

## Non-Halogenated, Non-Styrenated Flame Retardant Composites

by

Aaron C. Small, Luna Innovations Incorporated  
Thomas Plaisted, Luna Innovations Incorporated  
Frances Davis, Luna Innovations Incorporated  
Lisa Sterner, Luna Innovations Incorporated

### Abstract

It has previously been demonstrated that superabsorbent polymers, SAPs, can be loaded with inexpensive inorganic phosphates as the flame retardant component in composite systems.<sup>1</sup> The resulting microsphere flame retardants dramatically improved flame exposure when blended with common matrix resins (unsaturated polyester and vinyl ester resins) for pultrusion applications.<sup>2</sup> The microsphere flame retardant produces no halogen or sulfur byproducts on thermal decomposition, and generates less smoke than conventional halogenated polymers. There is a common belief that switching from a styrenated resin system to a non-styrenated blend may further improve the smoke generation and smoke toxicity properties such that the specifications found in Navy standard DDS 078-2 may be met. The fire, smoke, and mechanical performance have been characterized for a number of non-styrene systems with the microsphere flame retardants, including epoxies, polyureas, and urethane acrylates, in order to verify this assumption.

### Background

In FRP composite materials, fillers and halogenated resins are the most common methods used to achieve flame resistance. Toxic fumes released during the combustion of halogenated resins can be lethal in the confined spaces found in aircraft fuselages or marine hull compartments. New Naval standards governing the smoke toxicity preclude the use of brominated vinyl esters and halogenated fire retardant additives almost entirely for below deck naval applications. Highly filled composites (such as those filled at 50% by weight or greater with flame retardant) do not meet the structural requirements for most applications and are also unsuitable for replacing steel. For composites to become more widely used in applications traditionally requiring steel

and aluminum for strength and fire performance, non halogenated solutions must be found that allow the composite to retain excellent mechanical properties while meeting stringent fire, smoke, and toxicity (FST) requirements.

A number of approaches are currently being developed for this challenging goal. Materials such as nanoclays, carbonaceous nanomaterials, borates, silicates, and phosphates are currently in development. Phosphorus based fire retardants are attractive from the standpoint of cost and their char forming nature. By forming a char layer, smoke generation and overall toxic gas evolution can conceivably be reduced over the time scale of the test. Compatibility however is a problem with phosphate materials since many polymeric materials, organic solvents, and organic reactive monomers are not polar enough to dissolve or interact well with a material that is ionic in nature. Through the use of superabsorbent polymers, a new non-halogenated flame retardant additive for composite resins is being developed that possesses finely dispersed phosphate (or borate or silicate) materials in a polymer compatibilizer. Typical SAPs include polyacrylates, polyacrylamides and poly(vinyl alcohol)s and have previously been demonstrated as flame retardants in thermoplastic polymers.<sup>3</sup> A polyacrylate type SAP was blended with polyethylene and an improvement in flame resistance was reported. SAPs have also been used as flame barriers in firefighter clothing.<sup>4</sup> Luna Innovations has advanced this technology for application to thermosetting and fiber reinforced composite systems.<sup>5</sup>

Previously, the efficacy of the SAP based flame retardant has been demonstrated as applied to a variety of resins used in fiber reinforced polymer composites and processed through a hand lay-up/vacuum bag processing.<sup>6</sup> Lab scale pultrusion trials were also conducted to determine processability.<sup>7</sup> SAP based flame retardants are effective in improving the fire resistance of commercial unsaturated polyester, vinyl ester, urethane hybrid, and epoxy resins through these processes and others. The composite materials demonstrate good mechanical properties and fire resistance, and are processable using current equipment. In the current work we report on the FST properties for non-styrenated systems such as epoxies, polyureas, and urethane modified acrylic resins.

### Experimental

Acrylic is a commercially available modified acrylic resin; PolyU is a commercially available polyurea; Ep/Am is a commercially available amine cured epoxy system; Ep/Anh is a commercially available anhydride cured epoxy system; XEP/An is an experimental anhydride cured epoxy system; VE is a Bisphenol A type

styrenated vinyl ester resin; PE is an isophthalic acid based styrenated polyester resin; FR is a flame retardant superabsorbent polymer prepared as described below; APP is commercially available ammonium polyphosphate; Clay is montmorillonite clay; Br additive is decabromodiphenyl oxide; Zinc borate and ATH were used as received from commercial suppliers.

#### *Synthesis of flame retardant microspheres*

Flame retardant polyacrylamide microspheres were synthesized using a single step inverse emulsion polymerization technique in a 650 gallon reactor. The resulting solid was milled to an average particle size of 13 microns.

#### *Preparation of flame retardant resin and composites*

The SAP flame retardant microspheres were combined with commercial resins using a high speed mixer. In epoxy samples, the flame retardant was blended with the A side (epoxy side).

Clear cast polyurea samples were prepared in a square polyethylene mold. Specimens were allowed to cure for 2-4 days at room temperature, followed by 6 hours at 100 °C. Composite laminates were prepared using commercially available resin combined with the SAP flame retardant microspheres. Epoxy laminates were produced by either hand lay up followed by vacuum bagging or by compression molding. Laminate sequences were consistent within a series and post cured per manufacturer's recommendations. Other laminates were fabricated by pultrusion. Laminates were pultruded through a 0.3175cm x 15.24 cm die using a combination of roving, continuous strand mat, and woven mat in a proprietary sequence. Die temperatures ranged from 104°C - 148°C. Panels prepared via pultrusion were not subjected to a post cure schedule prior to FST characterization.

#### *Characterization*

##### *UL94 - Horizontal Burn Test*

The horizontal burn test is used to calculate the linear burning rate of polymer materials. Three samples were tested for repeatability. The samples were marked with two lines, one 25mm and one 100mm from the end to be ignited. The samples were clamped at the end farthest from the 25mm mark with the longitudinal axis horizontal and the transverse axis inclined at an angle of 45°. A Bunsen burner supplied with propane gas was used as the torch. The burner was adjusted to produce a blue flame with a height of 20mm. The flame was applied to the free end of the sample to a depth of 6mm for 30 seconds. The flame was removed after 30 seconds or when the combustion front reached the 25mm mark. The timing was started when the combustion front reached the 25mm mark. The time for the combustion front to travel between the 25mm mark and the 100mm mark and

the damaged length is recorded. If the sample does not burn to the 25mm mark the damaged length is zero. The linear burning rate,  $V$ , for each sample is calculated using the equation  $V = 60 L/t$ .  $L$  is the damaged length in millimeters and  $t$  is time in seconds.

##### *UL94 – Vertical Burn Test*

The samples were conditioned according to ASTM D 618 for 48 hours. The samples were clamped with the longitudinal axis vertical and the lower end 300mm above a layer of cotton. The burner was adjusted to a flame height of 20mm. The flame was then applied to the sample for 10 seconds and the afterflame time,  $t_1$ , is recorded. The flame is applied for an additional ten seconds and the afterflame time,  $t_2$ , is recorded as well as the afterglow time,  $t_3$ . Also recorded are whether the sample burns all the way to the clamp and whether the cotton is ignited.

##### *FST Properties*

Cone calorimetry was conducted per ASTM E 1354. Radiant panel testing was performed per ASTM E 162-02a or per ASTM E 1317. Smoke toxicity testing was performed per ASTM E 800. Optical smoke density was determined by ASTM E 662.

## **Results and Discussion**

Fire retardant polymer microspheres were synthesized by an inverse emulsion polymerization in a 325 kg yield. The resulting material was characterized by optical microscopy, percent phosphorus, and particle size analysis after milling. The average particle size of the current formula is approximately 10-15 microns with a phosphorus content of 10%. This manufacturing method represents a significant advance in commercial viability of the flame retardant microspheres by reducing the cycle time by well over 50%. The addition of 20-30% FR microspheres to any resin system tested was found to extinguish burning almost immediately after the torch was removed from the casting thus its performance was similar to that of material from the two step process used in previous studies.<sup>7</sup>

Pultrusion of the modified acrylic resin was conducted as the first large scale attempt at incorporating the flame retardant microspheres into a non halogenated system. Previously the flame retardant microspheres had been demonstrated in epoxy systems, but only in small castings suitable for evaluation by UL-94 and cone calorimetry.<sup>6</sup> As in previous studies, choice of the pultrusion process was mainly driven by the nature of the parts to be produced (continuous cross-sections, such as beams and panels). Table 1 summarizes the resin component of each pultrusion trial. The laminate sequence was kept constant throughout in order to have comparable samples. The flame retardant load levels were determined through a design of experiment in the lab, and the mini-

imum additive level that produced a V-0 rating with burn times of less than 5 seconds were selected for pultrusion. After pultrusion, the panels were tested by UL-94 to determine how they compared to lab produced samples. As expected, the control was not rated vertically. The three flame retardant specimens gave very good vertical burn results.

Smoke generation is of utmost importance in confined spaces, such as below ship decks. Bulkhead materials, doors, and even shipping and storage containers must have low smoke generation values if they are to be used in naval vessels. Results of smoke testing from the modified acrylic resin pultrusion testing are summarized in Table 2 and compared to previously reported results for two styrenated systems. ASTM E 662 was performed at 25 kW of irradiance. In both flaming and non flaming mode, smoke density values of less than 2 were observed for all samples at the 1.5 minute mark. After 4 minutes of testing, smoke generation is still very low in both modes. The maximum smoke density values are much better than the flame retardant microspheres with either vinyl ester or polyester,<sup>2</sup> and significantly better than a brominated VE/glass combination previously reported.<sup>8</sup>

One of the main advantages to using the flame retardant SAP microspheres is their lack of halogenated materials. This is very important in confined spaces where low smoke toxicity and generation values are required. Select results of smoke toxicity testing can be found in Table 2. Only values for CO and NO<sub>x</sub> are presented since other toxins sampled for were not present in significant levels. The CO values for all four samples are at least 30% better than those reported for either polyester or vinyl ester with the flame retardant microspheres.<sup>2</sup> All four samples containing the acrylic resins system meet the toxic gas concentration requirements put forth by the Navy in standard DDS 078-02.

Cone calorimetry is another method useful for screening materials in how they may compare to each other for FST properties. Generally cone calorimetry is performed at 4 levels of radiant heat flux: 25kW (small class A fire); 50kW (large trash can fire); 75kW (significant fire/room fire); and 100kW (pool oil fire).<sup>8</sup> The results of 0.3175 cm panels are presented in Table 3 for 50 kW and 75 kW testing. 50 kW and 75 kW flux levels were chosen for comparison since these most closely approximate tests such as ASTM E-84. No trend can really be determined from the testing within the sample set. Addition of flame retardant did not improve ignition time, nor did it affect peak heat release rate or smoke generation significantly. Ignition times were a bit lower than those previously reported on 0.3175 cm thick panels of vinyl ester and polyester<sup>2</sup> and of a brominated vinyl ester/glass combination reported in the literature at 25 and 75kW.<sup>9</sup> This suggests these may have better per-

formance in fire testing such as flame spread. Specific extinction area values were much better than polyester, vinyl ester, or brominated vinyl ester, and this is borne out in the ASTM E662/800 data reported in Table 2.

Flame spread and surface flammability can be evaluated by methods such as radiant panel (ASTM E 162) or lateral ignition flame travel methods (such as ASTM E 1317 or E 1321). Results from ASTM E 162-02a can be found in Figure 1 for the 4 samples produced in the pultrusion trial as well as the 0.3175 cm thick vinyl ester and polyester samples previously reported. The flame spread index (FSI) was higher than desired in all four cases with the modified acrylic resin, with values of 40-75 as opposed to the 10-15 obtained for vinyl ester and polyester samples.<sup>2</sup> The fire retardants did improve the properties over the control, although not as much as expected based on the UL-94 vertical burn results from Table 1. The ASTM E-162 data seems to correlate with the cone calorimetry data for ignition time from Table 2 in that it predicts the vinyl ester and polyester may outperform the modified acrylic with respect to fire resistance.

A second set of specimens was fabricated from commercially available polyurea (PolyU). Polyureas have both military and commercial applications, such as for impact resistant coatings (truck bed liners). Polyurea would also be considered closer to a 100% solids system unlike the modified acrylic resin, which is non-styrenated but does contain reactive volatile monomer. On exposure to fire during a UL-94 vertical burning test, polyurea castings burn readily and drip. Supplier recommended loading levels of a brominated additive were used and compared to various non halogenated flame retardants (clay, flame retardant microspheres, and ammonium polyphosphate). Castings were tested per ASTM E 1354. From Figure 2 it is evident that any of the flame retardant additives reduced the peak heat release rate by at least 65%. Figure 3 suggests that the flame retardant microspheres, clay, and combinations of the two are effective at reducing smoke generation against the control whereas the brominated additive contributed additional smoke density (as expected).

Based on the success of the flame retardant microspheres in reducing the peak heat release rate and smoke generation in a 100% solids system, three epoxy systems with the potential for pultrusion were evaluated in order to determine if the FST results for the modified acrylic system could be surpassed. Table 4 summarizes the experimental design where lab produced reinforced laminates were generated for testing. The three epoxy systems were evaluated against the modified acrylic resin for direct comparison. Sample 5 was designed to approximate the blend used in the pultrusion trial (Acrylic/FR in Tables 1-3). Zinc borate was evaluated as a synergist again due to its minimal effect on viscosity at the 10% load level.

Cone calorimetry screening results are also summarized in Table 4. As before with the modified acrylic system (as well as vinyl ester and polyester), the flame retardant microspheres are not showing an effect on peak heat release rates, but did show a significant effect on the smoke generation by reducing the SEA value over the control by 40%. The anhydride cured systems also performed better than the amine cured system with respect to smoke generation, but at best were comparable to the modified acrylic resin.

## Conclusions

In order to meet the stringent FST requirements of DDS 078-02, a non-halogenated flame retardant combined with either a non-styrenated or 100% solids resin system is the best composites approach. The modified acrylic resin should meet the smoke density and smoke toxicity requirements, but the samples produced to date do not meet the flammability requirements. Due to the large amount of black smoke generation from styrenated resin systems, it is anticipated based on these results neither vinyl ester nor polyester will meet the smoke density requirements of DDS 078-02. The flame retardant microspheres are more effective in a system without reinforcement (as seen in the polyurea sample set). This has been previously observed and may suggest the flame retardant microspheres are suitable for coating and cast polymer applications. The FR microspheres offer an advantage with respect to processability in that the loading level is lower than a corresponding load of ATH. Further work characterizing the FST and physical properties of the epoxy systems is currently being conducted, as well as studies on the synergistic effects of the FR microspheres with other non halogenated flame retardants such as ATH and zinc borate.

## Acknowledgements

Results presented here were supported by the following funding agencies: Naval Sea Systems Command under Contract No. N00024-06-C-4101; Naval Sea Logistics Center-Mechanicsburg under Contract No. N65538-07-M-0102; Naval Surface Warfare Center-Crane Division under Contract No. N00164-07-C-6067; and Missile Defense Agency Contract No. HQ0006-07-C-7624. All pultrusion trials were carried out at Strongwell (Bristol, VA) under the aforementioned programs. ASTM E 662, ASTM E 800, ASTM E 162-02a and ASTM E 1354 were conducted at Southwest Research Institute (San Antonio, TX). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the U.S. Navy, the Missile Defense Agency, Strongwell, or Southwest Research Institute.

**Author(s):**

Aaron C. Small is a Senior Research Scientist at Luna Innovations Incorporated receiving his B.S. in Chemistry from SMU and his Ph.D. in Organic Chemistry from The University of Michigan.

Lisa Sterner is an Associate Scientist in the Advanced Materials Group at Luna Innovations Incorporated. She received her B.S. in Environmental Science at Virginia Tech.

Thomas Plaisted is a Senior Research Engineer at Luna Innovations Incorporated. He received his Ph.D. in Material Science and Engineering from the University of California, San Diego.

Frances Davis is a Research Associate in the Advanced Materials Group at Luna Innovations Incorporated. Frances has a B.S. degree in Engineering, Science, and Mechanics from Virginia Tech.

---

<sup>1</sup> A.C. Small, M. Rogers, L. Sterner, T. Amos, and A. Johnson, "A Novel Non-Halogenated Flame Retardant for Composite Materials", *Composites Research Journal*, **1**, 12, (2007).

<sup>2</sup> A.C. Small, T. Plaisted, M. Rogers, F. Davis, and L. Sterner, "A Non-Halogenated Flame Retardant Additive for Pultrusion", *Composites Research Journal*, **2**, 15, (2008).

<sup>3</sup> J. Sheu and J. Meeks, "Methods for flame-retarding and products produced therefrom", *U.S. Pat. 6,290,887* (2001).

<sup>4</sup> J. Reilly, W. Grilliot, M. Grilliot, "Protective pad for protective garment", *U.S. Pat. 6,317,889* (2001).

<sup>5</sup> M.E. Rogers, P. Deschatelets, J.P. Phillips, "Flame retardant thermoset resins and methods for making the same", *U.S. Pat. 7,001,942* (2006).

<sup>6</sup> M. Rogers, A. Small, T. Amos, A. Johnson, and L. Sterner, "A New Flame Retardant Additive for Polymeric Composites", *SAMPE 2006*, (May 2006).

<sup>7</sup> A.C. Small, M. Rogers, L. Sterner, T. Amos, and A. Johnson, "A Novel Non-halogenated Flame Retardant for Composite Materials", *ACMA-Composites 2006*, (October 2006); A.C. Small, M. Rogers, L. Sterner, T. Plaisted, and F. Davis, "A Non-Halogenated Flame Retardant Additive for Thermoset Composites", *SAMPE 2007* (June 2007).

<sup>8</sup> U. Sorathia, "Fire Performance of Composites", *SAMPE 2006* (May 2006).

<sup>9</sup> U. Sorathia and I. Perez, "Navy R&D Programs for Improving the Fire Safety of Composite Materials", in *Fire and Polymers IV*, C. Wilkie and G. L. Nelson Eds. (2006).

## Figures and Tables

**Table 1: Composition and Results of UL-94 Vertical and Horizontal Burn Tests, Modified Acrylate Pultrusion Trial**

Sample ID	FR micro-spheres (%)	Second FR	FR #2 Loading (%)	Material Classification	V (mm/min)*
Control Acrylic	-	-	-	Not Rated	0
Acrylic/FR	30	-	-	V-0	0
Acrylic/FR/ATH	20	ATH	20	V-1	23
Acrylic/FR/ZnB	20	Zinc Borate	10	V-1	0

\* Average of Samples

**Table 2: Select Results of ASTM E 662 (Flaming and Non Flaming) and FTIR smoke toxicity (ASTM E800) Modified Acrylate Pultrusion Trial<sup>†</sup>**

Sample	Test	4 Min. D <sub>s</sub>	D <sub>s</sub> Max	CO (ppm)	NO <sub>x</sub> (ppm)
Control Acrylic	662F/800	17	87	420	110
	662NF	13	130		
Acrylic/FR	662F/800	43	150	560	105
	662NF	14	190		
Acrylic/FR/ATH	662F/800	22	170	500	ND*
	662NF	17	190		
Acrylic/FR/ZnB	662F/800	30	140	500	150
	662NF	10	140		
VE/FR	662F/800	230	340	1330	90
	662NF	5	401		
PE/FR	662F/800	68	239	815	85
	662NF	9	344		

\*ND – Not detected during testing of the sample set

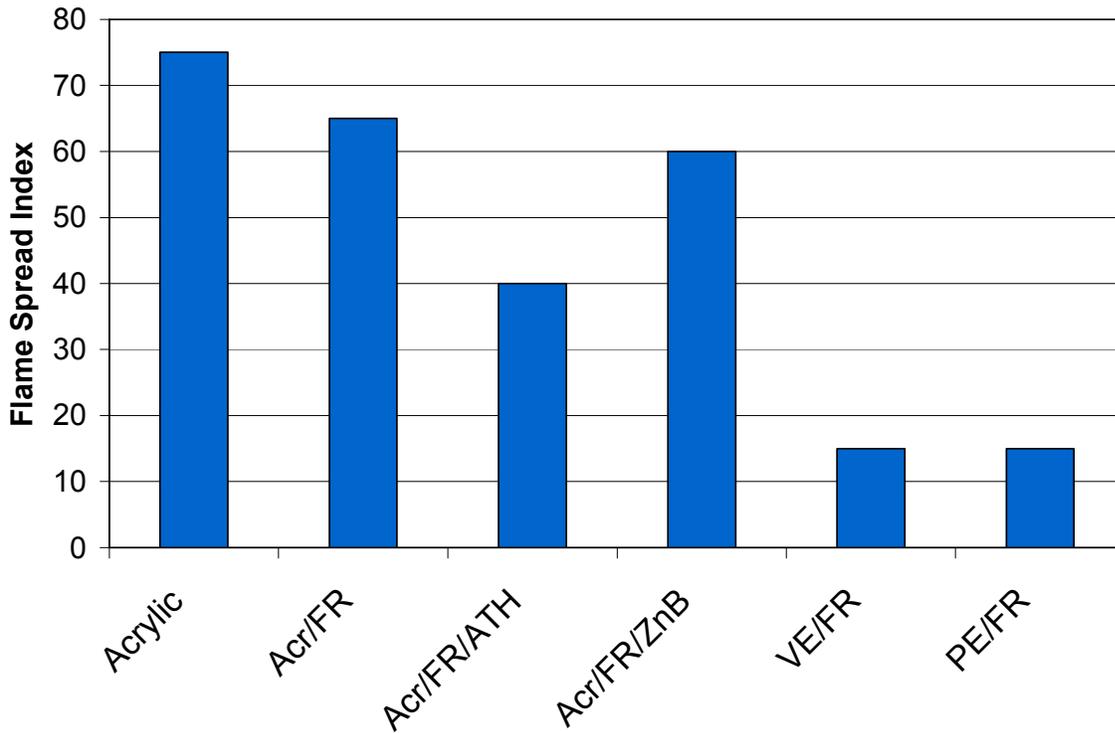
<sup>†</sup> Data for VE/FR and PE/FR taken from reference #2

**Table 3: Select ASTM E 1354 Results for 0.3175 cm Pultruded Panels from Modified Acrylate Pultrusion Trial**

Sample	Flux (kW/m <sup>2</sup> )	T <sub>ig</sub> (sec)	HRR <sub>peak</sub> (kW/m <sup>2</sup> )	SEA (m <sup>2</sup> /kg)
Control Acrylic	50	26	269	452
	75	16	335	514
Acrylic/FR	50	36	265	555
	75	16	314	593
Acrylic/FR/ATH	50	32	234	456
	75	17	290	545
Acrylic/FR/ZnB	50	37	266	457
	75	18	321	542
VE/FR <sup>†</sup>	50	63	272	904
	75	37	341	1229
PE/FR <sup>†</sup>	50	62	253	650
	75	35	304	965

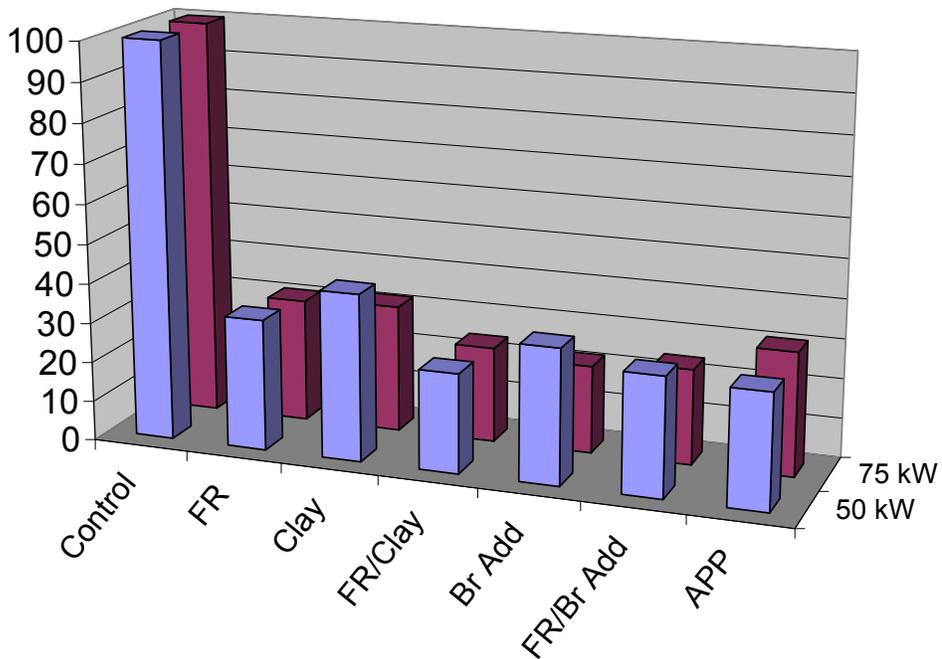
<sup>†</sup> Data for VE/FR and PE/FR taken from reference #2

**Figure 1-**  
**ASTM E 162-02a Results for 0.3175 cm Pultruded Panels from Modified Acrylate Trial Compared to Previously Reported Data for 0.3175 cm Vinyl Ester and Polyester with FR microspheres**

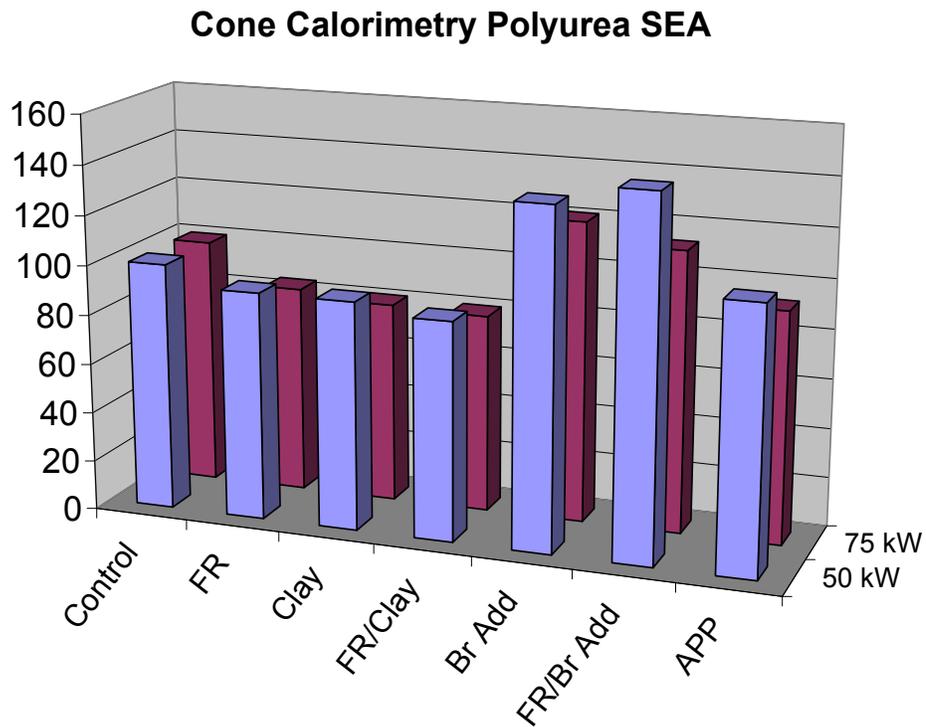


**Figure 2-**  
**ASTM E 1354 Peak Heat Release Rate Results for Polyurea Samples (Percent Change vs. Control)**

**Polyurea Cone Calorimetry PHRR**



**Figure 3-  
ASTM E 1354 Specific Extinction Area Results for Polyurea Samples (Percent Change vs. Control)**



**Table 4: Select ASTM E 1354 Results Epoxy and Modified Acrylate Study (50 kW heat flux)**

Sample ID	Resin	Luna FR Loading (%)	Zinc Borate Loading (%)	T <sub>ig</sub> (sec)	HRR <sub>peak</sub> (kW/m <sup>2</sup> )	SEA (m <sup>2</sup> /kg)
5	Acrylic	30	-	51	271	517
6	Acrylic	35	-	47	198	459
7	Ep/Am	-	-	47	295	1347
8	Ep/Am	35	-	50	245	812
9	Ep/Am	25	10	82	265	869
10	Ep/Anh	-	-	62	279	1038
11	Ep/Anh	35	-	24	335	679
12	Ep/Anh	25	10	39	225	683
13	XEp/Anh	-	-	58	234	1012
14	XEp/Anh	35	-	27	241	609
15	XEp/Anh	25	10	21	262	501