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FLAME AND BLAST RESISTANT MATERIALS FOR FORCE PROTECTION

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■ **Air Force Materiel Command** ■ **United States Air Force** ■ **Tyndall Air Force Base, FL 32403-5323**

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14. ABSTRACT

This report is concerned with the development of a fire retarded blast resistant polyurea. Any blast resistant material must offer protection not only against a blast but also against the possibility of an accidental fire. In this project more than fifty different materials were investigated but alone and in a variety of combinations to determine the best system to offer fire protection to polyurea. The various formulations were initially evaluated using the cone calorimeter and the two key ingredients were found to be expandable graphite and ammonium polyphosphate. The combination of these two additives reduces the peak heat release rate from more than 2000 kW/m^2 to about 100 kW/m^2. This indicates that there is a significantly smaller fire. When the system is evaluated by the ASTM E-84 Flame Spread protocol, a solid Class B performance is obtained. Since pristine polyurea is not classified according to this testing protocol, this represents a great improvement in fire retardancy.

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1. SUMMARY

This report is concerned with the development of a fire retarded, blast resistant polyurea. Any blast resistant material must offer protection not only against a blast, but also against the possibility of an accidental fire. In this project, more than fifty different materials were investigated, both alone and in a variety of combinations, to determine the best system to offer fire protection to polyurea. The various formulations were initially evaluated using the cone calorimeter and the two key ingredients were found to be expandable graphite and ammonium polyphosphate. The combination of these two additives reduces the peak heat release rate from more than 2000 kW/m^2 to about 100 kW/m^2, indicating a significantly smaller fire. When the system is evaluated by the American Society of Testing and Materials (ASTM) E-84 Flame Spread protocol, a solid Class B performance is obtained. Because pristine polyurea has no classification according to this testing protocol, this represents a great improvement in fire retardancy.

Numerous additives have been studied to see if polyurea's fire performance can be improved. The additives that have been studied include both conventional additives that one may choose from knowledge of fire retardancy principles, as well as unusual additives that were thought to be potentially useful. None of these have shown an improvement in fire performance beyond that obtained from the fire retardant system containing expandable graphite and ammonium polyphosphate.

The system developed in this project is as effective as the currently employed intumescent paint. It is believed that the additive package offers some advantages in that there is not a solubility concern and it seems unlikely that anything can be removed in normal maintenance. The additive package requires only one spraying while the intumescent paint must be sprayed on two separate and temporally-separated occasions.

2. INTRODUCTION

Blast resistant materials, notably plastics made of polyurea, are of great interest to organizations subject to explosive threats. In general, blast protection material must be ductile enough to yield under high-strain loads, but strong enough to retain blast impulses and mitigate any secondary fragmentation. Polyurea has proven itself to be a potential material solution, but is often considered to be a risky alternative, as its flammability makes it a hazard in blast events commonly associated with fire. Thus, the goal of this project is to develop a fire retardant package that can be used in elastomers without weakening its blast resistant characteristics. Two distinctly independent threats are therefore analyzed: First, the threat of an explosion in the vicinity of the structure, and second, the possibility of an accidental fire in a structure protected against blast.

Prior to this effort, a common method of providing fire retardancy involved the application of intumescent paint over the blast resistant coating. This practice has several potential problems: intumescent coatings contain components that have some water solubility and thus they may be partially removed by cleaning; an intumescent coating may not be the best method to achieve good fire retardancy; fire retardancy is dependent on the thickness of the material used; and an intumescent coating is a second application, so additional start-up time and expense is necessary. With these insufficiencies in mind, the objective in this project was to develop a fire retardant additive package that would provide suitable fire retardancy to polyurea.

Fire retardancy may be evaluated by various techniques. The usual laboratory methods include oxygen index, UL-94 protocol and the cone calorimeter. Of course, the ultimate evaluation of a fire retardant system is a full-scale burn test. These tests are not often performed because everything is consumed, making them very expensive with respect to time and material. Between these evaluations are a number of ASTM protocols. One of the problems commonly encountered in fire retardancy is that each test measures a variable of fire retardancy but nothing, except the full-scale burn, takes every variable into account. To understand this further, the common laboratory methods of evaluation are described.

Oxygen index measures the ease of ignition of a material. In this protocol, a sample is ignited in a synthetic nitrogen-oxygen mixture and the minimum concentration of oxygen required to sustain combustion is obtained. The UL-94 protocol evaluates the ease of extinction of a flame. Here, a sample of specified thickness is ignited and the time that it takes for this to extinguish is measured. Thickness is extremely important in this evaluation, for a thick sample will extinguish much easier than a thin sample. Normally, the preferred thickness is less than about 3 mm. This UL-94 protocol is somewhat of a measure of merit for the commercial success of an additive. A ranking of V-0, which means rapid extinguishment, is required in many applications. The cone calorimeter, which measures heat release rate, could also be expressed as the size of the fire, and is usually considered to be the best laboratory-scale, evaluative technique for fire retardancy. In this technique, a sample is exposed to some high temperature, which is usually expressed as the heat flux, and it begins to burn as oxygen is consumed. Within the instrument, the percent of oxygen remaining in the effluent is measured, and from this the heat release curve is obtained.

For this work, we decided that since a large quantity of material was going to be used to protect the structure, it was more appropriate to test a larger quantity of material. The ASTM E-84 flame

spread test was consequently chosen. In this test, a sample approximately 24 ft long and 24 in wide is exposed to a flame and compared with a standard to obtain a flame spread index and a smoke index. The ratings for this test are given in Table 1. Given the large amount of materials involved, a simpler technique is required to pre-evaluate the various compositions in order to identify the relevant materials requiring the full E084 protocol. The technique chosen is the cone calorimetry test. In other unpublished work,[1] a correlation between cone calorimetry and E-84 testing was identified. This particular correlation for unsaturated polyesters allowed for the use of cone calorimetry as a predictor for E-84 results.

Table 1. Ratings for Various Fire Spread and Smoke Indices in the ATSM E-84 Test

Class	Flame spread index	Smoke developed index
A	0–25	0–450
B	26–75	0–450
C	76–200	0–450
Unclassified	>200	>450

This technical report is to describe the efforts that have been made in these laboratories, over the past approximately four years, to develop a suitably fire retarded polyurea which can be used for blast protection. In order to do this, it is necessary to describe work that was carried out before funding from the Air Force became available.

In 2005, the U.S. Navy approached and asked that the fire retardancy of polyurea be evaluated, using the cone calorimeter. The purpose of this study was to determine which, if any, conventional fire retardants were useful in this system. A total of thirteen different fire retardants were evaluated; these included five phosphates, two phosphonates, one phosphite, two halogenated compounds, one inorganic material, two melamines and one intumescent composition. The conclusions from this study were that the halogenated material, decabromodiphenyl ether (deca) with antimony, and ammonium polyphosphate (APP) should be considered for further evaluation.

The next stage in this odyssey was cooperation between Triton Systems and Marquette University, both partnered with this Air Force investigation, to further pursue research on polyurea. This work proceeded self-funded for a short time and then it was further funded by the Navy. The primary objective of this work was to evaluate a proprietary material developed by Triton called FX, which they knew to be a suitable fire retardant for polycarbonate and similar materials and believed would be useful in polyurea. Unfortunately, this material did not prove to be efficacious in polyurea, necessitating a search for other additives that could be useful[*]. This Navy-funded work segued into the Air Force-sponsored work, which is the subject of this final report.

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[*] Results not published.

3. METHODS, ASSUMPTIONS, AND PROCEDURES

3.1. Materials

Materials used in this study include the components of polyurea, which are the diisocyante, Isonate 143L from Dow Chemical, and the diamine, Versalink P1000 from Air Products. These were the materials suggested by the Navy for the initial investigation of this system, which can be conveniently studied in a chemical laboratory. The components produce a castable polyurea which is somewhat slow to set and can be worked with for a short time before quickening. However, a sprayable polyurea is more often used in the field and sets up must faster, as a sprayable material is typically aliphatic while a castable material is aromatic. For laboratory evaluations, the castable materials were routinely evaluated while the sprayable material, made by Specialty Products Incorporated SPI, was used for the blast tests. Despite the difference in hardening time, both the sprayable and castable polyureas were evaluated for fire performance and it was found that both forms of polyurea were quite similar in their fire retardancy.

A very large number of fire retardants were used, all shown in Table 2 along with the corresponding supplier. In addition to the commercial additives noted above, several new materials which are not commercially available were also evaluated in polyurea. It was felt that the package that had been developed based on commercial materials was close to what was needed and that a small improvement would come from a novel additive. The novel additives that were used include: α-zirconium phosphate[2,3], molybdenum disulfide[4], cerium oxide,[5,6,7] cucurbir[6]uril[8,9], cadmium sulfide[10] and LDH-MMT[11].

Table 2. Fire Retardant Additives, and Suppliers, That Have Been Evaluated

Fire Retardant	Supplier
Decabromodiphenyl oxide	Albemarle
Antimony Oxide	Laurel Industries
Ammonium Polyphosphate	ICL
Melamine	BASF
Melamine Polyphosphate	BASF
Triphenylphosphate	ICL
Antiblaze 78	Albemarle
DoverPhos S9228	Dover
Aluminum trihydroxide	Albemarle
Pentaerythritol	Aldrich
Zinc Borate	Rio Tinto
Santicizer 2158	Ferro
Fyrol PMP	ICL
FX	Triton Systems
Expandable graphite	Graph-Tech
Cloisites	Southern Clay
Layered double hydroxides	Akzo-Nobel
Polytetrafluoroethylene	Aldrich
Resorcinol diphosphate	ICL
Trixylphosphate	ICL
Carbon nanotubes	Nanocyl
POSS	Hybrid Plastics
$ZnCO_3$	Aldrich
Bisphenol A diphosphate	ICL
Ethylenediamine diphosphate	ICL
Red phosphorus	Aldrich
Triphenylphosphite	Dover
Dimethyl methyl phosphonate	Albemarle
Antiblaze N	Albemarle
DOPO	Krems Chemie
Exolit OP1230	Clariant
Reofos NHP	Chemtura
Triphenylphosphine oxide	Aldrich
Boron Nitride	Aldrich
Silicon carbide	Aldrich
Melamine cyanurate	Buddenheim
Fumed silica	Evonik
Silica	Evonik
Titania	Evonik
Intumescent paints	Sherwin-Williams
FireStop intumescent paint	A-B Thermal Technologies
FireFree intumescent paint	Fire Free Coatings
Intumescent powder	SPI
Aluminum nitride	Aldrich
Nano	SPI
Sidistar	Elkem

3.2. Preparation of the Polyureas

The polyurea samples were prepared in a beaker by reacting four parts (by weight) of polytetramethylene oxide-di-*p*-aminobenzoate) (Versalink P-1000; Air Products) with 1 part of a polycarbodiimide-modified diphenylmethane diisocyanate (Isonate 143 L; Dow Chemical). The diamine and diisocyanate undergo rapid linear polycondensation to yield a microphase-separated block copolymer having ca. 20% hard segments by mass. For polyurea with additives, the additive is mixed first in the diamine for several minutes. The dispersion of the additives was achieved using mechanical mixing followed by ultrasonication. Then, the isocyanate was added to the mixture with continuous stirring for one minute, and the contents of the beaker were poured into a mold. The samples were cured at room temperature for 12 hours, then placed in a vacuum oven at 70 °C for an additional 24 hours. In some cases, only mechanical mixing was used, while in other cases, only ultrasonic mixing or the combination of the two was used. No significant difference in the mixing protocol appeared to exist. In a few cases, the additive was mixed into the diisocyanate rather than the diamine, but again no difference was observed. For the vast majority of cases, a mixture of additives was used and the additives were added in a different order to ascertain if the order of mixing was important. No differences were found based on the order of addition of the additives to the polyurea component.

3.3. Instrumentation

A Rigaku Miniflex II desktop X-ray diffractometer with Cu Kα radiation (λ= 1.54 Å) at a generator voltage of 30 kV and a current of 15 mA was used to study the diffraction behavior of pristine polymers and polymer nanocomposites. All tests were conducted in the reflection mode at ambient temperature with 2θ varying between 2° and 45°. The scanning speed was 2° /min and the step size was 0.05°.

Transmission electron microscopy (TEM) images were obtained using a JEOL JEM- 2100F transmission electron microscope with an accelerating voltage of 200 kV. The nanocomposite specimens were cut at room temperature using an ultramicrotome (Model MT-6000, Du Pont) with a diamond knife from an epoxy block where the films of the composites were embedded.

Tapping mode atomic force microscopy (AFM) was performed with an Innova Scanning Probe system from Veeco. Topographic (height) and phase images were recorded simultaneously under ambient conditions. Silicon nitride Si_3N_4 cantilever probes with a nominal tip radius of 5–10 nm and spring constant in the range of 20–100 N/m were oscillated at their fundamental resonance frequencies, which ranged between 250 and 300 kHz. All data were collected with 256×256 pixels per image. Typical scan rate and set point amplitude ratio during recording were 1.0 Hz and 3.0–4.0 V, respectively.

Thermogravimetric analysis (TGA) tests were conducted on a TA instruments SDT Q600 from room temperature (~25 °C) to 700 °C at a rate of 10 °C/min in a nitrogen atmosphere. The nitrogen flow rate is 100 mL/min. Samples were run in duplicate and the average values are reported; temperature is reproducible to ±2 °C and mass to ±0.2%. The thermal phase behavior of polyurea was investigated using a Netzsch instrument 200 F3 Maia differential scanning calorimeter (DSC), operating at a heating and cooling rate of 10 °C/min under a nitrogen atmosphere. polyurea samples were subjected to two heating and cooling cycles between -70 and

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250 °C. Transitions were investigated during the second heating and cooling cycles. Dynamic mechanical analysis (DMA) was carried out using a TA instrument Q800 instrument.

TGA/FTIR studies used a Netzsch TG 209 F1 Iris coupled with a Bruker Tensor 27 Fourier Transform Infrared Spectroscopy (FTIR) to study the thermal degradation. The analyses were performed under flowing nitrogen at 20 mL/min. The (TGA) resolution is 0.1 µg. The sample size was around 5 mg and the heating rate was 10 °C/min from room temperature to 700 °C. The coupling system between TG and FTIR was maintained at 200 °C to prevent condensation of evolved gases.

Pyrolysis combustion flow calorimetry experiments were carried out on a Govmark MCC-2 microscale combustion calorimeter (MCC). Samples weighing around 5 mg were heated to 750 °C at a heating rate of 60 °C/min in a stream of nitrogen flowing at 80 ml/min. The combustor temperature was set at 900 °C and oxygen/nitrogen flow rate was set at 20/80 ml/ml. The reported data are averages of 3–6 measurements and the typical relative error for heat release capacity is ±10%.

Cone calorimetry was performed on an Atlas CONE-2 according to ASTM E-1354 at an incident heat flux of 50 kW/m^2 using a cone-shaped heater; exhaust flow was set at 24 L/s. All samples were burned in triplicate and the data are the average of the three replicated tests. Cone samples (about 30 g) were prepared by pouring into a mold of dimensions $100 \times 100 \times 6$ mm^3. Based on many thousands of samples that have been run, cone measurements are considered to have error bars of ±10%.

ASTM E-84 testing was carried out by Commercial Testing Laboratories, Dalton, GA.

4. RESULTS AND DISCUSSION

4.1.   Cone Calorimetry with Single Additives

The majority of the work carried out in this study utilized castable polyurea, the structure of which is shown in Figure 1. This is the reaction product of Isonate 143L and Versalink P1000. At the beginning of this project, it was necessary to revisit work that had been previously performed. This data is reported in Table 3. As can be seen in the table, similar results are obtained for mechanical and ultrasonic mixing and the most efficacious additives are expandable graphite (EG) and ammonium polyphosphate (APP). While there is a reduced peak heat release rate (PHRR) as the amount of these materials are increased, the change is not so large and suggests that one may be able to use a relatively small amount of material, which has the advantage that it is less likely to affect the blast characteristics.
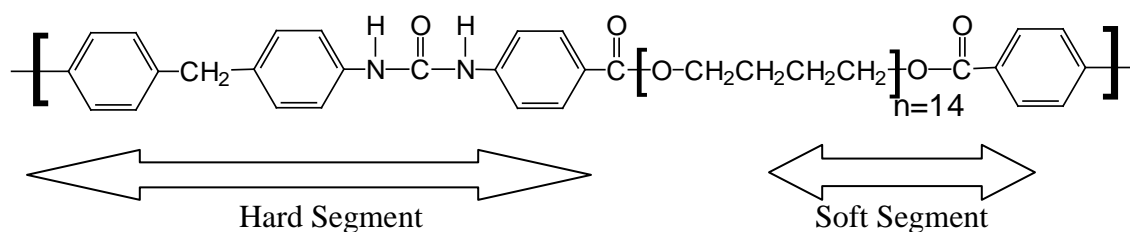
Figure 1. Structure of Segmented Polyurea

4.2.   Cone Calorimeter

Before continuing with the description of the results, it is valuable to describe the cone calorimeter, which has been used to evaluate the fire performance of the various polyurea packages. There are certain features of the cone calorimeter which must be understood in order to fully understand the data. In general, the information that is available from a cone study includes the following: the time to ignition (TTI), the heat release rate curve and especially its peak value (PHRR), the mass loss rate (AMLR), the total heat released (THR) and the quantity of smoke released (ASEA). Based upon many cone samples that have been run around the world, it can be stated that the reproducibility of the cone is about ±10%. This is what one may describe as the day-to-day reproducibility. It is quite common that if samples are run on successive days, then they will agree within this figure. For samples that are all run on the same day, this figure is usually much tighter. Thus, in the tables in this report, error bars are included, which show how closely the three samples that are run in each instance agree. However, the reader will notice that the values for polyurea, which has been run every time a set of polyurea samples were investigated, show quiet a spread of values. This is simply the normal reproducibility of the cone calorimeter.

It is generally observed that when one puts an additive together with a polymer, the time to ignition will be shorter[12]; this phenomena is not yet well-understood but it is a topic which is being studied in laboratories around the world and it is hoped that it will be understood at some point[13]. In many instances, it is found that there is about the same change in mass loss rate as there is in reduction in the peak heat release rate and the reduction in the PHRR is usually

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attributed to the change in mass loss rate. The total heat released is a measure of how much of the polymer actually burns. If the THR is similar for the pristine polymer and its combinations with additives, then a similar amount of polymer burns; this usually means that all the polymer burns.

The amount of smoke that evolves is also available from cone data. In this report, smoke data is not reported for a few reasons. First, out of practicality, for there is a lot of data and not enough room to include everything. Additionally, the presence of additives does not seem to affect the amount of smoke and therefore is not needed.

In an ideal situation, the time to ignition and time to peak heat release increases, whereas the peak heat release rate and the total heat and smoke released decreases. It rarely happens that all of these occur, and for the most part, what follows will focus on the PHRR.

Table 3. Cone Calorimetric Data for Polyurea with Single Additives

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2221±235	---	131±8	39±5	22±6
PU+0.5% CNT	1143±45	45	138±3	27±1	13±1
PU+1%CNT	1055±160	49	150±1	28±1	8±1
PU + 3% POSS	755±41	68	139±10	25±1	8±2
PU+5% POSS	600±13	73	134±9	20±1	10±2
PU+10% POSS	577±46	74	125±4	18±2	12±1
PU+3% EG	510±103	77	115±7	9±1	22±1
PU+5%EG	488±50	78	115±1	7±1	21±2
PU+10%EG	266±31	88	59±13	10±10	21±2
PU+15%EG	378±13	83	85±13		18±3
PU+ 3%EG (mechanical)	596±33	71	118±9	11±1	10±1
PU+3%EG (ultrasonic)	599±95	71	121±11	12±2	14±2
PU+3% APP	732±38	67	137±1	16±1	12±2
PU+5% APP	710±35	68	138±5	17±1	13±4
PU+10% APP	555±18	75	129±9	14±2	11±2
PU+15% APP	466±53	79	138±8	11±2	10±1
PU+3% ZB	1421±226	36	142±14	23±5	12±1
PU+5% ZB	1465±731	34	145±16	27±6	15±1
PU+10% ZB	1310±171	41	125±12	21±5	13±1
PU+3% mel	1710±593	23	108±1	30±8	16±1
PU+5% mel	1710±431	23	124±13	36±5	16±0
PU+3% FS	1510±32	32	170±13	21±0	18±0
PU+5% FS	1377±90	38	156±1	26±3	15±1
PU+10% FS	644±67	71	156±2	15±2	16±3
PU+3% deca	1421±71	36	122±2	26±6	13±2
PU+5% deca	1266±22	43	132±3	31±3	12±2
PU+ 10% deca	1043±58	53	131±2	23±2	15±3
PU+3% Fyrol	1110±15	50	133±26	15±3	19±1

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4.3. Cone Calorimetry with Two Additive Packages

The next stage in this investigation was to combine additives to determine if the effectiveness was increased by the combination. Plots of the heat release rates vs. time are shown in Figure 2–Figure 8. In general, it is observed that the PHRR decreases as the amount of an additive increases and that the most effective combination is EG and APP. This is most apparent in Figure 8.

Figure 2. Heat Release Rate Plot for Polyurea with APP and Clay 30B
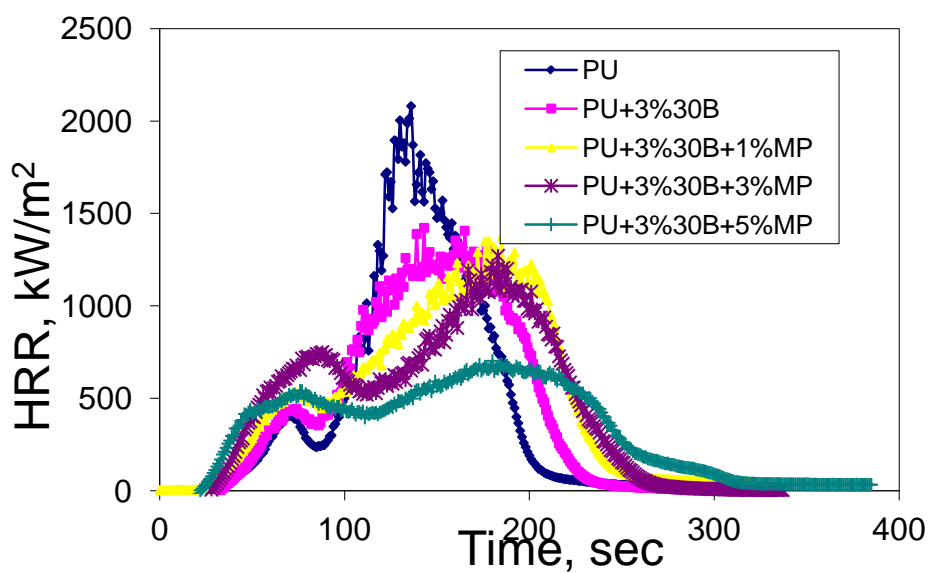
Figure 3. Heat Release Rate Plots for Polyurea with Clay 30B and Melamine Phosphate
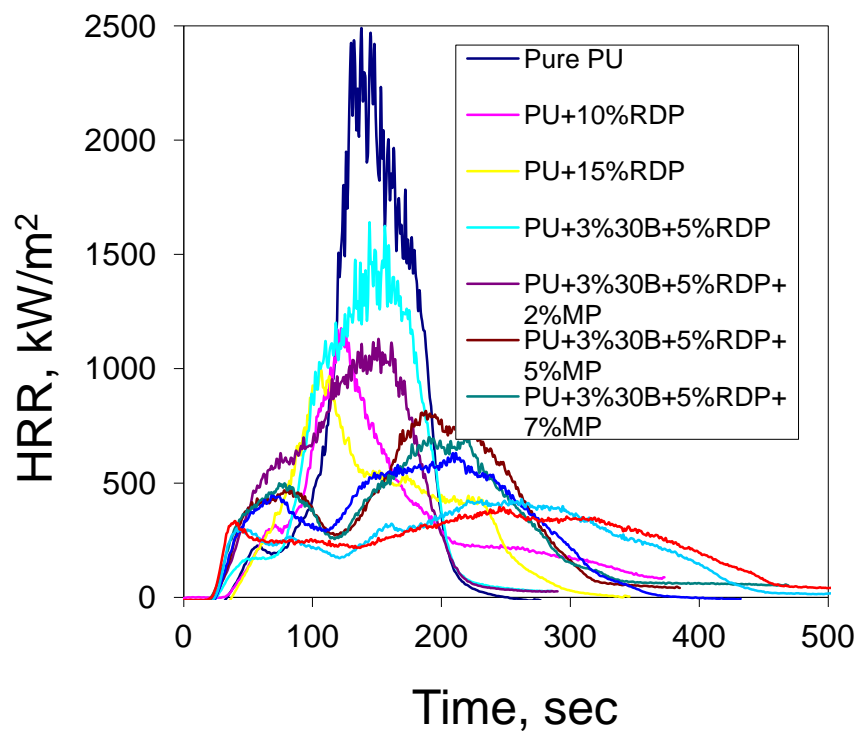
Figure 4. Heat Release Rate Plots for Polyurea with Clay 30B, Resorcinol Diphosphate and Melamine Polyphosphate
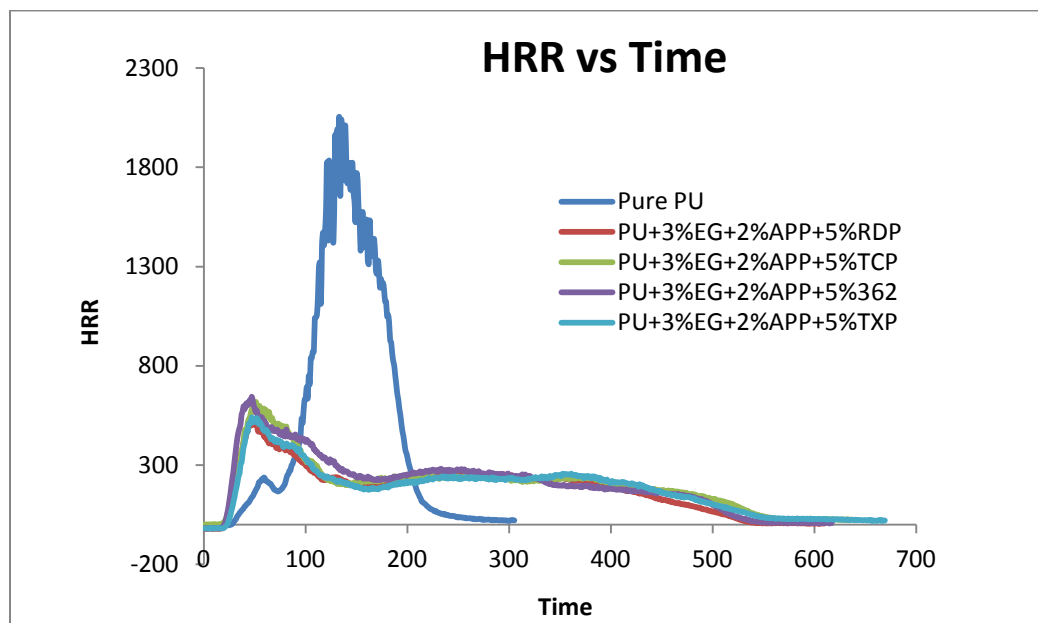
Figure 5. Heat Release Rate Plots for Polyurea with Ammonium Polyphosphate, Resorcinol Diphosphate and Tricresylphosphate

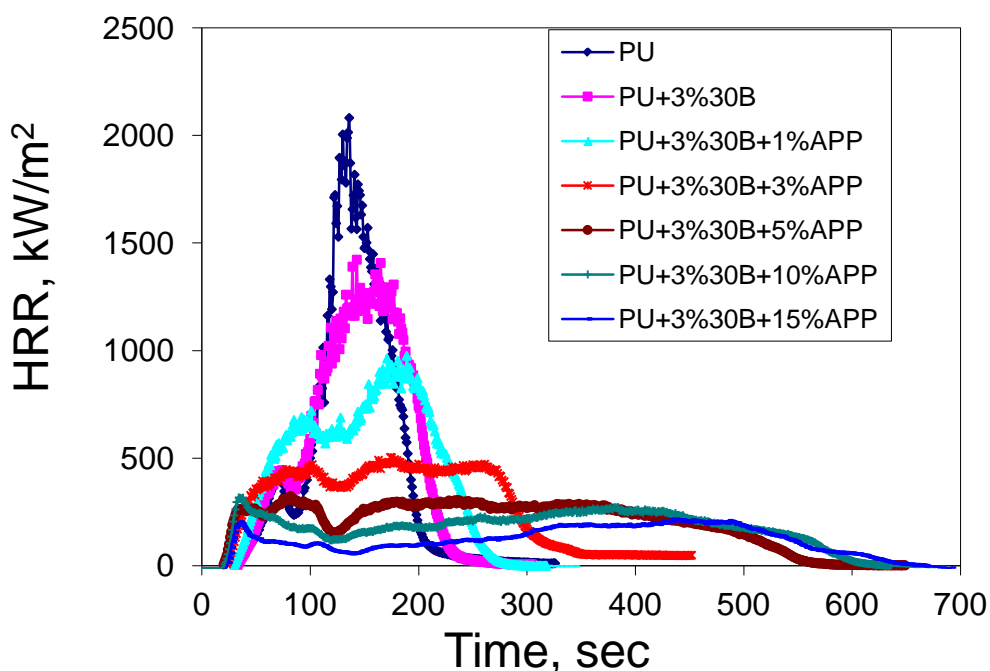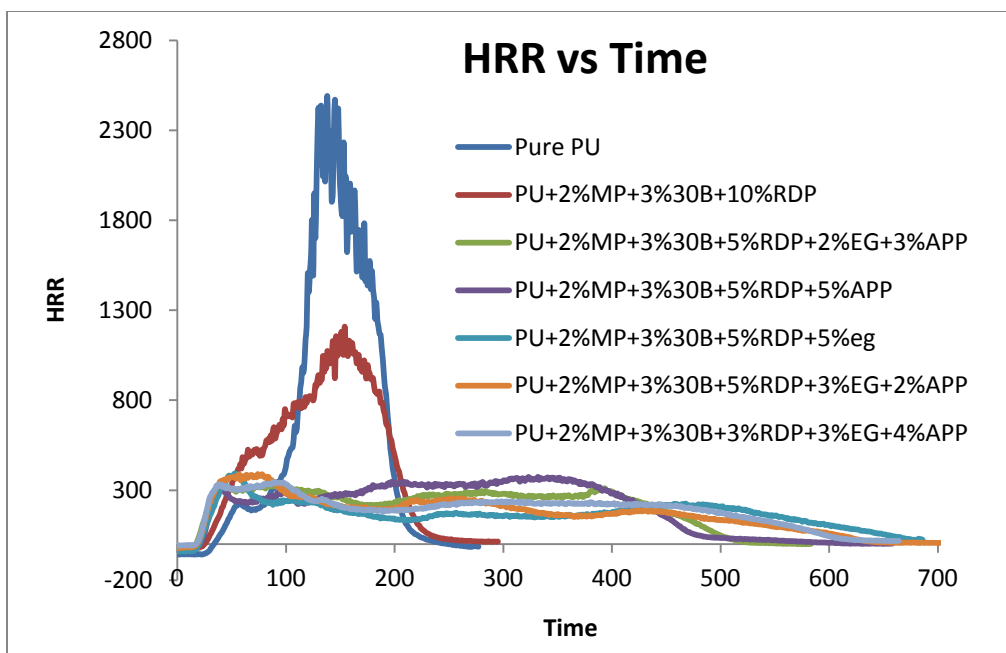**Figure 6. Heat Release Rate Plots for Polyurea with Clay 30B, Resorcinol Diphosphate, Expanded Graphite and Ammonium Polyphosphate**
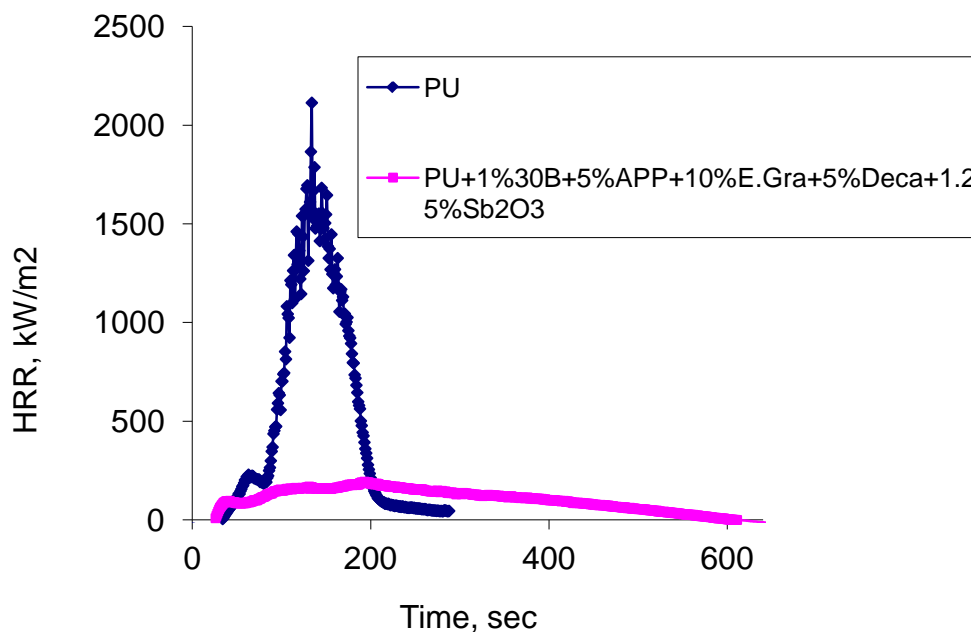
Figure 7. Heat Release Rate Plots for polyurea with Clay 30B, Expanded Graphite, Ammonium Polyphosphate, and Deca with Antimony Synergist

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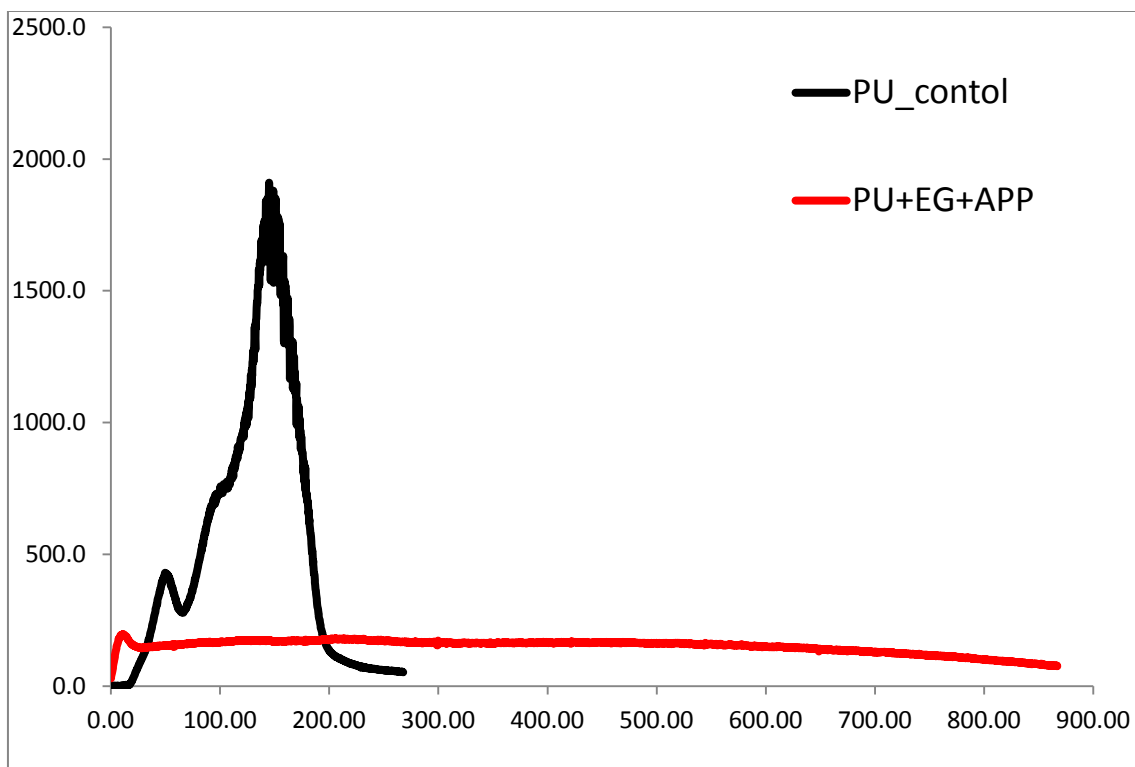
Figure 8. Heat Release Rate Plots for Polyurea and Polyurea Containing EG and APP

The composition which contained 10% APP, 10% EG and 3% layered double hydroxide clay (LDH) was evaluated by an ASTM E-84 test and the results gave a flame spread index of 105 and a smoke developed index of 200. This corresponds to a Class C rating, which is significantly better than the unclassified rating which pristine polyurea achieves. Of course, it is also not as good as is desired and means that there is room for improvement. The flame spread index which may be calculated for this composition is 117. Considering that the equation was developed for a completely different system, this seems to be pretty good agreement.

4.4. Polyurea Combined with More Than Two Additives

The composition, APP + EG + clay was the best system that we discovered during the early part of this investigation, which we then sought to improve. The reality is that we can use general knowledge of fire retardancy to come up with this system. EG is as well-known as a component of an intumescent system as APP. Because they have been used with some success in a variety of polymers, it was not difficult to identify these materials. Likewise, because the laboratory has done a lot of work using clays as fire retardants over the past twelve years, it was not difficult to realize that clay offers the advantage of drip suppression as well as fire retardancy and likely be a valuable part of the composition. The challenge was to identify additional materials that may favorably interact with APP, EG and the clay to produce a better system. A wide variety of materials were evaluated, including conventional fire retardants, novel nano-materials and whatever else that could be found that seemed to offer some possibility of success. The list of putative fire retardants that were evaluated is included as Table 1 in the experimental section of this report. Some cone calorimetric data for compositions containing various silicas is shown in

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Table 4. From the data, it is clear that the addition of silica alone, without the accompanying EG + APP is ineffective. The table also suggests that the addition of silica or titania to a filled-polyurea system does not improve the fire performance regardless of the characteristics of the silica. Table 5 shows the corresponding data for the case of fumed silica and the conclusion is similar, the addition of fumed silica has no effect on fire retardancy of a system composed of polyurea + APP + EG.

Table 4. Polyurea with Various Types of Silica

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	1932±144	--	163±3	21±8	23±2
PU+3% Aerosil 380	995±102	48	146±3	25±1	14±0
PU+3% Aerosil COK84	1103±47	43	153±5	28±1	15±0
PU+3% Aerosil R812	975±57	50	152±6	25±0	11±1
PU+3%R812+3% TiO$_2$	656±20	66	145±0	21±2	10±0
PU+10%APP+10%EG+3% R812+3%%TiO$_2$	174±15	91	122±0	22±2	10±6
PU+5% Sidistar T120D	767±68	60	151±0	23±1	21±1
PU+5% Sidistar T120U	860±0	55	142±14	25±1	20±1
PU+5% silica gel +5% Alumina	825	57	142	23	18
PU+5% graphite	1187	39	139	26	23
PU+10%APP+10%EG+3% Deca+1% Sb	399	79	125	8	16
PU+10%APP+10%EG+3% Silica gel	317	84	133	6	15

Table 5. Cone Calorimetric Data for Polyurea with Fumed Silica

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	1861±123	--	151±22	30±5	21±2
Pu+3% FS	1269±10	32	170±13	31±0	18±0
PU+5%FS	1160±90	38	156±1	26±3	15±1
PU+10%FS	548±67	71	155±2	15±2	16±3
PU+10%APP+10%EG+3%FS	267±17	86	132±2	7±0	15±2
PU+10%APP+10%EG+5%FS	228±12	88	122±1	5±0	11±0
PU+10%APP+10%EG+3%ZB+3%FS	248±54	87	126±3	7±2	13±0
PU_5%APP+5%EG+5%FS	282±2	85	142±1	8±0	12±1
PU+10%APP+10%EG+3%FS+3%POSS	333±15	82	140±3	8±1	12±0

The next set of data, shown in Table 6, covers many additives in combination with polyurea with APP and EG. The additives that have been combined here include resorcinol diphosphate (RDP), melamine polyphosphate (MP), red phosphorus (RP), boron nitride (BN), silicon carbide (SiC), aluminum nitride (AlN), and four different Cloisites (montmorillonite) clays, 30B, 15A, 10A and 93A. It can be noted that the mass loss rate does parallel the reduction in PHRR, implicating mass loss rate as the reason for the reduction in PHRR. The additives RP boron nitride, aluminum nitride, and silicon carbide bring about a relatively nominal reduction in the PHRR

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and are unlikely to be useful. Please note that in many instances, a variety of compositions have been evaluated. This is because it is known that in some instances, a material may be effective only at a certain level and much less effective at other levels. Thus, attempts have been made to sample a variety of levels to ascertain if the material can be efficacious at some level.

Table 6. Polyurea with a Variety of Additives

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2079±118	--	131±8	34±2	26±1
PU+0.2%CNT+2%EG+2%APP+1%30B	505±8	76	124±6	12±1	7±4
PU+0.2%CNT+5%EG+2%APP+1%30B	416±36	80	128±3	9±1	9±1
PU+0.2%CNT+7%EG+7%APP+1%30B	238±17	89	123±3	7±1	8±0
PU+0.2%CNT+2%EG+3%APP+3%30B+5%RDP	404±6	81	119±3	14±1	7±4
PU+0.2%CNT+2%EG+3%APP+2%30B+5%RDP+2%MP	374±44	82	117±1	12±0	9±0
PU+0.1%CNT+2%EG+3%APP+5%RDP+2%MP+1%15A	415±17	80	123±3	12±2	9±1
PU+0.1%CNT+2%EG+3%APP+5%RDP+2%MP+1%10A	438±14	79	126±12	12±1	8±1
PU+0.1%CNT+2%EG+3%APP+5%RDP+2%MP+1%93A	365±27	82	133±7	12±1	10±1
PU+5% BN	1167±87	46	135±14	39±7	12±1
PU+10%APP+10EG+5% BN	388±13	82	109±2	22±6	10±1
PU+10%APP+10%EG+3%ZB+3%BN	245±36	89	105±16	6±1	11±1
PU+5%AlN	1239±0	43	119±6	6±0	12±0
PU+10%APP+10%EG+5%AlN	348±51	84	103±2	28±4	8±1
PU+10%APP+10%EG+3%ZB+3%AlN	340±24	84	111±1	7±1	8±0
PU+5%SiC	1584±143	27	126±12	7±1	11±0
PU+10%APP+10%EG+5%SiC	293±15	86	104±3	38±1	8±1
PU+10%APP+10EG+3%ZB+3%SiC	323±22	85	118±5	5±0	9±0
PU+5%AlN+5%BN+5%SiC	1199±49	44	134±46	6±1	12±2
PU+3%RP	658±35	68	137±6	19±5	19±1
PU+10%APP+10%EG+1%RP	486±15	76	139±1	11±0	17±0
PU+3%SiO$_2$(12OU)+3%TiO$_2$	1224±191	40	160±3	28±1	13±2
PU+10%APP+10%EG+3%SiO$_2$(12OU)+3%TiO$_2$	267±1	87	124±0	4±1	11±0
PU+3%SiO$_2$(120D)+3%TiO$_2$	1365±104	33	160±7	22±9	14±1
PU+10%APP+10%EG+3%SiO$_2$(120D)+3%TiO$_2$	257±34	87	119±2	4±0	12±1
PU+5% nano	1352±199	34	163±3	18±8	9±1
PU+10% nano	998±22	51	156±6	26±1	9±1
PU+10%APP+10%EG+5% nano	190±20	91	121±4	7±6	7±1

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Table 7 shows data for some melamine containing systems. Again, it should be noted that a variety of amounts have been sampled and no efficacy has been observed.

Table 7. Cone Calorimetric Data for Polyurea with Melamine

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2
Pure polyurea (PU)	2680±506	--	113±28	40±13
PU+5%EG+5%APP+5%mel	380±4	86	107±7	11±4
PU+5%EG+10%APP+5%mel	310±4	88	102±11	9±1
PU+3%EG+5%APP+3%mel	563±46	79	111±7	9±3
PU+3%EG+10%APP+5%mel	337±6	87	96±1	9±0
PU+5%EG+3%APP+5%mel	470±28	82	110±6	9±0
PU+3%EG+5%APP+5%mel	439±23	84	110±8	11±1
PU+5%EG+10%APP+3%mel	357±39	87	118±9	9±2
PU+5%EG+3%APP+3%mel	532±26	80	122±4	9±1
PU+3%EG+3%APP+5%mel	506±38	81	107±11	10±1
PU+5%EG+5%APP+3%mel	542±12	80	123±2	9±1
PU+3%EG+10%APP+3%mel	381±9	86	110±6	11±1
PU+3%EG+3%APP+3%mel	616±33	77	114±13	10±0

The addition of zinc borate (ZB) to compositions containing APP and EG also does not improve the cone calorimetric situation, as shown in Table 8. If anything, the PHRRs are a bit higher after the addition of ZB to this system.

Table 8. Cone Calorimetric Data for PU with ZB

Formulation	PHRR, kW/m^2	% Reduct	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2014±21	--	128±6	40±4	18±2
PU+5%EG+10%APP+3%ZB	384±15	81	106±11	9±1	14±0
PU+3%EG+5%APP+5%ZB	432±18	79	107±4	10±1	13±1
PU+3%EG+5%APP+3%ZB	498±23	76	94±2	11±1	14±1
PU+5%EG+5%APP+3%ZB	456±23	78	106±1	8±1	14±0
PU+5%EG+5%APP+5%ZB	447±18	78	113±4	8±1	14±0
PU+5%EG+3%APP+3%ZB	444±11	78	114±4	9±1	14±0
PU+3%EG+3%APP+5%ZB	456±7	78	114±4	10±1	15±1
PU+3%EG+10%APP+5%ZB	372±2	82	114±4	10±1	15±1
PU+3%EG+10%APP+3%ZB	387±16	81	115±2	11±1	14±1
PU+5%EG+10%APP+5%ZB	384±16	81	114±1	8±0	14±1

The next set of data shown contains EG, APP, ZB and polyhedral oligomeric silisesquoxane (POSS). POSS is a relatively new material which has been shown to have some fire retardancy effect in some polymers[14]. Here it is used as an adjunct with the other additives and the data is shown in Table 9; it can be seen that this has little effect on the PHRR.

Table 9. Cone Calorimetric Data for Polyurea with ZB and POSS

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	1833±208	--	158±5	39±9	26±1
PU+5%EG+3%APP+3%ZB+1%POSS	421±12	77	138±3	7±1	13±1
PU+3%EG+5%APP+5%ZB+1%POSS	455±6	75	138±3	10±1	10±0
PU+5%EG+5%APP+5%ZB+3%POSS	392±42	79	134±3	7±1	13±1
PU+5%EG+3%APP+5%ZB+3%POSS	434±29	76	144±2	7±1	12±1
PU+5%EG+3%APP+5%ZB+1%POSS	382±52	79	143±2	8±2	13±1
PU+5%EG+10%APP+3%ZB+1%POSS	348±53	81	147±10	7±1	13±2
PU+5%EG+10%APP+3%ZB+3%POSS	425±40	77	149±2	8±1	12±2
PU+5%EG+10%APP+5%ZB+1%POSS	365±21	80	134±6	8±2	15±1
PU+3%EG+10%APP+5%ZB+1%POSS	323±1	82	146±1	8±0	14±1
PU+3%EG+10%APP+3%ZB+1%POSS	349±3	81	132±3	8±1	12±0
PU+3%EG+10%APP+3%ZB+3%POSS	409±23	78	136±2	9±0	12±1
PU+5%EG+5%APP+3%ZB+5%POSS	476±6	74	146±10	8±1	13±1

In the next set of experiments, the combination of carbon nanotubes (CNT) with EG and APP and a phosphorus-containing fire retardant were investigated. This set of data is shown in Table 10. All systems give a reduction in the PHRR of about 90%, which is what is obtained for the system APP + EG and thus there is no advantage from the addition of the additional materials.

**Table 10. Cone Calorimetric Data for Polyurea Containing a Combination of Materials**

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	3271±119	--	142±10	36±9	19±0
PU+0.2%CNT+2%EG+3%APP+3%30B+5%RDP	404±6	88	119±3	14±1	7±4
PU+0.2%CNT+2%EG+3%APP+2%30B+5%RDP	374±44	89	117±1	12±0	9±0
PU+0.2%CNT+2%EG+3%APP+5%RDP+2%MP	415±17	87	123±3	12±2	9±1
PU+0.2%CNT+2%EG+3%APP+5%RDP+2%MP	438±14	87	126±12	12±1	8±1
PU+0.2%CNT+2%EG+3%APP+5%RDP+2%MP	365±27	89	133±7	12±1	10±1
Pure PU	1859±218	--	135±30	31±12	24±2
PU+10%EG+10%APP+3%ZB+3%M+3%POSS	228±27	88	119±1	4±1	12±2
PU+10%EG+10%APP+3%ZB+5%M	208±34	89	127±4	6±2	17±0
PU+10%EG+10%APP+5%ZB+3%M	215±35	88	124±3	6±1	15±0
PU+10%EG+10%APP+3%ZB+3%M	190±12	90	131±6	5±0	14±1
PU+10%EG+10%APP+3%ZB+5%M+0.2%CNT	183±0	90	114±3	5±2	11±1
PU+10%EG+10%APP+3%ZB+3%M+0.2%CNT	213±14	89	112±2	5±1	11±1
PU+10%EG+10%APP+3%ZB+3%M+3%POSS+02.%CNT	235±18	87	129±12	7±1	10±0
PU+10%EG+10%APP+5%ZB+3%M+0.2%CNT	192±18	90	115±3	4±1	10±2
PU+10%EG+10%APP+3%ZB+3%M+3%POSS+0.2%CNT	209±21	89	120±0	5±2	10±1

4.4.1. ASTM E-84 Testing on the Best Composition

The best composition at this stage contained 10% EG and 2% APP. This composition was tested by the E-84 protocol and the Flame Spread Index was 50 with a Smoke Developed Index of 300. This is a solid Class B performance. This test used a sprayable polyurea; in a previous test, using the castable polyurea, the Flame Spread Index was 105 with a Smoke Developed Index of 200. Both of these are Class B performance. If one takes these at face value, which is difficult with a test which has not been reproduced, one may think that the sprayable polyurea has a better FSI while the castable polyurea has a better SDI. Any differences between these two systems is likely due to the differences in structure; the sprayable polyurea is aliphatic while the castable polyurea is aromatic. The comparison of the two is shown in Section 4.5.1.

4.5. Polyurea Combined with Intumescent Paints

The next series of experiments evaluated a variety of intumescent coatings. This data is shown in Table 11–Table 14. It should be noted from this that the efficacy in fire retardancy is quite dependent on the thickness with thin coating offering somewhat minimal fire protection. It was stated above that the intumescent paints are what is currently used but it is unknown at what thickness it is used. The long term stability of the intumescent paint, especially to scrubbing is unknown but one may guess that the thickness will decrease over time. Figure 9 shows a plot of heat release rate vs. thickness and demonstrates that a minimum thickness of about 1.5 mm is required.
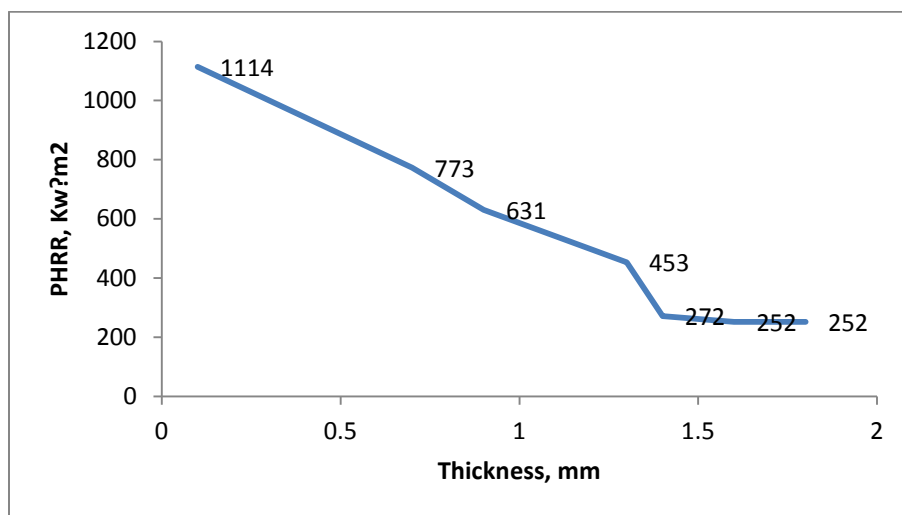
Figure 9. PHRR vs. Thickness for Polyurea with an Intumescent Paint

It is notable that the THR increases when the coating is applied, which means that some of the coating burns. This does not seem to have a deleterious effect on its performance as the PHRRs are significantly decreased. The increase in time to ignition for the water-based intumescent paint, shown in Table 12, is striking and looks at first glance as if it were in error. In fact, this is the correct data and the addition of the water-based paint makes it much more difficult to ignite the material. However, once it ignites, it burns away and the entire polymer is consumed.

Table 11. Solvent-Based Intumescent Paint on Polyurea

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2800±218	--	128±8	45±3	19±3
PU+0.1mm	1114±60	60	130±7	23±1	15±1
PU+0.7mm	773±53	72	121±17	22±1	15±2
PU+1.4mm	272±33	90	146±4	9±1	5±1
PU+1.6mm	252±7	91	160±6	9±1	6±1
PU+1.8mm	252±10	91	175±5	8±1	5±1

Table 12. Water-Based Intumescent Paint on Polyurea

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2599±211	--	141±8	47±4	14±2
PU+0.5mm	613±51	76	126±4	12±2	28±30
PU+2.2mm	485±30	81	150±1	8±3	155±35
PU+2.7mm	335±40	87	159±3	11±1	365±45

Table 13. Polyurea with Fire-Free Intumescent Paint

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2599±211	--	141±8	47±4	14±2
PU+1.5mm	594±15	77	141±5	8±1	11±1
PU+2.5mm	316±10	88	155±4	8±1	13±1
PU+3 mm	251±30	90	156±21	7±0	13±3

Table 14. Polyurea with Fire Stop Intumescent Paint

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea (PU)	2076±57	--	138±33	29±13	16±1
PU+0.9 mm	460±55	78	128±10	11±5	82±15
PU+1.1 mm	365±24	82	149±11	8±1	27±30
PU+2.3 mm	254±11	88	162±1	7±3	144±9
PU+2.5 mm	226±49	89	157±7	7±5	81±14

4.5.1. Sprayable Polyurea with Intumescent Paints

The data that has been reported so far in this report is entirely for the castable polyurea. However, it is the sprayable material that has been evaluated by the blast tests and will be evaluated further by the ASTM E-84 protocol. Thus, it is necessary to compare these two materials. The data for three different intumescent paints on a sprayable polyurea, known commercially as Dragon Shield and produced by SPI, is shown in Table 15. The reductions in the PHRR is quite comparable to those seen for the castable polyurea but the THRs are much lower for this system; the sprayable polyurea do not have as high an energy content as does the

castable material, which is probably related to the aliphatic nature of the sprayable and aromatic character of the castable. Flame stop intumescent paint gives the largest time to ignition.

Table 15. Intumescent Paint on Dragon Shield

Formulation	PHRR, kW/m^2	% Red	THR, MJ/m^2	AMLR, g/sm^2	TTI, s
Pure polyurea	1821±324	--	73±8	30±5	10±1
Flame stop 1 mm	281±46	85	67±4	9±1	155±47
Flame stop 2.5 mm	151±33	92	73	5±1	190±23
Fire free 3 mm	218±1	88	87±1	7±1	22±0
Fire free 4.5 mm	142±14	92	100	6±1	20±4
Fire free 5 mm	87±12	95	88	4±1	70±41
Flame control 2.2 mm	271	87	92±3	6±1	6
Flame control 5mm	172±17	91	95±32	5±1	5

4.6. Polyurea Combined with Intumescent Paint and Additives

The combination of the intumescent paint with the additives package that has been developed in this project offers no advantage over either of these separately, as is shown in Figure 10. The heat release rate curves completely overlap for all. We rationalize that if there is an intumescent event on the surface, this cannot be improved by another intumescent event that occurs within the bulk of the polymer.
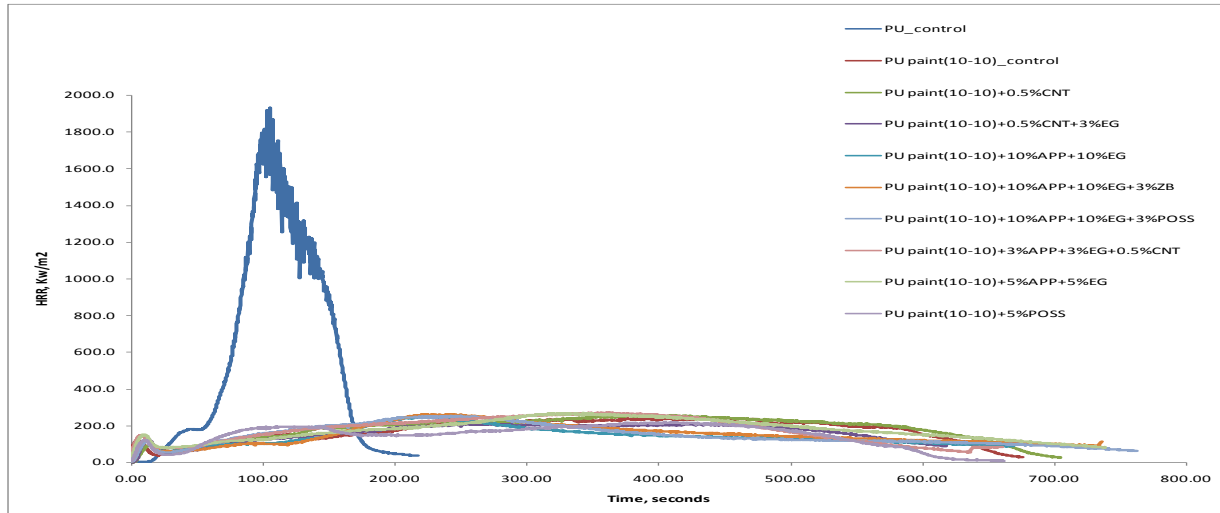
Figure 10. Heat Release Rate Curves for Polyurea, Polyurea with an Intumescent Paint, Plyurea with the Additive Package and polyurea with both the Intumescent Paint and Additive Package

## 4.7. Polyureas Combined with Some Novel Additives

It has been noted earlier in this report that several novel additives have been prepared in this laboratory for evaluation in polyurea. Since these are all materials that have not been commonly

used in fire retardancy, it was first necessary to evaluate these in common polymers with which we already have a lot of background information to see if these can be useful at all. The additives that have been studied include MoS_2, CdS, LDH-MMT, cucurbit[6]uril (CB[6]), CeO_2 and α-zirconium phosphate (ZrP). This latter material is the only for which background information has already been developed and therefore is the only material which has reached the stage where it could be evaluated in polyurea. In addition, the caged additive CB[6] has been evaluated in polyurea. The others have been dispersed in simpler polymers, polystyrene and poly(methyl methacrylate), and it is only now, when the funding for this project has expired, that we are able to determine if they show any efficacy in polyurea. Publications on MoS_2, CeO_2, CB[6]and LDH-MMT in these simpler polymers are in the process of submission and will acknowledge support from the Air Force. Because these polymers have shown some efficacy in the simpler polymers, it is expected for them to be incorporated in polyurea for further testing in order to determine if they can be useful.

4.7.1. α-Zirconium Phosphate (ZrP) in Polyurea

Here, the report covers ZrP in polyurea and the heat release rate plot is shown in Figure 11. It can be seen that the addition of ZrP to an EG+APP system is a little more effective than APP alone. Thus, there may be some advantage to using this as part of the additive package, but further work must be done to discover the most effective proportion.
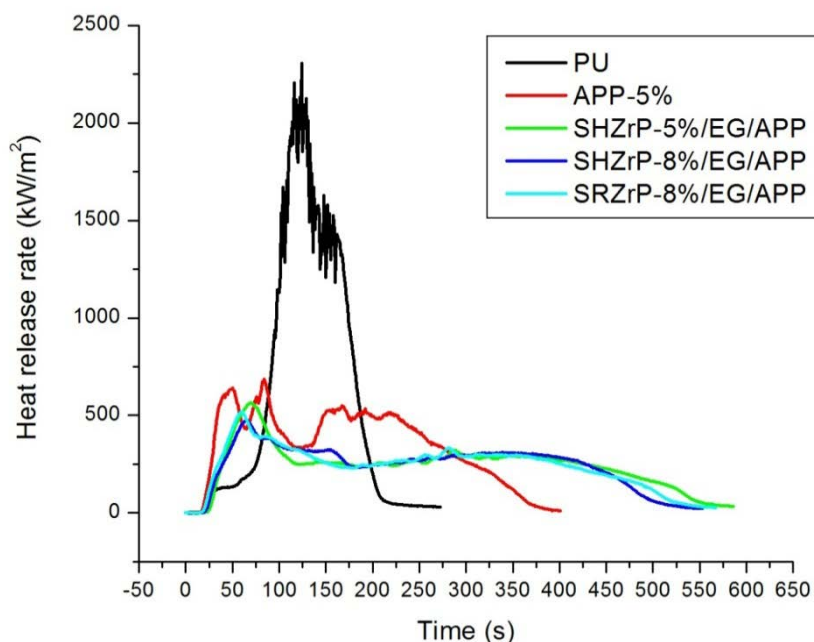

Figure 11. Heat Release Rate Plots for Polyurea with ZrP and EG+APP

4.7.2. Cucurbit[6]uril (CB[6]) in Polyurea

CB[6] is a novel cage structure which is capable of trapping amines and ammonium salts; many different cage sizes may be produced but for this study the cage size 6 was chosen. The original idea was that the use of CB[6] would enable the formation of a better-dispersed nano-dimensional material in a polymer and that this would enhance the fire retardancy. One can also look at the CB[6] structure and feel that it is possible that this cage structure might be able to

produce char and enhance char formation of polyurea. The structure is shown in Figure 12. Synthesis was carried out following a modified literature procedure and this was then combined with polyurea in the normal fashion.
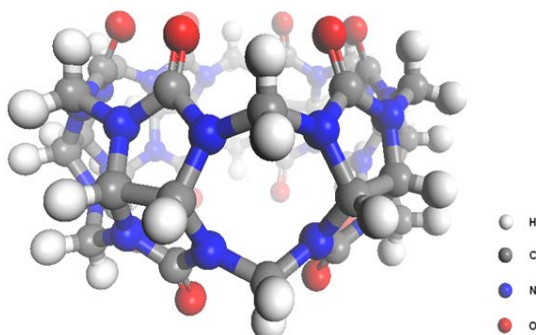
Figure 12. Structure of CB[6]

The original intention had been to cage an ammonium salt within the CB[6] cage in order to render the ammonium salt more hydrophobic so that it could more effectively combine with a polymer to produce a nanocomposite. It was necessary to study pristine CB[6] as a control to compare with a clay which was modified with a CB[6]-caged surfactant. Surprisingly, the pristine CB[6] had some effectiveness as a fire retardant. The plots of heat release rate for polyurea containing CB[6], as well as CB[6] with APP are shown in Figure 13. It is clear that CB[6] is about as effective as APP in reducing the PHRR and that the combination may be slightly improved. This combination is certainly not as effective as is the combination of EG and APP, but has the potential to be worth further investigation.
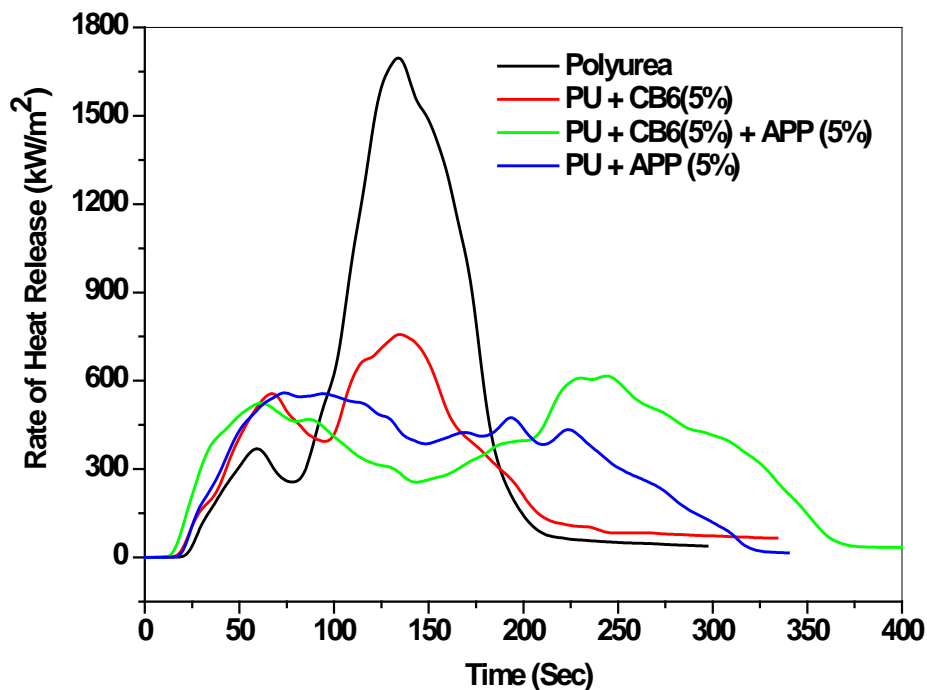
Figure 13. Heat Release Rate Plots of polyurea containing CB[6] as well as CB[6] with APP

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4.7.3 Use of these Novel Additives in Other Polymers

The novel additives noted above have been little used in fire retardancy. Additionally, polymers like polyurea are difficult to work with and have a very limited amount of available data. For these reasons, it was more useful to evaluate the additives in common polymers, PS and PMMA. By combining the additives with PS and PMMA, it was possible to compare the difference in material characteristics to readily-available data. A number of publications will result from this work, but since they do not have any effect now on the fire retardancy of polyurea, no further information will be provided here.

5. CONCLUSIONS

A wide variety of additives have been combined with polyurea and a considerable improvement in fire retardancy has been obtained for a composition which contains 10% EG and 2% APP. This composition gives a peak heat release rate of approximately 100 kW/m^2 in the cone calorimeter and a Class B rating in the ASTM E-84 protocol. This is comparable to what has been obtained for the commercially-used intumescent paints and has the advantage of easier application and more durability. Despite numerous attempts with many additives, higher rating improvements were not achieved.

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LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

30B, 10A, 15A, 93A	Cloisites
Å	Angstrom
AFM	atomic force microscopy
AMLR	average mass loss rate
AlN	aluminum nitride
Antimony	antimony oxide, Sb_2O_3
APP	ammonium polyphosphate
ASTM	American Society of Testing Materials
ATH	aluminum trihydroxide
BDP	bisphenol A diphosphte
BN	boron nitride
CB[6]	cucurbit[6]uril
CNT	carbon nanotubes
Deca	decabromodiphenyl oxide
DMA	dynamic mechanical analysis
DMMP	dimethyl methyl phosphonate
DSC	differential scanning calorimetry
EG	expandable graphite
FS	fumed silica
ft	foot
FTIR	Fourier Transform Infrared Spectroscopy
g/sm^2	gram per second per square meter
HRR	heat release rate
Hz	hertz
in	inch
kV	kilovolt
kW/m^2	kilowatts per meter squared
LDH	layered double hydroxides
M	melamine
ma	milliampere
MC	melamine cyanurate
MCC	microcone calorimetry
MJ/m^2	nega joules per square meter
ml	milliliter
mm	milimeter
MP	melamine polyphosphate
μg	microgram
N/m	Newton per meter
Nano	a proprietary SPI material
PHRR	peak heat release rate
POSS	polyhedral oligomeric silisequioxanes
PTFE	polytetrafluoroethylene
PU	polyurea
RDP	resorcinol diphosphate
RP	red phosphorus

s	seconds
SiC	silicon carbide
SPI	Specialty Products Incorporated
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TGA/FTIR	thermogravimetric analysis coupled to infrared spectroscopy
THR	total heat released
TPP	triphenylphosphate
TTI	time to ignition
TXP	trixylphosphate
V	Volt
ZB	zinc borate
ZrP	α-zirconium phosphate