

Technical Paper

Fire Retardant Polyester Resin Formulations

Abstract

The original fire retardant polyester resin formulations incorporated bromine and chlorine (halogens) into the polymer. The disadvantages to these formulations were excessive toxic products and smoke given off on exposure to a flame. Alumina trihydrate (ATH) has successfully been added to non-halogenated polyester resins to resolve the toxicity and smoke issues.

Unfortunately the high concentration of ATH detrimentally affects the mechanical properties of composites. Ammonium polyphosphate (APP) is an intumescent filler that is widely used in coatings for fire resistance. Other papers have been presented that describe the benefits of using filler blends of ATH and APP in composites. This paper describes the development of fire retardant formulations with emphasis on non-halogenated filled systems with varying amounts of ATH and APP. Neat and filled viscosities, cast resin mechanical properties are reviewed. Also included in this paper are flammability test results on composites tested according to BSS 7239 toxicity test, ASTM E 84, ASTM E 162, ASTM E 662, and ASTM E 1354.

Introduction

Originally fire retardant polyester resins were made with halogenated raw materials such as tetrabromophthalic anhydride, tetrachlorophthalic anhydride or chlorendic acid or anhydride. These products performed well until toxicity issues became important. In order to satisfy the needs for low toxicity products, non-halogenated general purpose unsaturated polyester resins were introduced that were filled with products such as alumina trihydrate (ATH). This filler was the key component in meeting the fire retardant and toxicity requirements.

ATH products provide effective flame redundancy by several routes. First, they dilute the amount of fuel available to sustain combustion during fire by replacing part of the resin. Secondly, ATH contains 34.6% bound water that is released at high temperatures [beginning at

230°C (446°F)] providing a blanket effect, which limits the oxygen available for combustion. Additionally, metal hydrates such as ATH absorb heat from the combustion zone, which reduces the prospect of continued burning. Finally, ATH will produce a char during burning that results in further flame retardant protection and less smoke generation.

Another fire retardant filler is ammonium polyphosphate, which has been used for many years but not extensively in fiber reinforced composites. It is a fine-grained non-toxic white powder that uses the intumescent effect for flame retardancy in fire resistant coatings. It will foam on exposure to heat or flames. The carbon foam layer protects the composite through its heat-insulating effect and reduces further oxygen access. An APP supplier is suggesting that lower viscosities and improved fire resistance properties can be achieved by decreasing the ATH content and substituting part of the removed ATH with APP. The focus of this paper is to confirm this suggestion.

One significant disadvantage of using ATH as the only filler is that high loadings were required to meet specific fire retardant requirements such as ASTM E 84 class I ratings. Other disadvantages are that ATH does settle, reinforcements are harder to wet out and finished parts were more brittle.

Five different test methods were used to evaluate these new blends. ASTM E 84 "Surface Burning Characteristics of Building Materials" is a standard test for general fire resistance and is widely recognized. Three tests that are often specified for mass transit applications are ASTM E 162 "Surface Flammability of Material Using a Radiant Heat Energy Source," ASTM E 662 "Specific Optical Density of Smoke Generated by Solid Materials" and Boeing Support Standard (BSS 7239) toxicity test. A test that is being recognized increasingly as a more reproducible fire retardant test is ASTM E 1354 "Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter."

A summary of these tests follows:

- a) ASTM E 84- Laminates that are a minimum of 45.7 cm (18 inches) wide by 7.3 meters (24 feet) long are compared in burning characteristics to a mineral fiber cement board, which is rated 0, and a red oak board that is rated 100. To meet an ASTM E 84 class I rating, the laminate in question must have an ASTM E 84 rating of 25 or less.
- b) ASTM E 162- This test measures surface flammability employing a radiant heat source rather than a flame.
- c) ASTM E 662- This test measures the optical density of smoke using a radiant energy source. The smoke is measured in a flaming mode and a non-flaming mode. In order to obtain the flaming mode, a row of equidistant flamelets is placed across the lower edge of the specimen.
- d) BSS 7239- This test is a Boeing Support Standard that measures the amount of toxic gases that are generated from a burning laminate in a controlled environment.
- e) ASTM E 1354- 100 mm square coupons are burned while being subjected to an external heat flux that is set from 0-100 kW/m². Time to ignition, heat release, smoke obscuration and mass loss are recorded.

This paper compares the fire/smoke properties of three filled resin systems utilizing ATH and blends of ATH/APP.

Experimental

A non-halogenated general purpose unsaturated polyester resin Firepel® K133-AAA-00 containing both styrene and methyl methacrylate (MMA) was chosen. In order to minimize the number of variables, three types of composites were prepared keeping the total filler content constant. A standard formula that required a 40/60 ratio of resin/ATH was chosen as a control. Ammonium polyphosphate replaced 12.5% and 25% of the ATH in two different composites.

Liquid resin properties both neat and filled, cast neat mechanical values, and the fire tests are provided in tables. The resin made with 12.5% ammonium polyphosphate and 47.5% ATH are coded APP12.5/ATH 47.5. The resin made with 25% ammonium polyphosphate and 35% ATH are coded APP25/ATH 35. The resin was promoted with 0.6% cobalt 6%, 0.2% N, N-Dimethyl aniline (DMA) and 1.5% methyl ethyl ketone peroxide (MEKP). Composites were made by wetting one layer of 450 grams per square meter (1.5 oz) chopped strand mat.

The ASTM E 84 tunnel test (surface burning characteristics of building materials) was run since it is one of the most

standard tests. The ASTM E 162 (surface flammability of materials using a radiant heat energy source), ASTM E 662 (specific optical density of smoke generated by solid materials) and the BSS 7239 toxic gas generation tests were run because they are often specified for mass transport applications. ASTM E 1354 (heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter) was run because it is becoming more recognized as one of the most reproducible fire tests. It is also an excellent screening test since a minimum amount of composite is required to run the test.

Liquid properties were tested with standard equipment and methods that are typically used in the industry. The casting preparation is found in Figure a. Fire testing was run on composites only.

Results

- 1) Resin liquid properties of Firepel® K133-AAA-00 with different ratios of ATH/APP fillers are found in Figure b.
- 2) The neat casting of Firepel® K133-AAA-00 was tested for mechanical properties and those values are in Figure c.
- 3) Composite mechanical test results of neat resin versus 60% ATH filled laminate values are in **Figure d**.
- 4) Fire Test Results (Firepel® K133-AAA-00 composites with different ratios of ATH/APP fillers)
 - a) ASTM E 84 (surface burning characteristics of building materials) results are in Figure e.
 - b) ASTM E 162 (surface flammability of materials using a radiant heat energy source) results are in Figure f.
 - c) ASTM E 662 (specific optical density of smoke generated by solid materials) results are in Figure g.
 - d) BSS 7239 (toxic gas generation) results are in Figure h.
 - e) ASTM E 1354 (heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter) is in Figure i.

Discussion

- 1) The cast neat mechanical properties of a non-halogenated general purpose polyester resin are typical of properties that are required in the FRP industry.
- 2) A filled composite is more rigid as expected. The strength values are lower due to not being able to achieve as high of glass content.
- 3) The 60% ATH and the APP25/ATH 35 met ASTM E 84 class I flame spread and smoke spread rating but the

APP12.5/ATH 47.5 did not; however, ASTM E 84 is an inconsistent test. It is interesting to note that the smoke rating was higher with increasing amounts of APP.

- 4) The ASTM E 162 time to ignition, heat evolved and time to specific distances indicated that the composite was progressively less fire resistant with increasing quantities of APP.
- 5) The maximum smoke ratings, according to the ASTM E 662 results, were progressively higher in values as the quantity of APP increased. The smoke density results at the 1.5 and 4.0 minute intervals varied significantly.
- 6) Based on the BSS 7239 test results, the 60% ATH composite was the best performer.
- 7) ASTM E 1354 data was difficult to analyze for conclusions. The APP12.5/ATH 47.5 composite had the best result for the time to sustained ignition. The best average peak heat release was APP25/ATH 35 and the best smoke rating was with 60% ATH.

Generally the tests with APP were disappointing. In discussions with our APP supplier, indications are that too much ATH was used, making it difficult for the APP to exfoliate properly. High performance flame-retardants like APP rely on the presence of charable substrate (carbon based polymer) to create an intumescent foam.

Conclusion

- 1) With increasing concentration of APP, the viscosity increased which is a negative factor.
- 2) APP did not improve the fire and smoke properties of a non-halogenated general purpose polyester resin where the total filler content was kept at 60%.
- 3) Since desired results were not obtained in this series of testing, it is suggested that a formula containing APP be repeated using less ATH. If positive results were obtained, the use of APP in composites could be an important raw material in fiberglass reinforced composites.

Figure A
CASTING PREPARATION

| CATALYST AND CURE SCHEDULE | QUANTITY AND TIME |
|----------------------------|-------------------|
| Catalyst system | |
| Benzoyl Peroxide (BPO), % | 1.0 |
| Cure schedule | |
| 60°C (160°F), hours | 4 |
| 93°C (200°F), hours | 1 |
| 116°C (240°F), hours | 1 |
| 138°C (280°F), hours | 2 |

Figure B
RESIN LIQUID PROPERTIES

| PROPERTY | Firepel ® K133-AAA-00 | | | |
|---|--------------------------------------|-----------|----------------------|------------------|
| | NEAT FIREPEL ® K133-AAA- 00 | 60%ATH | APP12.5/ ATH 47.5 | APP25/ ATH 35 |
| Brookfield Viscosity Spindle #1 @ 50 rpm, 1 minute (cps) | 0.018 (18) | 0.1 (100) | 0.12 (120) | 0.185 (185) |

Figure C
CAST MECHANICAL PROPERTIES

| PROPERTY | NEAT Firepel ® K133-AAA-00 |
|--------------------------------------|----------------------------|
| Tensile Strength, Mpa (psi) | 68 (9,900) |
| Tensile Modulus, Gpa (psi) | 3.4 (490,000) |
| Elongation, % | 2.4 |
| Flexural Strength, Mpa (psi) | 106 (15,400) |
| Flexural Modulus, Gpa (psi) | 3.8 (550,000) |
| Heat Distortion Temperature, °C (°F) | 85 (185) |
| Barcol Hardness (934) | 45 |

Figure D

GLASS FIBER COMPOSITE MECHANICAL PROPERTIES

| PROPERTY | Firepel ® K133-AAA-00 | |
|------------------------------|-----------------------|-----------------|
| | NEAT* | 60%ATH* |
| Tensile Strength, Mpa (psi) | 107(15,600) | 7.9(11,500) |
| Tensile Modulus, Gpa (psi) | 90(1,300,000) | 137(2,000,000) |
| Elongation, % | 1.4 | 1.3 |
| Flexural Strength, Mpa (psi) | 165(24,000) | 134(19,500) |
| Flexural Modulus, Gpa (psi) | 7.6(1,100,000) | 11.7(1,700,000) |
| Barcol Hardness (934) | 45 | 62 |
| Glass Content, % | 30 | 16 |

* Composite made with 1 ply of 450 grams per square meter mat (1.5 ounce per square foot)

Figure E
ASTM E 84 RESULTS
SURFACE BURNING CHARACTERISTICS OF BUILDING MATERIALS
USING NON HALOGENATED GENERAL PURPOSE POLYESTER RESIN
COMPOSITE
 (# of samples-1)

| TEST | RESULTS | | |
|-------------------|-----------------------|----------------------|------------------|
| | Firepel ® K133-AAA-00 | | |
| | 60%ATH | APP12.5/ ATH 47.5 | APP25/ ATH 35 |
| Flame Spread | 25 | 40 | 25 |
| Smoke Development | 65 | 160 | 250 |

Figure F
ASTM E 162 RESULTS
SURFACE FLAMMABILITY OF MATERIALS USING A RADIANT
ENERGY SOURCE USING NON HALOGENATED GENERAL PURPOSE
POLYESTER RESIN COMPOSITE
 (# of samples-4)

| TEST | RESULTS | | |
|-------------------------------------|-----------------------|----------------------|------------------|
| | Firepel ® K133-AAA-00 | | |
| | 60%ATH | APP12.5/ ATH 47.5 | APP25/ ATH 35 |
| Time to ignition, seconds | 71 | 51 | 44 |
| % Standard deviation | 14 | 4.8 | 7.9 |
| Baseline temperature, °C | 190 | 185 | 185 |
| Maximum temperature, °C | 245 | 276 | 291 |
| % Standard deviation | 1.6 | 3.2 | 4.8 |
| Temperature Rise, °C | 55 | 91 | 106 |
| % Standard deviation | 7.4 | 9.8 | 13 |
| Time to 7.6 cm (3 inches), minutes | 2.7 | 2.0 | 2.0 |
| Standard deviation | 30 | 8.2 | 5.7 |
| Time to 15.2 cm (6 inches), minutes | 4.7 | 2.9 | 3 |
| % Standard deviation | 32 | 8.8 | 4.3 |
| Time to 22.8 cm (9 inches), minutes | 8.3 | 4.5 | 5.0 |
| % Standard deviation | 24 | 3.0 | 3.8 |
| Heat evolution factor, Q | 8.8 | 14.4 | 17 |
| % Standard deviation | 8 | 9.8 | 13 |
| Flame spread factor, Fs | 2.2 | 3.0 | 3.0 |
| % Standard deviation | 18 | 4.9 | 5.2 |

Figure G
ASTM E 662 RESULTS
SPECIFIC OPTICAL DENSITY OF SMOKE GENERATED USING NON
HALOGENATED GENERAL PURPOSE POLYESTER RESIN COMPOSITE
 (# of samples-3)

| TEST | RESULTS | | |
|---------------------------------|-----------------------|----------------------|------------------|
| | Firepel ® K133-AAA-00 | | |
| | 60%ATH | APP12.5/ ATH 47.5 | APP25/ ATH 35 |
| NON FLAMING EXPOSURE | | | |
| Maximum smoke density | 40 | 89 | 134 |
| % Standard deviation | 17 | 85 | 6.5 |
| Smoke density after 1.5 minutes | 0.2 | 0.14 | 0.03 |
| % Standard deviation | 60 | 82 | 173 |
| Smoke density after 4.0 minutes | 2.0 | 0.47 | 1.0 |
| % Standard deviation | 40 | 84 | 120 |
| FLAMING EXPOSURE | | | |
| Maximum smoke density | 61 | 106 | 163 |
| % Standard deviation | 28 | 18 | 20 |
| Smoke density after 1.5 minutes | 1.3 | 0.43 | 2.6 |
| % Standard deviation | 18 | 97 | 91 |
| Smoke density after 4.0 minutes | 16 | 8.5 | 23 |
| % Standard deviation | 41 | 37 | 10 |

Figure H
TOXIC GAS GENERATION BSS 7239 FLAMING MODE RESULTS
USING NON HALOGENATED GENERAL PURPOSE POLYESTER RESIN
COMPOSITE
 (# of samples-1)

| TEST | RESULTS | | |
|---|-----------------------|------------------|--------------|
| | Firepel ® K133-AAA-00 | | |
| | 60%ATH | APP12.5/ATH 47.5 | APP25/ATH 35 |
| Hydrogen Cyanide (HCN), ppm | <2 | 4 | 7 |
| Carbon Monoxide, (CO), ppm | 67 | 275 | 290 |
| Nitrous Oxides, (NOx), ppm | <2 | 35 | 60 |
| Sulfur Dioxide, (SO ₂), ppm | <1 | ND | ND |

Figure I
ASTM E 1354 RESULTS
OXYGEN CONSUMPTION CALORIMETER USING NON-HALOGENATED GENERAL
PURPOSE POLYESTER RESIN COMPOSITE

| TEST | RESULTS | | |
|---|-----------------------|-----------------------|----------------------|
| | Firepel ® K133-AAA-00 | | |
| | 60%ATH | APP 12.5/ ATH 47.5 | APP 25/ ATH 35 |
| Time to sustained ignition, seconds | 63 | 76 | 59 |
| % Standard deviation | 5 | 11 | 3.9 |
| Average peak heat release rate, kw/m ² | 341 | 358 | 314 |
| % Standard deviation | 6.7 | 12 | 2.9 |
| Average heat release rate after 60 seconds, kw/m ² | 235 | 258 | 262 |
| % Standard deviation | 11 | 3.0 | 2.5 |
| Average heat release rate after 180 seconds, kw/m ² | 138 | 143 | 171 |
| % Standard deviation | 3.4 | 3.7 | 3.5 |
| Average heat release rate after 300 seconds, kw/m ² | 104 | 113 | 126 |
| % Standard deviation | 2.7 | 3.8 | 5.1 |
| Total heat release, mj/m ² | 27 | 27 | 33 |
| % Standard deviation | 5.2 | 5.0 | 3.9 |
| Average effective heat of combustion, mj/kg | 17 | 17 | 21 |
| % Standard deviation | 4.7 | 8.8 | 1.8 |
| Smoke obscuration, average specific extinction area, m ² /kg | 433 | 498 | 642 |
| % Standard deviation | 0.8 | 6.9 | 4.3 |
| Mass Loss, % | 50.6 | 44.8 | 42 |
| % Standard deviation | 0.8 | 3.7 | 1.4 |