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Technical Paper

Comparison of Flame, Smoke and Toxicity in a Halogen-Free and a Halogenated Reinforced Composite

Abstract

The quest continues for fire resistant composites that generate minimal smoke and toxic products. A major concern is the toxic components that are given off from composites containing halogens. The benefit of using Alumina Trihydrate (ATH) to reduce the smoke and toxic components released from fiberglass composites has been well established. A non-halogenated polyester resin has been developed that meets many of the flame, smoke and toxicity requirements. This paper describes the first side-by-side detailed comparison of a halogenated and a non-halogenated ATH filled system. ATH glass fiber reinforced composites are tested according to ASTM E 84 tunnel test for flame and smoke density, ASTM E 162 surface flammability, ASTM E 662 optical smoke density, ASTM E 1354 cone calorimeter, and BSS 7239 toxic gas test. The results of the flame, smoke and toxicity for both the halogenated and non-halogenated ATH filled resin systems are presented in this paper.

Introduction

When low smoke properties are required in a composite, the use of methyl methacrylate (MMA) monomer is preferred to that of styrene. Also, the use of ATH is well documented as fire retardant filler for non-halogenated and halogenated systems to reduce the flammability properties and smoke mission.

ATH products provide effective flame retardancy 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, which is released at high temperatures (beginning at 230°C or 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. This paper compares the fire/smoke properties of two ATH filled resin systems both containing MMA/styrene monomer, one being a commercial, non-halogenated resin and the other a commercial, brominated fire retardant resin diluted with MMA. The advantages and disadvantages of using one system over the other will be reviewed. For the purposes of this paper, the non-halogenated resin will be coded NH1 and the halogenated resin will be H2.

ASTM E 84 fire resistant standard was chosen because it is a required test that must be passed in order for products to be considered in many fire retardant applications. The title for the ASTM E 84 standard is "Surface Burning Characteristics of Building Materials".

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 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 18 inches wide by 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 E84 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 are placed across the lower edge of the specimen.

d) 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 and smoke obscuration are recorded.

e) BSS 7239- This test is a Boeing Specification Support Standard that measures the amount of toxic gases that are generated from a burning laminate in a controlled environment.

Experimental

In many cases, about 60 phr (parts per hundred parts of resin) is added to a resin because the viscosity becomes too high when a higher concentration is added. A newly developed FIREPEL® K133-AAA-00 resin will accept 150 phr ATH. Using the same technology, H2 was developed to maximize the fire retardant properties of a composite. In both cases, a blend of styrene/MMA was used as the monomer. The significant difference between the two resins is that one is halogenated and one is halogen-free. Liquid resin properties, cast mechanical values, composite mechanical values and a number of fire tests are provided in tables at the end of the paper.

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 and is 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 cast and composite preparations are found in figures 1 and 2 respectively. The castings and the composites were tested for mechanical properties. Fire testing was run on composites only.

Results

1) **Liquid Properties**
The results are in figure 3.

2) **Cast Mechanical Properties**
Cast property results are in figure 4.

3) **Composite Mechanical Properties**
The mechanical properties of the composites are in figure 5.

4) **Fire Test Results**
a)ASTM E 84 (surface burning characteristics of building materials) results are in figure 6.

b)ASTM E 162 (surface flammability of materials using a radiant heat energy source) results are in figure 7.

c)ASTM E 662 (specific optical density of smoke generated by solid materials) results are in figure 8.

d)ASTM E 1354 (heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter) are in figure 10.

e)BSS 7239 (toxic gas generation) results are in figure 9.

Discussion

1) The mechanical properties of both the FIREPEL K133-AAA-00 and the H2 are typical of properties that are required in the FRP industry.
2) The FIREPEL K133-AAA-00 and the H2 met ASTM E 84 class I flame spread rating for both flame spread and smoke developed. As expected, the flame spread for the halogenated composite was much lower than the non-halogenated composite. The opposite was true for smoke developed.
3) The ignition was not steady on the H2 composite tested according to ASTM E 162 and thus ignition time results could not be obtained. The flammability characteristics of the halogenated composite were significantly superior to those of the non-halogenaged composite. The flame spread for the former was 19.7 versus 5.4 for the latter.
4) The smoke ratings, according to the ASTM E 662 results, were superior for the non-halogenated composite over the halogenated composite by a significant margin.
5) Based on the BSS 7239 test results, the toxic gases given off from the halogenated composite were much higher than those released by the non-halogenated composite. This is expected.

6) The ASTM E 1354 provided interesting data. The ignition time for the H2 was longer than that for the FIREPEL K133 AAA-00, but not significantly longer. The heat release values for the H2 were significantly lower than those of the FIREPEL K133-AAA-00 composite.

7) The smoke obscuration for the H2 was just slightly higher than that for the FIREPEL K133-AAA-00, but the difference was not significant.the difference in smoke generation values of ASTM E 1354 between FIREPEL K133-AAA-00 and H2.

8) The % Standard deviation is not reported with the ASTM E 84 and BSS 7239 because only one sample was run. The % Standard deviation on the results of ASTM E 1354 is much less than that of ASTM E 162 and E 662.

9) Even though there is no chlorine in the FIREPEL® K133-AAA-00 resin, the HCL found in the gas during the BSS 7239 testing may be due to the filler or the glass.

10) HBr would be expected to be given off from H2 resin. HBr was analyzed as HCL in the BSS 7239 test.

Applications

Currently the FIREPEL K133-AAA-00 resin system is being used for ducts in mines and architectural parts. The opportunities for the H2 depend on the specific requirements.

Conclusions

1) Mechanical properties of both FIREPEL K133-AAA-00 and H2 meet industry requirements.

2) FIREPEL K133-AAA-00 meets many of the fire resistant requirements for mass transit applications when used with metal halides such as ATH.

3) H2 provides improved flammability properties over FIREPEL K133-AAA-00.

4) FIREPEL K133-AAA-00 provides improved smoke and toxicity properties over H2.

5) FIREPEL K133-AAA-00 and H2 can be used for fire retardant applications provided that the fire retardant requirements are less or equal to those obtained in these tests.

6) ASTM E 1354 appears to be a more reliable test than ASTM E 162 and ASTM E 662, based on % Standard deviation values.

Figure 1 **- 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 2 - **COMPOSITE PREPARATION**

PREPARATION	DETAILS
Promoter system	0.3% cobalt 12% and 0.2 % of DMA
Filler	60% ATH
Catalyst system	1.5 % MEKP (9% active oxygen)
Composite construction	1 ply of 1.5 ounce chopped strand glass mat
Glass content, %	16
Thickness, inches	0.075
Postcure	3 hrs at 100°C/212°F

Figure 3 –**RESIN LIQUID PROPERTIES**

PROPERTY	FIREPEL® K133-AAA-00	H2
25°C BROOKFIELD VISCOSITY SPINDLE #1 @ 50 rpm, cps	18	20
GEL TIME WITH 0.3 cobalt 12%, 0.2% DMA and 1.5% MEKP, minutes	38	27
TOTAL TIME, minutes	52	38
PEAK EXOTHERM, °F	336	360
SPECIFIC GRAVITY	1.05	1.26

Figure 4 -CAST MECHANICAL PROPERTIES

PROPERTY	FIREPEL K133-AAA-00	H2
TENSILE STRENGTH, psi	9,900	9,800
TENSILE MODULUS, psi	490,000	620,000
ELONGATION, %	2.4	1.9
FLEXURAL STRENGTH, psi	15,400	16,500
FLEXURAL MODULUS, psi	550,000	630,000
HEAT DISTORTION TEMPERATURE, °F	185	185
BARCOL HARDNESS (934)	45	45

Figure 6 - ASTM E 84 RESULTS
SURFACE BURNING CHARACTERISTICS OF BUILDING MATERIALS
(# of samples-1)

TEST	RESULTS	
	FIREPEL K133-AAA-00	**H2**
Flame spread	25	10
Smoke development	65	200

Figure 7 –ASTM E 162 RESULTS
SURFACE FLAMMABILITY OF MATERIALS USING A RADIANT ENERGY SOURCE
(# of samples-4)

<table>
<tr><th>TEST</th><th colspan="2">RESULTS</th></tr>
<tr><th></th><th>FIREPEL K133-AAA-00</th><th>H2</th></tr>
<tr><td>Time to ignition, seconds</td><td>71</td><td>Ignition not steady</td></tr>
<tr><td>Baseline temperature, °C</td><td>190</td><td>190</td></tr>
<tr><td>Maximum temperature, °C</td><td>245</td><td>209</td></tr>
<tr><td>% Standard deviation</td><td>1.6</td><td>1.6</td></tr>
<tr><td>Temperature Rise, °C</td><td>55</td><td>18.8</td></tr>
<tr><td>% Standard deviation</td><td>7.4</td><td>18</td></tr>
<tr><td>Time to 3 inches, minutes</td><td>2.7</td><td rowspan="6">Ignition not steady</td></tr>
<tr><td>% Standard deviation</td><td>30</td></tr>
<tr><td>Time to 3 inches, minutes</td><td>4.7</td></tr>
<tr><td>% Standard deviation</td><td>32</td></tr>
<tr><td>Time to 3 inches, minutes</td><td>8.3</td></tr>
<tr><td>% Standard deviation</td><td>24</td></tr>
<tr><td>Heat evolution factor, Q</td><td>8.8</td><td>3.0</td></tr>
<tr><td>% Standard deviation</td><td>8</td><td>17</td></tr>
<tr><td>Flame spread factor, Fs</td><td>2.2</td><td>1.1</td></tr>
<tr><td>% Standard deviation</td><td>18</td><td>14</td></tr>
<tr><td>Flame spread</td><td>19.7</td><td>5.4</td></tr>
<tr><td>% Standard deviation</td><td>20</td><td>15</td></tr>
</table>

Figure 8 - ASTM E 662 RESULTS
SPECFIC OPTICAL DENSITY OF SMOKE GENERATED
(# of samples-3)

TEST	RESULTS	
	FIREPEL® K133-AAA-00	**H2**
NON FLAMING EXPOSURE		
Maximum smoke density	40	93
% Standard deviation	17	28
Smoke density after 1.5 minutes	0.2	0.06
% Standard deviation	60	67
Smoke density after 4.0 minutes	2.0	4.7
% Standard deviation	40	74
FLAMING EXPOSURE		
Maximum smoke density	61	192
% Standard deviation	28	17
Smoke density after 1.5 minutes	1.3	2.8
% Standard deviation	18	61
Smoke density after 4.0 minutes	16	81
% Standard deviation	41	35

Figure 9 - ASTM E 1354 RESULTS
OXYGEN CONSUMPTION CALORIMETER
(# of samples-3)

TEST	RESULTS	
	FIREPEL® K133-AAA-00	H2
Time to sustained ignition, seconds	63	89
% Standard deviation	5	4
Average peak heat release rate, kw/m^2	341	174
% Standard deviation	6.7	9.2
Average heat release rate after 60 seconds, kw/m^2	235	117
% Standard deviation	11	1.5
Average heat release rate after 180 seconds, kw/m^2	138	88
% Standard deviation	3.4	1.4
Average heat release rate after 300 seconds, kw/m^2	104	66
% Standard deviation	2.7	3.9
Total heat release, mj/m^2	26.7	17.8
% Standard deviation	5.2	4.5
Average effective heat of combustion, mj/kg	17	9
% Standard deviation	4.7	6.7
Smoke obscuration, average specific extinction area, m^2/kg	433	463
% Standard deviation	0.8	8
Mass Loss, %	50.6	50.9
% Standard deviation	0.8	3.3

Figure 10 – TOXIC GAS GENERATION BSS 7239 RESULTS
(# of samples-1)

TEST	RESULTS			
	FIREPEL K133-AAA-00		H2	
	Flaming Mode	Non-Flaming Mode	Flaming Mode	Non-Flaming Mode
Hydrogen Cyanide (HCN), ppm	<2	<2	2	2
Carbon Monoxide, (CO), ppm	67	<10	225	300
Nitrous Oxides, (NOx), ppm	<2	<2	1	1
Sulfur Dioxide, (SO_2), ppm	<1	<1	<1	<1
Hydrogen Fluoride (HF), ppm	<1.5	<1.5	<1.5	<1.5
Hydrogen Chloride (HCL), ppm	4	2	15	16