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USE OF DECAHYDRODECABORATE AS FLAME RETARDANTS IN POLYURETHANES

Austin W. Bailey

Pittsburg State University, austinwesbailey@hotmail.com

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USE OF DECAHYDRODECABORATE AS FLAME RETARDANTS IN POLYURETHANES

A Thesis Submitted to the Graduate School
in Partial Fulfillment of the Requirements
for the Degree of
Master of Science

Austin Bailey

Pittsburg State University

Pittsburg, Kansas

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USE OF DECAHYDRODECABORATE AS FLAME RETARDANTS IN POLYURETHANES

Austin Bailey

APPROVED:

Thesis Advisor ____
Dr. Charles Neef, Chemistry Department

Committee Member ____
Dr. Petar Dvornic, Chemistry Department

Committee Member ____
Dr. Jeanne Norton, Engineering Technology Department

Committee Member ____
Dr. Tim Dawsey, College of Technology

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USE OF DECAHYDRODECABORATE AS FLAME RETARDANTS IN POLYURETHANES

An Abstract of the Thesis by
Austin Bailey

There is a growing need for non-halogenated flame retardants due to the toxicity and environmental impacts that are exhibited by current ones. The polyurethane industry is one that has expressed a need for flame retardants in many of its industrial and commercial applications. For these reasons, two different decaborate compounds, tetramethyl and tetrabutyl ammonium decahydrodecaborate, were synthesized and incorporated into polyurethane films for testing. The compounds were characterized using Fourier Transform Infrared (FT-IR) spectroscopy, Proton-Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy, Carbon-Nuclear Magnetic Resonance (^{13}C-NMR) spectroscopy, and Boron-Nuclear Magnetic Resonance (^{11}B-NMR) spectroscopy. The compounds were incorporated into a polyol mixture at various weight percentages, mixed with methylene diphenyl diisocyanate (MDI), and cast as either thin films on glass plates or in a fixture for cone calorimetry samples. Thermal stability and flammability of the films were tested using a standard burn chamber and via thermogravimetric analysis (TGA) in nitrogen. To investigate potential synergistic effects, the decaborate compounds were incorporated with triphenylphosphine oxide (TPPO) and tested. These combinations were tested using the standard burn test chamber, thermal stability in nitrogen, and cone calorimetry. The cone test provided heat release rates and smoke release rates. Per the results of these tests, the combination of the new decaborate, and triphenylphosphine oxide showed potential for flame retardancy at minimal amounts of flame retardant.

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LIST OF ABBREVIATIONS

LOI – Limiting oxygen index

MDI – Methylene diphenyl diisocyanate

TGA – Thermogravimetric analysis

TPPO – Triphenylphosphine oxide

DOE- Design of experiment

1-FAT-One factor at a time

TMAD- Tetramethylammonium decahydrodecaborate

TBAD- Tetrabutylammonium decahydrodecaborate

PHRR- Peak Heat Release Rate

SRR- Smoke Release Rate

HRR- Heat Release Rate

FT-IR-Fourier Transform Infrared

^{1}H-NMR-Proton Nuclear Magnetic Resonance

^{13}C-NMR-Carbon Nuclear Magnetic Resonance

^{11}B-NMR-Boron Nuclear Magnetic Resonance

NMR-Nuclear Magnetic Resonance

Chapter I

1. Introduction

1.1 Flame Retardants and Environmental Effects

As polymers grow in popularity, there is a need to address the inherent flammability of some of these materials. This flammability comes from materials that have lots of carbon present in their chains. Also, there are some polymeric materials that have anti-flammability properties, however these materials tend to be more expensive than adding a flame retardant to the commodity materials. To address the inherent limitation of some polymers, flame retardants are often required. Flame retardants are used in polymers for a multitude of reasons, depending on the specific application for the polymer. The flame-retardant properties required vary with the application: clothing requires the creation of an inert char layer that can protect the wearer, while the automotive industry is focused on providing time before spreading of the fire to give time for escape or rescue. In the electronics industry, they are used to prevent ignition inside the devices, while the construction industry uses them to slow or to stop the spread of the fire.[1-4]

Halogenated flame retardants have been used in polymers for years but not without having environmental and toxicology problems. It is due to those problems that consumers, governments, and countries have made a push to remove halogenated products.[5] Many of these compounds are environmentally persistent and can bioaccumulate, causing health problems when sufficient quantities are encountered. Health problems can include causing lower IQ[6] and thyroid problems in humans.[7] Multiple studies have concluded that halogenated compounds bioaccumulate including one that studied the accumulation of polychlorinated biphenyls and polybrominated diphenylethers in snails in the Taihu Lake area of China.[8] Also, upon combustion halogenated materials produce toxic gases and large amounts of smoke which is problematic. These toxic gases can include brominated furans, dioxins, and hydrogen chloride gas just to name a few.[9] Most of the gases have been found to be carcinogenic as well.[10] To circumvent these problems, non-halogenated materials are needed which are significantly more environmentally friendly.[11] However, the non-halogenated materials have one major problem in that they have to be designed for specific classes of polymers unlike the halogens which can be applied to a multitude of applications and polymers.[5]

With the push for more environmentally friendly fillers and/or additives, there has been considerable research to develop new flame retardants. Non-halogenated systems that are typically used include: phosphorous-based[12-14], nitrogen-based[5], silicon-based[15-16], boron-based[17-18], intumescent systems[19-21], mineral fillers[5], or metal hydroxides.[22-24] The phosphorous-based systems are used in either oxygen or nitrogen containing polymers and promote the formation of a char layer. Also, the thermal decomposition products for these materials act in the condensed/vapor phase. Nitrogen containing polymers also behave as flame retardants by acting in the condensed/vapor phase. The silicon-based flame retardants are known for substantially improving thermal stability as well as heat resistance. An important aspect of these flame retardants is that they produce much less toxic gases compared to halogenated flame retardants. Intumescent systems grow and increase in volume when heat is applied. This is indicated by the formation of an expanded carbon char layer creating an insulating layer that protects substrates. In addition, mineral fillers that are used as flame retardants are inorganic compounds and functional fillers. Metal hydroxides decompose endothermically releasing non-flammable molecules, and therefore reduce the number of molecules that can ignite.[25]

In order to understand the use of these materials, the different mechanisms of flame retardancy must be understood. There are four flame retardant mechanisms that are observed: poisoning/vapor phase, dilution, char formation, and intumescence. (1) The poisoning mechanism occurs by interfering with the flame by releasing gases that are denser then oxygen and thus starving the flame of the oxygen needed to continue. (2) The dilution mechanism is a combination of mechanisms in that water in the gas phase is released to cool the overall flame temperature, along with the creation of a char layer to insulate the specimen. (3) Char formation occurs when there are substances present that cause the creation of a charring insulating layer. (4) Intumescence occurs when there is a char that is formed but there is a foaming mechanism that is also present to prevent both flame and oxygen from reaching what is material underneath the char.[5]

There are two ways that flame retardants are incorporated into materials, including additive and reactive means.[26] Additive incorporation is through blending of the materials into a polymer that requires the increased flame retardant characteristics. This method is advantageous in that it is less expensive than reactive means, but it has the disadvantages of affecting the mechanical properties, compatibility, as well as leaching from the polymer. Additive incorporation can vary from 5 wt% up to 70 wt% depending on the type of flame retardant, with the typical range of 15 wt% to 30 wt% incorporation used the most. The second method of incorporation is when the flame retardant is bound into the polymer chain. This is accomplished by copolymerization with a monomer that has flame retardant properties, or through the creation of a new monomer that has flame retardant properties.

1.2 Current Flame Retardants for Polyurethanes

Polyurethanes are used in a variety of items that are common to everyday life. These polyurethane materials have a wide variety of applications, including: elastomeric fibers like SPANDEX^{TM}, foams in furniture, and insulative automotive doors and seats, elastomers, coatings, and sealants. These materials are organically based and thus combust with ease and also produce large amounts of smoke upon combustion.[27]

Polyurethane films have switched to non-halogenated flame retardants in almost all of those aforementioned applications. However, these materials still vary substantially in loading and type. As these are designed for use in polyurethane films, they typically do not work as well with foams as they require different elements of flame retardance.[5] Melamine cyanurate, a nitrogen compound, is typically added with other flame retardants to achieve the desired properties. One such example is a material developed by Clariant^{TM} that has 15% melamine cyanurate, and 15% of aluminum phosphinate (EXOLIT OP). These material combinations have also been explored in lower quantities at 15%, and 6% respectively, and combined with 6% melamine polyphosphate, and 3% ultra-fine talc to provide synergistic effects.[28] BASF^{TM} also has a formulation that includes 25 wt.% melamine cyanurate with 5 wt.% resorcinol bis-diphenylphosphate.[5]

In contrast, polyurethane foams typically have halogens incorporated into them as those provide the best overall flame retardancy benefits. For rigid foams, that additive is tris (chloroisopropyl) phosphate.[5] However, non-halogenated materials do provide some flame retardant effects as well. Bayer has developed an alternative in dimethyl propane phosphonate (Levagard® DMPP) to replace the halogenated materials in rigid foams.[29] In flexible foams, a non-halogenated material that is used is a slightly different formulation of EXOLIT OP; that is used specifically for automotive applications.[30] ICL Industrial Products has produced an alkylphosphate oligomer that has 19% phosphorous content called Fyrol™ PNX.[31]

1.3 Previous Studies with Boron as a Flame Retardant

Boron-based flame retardants have a wide variety of uses including the promotion of a char layer and preventing dripping in some polymers. One major advantage of these flame retardants is that they have shown synergistic effects with nitrogen, phosphorus, and silicon compounds in fire test performances. Some of the boron-based compounds even help to stabilize the polymer package during processing.[5]

A boron-based flame retardant that is currently used in industry due to its lower environmental effects is boric acid. Even though boric acid provides flame-retardant effects it has several disadvantages. Being that it is an acidic compound; it can corrode metal substrates. Also, boric acid is not recommended for incorporation into non-polar hydrocarbon polymers since it is highly likely to migrate to the polymer surface.[5] Researchers in Malaysia showed that varying levels of boric acid in epoxy could provide increased flame retardance, and that while boric acid decreased the amount of expansion of the intumescent char layer, it provided increased attachment of the polymer to the substrate, as well as prevented cracking. Thus, boric acid was able to protect the polymer substrate underneath the char layer, and this effect subsequently increased as the content of boric acid was increased from 5% to 11%.[32] The structure of boric acid is shown below in Figure 1.

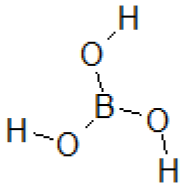


Figure 1: Boric Acid Structure

Boron nitride is another compound that has received attention for flame retardant applications. This compound has shown the ability to increase material properties such as hardness, along with thermal stability, and insulating capability. The specific boron nitride explored was hexagonal boron nitride, as this is the preferred polymorph among the boron nitrides. Amounts of up to 10% of this boron nitride showed an increase in the char yield in TGA, as well as an increase in the limiting oxygen index (LOI) from 18% to 27%.[33] LOI is "the minimum percentage of oxygen it takes in an air-like gas mixture to support flaming combustion." With an index that is below 21% the polymer will easily burn in normal amounts of air, whereas anything above 21% requires an increased amount of oxygen compared to normal air in order to burn.[5] The structure for hexagonal boron nitride is shown below in Figure 2.

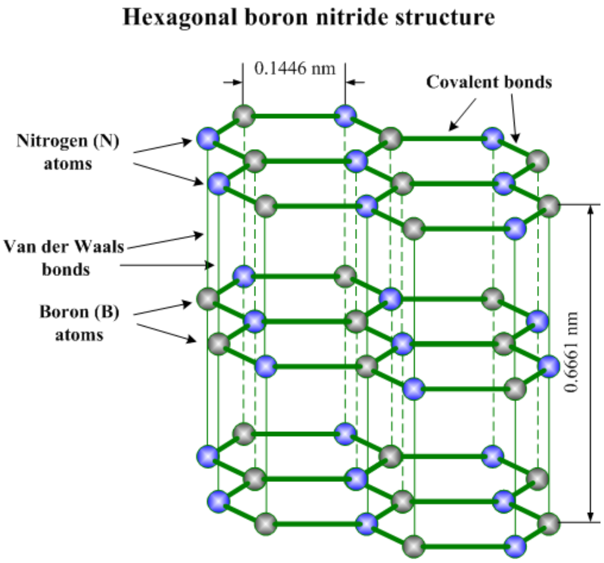


Figure 2: Hexagonal Boron Nitride Structure[34]

Metal hydroxides are prevalent in use for flame retardant polymers, and one boron-based material that is of interest in this category is zinc borate. Even though these materials are prevalent, they are used with caution as they can reduce the overall mechanical properties of the polymer. When zinc borate is added in small amounts (15g in approximately 300g of sample), the LOI increases from 18.4% for the base compound to 25.3% for the compound with zinc borate. This increase is likely due to the release of steam upon heating of the material from the crystal water in the chemical structure of the zinc borate.[35] The structure for zinc borate is shown below in Figure 3.

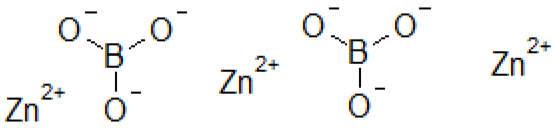


Figure 3: Zinc Borate Structure

Sodium borate decahydrate has also been studied for incorporation into cotton fabrics to improve flame retardant properties. This material was applied as a non-durable finish on 100% cotton fabric. Using a vertical flame test, at only 4% of incorporation into the cotton, the incorporated borate resulted in a sample that flamed out and only burned when directly exposed to the flame. Even at lower levels of up to 1% of borate, there was char promotion and smoldering.[36] The structure for sodium borate decahydrate is shown below in Figure 4.

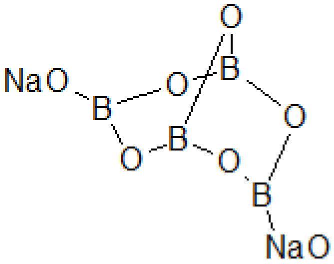
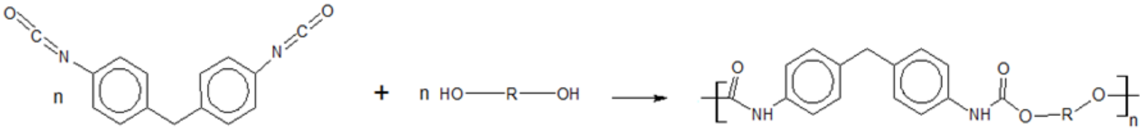


Figure 4: Sodium Borate Decahydrate Structure

1.4 Polyurethane Synthesis

The polyurethane used in this work was prepared from a polyol mixture and methylene diphenyl diisocyanate (4-4-MDI) as shown below in Scheme 1.



Scheme 1: Reaction of 4-4-MDI with a diol

This generalized reaction scheme shows the formation of urethane linkage (-NH-C(O)O-) by the addition of polyol reacting with an isocyanate and elimination of the water byproduct. The R-group is used in the scheme because the exact composition of the polyol mixture was not known to us, being proprietary unavailable information. During the polymerization reaction, there is the potential for water to react with isocyanate, which would lead to the formation of urea linkages rather than urethane.

1.5 Project Rationale

Halogenated flame retardants have shown extensive use in most applications but suffer from bioaccumulation and toxic byproducts upon burning. As a replacement, borates have been extensively employed, but they suffer from drawbacks such as acidity and limited general use. Thus, the goal of the research was to incorporate novel decaborate compounds (tetramethylammonium decahydrodecaborate and tetrabutylammonium decahydrodecaborate) into a standard polyurethane film and determine their potential use as flame retardants. In addition, triphenylphosphine oxide was also added to determine potential synergistic effects with decaborate.

Chapter II

2. Experimental

2.1 Materials and Methods

Bis(triethylammonium) decahydrodecaborate was supplied by 3M. Triphenylphosphine oxide, tetramethyl and tetrabutyl ammonium hydroxide were obtained from Acros Organics. Acetonitrile was obtained from Sigma Aldrich. Boric acid was obtained from the Fisher Scientific Company. Polyol mixture and methylene diphenyl diisocyanate (MDI) for polyurethane films were provided by ETCO-Specialty Products Inc. in Girard, Kansas.

Characterization of the monomer products was achieved using a Bruker Ultrashield™ 300MHz Nuclear Magnetic Resonance (NMR) spectrometer for ^{13}C, ^{11}B, and ^{1}H spectra. Infrared spectra were taken on a Perkin-Elmer Spectrum Two™ Fourier Transform Infrared (FT-IR) L1600400 spectrometer. For the polymer films, thermogravimetric analysis (TGA) was performed on a TGA-Q50, a product of TA™ Instruments. Standard burn tests were performed in an SDL-Atlas™ vertical flame chamber, M223M. Cone calorimetry was performed on a Fire Testing Technology, Limited Cone Calorimeter.

2.2 Synthesis of Decaborate

An ion exchange column was prepared by rinsing with 1M sulfuric acid followed by deionized water until a pH of 7.0 was achieved. Bis(triethylammonium) decahydrodecaborate (10g) was dissolved in water (500 mL) and added to the column. Water was added and the aqueous solution was collected until a pH of 7.0 was measured. The collected solution was titrated with tetramethyl or tetrabutylammonium hydroxide until the solution was at a pH of 7.0. The tetrabutyl derivative (TBAD) was collected by vacuum filtration and the tetramethyl derivative (TMAD) had the water removed using a rotary evaporator. Both compounds were dried in a vacuum oven at 80^{o}C for 12 hours. TMAD: ^{1}H-NMR (D_2O, δ. ppm): 4.69, (2H and Methyl) 3.07, (5H from triethyl) 1.11, (8H) 0.5-$^{-}$0.5. ^{13}C-NMR (D_2O, δ. ppm): (C on Me) 55.285, (C on residual triethyl) 46.78, and 8.33. ^{11}B-NMR (2B) 2.86, (8B) -26, (Residual B_{12}) -12. IR (solid, cm^{-1}): 2957 (C-H), 2437 (B-H), 1479 (CH_3), 1455 (C-N), 1380 (C-H), 1004 (B-B), 882 (B-H deformation), 738 (B-H deformation). TBAD: ^{1}H-NMR (D_2O, δ. ppm): 4.72 and 4.69, (2H of $B_{10}H_{10}$ and 2H of methylene closest to nitrogen) 3.07, (2H of 2nd methylene group from nitrogen) 1.52, (2H of 3rd methylene group from nitrogen) 1.2, (3H of methyl group) 0.8, (8H of $B_{10}H_{10}$) -0.5 to 0.3. ^{13}C-NMR (D_20, δ. ppm): (CH_2 closest to nitrogen) 58.12, (3rd carbon from nitrogen) 23.18, (2nd carbon from nitrogen) 19.26, (Methyl groups) 12.95. ^{11}B NMR (D_2O, δ. ppm): (B-B) 3.0172 and 1.5194, (Residual B_{12}) -11.3542 and -12.8236, (B-B) -26.36 and -27.69. IR (solid, cm^{-1}) 3023 (C-H), 2446 (B-H), 1484 (CH_3), 1448 (C-N), 1010 (B-B), 948 (B-B), 662 (B-H deformation).

2.3 Casting of Thin Films

Polyurethane films for control samples were cast with an 8:2 ratio (w/w) of polyol mixture (Part A) to MDI (Part B). For polyurethane films containing decaborate, the amount of MDI was determined based upon the amount of polyol (8:2 ratio (w/w) of polyol mixture to MDI) and the amount of decaborate (as determined by DOE setup). For the decaborate containing films, a spatula was used to grind the compound prior to mixing. In cases where triphenylphosphine oxide (TPPO) was incorporated, TPPO amounts were determined using a design of experiment (DOE) and varied from 5 wt% to 12.5 wt%. In tetramethylammonium decahydrodecaborate (TMAD) film preparation acetonitrile was used to dissolve the solids in an amount equal to the weight of solid material. All tetrabutylammonium decahydrodecaborate (TBAD) films had an amount of acetonitrile, equal to one half the weight of solid material. Components of the films were mixed together without MDI, which was then added to the mixture and stirred for 45-60 seconds. This mixture was then poured onto glass plates and cast using a doctor blade for consistent thickness, nominally 0.025 inches, and allowed to sit at room temperature for 24 hours. Films were cut to make four films of dimensions 5.5 by 1.5 inches, as well as excess small pieces for use in thermal testing.

2.4 Casting of Cone Calorimeter Samples

Amounts of decaborate and TPPO for samples to be tested by cone calorimetry were determined using a DOE and varied from 5 wt% to 12.5 wt% for the decaborate and from 5 wt% to 12.5 wt% for the phosphonium oxide. The mixture of flame retardants was dissolved in acetonitrile for ease of mixing in the polyurethane. The dissolved flame retardants were added to the polyol to give a quantity equal to 80% of the remaining mixture needed to obtain a final weight of 80 grams. Isocyanate was added to the mixture in an amount equal to the remaining mixture weight needed to obtain 80 grams. The polyurethane mixture was stirred by hand for 15-20 minutes until the mixture began to become viscous. The mixture was then poured into a mold at dimensions of 100 x 100 x 7-8mm. The mold was then placed into an oven at 50°C for 24 hours to complete curing.

2.5 Design of Experiment

A design of experiment (DOE) is used as a replacement for the traditional change one factor at a time (1-FAT) approach. This statistical tool is used to identify critical parameters, identify interactions, and to create a robust process. Ultimately this provides the capability to optimize the process. By using a DOE in chemistry time and material can be saved by testing fewer samples at the changing levels of the factors. One does not need to have a statistical background to create a DOE either, as there are many computer programs that have been developed to aid in this process. One advantage of using a DOE is that, no matter the result, something of value is always learned.[37]

There were three DOEs used for this work. They were based upon a central composite design, and created in Minitab™ DOE software. The DOE dictated the percentages of each component to be incorporated into the thin films and the cone calorimeter samples. The first DOE was a screening DOE with varying amounts of TPPO and decaborate at 5 %, 8.75 %, and 12.5% each by weight. The second DOE was a full DOE with recentered amounts of TPPO at 6.25%, 12.5%, and 18.75%, while the amounts of decaborate were reduced to 2.5%, 5%, and 10%, all by weight. While the previous two DOEs were used for the thin film burning, the third DOE was used for the cone calorimeter samples. The third DOE had varying amounts of TPPO and decaborate at

5%, 8.75%, and 12.5% each by weight. DOEs 1 and 2 are for 10 g samples while DOE 3 is for 80 gram samples. Shown below are the three DOEs in Tables 1, 2, and 3.

Table 1: Amounts of Flame Retardant 1 and 2 in Polyurethane Blends.

Sample No.	Decaborate (wt%)	TPPO (wt%)	Part A (g)	Part B (g)
1	8.75	8.75	6.6	1.65
2	5	5	7.2	1.8
3	5	12.5	6.6	1.65
4	8.75	8.75	6.6	1.65
5	12.5	5	6.6	1.65
6	12.5	12.5	6	1.5

Table 2: Amounts of Flame Retardant 1 and 2 in Polyurethane Blends.

Sample No.	Decaborate (wt%)	TPPO (wt%)	Part A (g)	Part B (g)
1	12.5	5	6.6	1.65
2	18.75	2.5	6.3	1.58
3	12.5	2.5	6.8	1.7
4	12.5	5	6.6	1.65
5	12.5	10	6.2	1.55
6	18.75	10	5.7	1.43
7	6.25	5	7.1	1.78
8	12.5	5	6.6	1.65
9	6.25	2.5	7.3	1.83
10	12.5	5	6.6	1.65
11	12.5	5	6.6	1.65
12	6.25	10	6.7	1.68
13	18.75	5	6.1	1.53

Table 3: Amounts of Flame Retardant 1 and 2 in Polyurethane Blends.

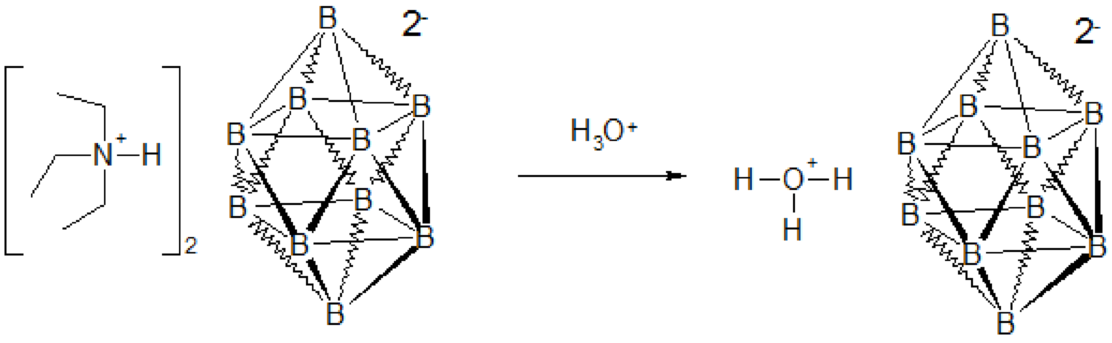
Sample No.	Decaborate (wt%)	TPPO (wt%)	Part A (g)	Part B (g)
1	8.75	8.75	52.8	13.2
2	5	5	57.6	14.4
3	8.75	5	55.2	13.8
4	5	12.5	52.8	13.2
5	8.75	12.5	50.4	12.6
6	8.75	8.75	52.8	13.2
7	8.75	8.75	52.8	13.2
8	5	8.75	55.2	13.8
9	12.5	5	52.8	13.2
10	8.75	8.75	52.8	13.2
11	8.75	8.75	52.8	13.2
12	12.5	12.5	48	12
13	12.5	8.75	50.4	12.6

Chapter III

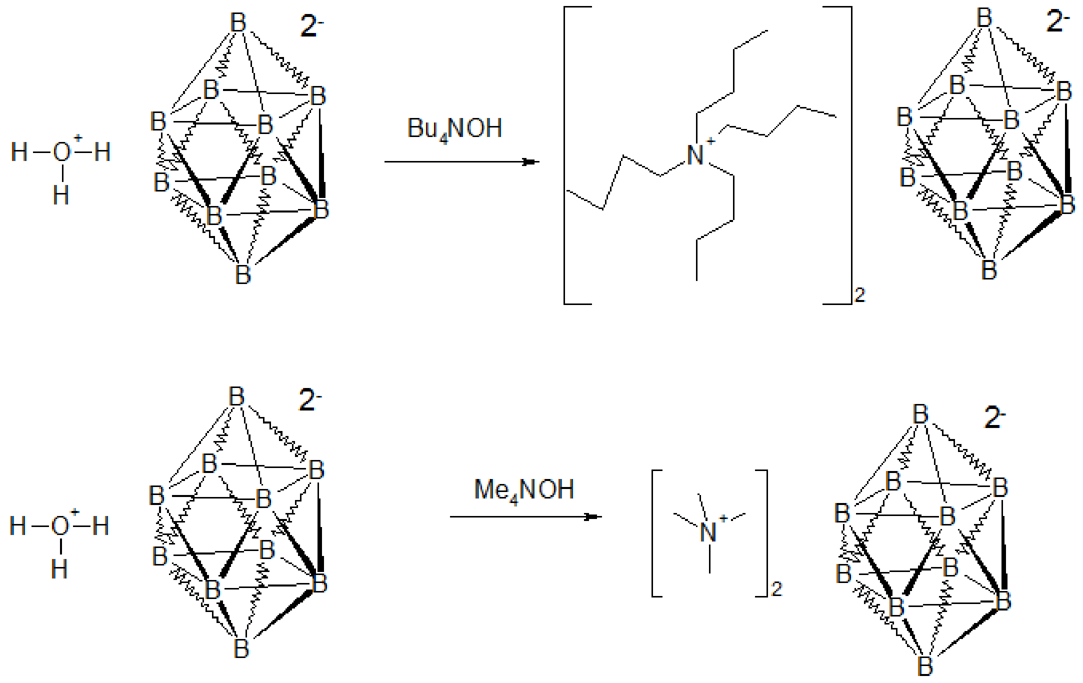
3. Results and Discussion

3.1 Product Synthesis

The synthesis of the TMAD and TBAD was straightforward. Triethylammonium decahydrodecaborate was converted to the hydronium salt via ion exchange (Scheme 2). Neutralization of the hydronium decaborate with tetramethylammonium or tetrabutyl ammonium hydroxide gave TMAD or TBAD, respectively (Scheme 3). The products were obtained in 72.7% and 56.5% yields for TBAD and TMAD, respectively.



Scheme 2: Ion Exchange Process



Scheme 3: Conversion to of Hydronium Decaborate to TMAD or TBAD

The decaborate anion is known to have bi-pyramidal formation.[38] This complex self-bonded network is shown in Figure 5. For characterization, there are two types of borons and protons shown in the cage structure, axial shown as 1 and 10 in Figure 5, and the others are considered equatorial.

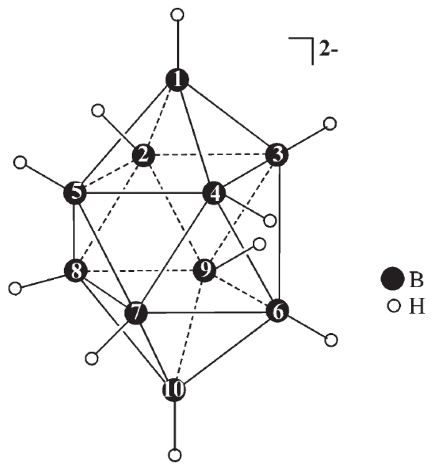


Figure 5: Structure of [B10H10]$^{2-}$ Anion

3.2 Product Characterization

TMAD and TBAD were characterized by FT-IR spectroscopy and the spectra are shown in Figure 6. The spectra have peaks at approximately 2400 cm^{-1} indicative of a B-H stretch and a peak at 1000 cm^{-1} which was consistent with a B-B stretch. Additional peaks in the spectra were observed at 2950 cm^{-1} and 1450 cm^{-1} which can be attributed to C-H and C-N stretching respectively.

The ^{1}H-NMR spectrum for TMAD showed three signals in Figure 7. The two multiplets at approximately 3.10 and 0.0 ppm are the protons that are a part of the boron cage. The signal at 3.10 ppm is due to the axial protons within the $B_{10}H_{10}^{2-}$ anion and the signal at 0.0 ppm is from the equatorial protons. The triplet at 1.17 ppm was due to residual triethylammonium. The methyl protons were observed at 3.07 ppm. Integration of the NMR peaks showed the peak at 3 ppm as 1.00. After removal of the triethylammonium proton integration, the peaks at 3 ppm and 0 ppm are calculated to show 16 protons and 7 protons which was close to the anticipated 14 protons and 8 protons, respectively.

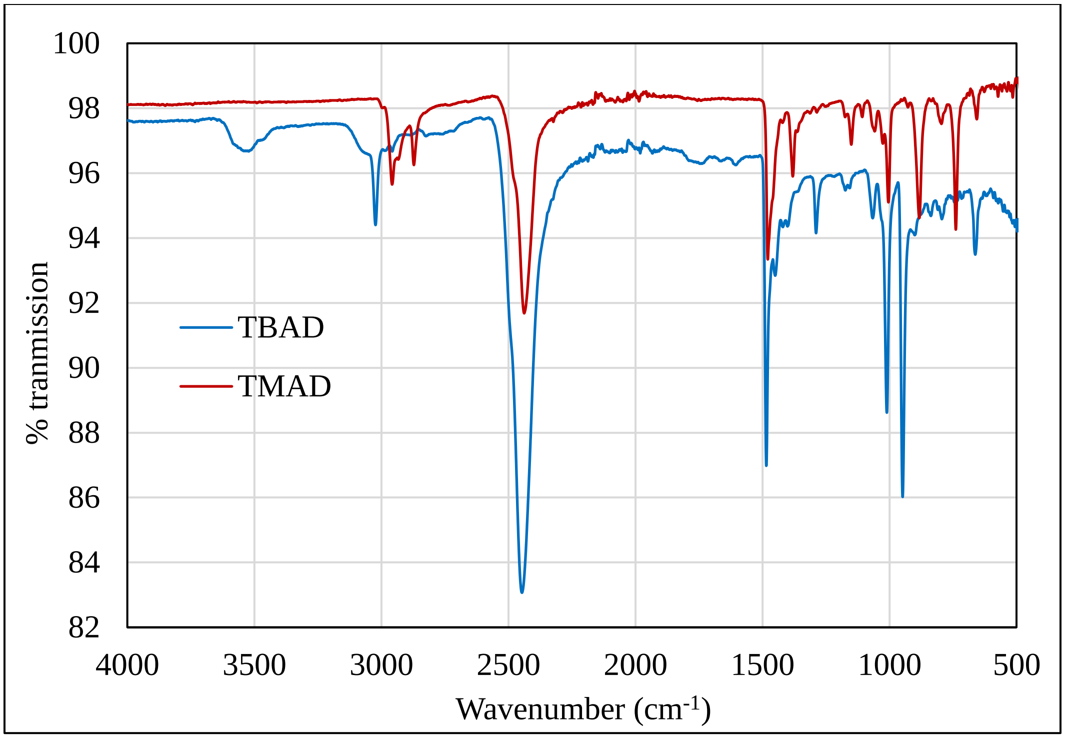


Figure 6: FT-IR Spectra of TBAD and TMAD

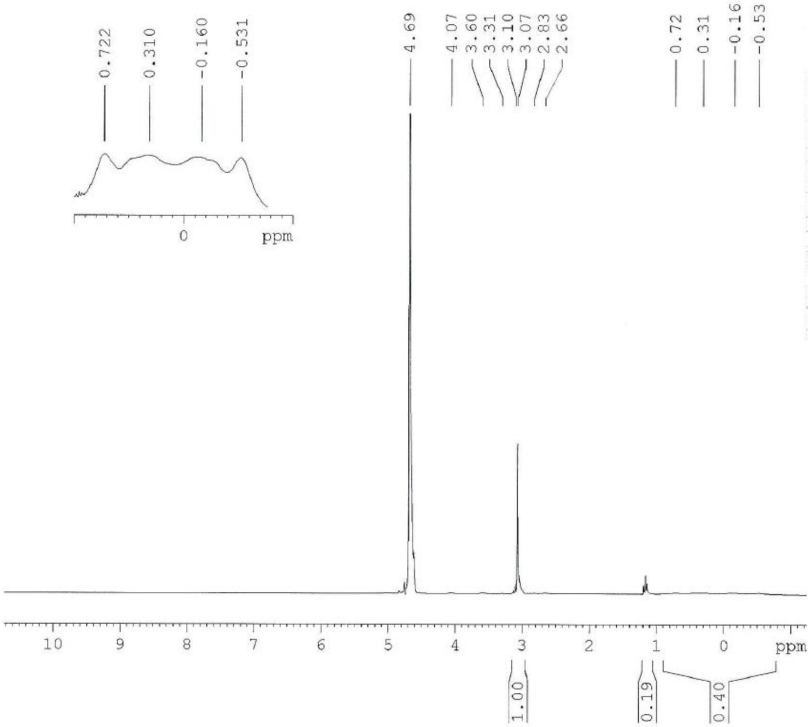


Figure 7: ^{1}H-NMR spectrum for TMAD

The ^{13}C-NMR spectrum for TMAD is shown in Figure 8. The signal at 55ppm was indicative of the methyl carbons. However, the small peaks at approximately 46ppm and 8ppm showed residual triethylammonium, which was consistent with the ^{1}H-NMR spectrum.

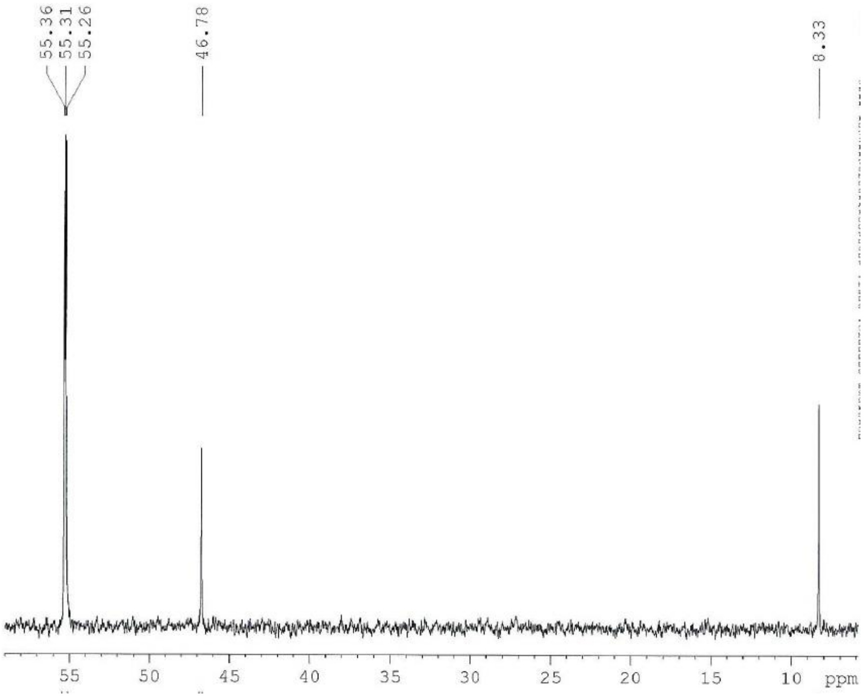


Figure 8: ^{13}C-NMR spectrum of TMAD.

^{11}B-NMR was also obtained for this sample and it can be seen in Figure 9. The doublets that are observed are due to the coupling of the ^{1}H-^{11}B within the boron cage. The axial and equatorial boron signals were observed at 1 and -27, respectively. The small doublet at -12 is indicative of residual B_{12} present in the starting material as an impurity from the manufacturing of the starting compound.

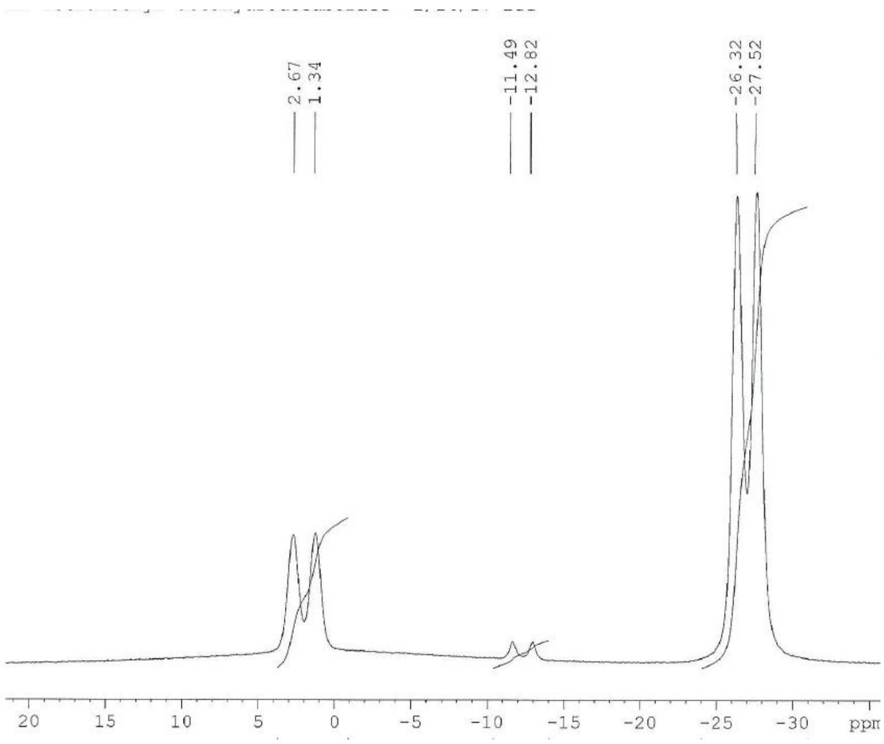


Figure 9: ^{11}B-NMR of TMAD

The ^{1}H-NMR spectrum of TBAD showed five signals in Figure 10. The multiplets at 3.07 and 0.0 ppm were the axial and equatorial protons, respectively, within the boron cage. The axial boron proton signals overlapped with the methylene protons adjacent to the nitrogen at 3.07 ppm. The beta protons from the nitrogen were located at 1.5 ppm, while the gamma protons were centered at 1.2 ppm. The protons on the methyl group were observed at 0.84 ppm. Integration of the signals at 3 ppm, 1.5 ppm, 1.2 ppm, 0.8 ppm, and 0.0 ppm gave a ratio of 10:9:9:14:1 proton. This was slightly different than the theoretical ratio of 10:8:8:12:8 protons for those peaks, respectively. The discrepancy may be due to the lack of solubility of TBAD which resulted in weak signals within the ^{1}H-NMR spectrum.

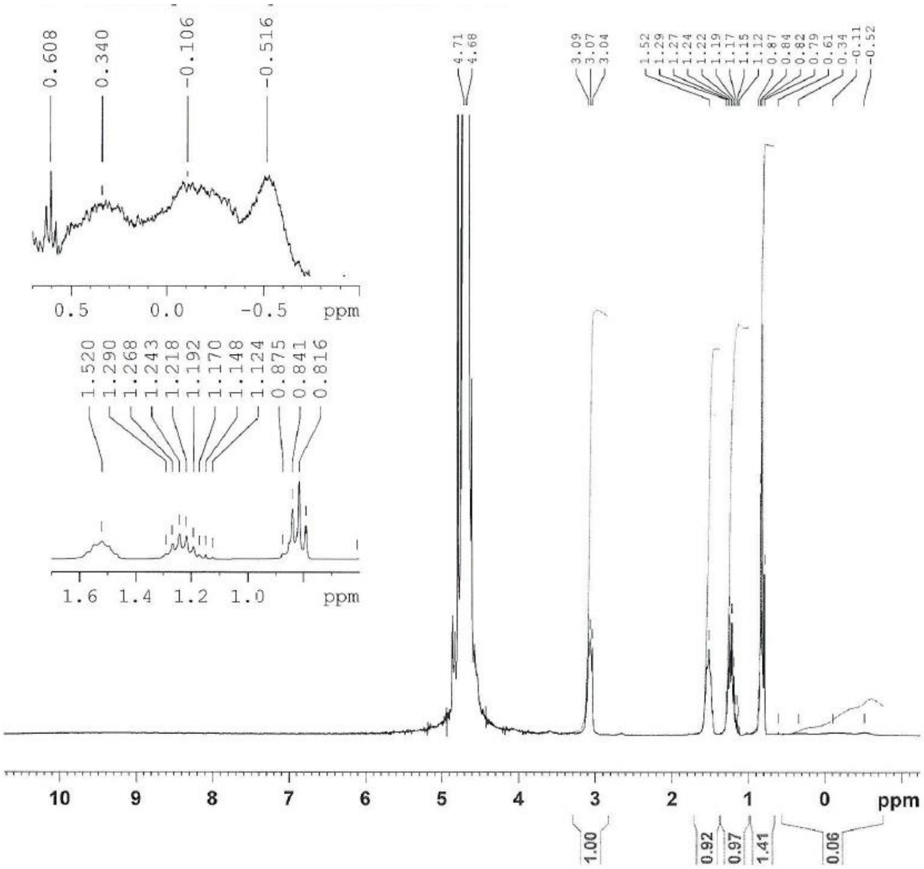


Figure 10: ^{1}H-NMR spectrum for TBAD

Figure 11 shows the ^{13}C-NMR spectrum for TBAD. Four signals were observed at 58 ppm, 23 ppm, 19 ppm, and 12 ppm in the ^{13}C-NMR of TBAD. The peak at 58 ppm is indicative of the CH_2 group alpha to the nitrogen, while the peak at 23 ppm was from the carbon beta to the nitrogen. The peak at 19 ppm was from the gamma carbon and the methyl carbon was located at 12 ppm.

The ^{11}B-NMR spectrum was collected for TBAD and can be seen in Figure 12. The signals from the axial borons were observed as a doublet at 2.5 ppm and the equatorial borons were shown at -26 ppm.

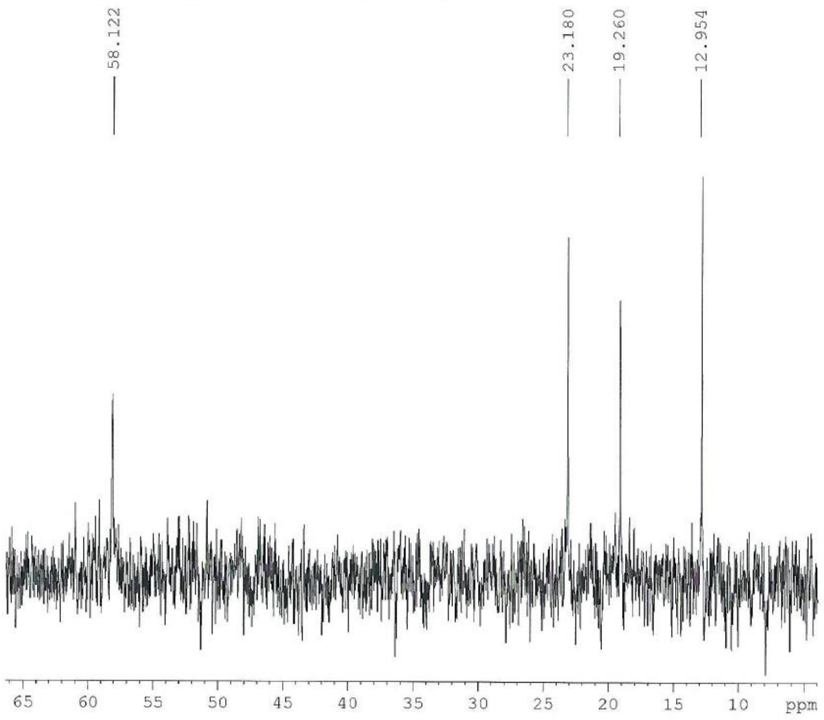


Figure 11: ^{13}C-NMR for TBAD

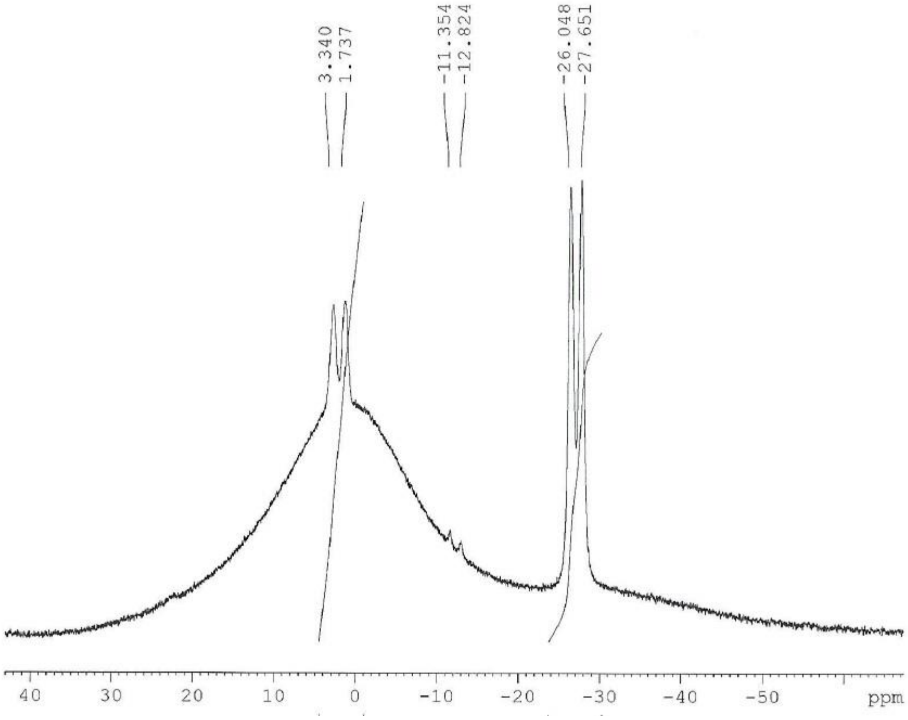


Figure 12: ^{11}B-NMR for TBAD

The doublets that are observed are due to the coupling of the ^{1}H-^{11}B within the boron cage. These results were similar to the TMAD ^{11}B-NMR spectrum. However, the baseline in the TBAD spectrum was inconsistent, presumably due to the limited solubility of TBAD in D_2O. The small doublet at -12 ppm and -11 ppm was indicative of residual B_{12} present in the starting material as an impurity from the manufacturing of the starting compound.

3.3 Thermal Properties

3.3.1 Polyurethanes containing TMAD or TBAD

Initial polyurethane samples containing TMAD and TBAD were tested for thermal stability in nitrogen using thermogravimetric analysis (TGA). Evaluation of each sample was determined at 5% weight loss and char yield. The weight loss at 5% was chosen since it is a typical weight loss analyzed in TGA. The TGA of the control sample of polyurethane with no additives is shown below in Figure 13. The base polyurethane showed 5% weight loss at 286^{o}C and a char yield of 16.8%.

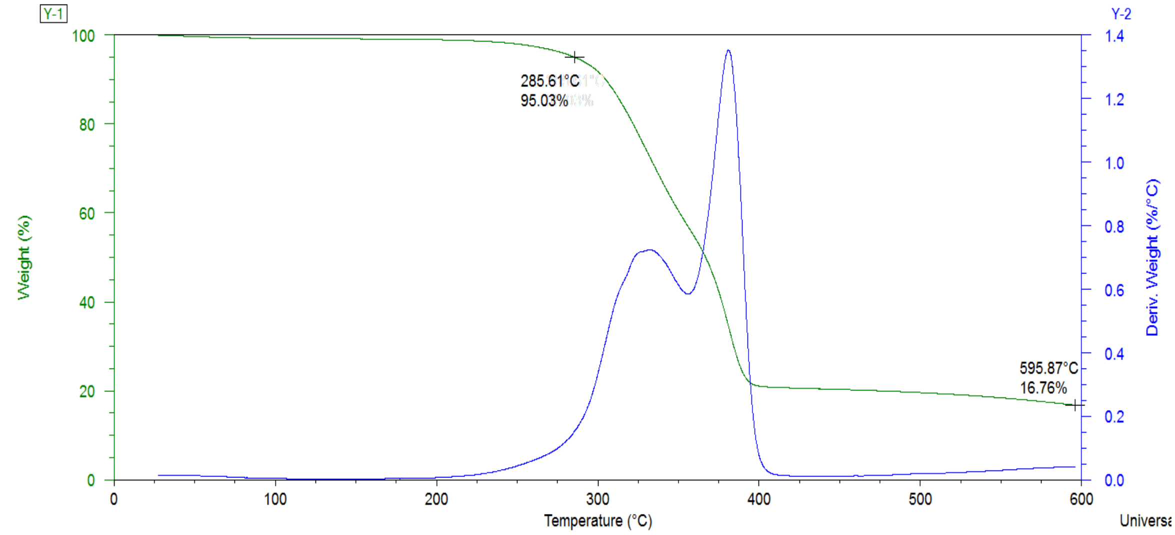


Figure 13: TGA of Control Sample

Figure 14 shows the trend for char yield in nitrogen for the decaborate samples at 10% and 20% decaborate incorporation along with the neat urethane sample. There was a steady increase in char yield at 10% of decaborate incorporation into the polymer. However, there was a slight decrease in char yield at 20% incorporation of TBAD into the polymer suggesting that the polymer was not as thermo-oxidatively stable at the higher loadings of TBAD. However, the char yield remained higher than the neat urethane sample. The TMAD sample at 20% provided a char yield of 40% indicating that it was having a significant impact on the ability to act as a char promoter and was the only sample with a char yield greater than that of boric acid.

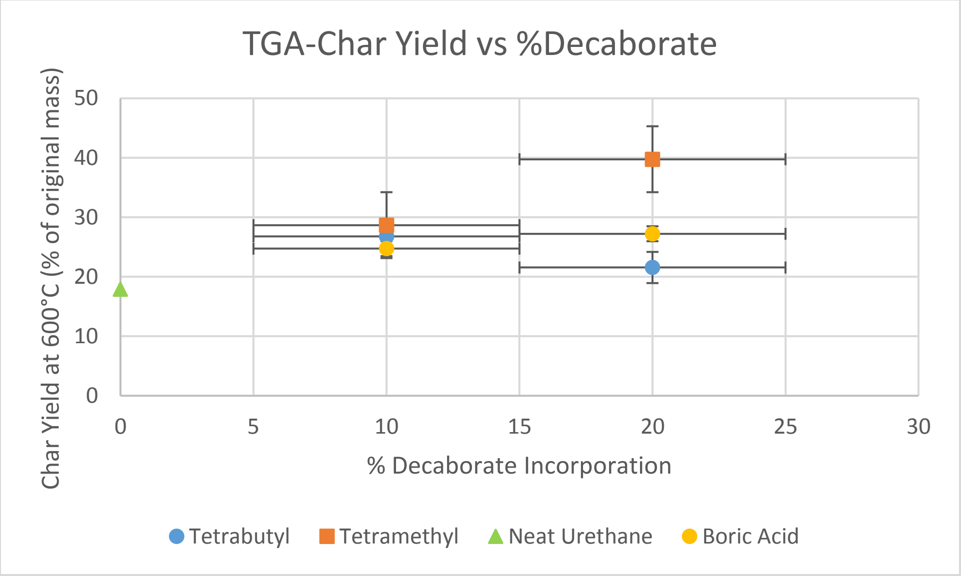


Figure 14: Plot of TGA char yield versus amount of decaborate incorporation

Figure 15 shows the 5% weight loss for decaborate samples, boric acid samples, and neat urethane. Figure 15 showed that TMAD and TBAD samples have a steady decrease in thermal stability as compared to the neat urethane sample. Within the two graphs, the 20% decaborate incorporation reaches the expected weight loss at approximately the same temperature, respectively for each weight loss, for both TBAD and TMAD. Overall, a decrease in thermal stability was observed with increasing amount of TMAD or TBAD, indicating negative effects by the decaborate materials.

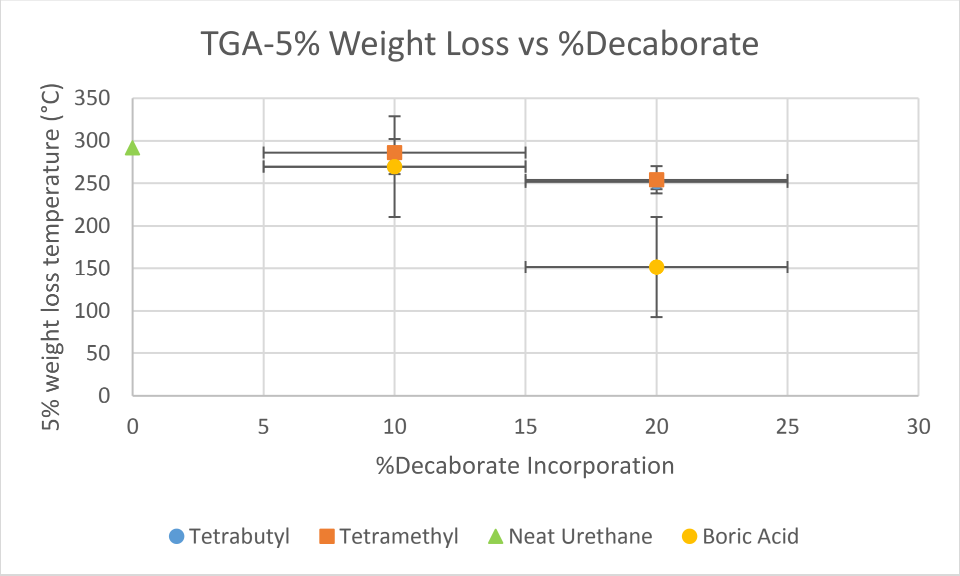


Figure 15: Plot of TGA 5% weight loss versus amount of decaborate incorporation

3.3.2 Polyurethanes containing TMAD or TBAD with TPPO

Per a DOE created in the Minitab^{TM} DOE software, varying amounts of TPPO and decaborate were incorporated into polyurethane samples. TPPO and decaborate were incorporated at varying levels of 5%, 8.75%, and 12.5% each by weight. These samples were tested using TGA in nitrogen. Figures 16 and 17 show the contour plots of the results for char yield in nitrogen for TBAD and TMAD respectively. The contour shown in Figure 16 for the TBAD samples showed a consistent trend that as %TPPO was decreased and %TBAD was increased there was an increase in the char yield. With the greatest amount of char produced being at 5-6% of TPPO and 10.5-12%+ of TBAD. For the samples containing TMAD, an increased in char yield was seen at high levels of TMAD (9-12%), regardless of the amount of TPPO. All the TMAD samples and most of the TBAD samples did provide an increased char yield as compared to the base urethane resin.

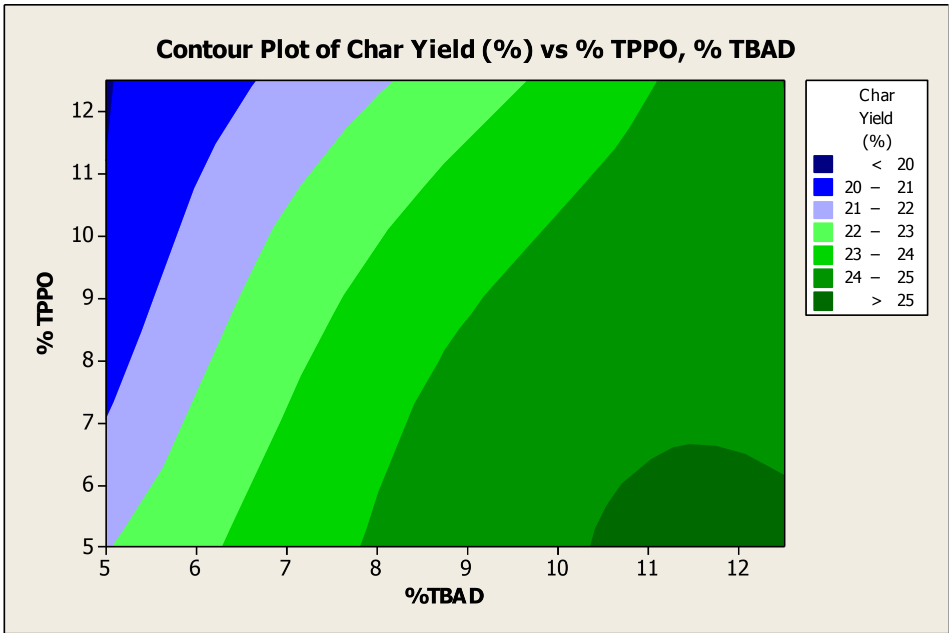


Figure 16: Contour plot of char yield in nitrogen vs %TPPO and %TBAD

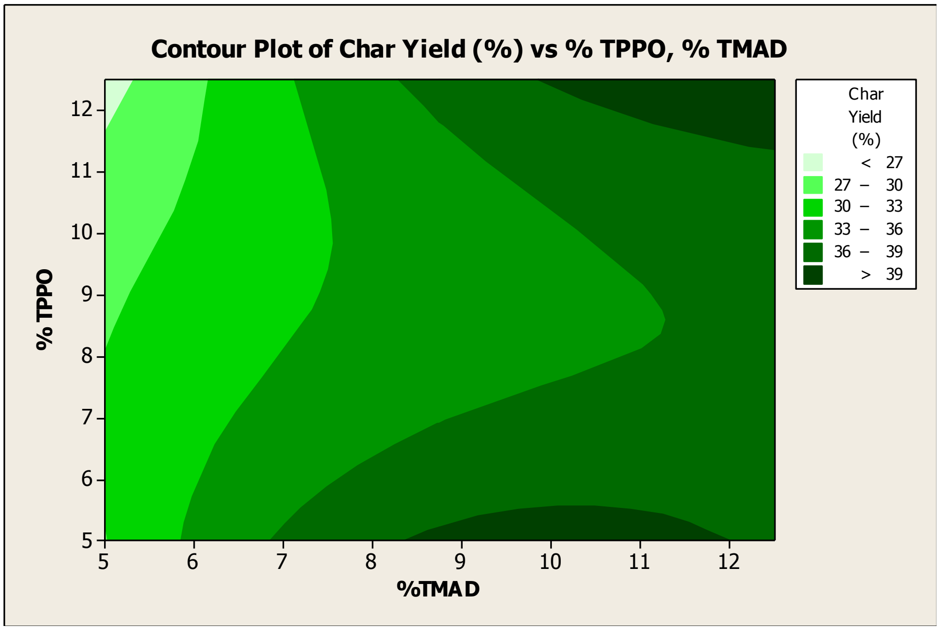


Figure 17: Contour Plot of Char Yield in Nitrogen vs %TPPO and %TMAD

The 5% degradation temperature was recorded and the effects that were seen are dependent upon the decaborate that was incorporated. Figures 18 and 19 show the 5%

weight loss temperatures for TBAD and TMAD samples, respectively. The contour plot for TBAD samples showed thermal stability ranging from 245-255°C. These results indicate that the varying amounts of TBAD and TPPO had little effect on the thermal stability of the polymer.

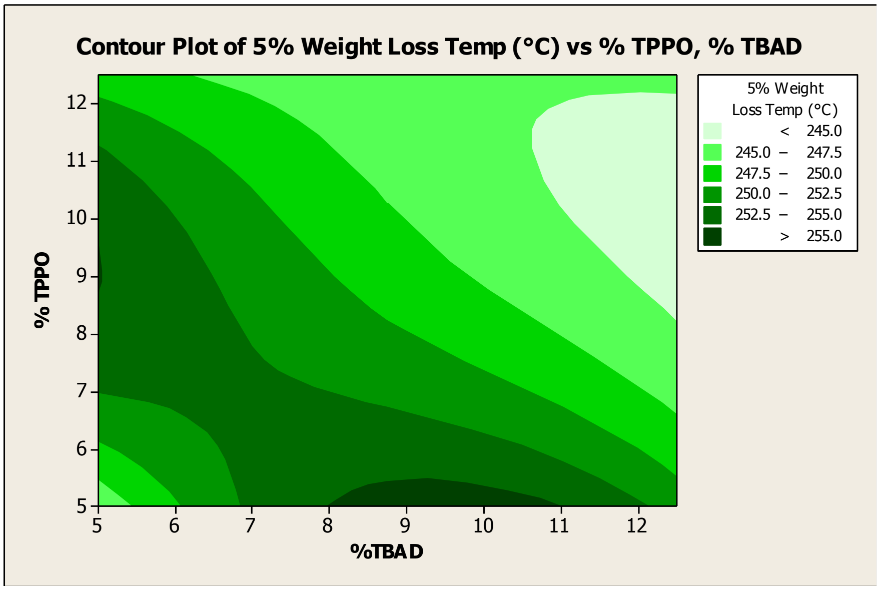


Figure 18: Contour Plot of 5% Weight Loss Temp for TBAD

For the TMAD samples, the thermal stability ranged from 250-280°C. The highest thermal stability was achieved when there was 5-6% of both TPPO and TMAD in the polyurethane sample. These data indicate an increase in thermal stability with increasing amounts of TMAD and TPPO.

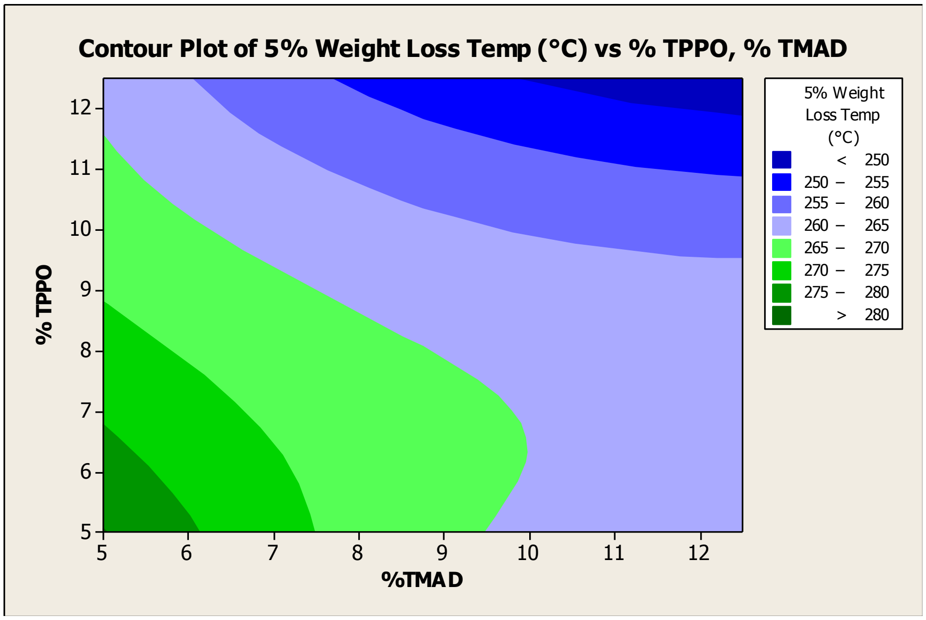


Figure 19: Contour Plot of 5% Weight Loss Temp for TMAD

3.4 Thin Film Burn Test

3.4.1 Polyurethanes containing TMAD or TBAD

Burn tests were performed on thin films 5.5 inches long and 1 inch wide with varying amounts of decaborate incorporation at 10% and 20% by weight. These tests consisted of lighting one end of the film with a Bunsen burner and allowing ignition to continue for 10 seconds. The films were allowed to burn to completion, with burn time and burn distance both being recorded.

The burn time and weight loss percentage was recorded for two to four samples of each material and averaged. Figure 20 and 21 show the burn rate and weight loss percentage for the materials containing TBAD, and TMAD, respectively. The control film was indicated at the 0% decaborate incorporation.

Burn rate of the TBAD incorporated films showed an increase as compared to the neat urethane sample. However, there was a decrease in burn rate as the TBAD was increased from 10 to 20% with a burn rate much closer to that of the neat urethane sample. Both samples had a lower weight loss percent than the neat urethane sample. This was because the TBAD material had an affinity to form char thus reducing the actual weight loss.

The TMAD sample had a weight loss of about 80% at 10 and 20% loadings which was similar to the weight loss of the neat urethane. These results seem to contradict the TGA results, as the TGA results in nitrogen showed both materials with an affinity to char as compared to the base sample. This contradiction could stem from the difference of atmospheres of nitrogen vs air for the two techniques; as well as from the inconsistencies within the thin film burning process. However, TGA data was collected in nitrogen and will differ from data collected in air. TMAD had an increased burn rate at both loadings. Even with the burn rate a concern with both samples, the potential for samples that formed char and reduced the overall weight loss percentage was present.

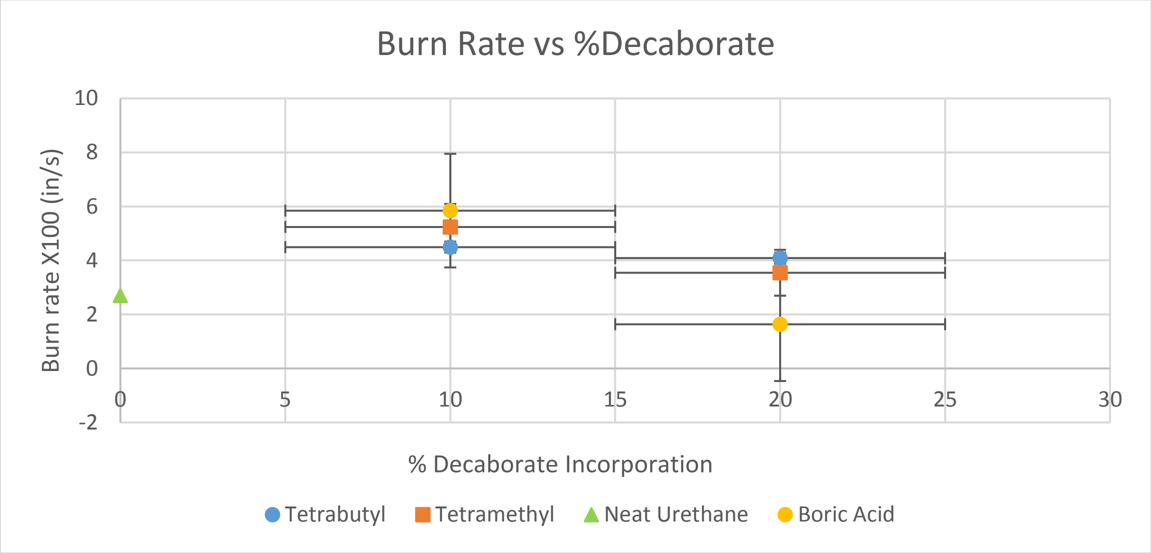


Figure 20: Plot of burn rate versus amount of decaborate incorporation

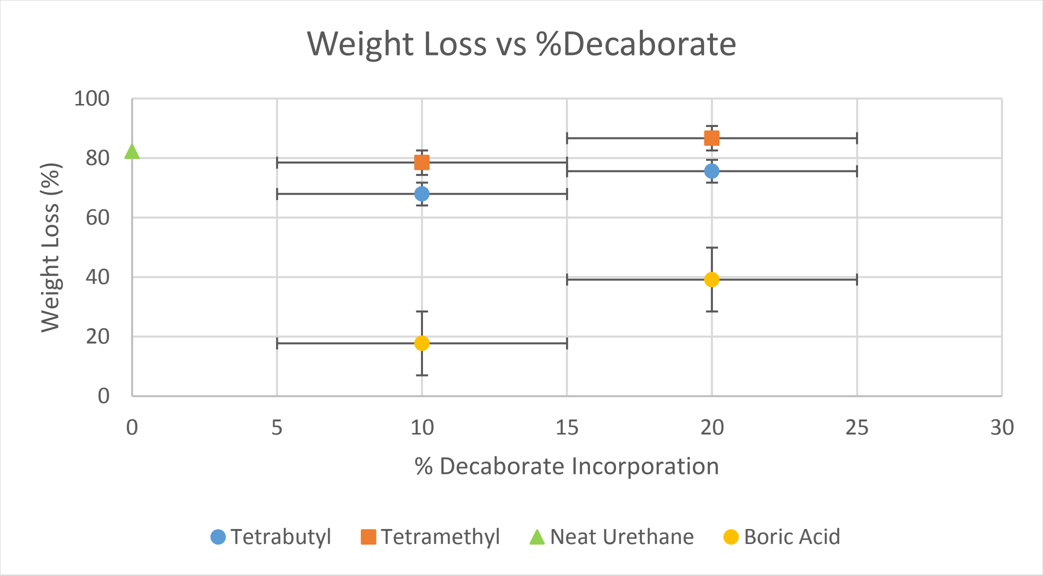


Figure 21: Plot of weight loss versus amount of decaborate incorporation

The boric acid samples had the highest burn rate at 10% loading, but at 20% loading they actually had the lowest burn rate at almost one half the burn rate of the decaborate samples. In the burn testing, the boric acid samples had the lowest weight loss

% at both loadings. At 10% loading, it was approximately 18%, and at 20% loading, it was 39% weight loss.

3.4.2 Polyurethanes containing TMAD or TBAD with TPPO

As potential for flame retardancy benefits were seen from the previous results, it was decided that a screening DOE would be used to test for potential of this flame retardant with TPPO. This DOE of just six runs would allow the ability to see if there were some sort of synergistic effect between the two flame retardants, decaborate compounds, and TPPO. The DOE had varied amounts of TPPO and decaborate both at 5%, 8.75%, and 12.5% each. The results for burn rate and for percent weight loss are shown in Figures 22 and 23 for TBAD, and in Figures 24 and 25 for TMAD.

The results for the TBAD samples shown in Figures 22 and 23 provide quite different results when compared to the TMAD samples in Figures 24 and 25. For the TBAD burn rate, the contour showed that the lowest burn rate of the material was achieved when only 5-6% of TBAD was used and when there was either 5-6% TPPO, or 12% TPPO. This data was interesting because when taken with the weight loss % data where the lowest % was trying to be achieved, they contradict. For the weight loss contour, of TBAD the lowest weight loss was achieved when there was only 5% TPPO, and 11-12% of the TBAD. One of the interesting parts of research was shown here, in that when trying to work towards improvement of some properties, others may suffer. The TMAD samples showed a trend that was consistent for both burn rate and weight loss. That trend was that an increase in %TPPO will give a reduced weight loss, and a decreased burn rate. The sample ranges for slowest burn rate from TMAD are 5-6% TMAD, and 5-6% or 12% TPPO. The samples providing lowest weight loss were at 5%

TMAD, and at 12% TPPO. Of note for both TBAD and TMAD is that they have samples that are as good, if not better, for burn rate when compared to the base urethane sample.

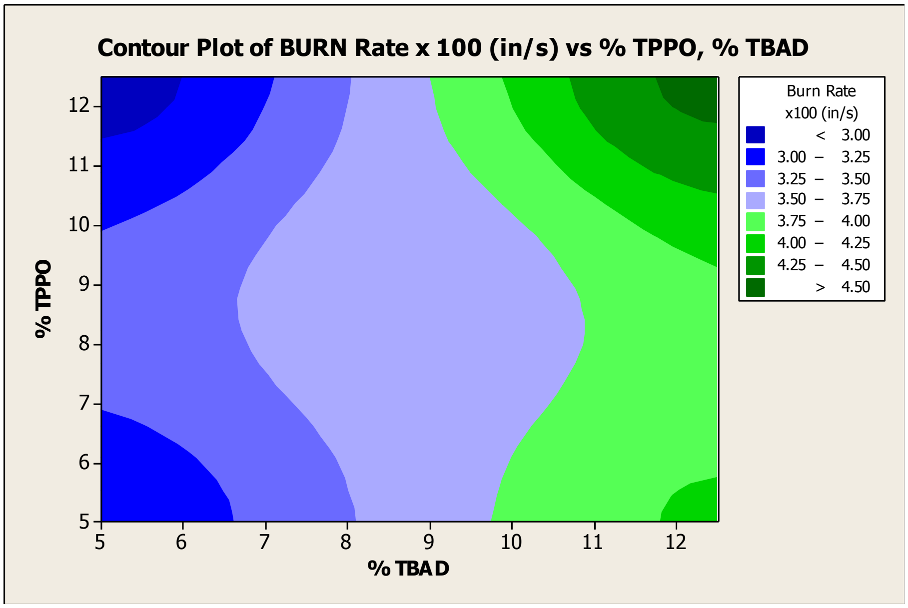


Figure 22: Contour Plot of Burn Rate for TBAD

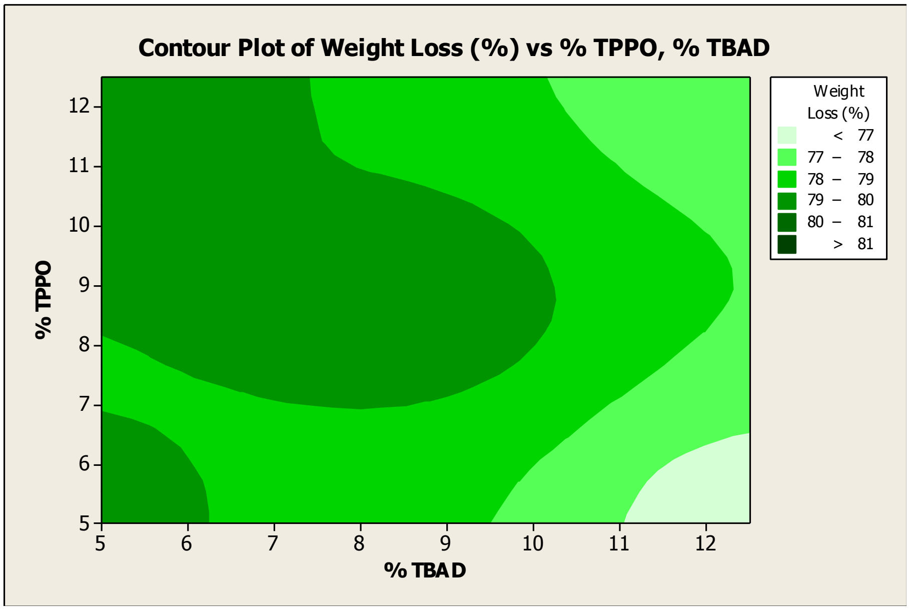


Figure 23: Contour Plot of Weight Loss % for TBAD

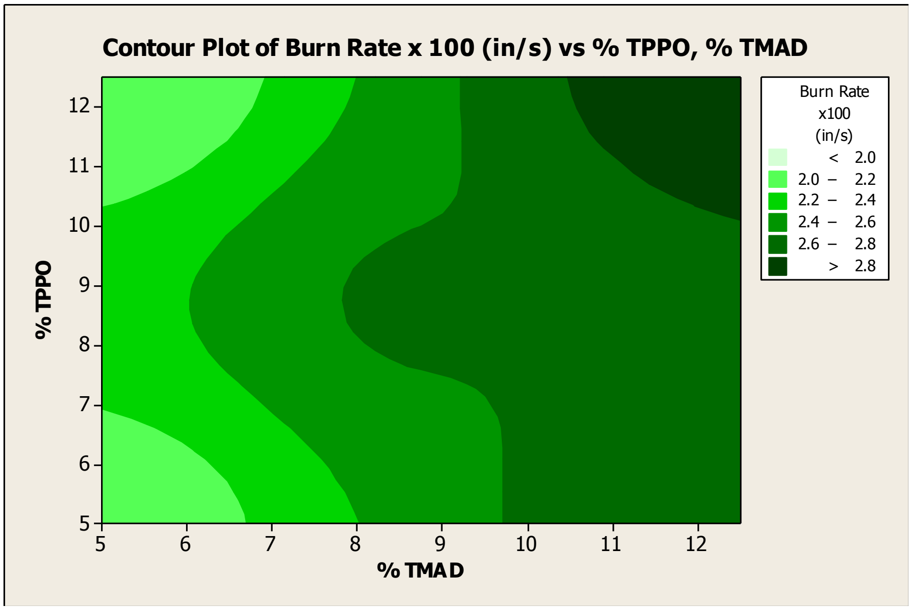


Figure 24: Contour Plot of Burn Rate for TMAD

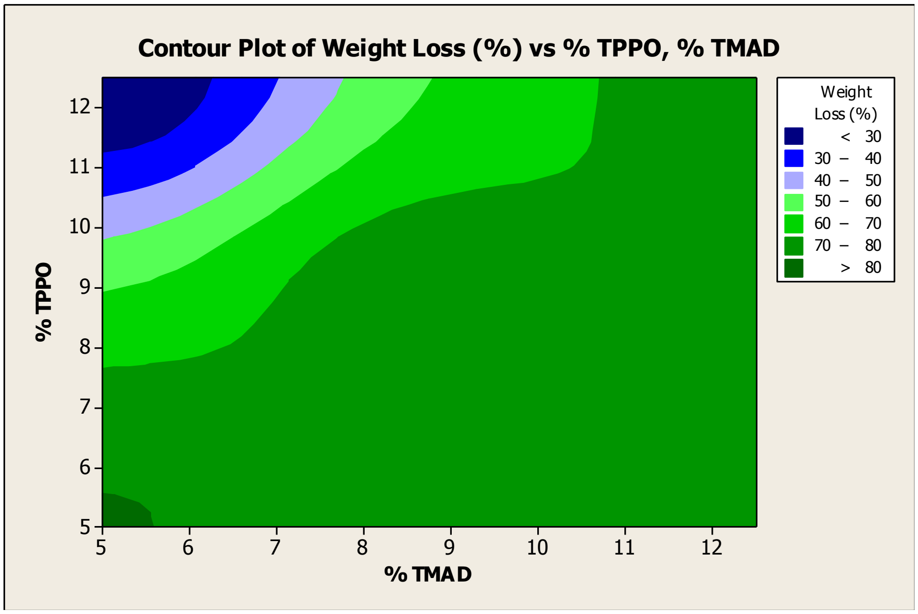


Figure 25: Contour Plot of Weight Loss % for TMAD

Based upon the results for the contours above, it was decided to recenter the DOE amounts and run a full DOE. The recentered DOE is shown in Table 2 in the experimental section. The %TPPO was at levels consisting of 6.25%, 12.5%, and

18.75%, while the %TBAD or TMAD was at levels of 2.5%, 5%, and 10%. The full DOE consisted of 13 runs, at those varying levels. The thin films were burned and data analysis was performed for burn rate and weight loss %. Those results are shown as contour plots of burn rate x 100 and weight loss % as a function of %TPPO, and %TBAD in Figures 26 and 27, and as a function of %TPPO and %TMAD in Figures 28 and 29, respectively.

The burn rate contour for TBAD showed that the lowest burn rate was achieved when there was 3% or less of TBAD, and 10-14% of TPPO. The lowest amount of weight loss for TBAD was achieved when there was less than 3% TBAD, and 12-18% TPPO. The burn rate contour for TMAD shown in Figure 28, shows that at 10% TPPO, and 3% TMAD there was a slower burn rate, and that was also achieved at 14-18% TPPO, and approximately 3-6% TMAD. The least amount of weight loss from burning the samples was achieved when 18% of TPPO was used with less than 3% of TMAD. Of note for both decaborate materials is that they provide a good distinction of several samples that had burn rates just as good, and better than the neat urethane sample.

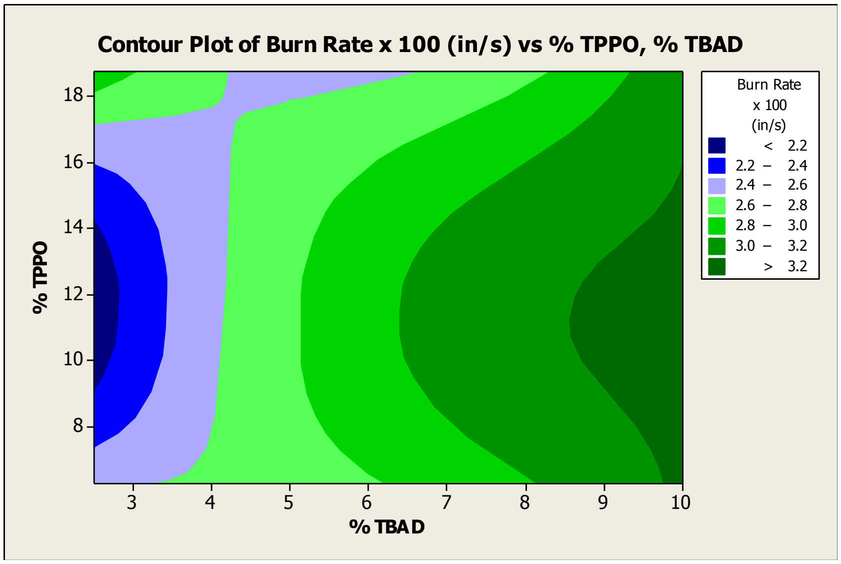


Figure 26: Contour Plot of Burn Rate vs % TPPO and %TBAD

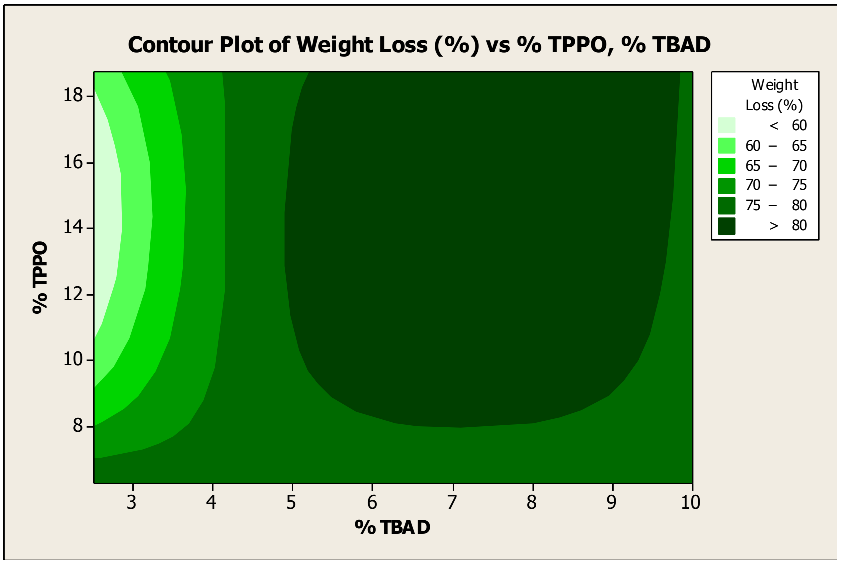


Figure 27: Contour Plots of Weight Loss vs %TPPO and %TBAD

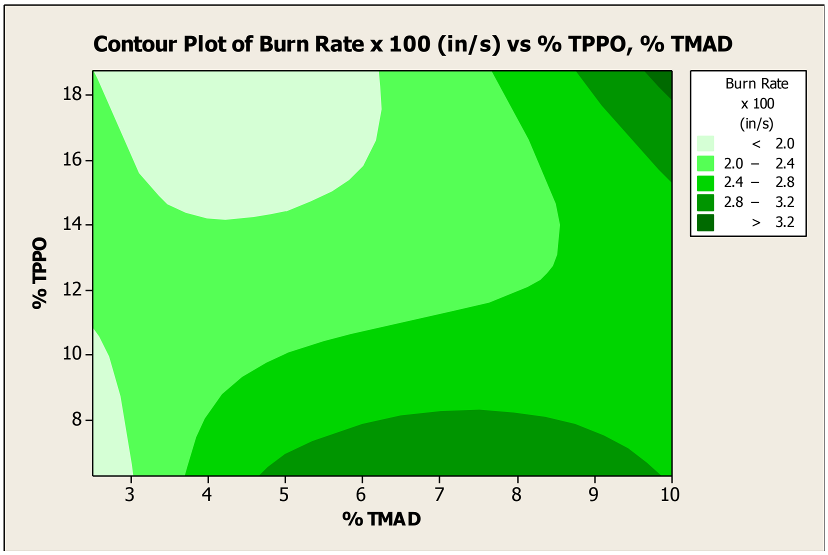


Figure 28: Contour Plot of Burn Rate vs % TPPO and %TMAD

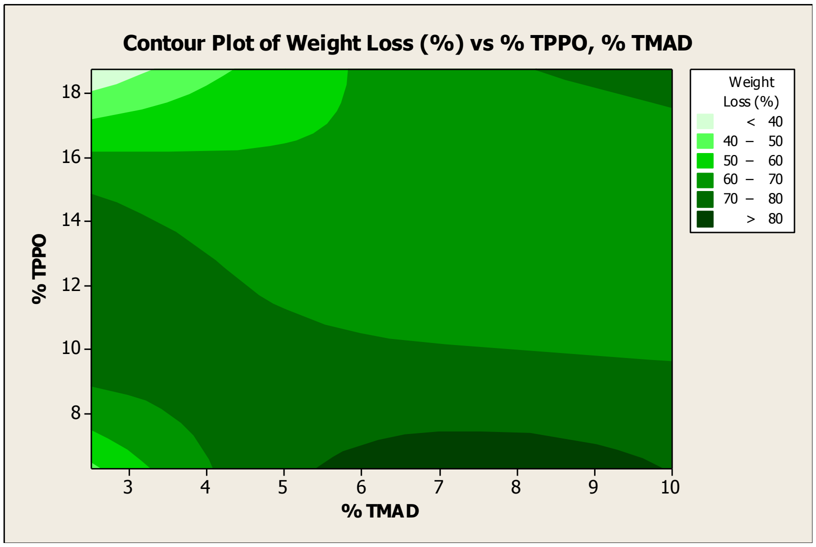


Figure 29: Contour Plot of Weight Loss vs % TPPO and %TMAD

3.5 Cone Calorimetry

Due to inaccuracies associated with data from the thin film burning test, a cone calorimeter was used for further characterization of these materials. Cone calorimetry is one of the most widely accepted methods in industry for determining flame retardancy.[39-41] All the tests were performed per ISO 5660-1:2002, with a thermal radiation power of 35 kW/m^2. The flammability properties measured were heat release rate (HRR), peak heat release rate (PHRR), and smoke release rate (SRR) which are the most used values in research and the most important in fire safety. Cone Calorimetry ultimately provides much more data than just a TGA in air. It also gives the ability to see the amount of residue following combustion like TGA. Rather than providing a degradation temperature, it provides the overall heat that is released from the sample throughout the burning process.

The samples for cone calorimeter testing were derived from the Minitab^{TM} DOE that was used for the TGA samples shown in section 3.3. Those samples contained varying amounts of TPPO with TMAD or TBAD at levels of 5%, 8.75%, and 12.5%. Figure 30 shows the cone calorimetry results for heat released for the base material and the samples that had a lower HRR for TBAD. Compared to the base material, most of the TBAD samples had a lower PHRR, indicative of flame retardancy potential. Most of the TBAD compounds have a sharp peak as burning begins followed by a decrease in the HRR. However, the maximum peak heat release rate was observed by a strong increase between 300-400 seconds or between 500-600 seconds. The sample with 5% TPPO and 5% TBAD did not level off until about 1000 seconds. The sample containing 8.75% TBAD and 12.5% TPPO had a PHRR just below that of the base sample but it occurred over four and a half minutes longer to reach. PHRR occurred at 45 seconds for the 5% TBAD, 5% TPPO sample but it was 93.56 kW/m^2 lower of a PHRR as compared to the base urethane. The 8.75% TBAD, and 5% TPPO sample had a PHRR lower than the base urethane by 58.23 kW/m^2, but it took nine and a half minutes for that PHRR to be achieved. Heat release rate is considered as one of the driving forces of a fire and PHRR represents the point where fire is likely to grow and potentially cause flashover to occur.[42]

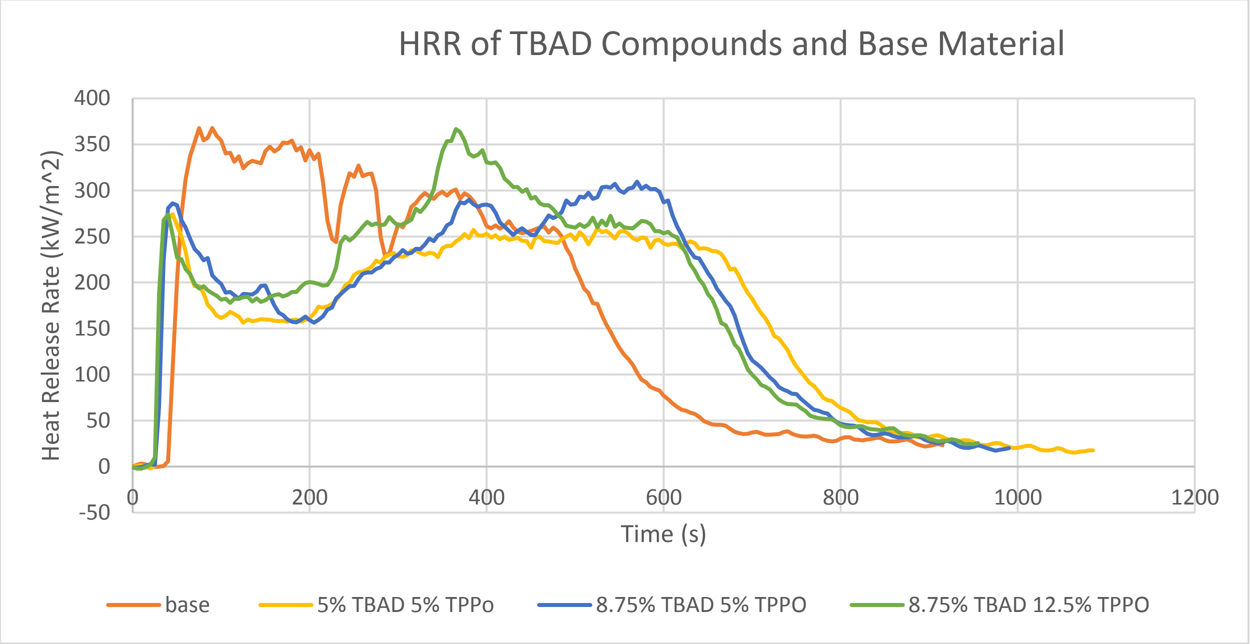


Figure 30: Plot of HRR for TBAD Materials and Base Material

Average HRR were also determined from the graph shown in Figure 30. The 5% TBAD, 5% TPPO and 8.75% TBAD, 5% TPPO samples had an average HRR of 23.25 kW/m^2, and 4.15 kW/m^2 less than base urethane, respectively. However, the sample at 8.75% TBAD and 12.5% TPPO had an average HRR of 7.34 kW/m^2 greater than the base urethane. Of note, however, was the differences between the total heat that was released. There were negligible differences of 8-10 Mj/m^2 increases in the total HR as compared to the base urethane sample for the 5% TBAD, 5% TPPO, and 8.75% TBAD, 5% TPPO samples. The 8.75% TBAD, 12.5% TPPO sample however released 84 Mj/m^2 less of heat than the base urethane sample, showing that the sample at this loading could potentially be used as a flame retardant.

Figure 31 shows a contour plot of the PHRR for samples containing TBAD. Materials with lower amounts of TBAD and phosphine oxide compounds provided the lowest PHRR, with the lowest PHRR at 5% of both materials. If samples contained greater than 8% of TBAD or TPPO an increase in PHRR was observed. The contour plot also shows that the highest PHRR occurred at two formulations, when there was 5% TBAD and 12% phosphine oxide compound, and when there was 12% TBAD and 12% phosphine oxide compound. This shows that adding more flame retardant did not result in a decrease to the PHRR.

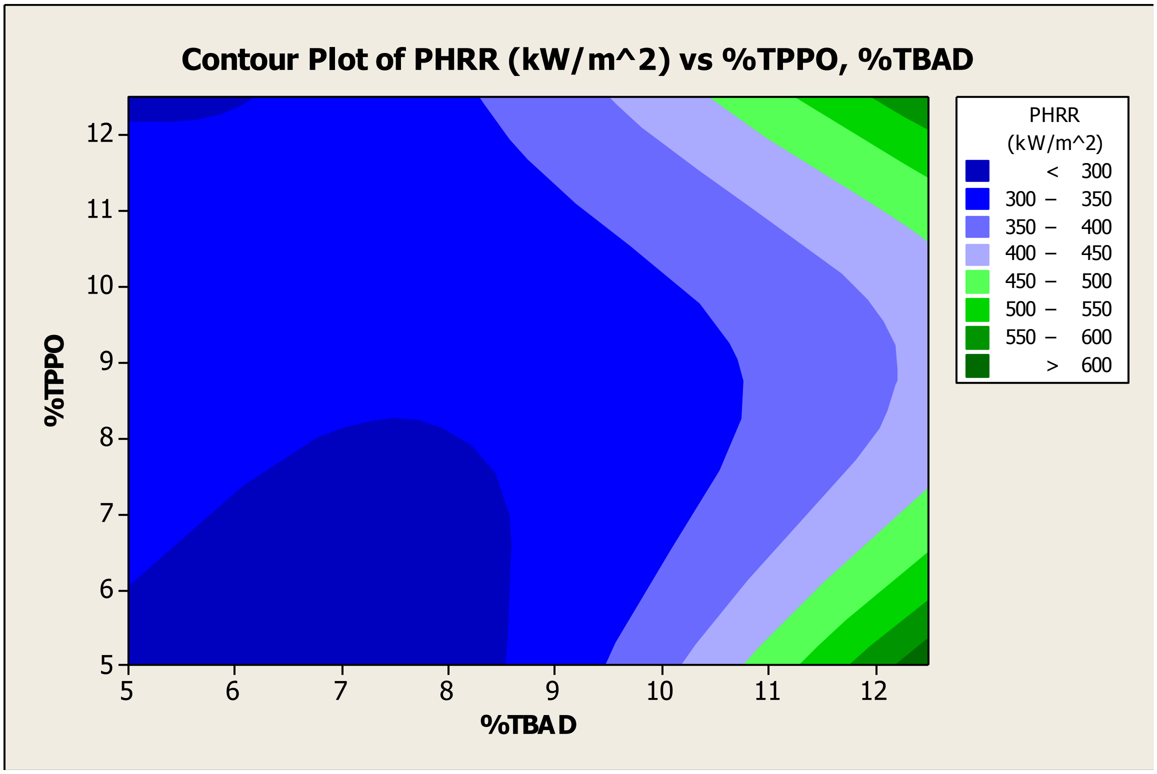


Figure 31: Contour Plot of PHRR vs %TBAD, %TPPO

Figure 32 shows the HRR differences between the base material and the sample with the lowest PHRR for TMAD. There was only one sample for TMAD that had a lower PHRR as compared to the base sample. That was the sample with just 5% of each flame retardant mixed into the compound. The base material and the TMAD curves from Figure 32, very closely resembled each other except for the TMAD staying somewhat high for heat release rate until about 200 seconds. Both materials decrease and then level off around 650 seconds.

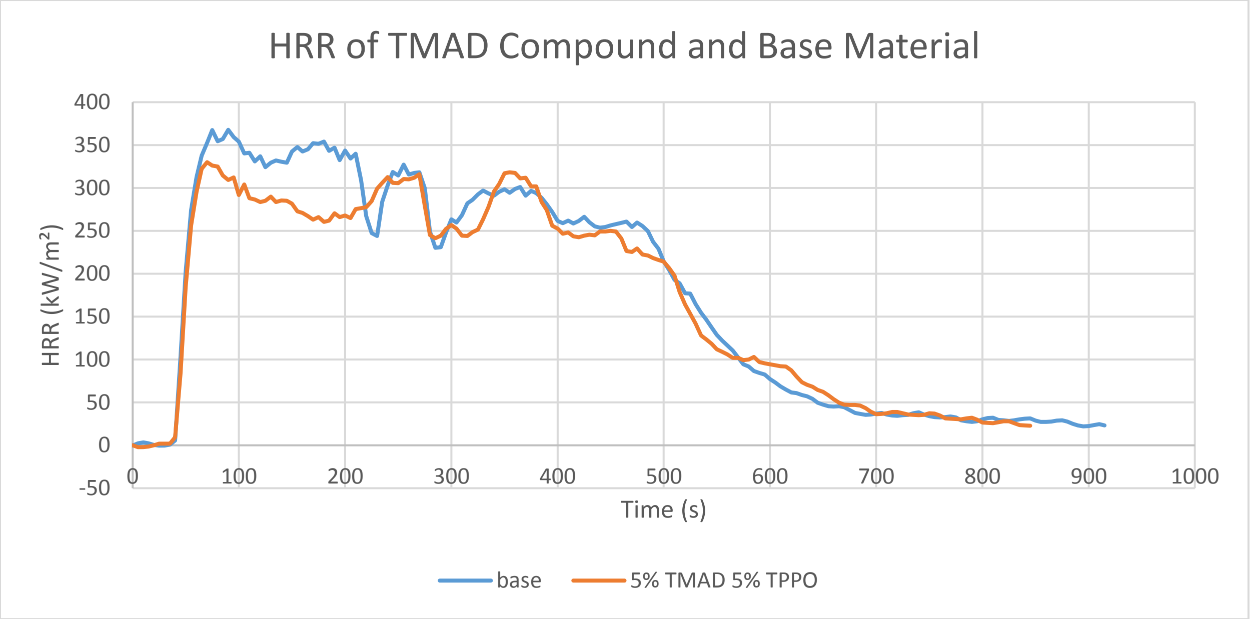


Figure 32: HRR of TMAD and base material

Figure 33 shows a contour plot of the peak heat release rates based upon the varying weight percent of TMAD and TPPO. As observed for TBAD, the lowest PHRR was achieved at lower amounts of flame retardants. The lowest PHRR for TMAD and TPPO was achieved at 5% of each in the compound. Interestingly there were two areas on the contour plot where the highest PHRR was observed. One was at 5% TPPO and 9-12 wt% TMAD and the other area was at 12% of TPPO, and 8-11 wt% TMAD.

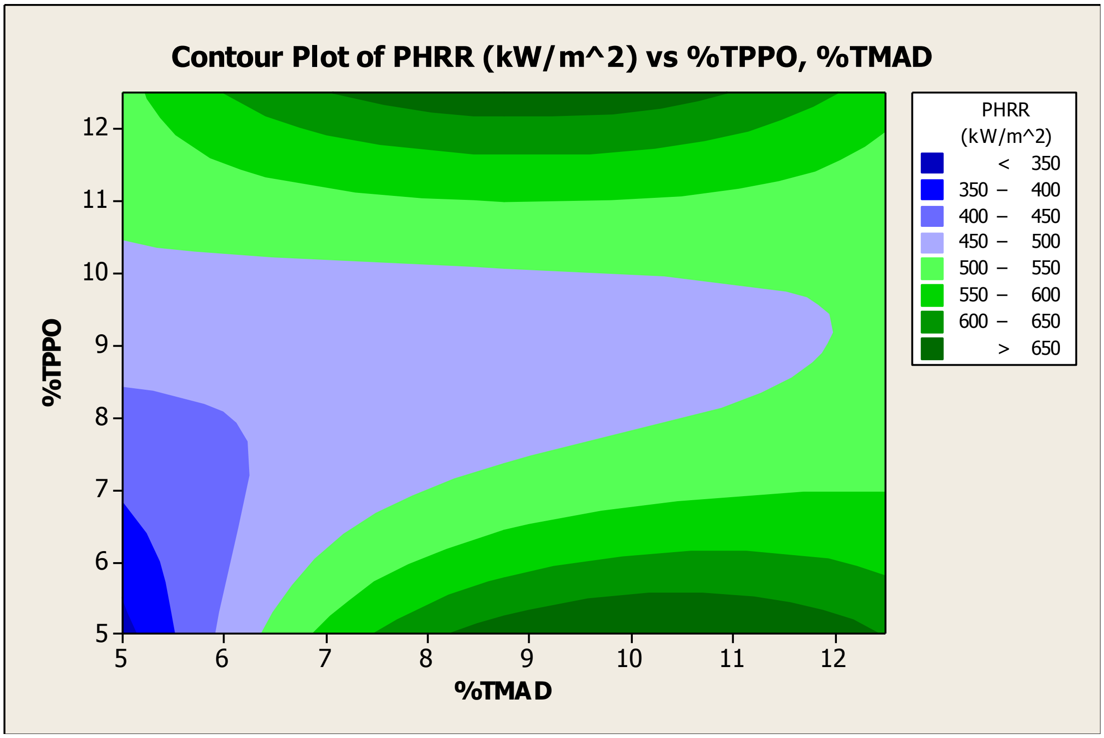


Figure 33: Contour Plot of PHRR vs %TMAD, %TPPO

Figure 34 shows the peak heat release rates for boric acid as compared to the trials of the decaborate compounds with the lowest heat release rates. It can be seen for 5% boric acid that the peak heat release rate was 302.9 kW/m^2, average HRR was 134.16 kW/m^2. The time when PHRR was achieved was 85s, in addition the total HR was 132.8 Mj/m^2. For the 10% boric acid sample, the peak heat release rate was 318.9 kW/m^2 at 165s, an average HRR of 142.56 kW/m^2, and a total HR of 139.0 Mj/m^2. There was a PHRR difference of 28.68 kW/m^2 between the 5% TBAD, 5% TPPO sample and the 5% boric acid sample, showing the lowest PHRR of the decaborate samples shown in Figure 34, and the boric acid for peak heat release rate. This indicates that TBAD has potential for flame retardance applications.

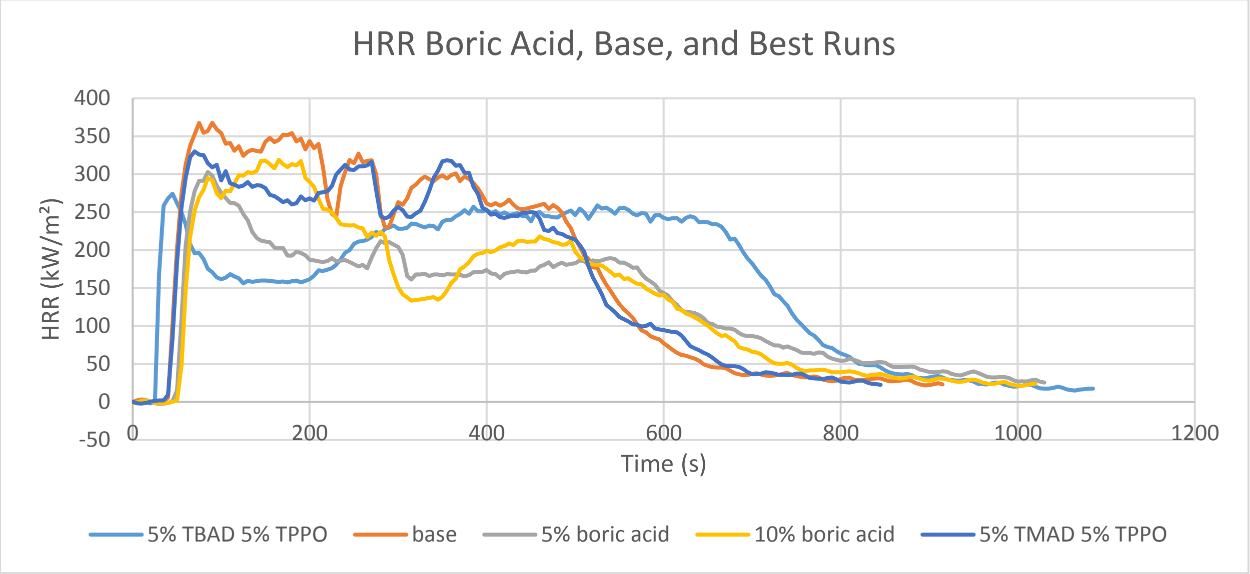


Figure 34: HRR of Boric Acid, Base and Representative Runs

Figure 35 shows the lowest smoke release rates from the two decaborate compounds and the boric acid. The peak smoke release rate of TBAD was 0.0483 m^2/s and the time required to reach it was 30 seconds. For TMAD, a peak smoke release rate of 0.0826 m^2/s at time 50 seconds was observed and the base material showed a peak smoke release rate of 0.0421 m^2/s at 245 seconds. For the 5% boric acid sample, the peak smoke release rate was 0.0342 m^2/s at 60 seconds. Comparing the smoke production rates of each material showed that boric acid provided the lowest amount of smoke production. However, TBAD had a small difference compared to boric acid of 0.0141 m^2/s. This small difference in smoke production supports the potential use of this material as a flame retardant.

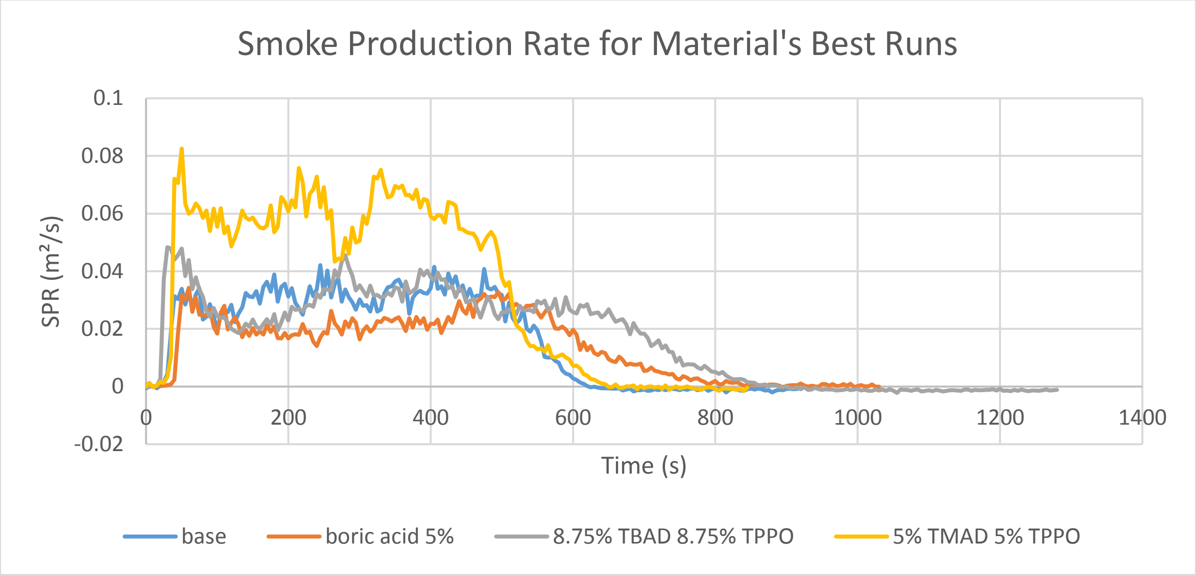


Figure 35: Smoke Production Rate for Representative Runs

Chapter IV

4. Conclusion

Synthesis of the TBAD and TMAD was achieved via an ion exchange process, replacing the triethylammonium ion with tetrabutyl or tetramethyl ammonium ions. This was performed using an ion exchange column followed by neutralization with tetrabutyl or tetramethyl ammonium hydroxide to make TBAD and TMAD, respectively. Both products were characterized by ^{1}H-NMR, ^{13}C-NMR, ^{11}B-NMR, and FT-IR.

TBAD and TMAD were incorporated into polyurethane films at varying levels providing a baseline performance for the samples. The thermal stability of these materials was similar to the neat polyurethane but a significant increase in char formation was observed. Burning of thin films showed that each sample burned to completion. When TPPO was incorporated into the polyurethane with the decaborates, self-extinguishing was observed for some samples under thin film burning conditions. The combination with TPPO provided some synergistic effects and some additive effects, as indicated by the contour plots in Section 3.4.1. The combination of TPPO and TBAD or TMAD provided samples with burn rates that were as good, as the base urethane.

Cone calorimeter testing of polyurethane samples with TMAD/TBAD and TPPO showed heat release rates similar to, or less than, that of the boric acid samples used for comparison. The decaborate compound with the lowest PHRR gave a value of 274.22

kW/m^2. While the decaborate sample with the lowest smoke released was slightly greater for HRR but had a lower smoke release rate with a value of 0.0483 m^2/s. Results from cone calorimeter testing indicate the potential use of these materials in flame retardant applications.

4.1 Future Research

Continuing research with these materials should include testing with other polymer resins. As nonhalogenated flame retardants are typically good for only select polymers for the ideal properties, testing the flame retardant with other polymers could find one that it actually works with better than the polyurethanes. Also, if the flame retardant could be incorporated into a higher volume commercial resin, like polypropylene or polyethylene, that would open up an opportunity for increased usage. Specific polymers would be polypropylene, polystyrene, and further exploration of polyurethanes with foams. Further testing outside of cone calorimetry would include LOI testing and testing for usage in thermal barrier coatings. Testing for thermal barrier coatings may be justified as these materials do not exhibit the acidic properties of boric acid, and with the flame retardants affinity to char, it can protect the item underneath the coating as well.

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APPENDIX

APPENDIX A
THERMAL STABILITY AND FLAMMABILITY DATA

A.1 BURN DATA

Table S1: Burn Data from Screening DOE

% TPPO	% Decaborate	% Loss	Burn Rate x 100 (in/s)
12.5	5 TBAD	79.38	2.93
5	5 TBAD	79.08	3.12
8.75	8.75 TBAD	81.02	3.88
8.75	8.75 TBAD	77.91	3.33
5	12.5 TBAD	76.53	4.02
12.5	12.5 TBAD	77.26	4.55
12.5	5 TMAD	22.30	7.33
5	5 TMAD	80.47	2.06
8.75	8.75 TMAD	77.45	2.75
8.75	8.75 TMAD	74.71	2.51
5	12.5 TMAD	75.82	2.78
12.5	12.5 TMAD	72.94	2.99

Table S2: Burn Data from Recentered DOE

% TPPO	% Decaborate	% Loss	Burn Rate x 100 (in/s)
12.5	5 TBAD	82.11	2.55
18.75	2.5 TBAD	61.33	2.94
12.5	2.5 TBAD	55.88	2.09
12.5	5 TBAD	82.37	2.44
12.5	10 TBAD	78.01	3.23

18.75	10 TBAD	79.42	3.16
6.25	5 TBAD	76.96	2.70
12.5	5 TBAD	79.03	3.06
6.25	2.5 TBAD	79.29	2.58
12.5	5 TBAD	79.02	2.77
12.5	5 TBAD	79.51	3.03
6.25	10 TBAD	76.67	3.23
18.75	5 TBAD	79.30	2.26
12.5	5 TMAD	77.88	2.50
18.75	2.5 TMAD	30.39	2.00
12.5	2.5 TMAD	78.58	2.07
12.5	5 TMAD	77.35	2.09
12.5	10 TMAD	66.35	2.56
18.75	10 TMAD	72.74	3.38
6.25	5 TMAD	77.64	2.90
12.5	5 TMAD	84.57	2.05
6.25	2.5 TMAD	47.36	1.62
12.5	5 TMAD	44.55	2.00
12.5	5 TMAD	54.18	2.09
6.25	10 TMAD	79.33	2.76
18.75	5 TMAD	54.87	1.80

A.2 CONE CALORIMETRY DATA

Table S3: Cone Calorimetry HRR Data for Base Material and TBAD and TMAD

Sample/ Run No.	Peak HRR (kW/m^2)	Time to Peak (s)	Average HRR (kW/m^2)	Total HR (Mj/m^2)
Base	367.78	90	181.06	160.2
TBAD 1	299.51	50	123.53	155.6
TBAD 2	274.22	45	157.81	168.1
TBAD 3	309.55	570	176.91	170.8
TBAD 4	292.69	355	109.79	164.1
TBAD 5	366.65	365	188.4	76.2
TBAD 6	288.96	600	156.31	173.5
TBAD 7	328.71	30	75.52	168.5
TBAD 8	331.49	330	137.14	167.3
TBAD 9	636.11	450	248.18	179.9
TBAD 10	298.27	335	175.53	174.7
TBAD 11	337.67	330	187.24	167.6
TBAD 12	590.78	350	244.09	188.0
TBAD 13	411.91	325	230.31	178.5
TMAD 1	556.07	65	189.11	163.6
TMAD 2	330.04	70	180.65	148.1
TMAD 3	675.84	50	220.28	161.9
TMAD 4	533.52	60	221.46	171.6

TMAD 5	684.97	60	199.21	176.3
TMAD 6	471.45	70	252.76	183.3
TMAD 7	520.21	65	199.97	164.0
TMAD 8	458.95	70	210.09	170.2
TMAD 9	646.15	385	246.54	152.9
TMAD 10	385.43	425	192.04	145.0
TMAD 11	429.15	440	198.14	145.6
TMAD 12	570.62	75	192.37	141.4
TMAD 13	508.52	85	185.91	142.2

Table S4: SRR results for All Samples

Sample/ Run No.	PSRR (m^2/s)	Time (s)
Base	0.0421	245
Boric Acid 5%	0.0342	60
Boric Acid 10%	0.0417	460
TBAD 1	0.0483	30
TBAD 2	0.0832	605
TBAD 3	0.0733	580
TBAD 4	0.0655	330
TBAD 5	0.0940	355
TBAD 6	0.0925	585
TBAD 7	0.1021	585
TBAD 8	0.0769	315

TBAD 9	0.1355	435
TBAD 10	0.0970	570
TBAD 11	0.1008	525
TBAD 12	0.1744	415
TBAD 13	0.1267	455
TMAD 1	0.1072	405
TMAD 2	0.0826	50
TMAD 3	0.1254	455
TMAD 4	0.1330	365
TMAD 5	0.1364	400
TMAD 6	0.0852	460
TMAD 7	0.1183	430
TMAD 8	0.1078	185
TMAD 9	0.1369	375
TMAD 10	0.1000	425
TMAD 11	0.1165	435
TMAD 12	0.1533	455
TMAD 13	0.1170	465

A.3 TGA DATA

Table S5: TGA Data for Base Samples

Sample	% Boron Compound Incorporation	Char Yield at 600°C (% of original mass)	5% weight loss temperature (°C)
TBAD	10	26.8	269.67
TBAD	20	21.56	251.8

TMAD	10	28.68	286.17
TMAD	20	39.76	254.09
CONTROL	0	17.89	291.67
BORIC ACID	10	24.72	269.67
BORIC ACID	20	27.23	151.44

Table S6: TGA Data for Cone Samples

%TBAD	% TPPO	5% Weight Loss Temp (°C)	Char Yield (%)
8.75	8.75	249.05	23.59
12.5	5	251.34	25.22
12.5	12.5	245.39	25.02
12.5	8.75	244.47	24.75
8.75	8.75	249.51	24.09
5	12.5	248.59	19.94
8.75	5	255.93	24.46
8.75	12.5	245.84	22.37
5	8.75	255.01	20.44
5	5	245.39	21.94
%TMAD	% TPPO	5% Weight Loss Temp (°C)	Char Yield (%)
8.75	8.75	269.67	30.72
12.5	5	262.8	38.17
12.5	12.5	246.3	41.27
12.5	8.75	260.97	32.86
8.75	8.75	258.68	45.63
5	12.5	263.72	25.76
8.75	5	266.47	39.5
8.75	12.5	252.26	37.02

5	8.75	270.13	29.67
5	5	280.21	29.86