A Non-Halogenated Flame Retardant Additive for Pultrusion

Aaron C. Small, CCT-M, Thomas Plaisted, Martin Rogers, Frances Davis and Lisa Sterner, Luna Innovations Incorporated

Abstract
Flame retardants are incorporated into polymeric materials either as additives or reactive materials. Inorganic fillers and halogenated resins are the most common methods used to achieve flame resistance in fiber reinforced polymer (FRP) composite materials. Inorganic fillers, such as alumina tri-hydrate (ATH), are blended with the resin prior to fiber impregnation at relatively high levels, often presenting problems of poor compatibility, leaching, and reduced mechanical properties. Halogenated monomers, resins, and additives cause problems with smoke toxicity, making them unsuitable for many naval and transportation applications. It has previously been demonstrated that superabsorbent polymers, SAPs, can be loaded with inexpensive inorganic phosphates as the flame retardant component in composite systems. The resulting SAP flame retardants dramatically improved flame exposure when blended with common matrix resins (epoxy, unsaturated polyester and vinyl ester resins) at relatively low levels. The SAP flame retardant produces no halogen or sulfur byproducts on thermal decomposition and generates less smoke than conventional halogenated polymers. The fire, smoke, and mechanical performance of this novel FR material has been characterized on 0.3175 cm - 0.635 cm flat strip pultruded composites and the processability in both polyester and vinyl ester resin systems has been evaluated.

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Introduction
Flame retardants are incorporated in FRP composites to achieve a desired fire resistance. Flame retardants suppress combustion by acting either through the vapor phase or the condensed phase by chemical and/or physical mechanisms. Lu and Hammerton provide an excellent summary of common types of flame retardants and their fire suppressing mechanisms:[1]

Fillers dilute the polymer and reduce concentration of decomposition gases.
**Hydrated fillers** release non-flammable gases or decompose endothermically to cool the pyrolysis zone at the combustion surface.

**Halogen, phosphorus and antimony** act in the vapor phase by a radical mechanism to interrupt the exothermic processes and to suppress combustion.

**Phosphorus** also acts in the condensed phase to promote char formation, creating a barrier to inhibit gaseous products from diffusing to the flame and shielding the polymer from heat and air.

**Intumescent materials** swell when exposed to fire or heat to form a porous foamed mass acting as a barrier to heat, air and pyrolysis products.

In FRP composite materials, fillers and halogenated resins are the most common methods used to achieve flame resistance. Fillers such as alumina trihydrate release water upon heating. Other fillers, such as phosphates, may form glasses and increase char yield. However, such fillers must be incorporated in high amounts and have a negative effect on mechanical properties. Brominated polyester and vinyl ester resins are known to perform well in fire conditions and in some cases exhibit very low peak heat release rates. Halogenated resins also have clear disadvantages, particularly the toxic hydrogen halide formed during combustion.[1] Toxic fumes released during the combustion of halogenated resins can be lethal in the confined spaces found in aircraft fuselages or marine hull compartments. For below deck naval applications, the smoke toxicity specifications preclude the use of brominated vinyl esters almost entirely.

Flame retardants may be incorporated into polymeric materials either as additives or as reactive materials. Additive type flame retardants are widely used by blending with polymeric materials. In FRP resins, the flame retardant additive is blended into the resin prior to fiber impregnation. Additives present problems including poor compatibility, leaching and reduced mechanical properties. Reactive flame retardants have been created in an attempt to overcome these problems through copolymerization of the flame retardant with the polymer either prior to thermosetting (during base resin synthesis), or in some cases during thermosetting if the reactive flame retardant can function as a reactive monomer. Copolymerized flame retardants are designed not to leach or reduce mechanical properties. At this time, most copolymerized flame retardants are based on halogenated monomers with the aforementioned problems of toxicity.

Through the use of superabsorbent polymers, a new non-halogenated flame retardant additive for composite resins is being developed. The flame retardant additives are based on common superabsorbent polymer (SAP) materials which are capable of absorbing 2-10 times their weight in water. Typical SAPs include polyacrylates, polyacrylamides and polyvinyl alcohols. SAPs have been applied as flame retardants in thermoplastic polymers.[2] 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.[3] Luna Innovations has advanced this technology for application to thermosetting and fiber reinforced composite systems.[4]

Previously, Luna has demonstrated the efficacy of the SAP based flame retardant when processed through a hand lay-up/vacuum bag processing into a variety of resins used in FRP composites.[5] Preliminary pultrusion trials were also conducted to determine process-ability.[6] 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 additional fire, mechanical, and electromagnetic properties of pultruded and hand lay-up composites containing the SAP based flame retardant.

**Experimental**

Resin #1 (used in the samples designated as 1A and 1B) is a bisphenol A type vinyl ester in styrene monomer; Resin #2 (used in samples 2A-2C) is a one pack styrenated proprietary urethane hybrid blend used for high performance low profile pultrusion applications; Resin #3 (used in sample designations 3A and 3B) is an isophthalic based unsaturated polyester resin in styrene monomer used for pultrusion applications; Resin #4 (used in samples 4A-4C) is a toughened bisphenol A type vinyl ester in styrene monomer; Resin #5 is a brominated vinyl ester resin in styrene monomer; FR is a flame retardant superabsorbent polymer prepared as described below, either in laboratory 20L reactors or on a 136 kg scale at a contract production facility.

*Synthesis of polyacrylamide microspheres*

Polyacrylamide microspheres were synthesized using
an inverse emulsion polymerization technique. The monomer solution was made by combining acrylamide monomers with a crosslinking agent in deionized water. A water soluble initiator was added to the monomer solution. An emulsion reactor was set up containing toluene and small amount of surfactant. The monomer solution was added to the emulsion reactor through an addition funnel over a period of one hour. The reaction was then stirred vigorously for 4 hours to consume all of the monomer. The particles were then isolated, washed with acetone and dried.

**Preparation of SAP flame retardant**
The dried SAP microspheres were combined with a water solution containing an inorganic phosphate. The SAP microspheres absorbed the water solution and the water was subsequently removed by a drying process to yield the dry SAP flame retardant powder. The SAP flame retardant was passed through a sieve to remove agglomerates.

**Preparation of flame retardant resin and composites**
The SAP flame retardant microspheres were combined with commercial resins using a high speed mixer. Cast resin samples were prepared in molds by curing the resin with a combination of benzoyl peroxide initiator and dimethylaminoline catalyst. Post-curing was performed at 120 - 150°C for two hours.

Composite laminates were prepared using commercially available resin combined with the SAP flame retardant microspheres. Laminates were produced by hand lay up followed by vacuum bagging. Eight plies of E-Glass weave fabric (820 gsm, 0/90°) were used as the reinforcement. The panels were post cured at 150°C for two hours. The fiber content was 54% by weight. Other laminates were fabricated by pultrusion. Laminates were pultruded through a 0.3175 cm x 15.24 cm die with the following construction: surfacing veil, two 643 gsm biaxial/CSM plies, 40 - 113 yield rovings, two 643 gsm biaxial/CSM plies, and surfacing veil. Panels prepared via pultrusion were not subjected to a post cure schedule prior to physical testing or other 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 were 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 $V = \frac{60L}{t}$. 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, $t_1$, was recorded. The flame was applied for an additional ten seconds and the afterflame time, $t_2$, was recorded as well as the afterglow time, $t_3$. Also recorded were whether the sample burned all the way to the clamp and whether the cotton was ignited.

**Mechanical, Fire, and Electromagnetic Properties**
Flexural properties of clear castings and reinforced laminates were determined using ASTM D 790-00. Tensile properties and elongation values of clear castings and reinforced laminates were determined using ASTM D 638-01. Compressive properties of clear
cast and fiber reinforced laminates were determined using ASTM 695-96. Resin and glass contents for reinforced samples were determined using ASTM D 2584-02. Cone calorimetry was conducted per ASTM E 1354. Radiant panel testing was performed per ASTM E 162-02a. Smoke toxicity testing was performed per ASTM E 800 or BSS 7239 methods. Optical smoke density was determined by ASTM E 662 or BSS 7238. Shielding Effectiveness (or insertion loss) values were determined per ASTM D 4935-99 over the frequency range of 60 MHz-2GHz.

Results and Discussion

Super absorbent polymer microspheres are synthesized by an inverse emulsion polymerization. The resulting materials are characterized by optical microscopy and particle size analysis. The average particle size of the current formula is approximately 10-20 microns. Afterwards, they are further converted into the flame retardant microsphere (referred to as “FR” in the tables below) and dried. Upon drying, the FR microspheres are ready for incorporation into resins by simple blending as with any filler. In addition to particle size analysis and optical microscopy, both TGA and a custom clear cast burn test are carried out to ensure the quality of the material, as well as phosphorus analysis at an outside laboratory. 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.

Pultrusion was targeted as the first potential production scale processing method for incorporation of the FR microspheres into thermoset resin systems. This was mainly driven by the nature of the parts to be produced (continuous cross-sections, such as beams and panels); however, it was also easier to work with a process that allows for a resin mixture with a wide viscosity range and no room temperature gel time that requires adjustment. As previously reported, 6 blends of Resin 2 with the FR microspheres were processed on a 0.3175 cm thick die resulting in a neutral colored panel (Figure 1). A simple test of the flame retardant behavior was conducted by applying the inner cone of a propane torch to the face for 1 minute. After removal of the torch, the face extinguished immediately with very little damage or heat transfer to the backside (Figure 2). This is due to the formation of a char layer on the exposed surface which assisted in dissipating the heat and preventing heat penetration through the 0.3175 cm panel. Comparison of physical properties for samples with FR loading levels between 20 and 30% showed little variation in strength and modulus (Tables 1 and 2). Because of the polymer nature of the flame retardant microspheres (as opposed to a mineral filler such as ATH), there was a possibility that relatively small changes in loading levels would affect the properties, much as tougheners and low profile additives can.

A second set of specimens were fabricated at Strongwell using pultrusion in order to fabricate sufficient samples for analyzing by numerous fire test methods. Two general styrenated resin types (vinyl ester and unsaturated polyester) were pulled at two different thicknesses: 0.3175 cm (1A, 3A) and 0.635 cm (1B, 3B). The die for the pultrusion was a basic rectangular cross-section. Table 3 summarizes the level of FR microsphere loading and thickness for each pultrusion specimen type. Laminates were a combination of CSM and rovings similar in make up to the first set of pultrusion experiments. Mechanical properties of the 0.3175 cm panels were compared to brominated polyester pulled with the same laminate sequence and found to be comparable.

UL-94 horizontal and vertical burn data is presented in Tables 4 and 5. UL-94 data is useful in pre-screening candidates for further flame spread testing in methods such as ASTM E 162-02a and ASTM E 84.
As seen from the UL-94 data, the samples had very low ignitability. Consequently, specimens were sent for evaluation by other fire test methods required for qualification of fire retardant composites in a number of applications.

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. Currently, brominated vinyl esters are used in most naval applications. These resins, however, generate significant quantities of dense, toxic smoke and thus cannot be used without a coating system. Results of smoke testing from the second round of pultrusion testing are summarized in Table 6. ASTM E 662 and BSS 7238 are performed at 25 kW of irradiance and it is obvious that in non flaming mode, this is not enough to produce ignition in the sample at the 4 minute sample mark. In flaming mode, however, the samples do not perform as well, and in all cases the maximum smoke density is higher than desired, although still better than a brominated VE/glass combination reported.[7]

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 7. Only values for CO and NOx are presented since other toxins sampled for were not present in significant or detectable levels. The samples containing the FR microspheres meet the toxic gas concentration requirements put forth by the IMO FTP Code and Bombardier SMP 800-C with respect to testing in 25 kW flaming and non flaming modes for carbon monoxide; however CO levels are above the limits specified by Airbus Industrie ABD 0031 for a number of the samples.[8] The primary target for the study however was a carbon monoxide level of less than 600 ppm per the Navy standard DDS 078-2. BSS 7239 is not an acceptable test for U.S. Navy applications, and thus the CO levels were above the target specification for both vinyl ester and polyester as determined by E 800. There are also no required levels of NOx compounds in DDS 078-2 so all other smoke toxicity requirements were met by the FR microsphere combinations.

To better determine the performance of the FR microspheres, a third pultrusion trial was carried out with vinyl ester Resin #4 in three combinations: 1) containing no fire retardant (4A); 2) with 50% by weight ATH (4B); and 3) with 30% by weight FR microspheres (4C). An additional sample consisting of the same laminate sequence and die thickness was made with a brominated vinyl ester resin, designated as Resin #5 (5A). A comparison of smoke data in Table 8 shows the ATH modified sample outperformed the rest in both flaming and non-flaming mode. The FR microsphere sample performed second best in flaming mode since the mechanism for fire retardancy requires a flame to form the char layer. The brominated vinyl ester (Resin #5) was by far the worst performing sample, as expected. In Table 9, the FR microsphere outperformed the ATH and brominated sample (Resin #5) with respect to both carbon monoxide and halogenated byproducts in smoke toxicity testing. Although it did not quite meet the 600 ppm cap for CO, the FR microsphere sample was very close to the required level for this particular resin system. Although the Resin #4 control provided the best smoke toxicity with respect to DDS 078-2, it was also highly flammable and was not rated by UL-94 whereas the two FR containing combinations of Resin #4 had been rated V-0 in prescreen testing.

Cone calorimetry is another method useful for screening materials in how they may perform in structural fire tests, such as ASTM E-84. 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).[7] The results of 0.3175 cm panels are presented in Table 10 and the 0.635 cm pultruded specimens in Table 11. One trend that is evident from the table is the FR microsphere/PE combination seemed to perform much better in this test method than the FR microsphere/VE combination. Ignition times were comparable to those of a brominated vinyl ester/glass combination reported in the literature at 25 and 75kW.[9] Specific extinction area values were better for the FR microsphere panels, but peak heat release rates were inferior to the brominated VE laminate.

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 3 for the 4 samples produced in the second pultrusion trial. The FSI (flame spread index) was satisfactory in all four cases, with values of 10-15 in all cases. These values meet all naval requirements
for topside and below deck materials, for which values of less than 25 are required.

For commercial shipping applications, and even some DoD shipping situations, the ability to read RFID tags on container contents is important from the standpoint of inventory control and logistics. Such instances require the container walls to have low insertion loss (or shielding) much like a radome would. Values as close to zero as possible in the frequency range of interest are desired. Obviously, this precludes the use of carbon fiber or metals in the container walls. Resin and additives, though, can also affect RF transparency in composites, and thus a number of resin specimens from the pultrusion trials were screened for insertion loss to determine the effect of the FR microspheres (if any) on the electromagnetic properties of the composite.

Figures 4 and 5 plot the data obtained for various 0.3175 cm and 0.625 cm pultruded panels against aluminum foil and monolithic carbon fabric containing panels. This technique involves determining the shielding effectiveness or radio frequency transparency of a base material (flat panel or coupon) using an insertion-loss method.[10] The flat, thin sample is irradiated with an electromagnetic wave over the frequency range of interest. The method uses a coaxial transmission line with an interrupted inner conductor and a flanged outer conductor. The sample is placed between the flanges in the middle of the cell. Sample 418-3A was a square of 0.25mm thick aluminum foil with a purity of 99.45%. Samples 418-3B and 418-3C correspond to 1A and 3A from Table 4, respectively. Samples 418-3D and 418-3G were cut from panels fabricated during initial pultrusion trials performed with Resin 2. Samples 418-3E and 418-3F correspond to 3B and 1B from Table 4, respectively. Sample 418-J consisted of a single ply of 200 gsm carbon fiber/epoxy on each side of a 0.635 cm ply of closed cell urethane foam. Sample 418-3K consisted of roughly 0.51 cm of monolithic 12K carbon fiber unidirectional fiber and epoxy resin. The samples and their corresponding materials are summarized in Table 12 for ASTM D 4935-99. The aluminum and carbon samples were known to shield and were utilized as controls.

In the two plots (Figures 4 and 5) for ASTM 4935-99, it is evident that only the carbon fiber containing samples (the black lines) and the aluminum foil (the red line in each plot) had significant insertion loss by this test method and thus would not be the best choice for an RFID transparent container or structure. The FR/glass containing laminates exhibited less than 5 dB of

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**Figure 3: ASTM E 162-02a Results for 0.3175 cm and 0.625 cm Pultruded Panels from Second Trial**

**Figure 4: ASTM D 4935-99 Results for 0.3175 cm Pultruded Panels from First and Second Trials**

**Figure 5: ASTM D 4935-99 Results for 0.635 cm Pultruded Panels from First and Second Trials**
insertion loss regardless of resin or fabrication method. In order to determine whether or not the E-glass laminates would be truly suitable, radiated field measurements over the frequency range of interest would be required. The FR microspheres are not expected to contribute significantly to insertion loss based on this screening method.

Conclusions

A new flame retardant for composite resins has been identified and shown effective in various thermoset resin classes utilized in pultrusion. The flame retardant is based on SAP microspheres containing inexpensive phosphorus compounds. The SAP flame retardant mixes readily into epoxy, urethane hybrid, polyester, and vinyl ester resins producing pultruded materials with ratings up to V-0 per the UL-94 method. Flame Spread Indices as low as 10 as determined by ASTM E 162-02a have been demonstrated in both 0.3175 cm and 0.635 cm panels. The pultruded panels evaluated to date have low smoke toxicity, and lower smoke index values than brominated vinyl esters. The resins are also expected to be RFID transparent based on results from ASTM D 4935-99. Further work characterizing the physical properties of the new flame retardant pultruded composites, as well as more complex fire testing (such as ASTM E 1317) and environmental testing is currently being conducted.

References

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   Ogunsola, A. “Harmonization of Shielding-Effectiveness Standards for Enclosures”.

Acknowledgements

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See Tables next page
### Table 1: Pultruded Resin Properties, 0°

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<thead>
<tr>
<th>Property</th>
<th>Blend 2A</th>
<th>Blend 2B</th>
<th>Blend 2C</th>
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<tr>
<td>% FR</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>Comp. Str. kpsi (MPa)</td>
<td>74.7 (515)</td>
<td>76.1 (525)</td>
<td>74.1 (511)</td>
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<tr>
<td>Comp. Mod. Mpsi (GPa)</td>
<td>3.80 (26)</td>
<td>3.95 (27)</td>
<td>3.95 (27)</td>
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<tr>
<td>Tensile Str. kpsi (MPa)</td>
<td>49.6 (342)</td>
<td>55.2 (381)</td>
<td>44.6 (308)</td>
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<td>Tensile Mod. Mpsi (GPa)</td>
<td>4.05 (28)</td>
<td>4.03 (28)</td>
<td>3.97 (27)</td>
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<tr>
<td>Perp. Shear kpsi (MPa)</td>
<td>10.2 (70)</td>
<td>10.1 (70)</td>
<td>10.9 (75)</td>
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<td>Short Beam Shear kpsi (MPa)</td>
<td>6.01 (41)</td>
<td>6.92 (48)</td>
<td>7.17 (49)</td>
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### Table 2: Pultruded Resin Properties, 90°

<table>
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<tr>
<th>Property</th>
<th>Trial 2A</th>
<th>Trial 2B</th>
<th>Trial 2C</th>
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<tr>
<td>Comp. Str. kpsi (MPa)</td>
<td>21.7 (150)</td>
<td>20.7 (143)</td>
<td>21.3 (147)</td>
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<td>Comp. Mod. Mpsi (GPa)</td>
<td>1.28 (8.8)</td>
<td>1.38 (9.5)</td>
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<td>Tensile Str. kpsi (MPa)</td>
<td>6.83 (47)</td>
<td>8.73 (60)</td>
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<td>Tensile Mod. Mpsi (GPa)</td>
<td>1.20 (8.3)</td>
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<td>Perp. Shear kpsi (MPa)</td>
<td>12.4 (85)</td>
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<td>Short Beam Shear kpsi (MPa)</td>
<td>2.85 (20)</td>
<td>3.91 (27)</td>
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<tr>
<td>Water Absorp. (%)</td>
<td>.34</td>
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<td>.27</td>
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<tr>
<td>Density (mg/m³)</td>
<td>1.74</td>
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### Table 3: Second Pultrusion Experiment

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<th>Sample ID</th>
<th>Resin Type</th>
<th>Thickness</th>
<th>FR Loading (%)</th>
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<tr>
<td>1A</td>
<td>Resin 1</td>
<td>0.3175 cm</td>
<td>25</td>
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<tr>
<td>1B</td>
<td>Resin 1</td>
<td>0.635 cm</td>
<td>25</td>
</tr>
<tr>
<td>3A</td>
<td>Resin 3</td>
<td>0.3175 cm</td>
<td>25</td>
</tr>
<tr>
<td>3B</td>
<td>Resin 3</td>
<td>0.635 cm</td>
<td>25</td>
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Table 4: Results of UL-94 Horizontal Burn Tests, Second Pultrusion Trial

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Resin</th>
<th>FR Loading (%)</th>
<th>V (mm/min)*</th>
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<tr>
<td>1A</td>
<td>Resin 1</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>1B</td>
<td>Resin 1</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>3A</td>
<td>Resin 3</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>3B</td>
<td>Resin 3</td>
<td>25</td>
<td>0</td>
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* Average of Samples

Table 5: Results of UL-94 Vertical Burn Tests, Second Pultrusion Trial

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<th>Sample ID</th>
<th>Resin</th>
<th>FR Loading (%)</th>
<th>Material Classification</th>
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<tr>
<td>1A</td>
<td>Resin 1</td>
<td>25</td>
<td>V-0</td>
</tr>
<tr>
<td>1B</td>
<td>Resin 1</td>
<td>25</td>
<td>V-0</td>
</tr>
<tr>
<td>3A</td>
<td>Resin 3</td>
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<td>V-1</td>
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<tr>
<td>3B</td>
<td>Resin 3</td>
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<td>V-0</td>
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Table 6: Results of ASTM E 662 (Flaming and Non Flaming) and BSS 7238, Second Pultrusion Trial

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>4 Min. D₅</th>
<th>D₅ Max</th>
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<tr>
<td>1B</td>
<td>662F</td>
<td>76</td>
<td>295</td>
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<tr>
<td>1B</td>
<td>662NF</td>
<td>1</td>
<td>353</td>
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<tr>
<td>1A</td>
<td>662F</td>
<td>230</td>
<td>340</td>
</tr>
<tr>
<td>1A</td>
<td>662NF</td>
<td>5</td>
<td>401</td>
</tr>
<tr>
<td>1A</td>
<td>7238</td>
<td>129</td>
<td>247</td>
</tr>
<tr>
<td>3B</td>
<td>662F</td>
<td>46</td>
<td>368</td>
</tr>
<tr>
<td>3B</td>
<td>662NF</td>
<td>2</td>
<td>344</td>
</tr>
<tr>
<td>3A</td>
<td>662F</td>
<td>68</td>
<td>239</td>
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<tr>
<td>3A</td>
<td>662NF</td>
<td>9</td>
<td>344</td>
</tr>
<tr>
<td>3A</td>
<td>7238</td>
<td>112</td>
<td>274</td>
</tr>
</tbody>
</table>

Table 7: Select Results of ASTM E 800 (Flaming) and BSS 7239 Tests, Second Pultrusion Trial

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>CO (ppm)</th>
<th>NOₓ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1B</td>
<td>800</td>
<td>1260</td>
<td>155</td>
</tr>
<tr>
<td>1A</td>
<td>800</td>
<td>1330</td>
<td>90</td>
</tr>
<tr>
<td>1A</td>
<td>7239</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>3B</td>
<td>800</td>
<td>1425</td>
<td>145</td>
</tr>
<tr>
<td>3A</td>
<td>800</td>
<td>815</td>
<td>85</td>
</tr>
<tr>
<td>3A</td>
<td>7239</td>
<td>100</td>
<td>40</td>
</tr>
</tbody>
</table>
**Table 8: Select Results of ASTM E 662 (Flaming and Non Flaming) for Resin 4 and 5 Pultrusion Trial**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>1.5 Min. $D_x$</th>
<th>4 Min. $D_x$</th>
<th>$D_{x_{Max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>662F</td>
<td>20</td>
<td>300</td>
<td>340</td>
</tr>
<tr>
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<td>662NF</td>
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<td>3.6</td>
<td>190</td>
</tr>
<tr>
<td>4B</td>
<td>662F</td>
<td>0</td>
<td>11</td>
<td>110</td>
</tr>
<tr>
<td>4B</td>
<td>662NF</td>
<td>0</td>
<td>4.7</td>
<td>140</td>
</tr>
<tr>
<td>4C</td>
<td>662F</td>
<td>3.5</td>
<td>110</td>
<td>240</td>
</tr>
<tr>
<td>4C</td>
<td>662NF</td>
<td>0</td>
<td>3.5</td>
<td>300</td>
</tr>
<tr>
<td>5A</td>
<td>662F</td>
<td>22</td>
<td>650</td>
<td>770</td>
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<td>5A</td>
<td>662NF</td>
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<td>6.8</td>
<td>370</td>
</tr>
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</table>

**Table 9: Select Results of ASTM E 800 (Flaming) for Resin #4 and #5 Pultrusion Trial**

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO Req</th>
<th>HBr</th>
<th>NOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>600</td>
<td>30</td>
<td>N/A</td>
</tr>
<tr>
<td>4B</td>
<td>495</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4C</td>
<td>815</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5A</td>
<td>635</td>
<td>0</td>
<td>175</td>
</tr>
</tbody>
</table>

**Table 10: Select ASTM E 1354 Results for 0.3175 cm Pultruded Panels from Second Trial**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux (kW/m²)</th>
<th>$T_{ig}$ (sec)</th>
<th>HRR$_{peak}$ (kW/m²)</th>
<th>SEA (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>25</td>
<td>265</td>
<td>240</td>
<td>688</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>62</td>
<td>253</td>
<td>650</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>35</td>
<td>304</td>
<td>965</td>
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<tr>
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<td>100</td>
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<td>383</td>
<td>1011</td>
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<tr>
<td>1A</td>
<td>25</td>
<td>216</td>
<td>230</td>
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<td>63</td>
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<td>904</td>
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<td>341</td>
<td>1229</td>
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<td>100</td>
<td>25</td>
<td>385</td>
<td>1372</td>
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</table>
Table 11: Select ASTM E 1354 Results for 0.635 cm Pultruded Panels from Second Trial

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux (kW/m²)</th>
<th>T&lt;sub&gt;lg&lt;/sub&gt; (sec)</th>
<th>HRR&lt;sub&gt;peak&lt;/sub&gt; (kW/m²)</th>
<th>SEA (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3B</td>
<td>25</td>
<td>343</td>
<td>173</td>
<td>586</td>
</tr>
<tr>
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<td>85</td>
<td>249</td>
<td>529</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>39</td>
<td>295</td>
<td>938</td>
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<td></td>
<td>100</td>
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<td>335</td>
<td>963</td>
</tr>
<tr>
<td>1B</td>
<td>25</td>
<td>354</td>
<td>211</td>
<td>955</td>
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<td>73</td>
<td>274</td>
<td>859</td>
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<td>75</td>
<td>44</td>
<td>321</td>
<td>1250</td>
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<tr>
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<td>320</td>
<td>1495</td>
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</table>

Table 12: Summary of Samples Analyzed by ASTM D 4935-99

<table>
<thead>
<tr>
<th>D 4935-99</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>418-3A</td>
<td>Al Foil</td>
</tr>
<tr>
<td>418-3B</td>
<td>0.3175 cm VE</td>
</tr>
<tr>
<td>418-3C</td>
<td>0.3175 cm PE</td>
</tr>
<tr>
<td>418-3D</td>
<td>0.3175 cm Resin2 + FR</td>
</tr>
<tr>
<td>418-3E</td>
<td>0.635 cm PE</td>
</tr>
<tr>
<td>418-3F</td>
<td>0.635 cm VE</td>
</tr>
<tr>
<td>418-3G</td>
<td>0.3175 cm Resin 2 +FR+ATH</td>
</tr>
<tr>
<td>418-3H</td>
<td>4 ply E-glass + FR</td>
</tr>
<tr>
<td>418-3I</td>
<td>8 ply E glass + FR</td>
</tr>
<tr>
<td>418-3J</td>
<td>Carbon Sandwich</td>
</tr>
<tr>
<td>418-3K</td>
<td>Monolithic Carbon</td>
</tr>
</tbody>
</table>