper center around the spectroscopic data. NMR was not always conclusive about the incorporation of the flame retardants into the polyurethane. Further, the exact chemical structure and loading level of the flame retardants incorporated into the polyurethane is unknown at this time as NMR and FTIR were not able to determine what form the molecules reacted into the polyurethane. We only know at this time that they did not wash out during chemical synthesis, and therefore indirectly we can state that these potential flame retardants have definitely become part of the final product, but we cannot say what the final chemical structure of the polymer + boron/phosphorus compound is. Even the case of the DBB molecule, which would not have been fully washed out due to its low solubility in methanol and water, gave such different results when present in the "Prep" procedure that we believe, based upon known organic chemistry reactions, that DBB is likely reacted into the final polyurethane; but again we do not know the final structure. Therefore, elemental analysis to verify loading levels of flame retardant that successfully incorporated into the polyurethanes should be used to study these compounds further as time and funding permit. Even then, elemental analysis would not confirm the exact chemical structure of the flame retardant, just that a particular molar percent of boron or phosphorus was present in the sample. The "Prep" vs. "Blend" procedures, which are a simple extraction method to verify incorporation, may be the most cost effective "reactive vs. non-reactive" method to check for flame retardant incorporation, but the information will always be, and will only be qualitative. A qualitative screen though does serve the purpose of saving funds and effort towards more detailed analysis when projects are fund limited, and therefore this qualitative screen in hindsight was useful, just not as informative as we had hoped it would be.

For the boron based compounds, DBA, MBA, and DBB all show some effectiveness, but DBB shows the most impressive results as a potentially reactive flame retardant. This is important to note as DBB is an easier molecule to make than DBA or MBA, and it further appears that the ester groups enable better reactivity into the polyurethane structure. Its mechanism of flame retardancy, based upon TGA/FTIR results, appears to be one of char formation by reactions with the urethane groups and prevention of release of isocyanates and aromatic amines during polyurethane thermal decomposition.

Among the phosphorus based flame retardants, DPA and DPME are the best performing additives, with DPME showing superior performance. DPME is notable in that it is much easier to synthesize than DPA, and perhaps those methyl ester groups also allow better reaction of the flame retardant into the polyurethane, although the exact chemistry of reaction between polyurethane and DPME is not fully understood. The mechanism of these compounds is complex, as evidenced by the TGA/FTIR studies on the DPA molecule which showed DPA changed polyurethane decomposition chemistry via multiple pathways when blended into the matrix, whereas when chemically reacted into the polyurethane, it mostly inhibited isocyanate release only.

Utilizing PCFC to screen for fire performance as outlined in this paper is a promising start by which flame retardants for polyurethanes should be found. Scale-up and full-scale fire tests would need to be conducted to verify DBB, DPA, and DPME as flame retardants which simultaneously reduce heat release and inhibit melt flow in a flexible polyurethane foam, but given the results observed, there are indications that suggest these molecules could be very potent new flame retardants. Based upon the results of this paper, we conclude that PCFC can help discover new flame retardant chemistries that lower heat release, inhibit polyurethane flow during burning, and discover flame retardants with reactive potential that could have better environmental profiles.

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References:

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(1) Hirschler, M. M. *Polym. Adv. Technol.* **2008**, *19*, 521-529.

(2) Lefebvre, J.; Le Bras, M.; Bastin, B.; Paleja, R.; Delobel, R. *J. Fire Sci.* **2003**, *21*, 343-367.

(3) Lefebvre, J.; Bastin, B.; Le Bras, M.; Duquesne, S.; Paleja, R.; Delobel, R. *Polym. Degrad. Stab.* **2005**, *88*, 28-34.

(4) Denecker, C.; Liggat, J. J.; Snape, C. E. *J. App. Polym. Sci.* **2006**, *100*, 3024-3033.

(5) http://www.epa.gov/dfe/pubs/flameret/ffr-alt.htm (accessed 06/10/13)

(6) http://en.wikipedia.org/wiki/Pentabromodiphenyl_ether (accessed 06/10/13)

(7) http://www.bhfti.ca.gov/about/laws/propregs.shtml (accessed 06/10/13)

(8) http://www.regulations.gov/#!documentDetail;D=CPSC-2008-0005-0002 (accessed 06/10/13)

(9) Krämer, R. H.; Zammarano, M.; Linteris, G. T.; Gedde, U. W.; Gilman, J. W. *Polym. Degrad. Stab.* **2013**, *95*, 1115-1122.

(10) Lyon, R. E.; Walters, R. N. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 27-46.

(11) Walters, R. N.; Lyon, R. E. *J. App. Polym. Sci.* **2002**, *87*, 548-563.

(12) Kramer, K. H.; Blomqvist, P.; Hees, P. V.; Gedde, U. W. *Polym. Degrad. Stab.* **2007**, *92*, 1899-1910.

(13) Cogen, J. M.; Lin, T. S.; Lyon, R. E. *Fire Mater.* **2009**, *33*, 33-50.

(14) Schartel, B.; Pawlowski, K. H.; Lyon, R. E. *Thermochimica Acta* **2007**, *462*, 1-14.

(15) Morgan, A. B.; Galaska, M. *Polym. Adv. Technol.* **2008**, *19*, 530-546.

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(16) Stapleton, H. M.; Sharma, S.; Getzinger, G.; Ferguson, P. L.; Gabriel, M.; Webster, T. F.; Blum, A. *Environ. Sci. Technol.* **2012**, *46*, 13432-13439.
(17) Dodson, R. E.; Perovich, L. J.; Covaci, A.; Van den Eeede, N.; Ionas, A. C.; Dirtu, A. C.; Brody, J. G.; Rudel, R. A. *Environ. Sci. Technol.* **2012**, *46*, 13056-13066.
(18) Benin, V.; Durganala, S.; Morgan, A. B. *J. Mater. Chem.* **2012**, *22*, 1180 - 1190.
(19) Branion, S.; Benin, V. *Synth. Communications* **2006**, *36*, 2121 - 2127.
(20) Ivan, N.; Benin, V.; Morgan, A. B. *Synth. Communications* **2013**, *43*, 1831 - 1836.
(21) Muler, P.; Bykov, Y.; Walter, O.; Doring, M. *Heteroatom Chem.* **2012**, *23*, 383 - 394.
(22) Worku, A.; Bharadwaj, A.; Thibault, R.; Wilson, M.; Potts, D. In *Aromatic phosphonates for fireproofing agents for polymers*; PCT Int. Appl., WO2010025165 (A1), Dow Global Technologies Inc.: USA, 2010, p 47.
(23) Maffei, M.; Buono, G. *Tetrahedron* **2003**, *59*, 8821 - 8825.
(24) Wagner, S.; Rakotomalala, M.; Bykov, Y.; Walter, O.; Doring, M. *Heteroatom Chem.* **2012**, *23*, 216 - 222.
(25) Li, Q.; Jiang, P.; Wei, P. *Polym. Eng. Sci.* **2006,** *46*, 344 - 350.
(26) Ranganathan, T.; Cossette, P.; Emrick, T. *J. Mater. Chem.* **2010**, *20*, 3681 - 3687.
(27) Morgan, A. B.; Tour, J. M. *J. App. Polym. Sci.* **2000**, *76*, 1257-1268.
(28) Marini, A.; Berbenni, V.; Capsoni, D.; Riccardi, R.; Zerlia, T. *Appl Spectrosc* **1994**, 48:1468-1471.
(29) Lorenzetti, A.; Modesti, M.; Besco, S.; Hrelja, D.; Donadi, S. *Polym. Degrad. Stab.* **2011**, *96*, 1455-1461.