A Novel Non-Halogenated Flame Retardant for Composite Materials

By

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Abstract

Flame retardants, such as inorganic fillers or halogenated resins, are incorporated into composites either as additives or reactive materials. In order to improve processability and mechanical properties, as well as reduce smoke toxicity, a method is being developed to introduce highly effective, inexpensive flame retardant materials into thermoset resins. Superabsorbent polymers (SAP) can be loaded with inexpensive inorganic phosphates as the flame retardant component in composite systems. The resulting SAP flame retardants dramatically improved fire resistance when blended with common matrix resins (epoxy, unsaturated polyester, urethane hybrid, and vinyl ester resins) at relatively low levels with very minimal off-gassing of toxic compounds during combustion.

Background

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 mechanism of action:[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 aluminum trihydrate release water upon heating. However, such fillers must be incorporated in high amounts and have a negative effect on mechanical properties. Halogenated resins 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.

Flame retardants can 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 added to the resin prior to fiber impregnation. Additives present problems including poor compatibility, leaching and reduced mechanical properties. Reactive flame retardants are an attempt to overcome the problems of additives through copolymerization of the flame retardant with the polymer. 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 additive is based on common superabsorbent polymer materials. Superabsorbent polymers (SAP) are materials capable of absorbing 2-10 times their weight in water. SAPs are commonly used in incontinence products, such as diapers, due to their water absorbing characteristics. Typical SAPs include polyacrylates, polyacrylamides and poly(vinyl alcohol)s. 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]

[1] S. Lu, I. Hamerton, "Recent developments in the chemistry of halogen-free flame retardant polymers", *Prog Polym Sci*, **27**, 1661-1712 (2002).

[2] J. Sheu and J. Meeks, "Methods for flame-retarding and products produced there from", *U.S. Pat. 6,290,887* (2001).
[3] J. Reilly, W. Grilliot, M. Grilliot, "Protective pad for protective garment", *U.S. Pat. 6,317,889* (2001).

The SAP based flame retardant has been applied to a variety of resins used in fiber reinforced polymer composites. SAP based flame retardant are highly effective in improving the fire resistance of commercial vinyl ester and epoxy resin. Subsequent composite materials demonstrate good mechanical properties and fire resistance.

Experimental

Resin #1 is a bisphenol A type vinyl ester; Resin #2 is a one pack styrenated proprietary urethane hybrid blend used for high performance low profile pultrusion applications; FR is a flame retardant superabsorbent polymer prepared as described below.

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 is 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 are combined with a water solution containing an inorganic phosphate. The SAP microspheres absorb the water solution and the water is removed by drying leaving a dry SAP flame retardant powder. The SAP flame retardant is passed through a sieve to remove agglomerates.

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

Composite laminates were prepared using commercially available resin combined with the SAP flame retardant microspheres. The laminates were produced by hand lay up followed by vacuum bagging. Eight plies of E-Glass weave fabric (24 oz. /sq. yrd, 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.

Characterization

UL94 - Horizontal Burn Test

The horizontal burn test is used to calculate the linear burning rate of plastic 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 reaches 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.

Pultruded panels were constructed of surfacing veil, a 1.0 oz CSM mat, 45 113 yield roving, a 1.0 oz CSM mat, 45 113 yield roving, a 1 oz CSM mat, and another surfacing veil using a 1/8"x 6' die. Panels prepared via pultrusion were not subjected to a post cure schedule prior to physical testing.

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.

Results and Discussion

Super absorbent polymer microspheres are synthesized by an inverse emulsion polymerization. The resulting materials are characterized by optical microscopy (Figure 1) and particle size analysis generally. The average

particle size of the current formula is approximately 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. The addition of 25% FR microspheres to any resin system tested was found to extinguish burning almost immediately after the torch was removed from the casting.

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. Resin 1 loaded with 22% of the FR microspheres exhibits smoke toxicity values below that of a common specified limit as seen in Table 1 (Figure 2). Two separate specimens were cast in order to ensure reproducibility of the results. Clear cast resins were used in order to present the worst case scenario, as the glass fiber will reduce the percent flammable material in a particular sample, thus causing a further drop in the values by weight.

UL-94 testing was carried out using Resin 1 as the matrix. Adding just 15% of the FR to Resin 1 resulted in no fire spread during the horizontal burn test as seen in Table 2 (Figure 3). The vertical burn test however revealed that 15% FR microspheres were not sufficient to achieve a rating, but using 25% resulted in a V-0 rating for the casting (Table 3, Figure 4).

Composite panels containing the flame retardant resin were made by hand lay-up followed by vacuum bagging. Vacuum bagging allowed for compaction of the panels so that homogeneous samples for testing could be obtained (i.e. it eliminated resin rich areas and air voids). By adjusting the vacuum level, it was also possible to control fiber content to within a few percentage points, thus eliminating that as a variable. Three panels created in this way are presented in Table 4 (Figure 5).

Physical testing was carried out first in order to determine the effect of the new flame retardant on the mechanical properties. A property drop was undesirable so a high level of flame retardant may be unacceptable for further testing if the properties were poor. From Table 5 (Figure 6), it can be seen that the microspheres had little impact on tensile or compressive properties. Although a drop in tensile strength was noted, the other properties were within normal deviations and all three samples were taken on for further testing. UL-94 vertical burn data is presented in Table 6 (Figure 7). As with the clear castings, 22% FR microspheres was sufficient to give a V-0 rating for this resin system with no real advantage seen to using 40% of the new FR. This was reinforced

by the cone calorimetry data in Table 7 (Figure 8) where the time to sustained ignition for both the 22% and 40% FR are the same. The higher level of FR microspheres did lower the peak heat release and SEA values however.

Pultrusion was targeted as the first potential processing method to attempt incorporation of the FR microspheres into thermoset resin systems. This was mainly driven by the nature of the parts to be produced; however, it is 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. Blends of Resin 2 with the FR microspheres were processed on a 1/8" thick die resulting in a neutral colored panel (Figure 9). 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 10). 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 1/8" panel. Testing of physical properties in both the 0° and 90° directions showed very little variation suggesting that increasing FR loading levels from 20-30% have no effect on the properties (Tables 8 and 9). Because of the polymer nature of the flame retardant microspheres (as opposed to a mineral filler such as ATH), there was a possibility relatively small changes in loading levels would affect the properties, much as tougheners and low profile additives can.

Conclusion

A new flame retardant for composites resins has been identified and shown to be highly effective in various thermoset resins. The flame retardant is based on SAP microspheres containing inexpensive phosphorus compounds. The SAP flame retardant mixes readily into epoxy, urethane hybrid, and vinyl ester resins producing cast materials with a V-0 UL-94 rating. The flame retardant resin can be fabricated into fiber reinforced composites with good mechanical properties and fire resistance. Further work characterizing the physical properties of the new flame retardant composites, as well as modifying the SAP microspheres for additional composite processes, is currently in progress.

Acknowledgments

recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the United States Air Force, the United States Navy, Strongwell or Intertek.

Figure – 1
SAP Microspheres-Optical Microscopy

Figure 2-
Table 1: Smoke Toxicity (BSS 7239) of Resin 1 + 22% FR Microspheres, non-reinforced

Gas	Specified Limit (ppm)	Specimen 1	Specimen 2
CO	3500	540	525
HF	200	ND	ND
HCl	500	ND	ND
SO_2	100	ND	ND
HCN	150	5	5
NO_X	100	85	80

Figure 3-
Table 2: UL-94 Horizontal Burn Test Results for Resin 1 clear casts

% FR	T (sec)	L (mm)	V (mm/min)
0	531	75	8.6
15	0	0	0
25	0	0	0

Figure 4-
Table 3: UL-94 Vertical Burn Test Results for Resin 1 clear casts

% FR	t1 (sec)	t2 (sec)	t3 (sec)	Class
0	279	consumed	Consumed	NC
15	1	122	0	NC
25	1	4	0	V-0

Figure 5-
Table 4: Composite Panels Prepared by Hand Lay-Up followed by Vacuum Bagging.

Sample	Fiber Content (% mass)	Average Thickness (in.)
Resin 1	55	0.29
Resin 1 + 22% FR	57	0.26
Resin 1 + 40% FR	53	0.29

Figure 6-
Table 5: Comparison of Physical Properties Prepared by Hand Lay-Up/Vacuum Bagging

Sample	Tens. Mod. (Mpsi)	Tens. Str. (Kpsi)	Comp. Mod. (Mpsi)	Comp. Str. (Kpsi)
Resin 1	3.9	35	3.3	21
Resin 1 + 22% FR	3.9	35	3.9	18
Resin 1 + 40% FR	3.7	19	3.4	20

Figure 7-
Table 6: UL-94 Vertical Burn Test Results for Resin 1 laminates

% FR	t1 (sec)	t2 (sec)	t3 (sec)	Class
0	0	93	-	V-1
22	0	0	0	V-0
40	0	0	0	V-0

Figure 8-
Table 7: Cone Calorimetry (50 kW/m^2) Results for Resin 1 laminates

% FR	Time to sustained ignition (sec)	Peak heat release rate (kW/m^2)	Effective Heat Capacity (MJ/kg)	SEA
0	108	369	28.9	151
22	97	282	22.8	136
40	98	239	25.0	99

Figure 9-
1/8" Pultruded Resin 2/FR Panel from Trials

**Figure 10-
Left: Front face of panel after 1 minute exposure to inner cone of propane torch.
Right: Back face of panel after 1 minute exposure to inner cone of propane torch.**
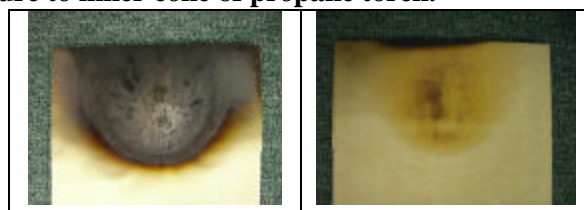

**Figure 11-
Table 8: Pultruded Resin Properties, 0°**

Property	Blend 2A	Blend 2B	Blend 2C
% FR	20	25	30
Comp. Str. (kpsi)	74.7	76.1	74.1
Comp. Mod. (Mpsi)	3.80	3.95	3.95
Tensile Str. (kpsi)	49.6	55.2	44.6
Tensile Mod. (Mpsi)	4.05	4.03	3.97
Perp. Shear (kpsi)	10.2	10.1	10.9
Short Beam Shear (kpsi)	6.01	6.92	7.17

**Figure 12-
Table 9: Pultruded Resin Properties, 90°**

Property	Trial 2A	Trial 2B	Trial 2C
Comp. Str. (kpsi)	21.7	20.7	21.3
Comp. Mod. (Mpsi)	1.28	1.38	1.47
Tensile Str. (kpsi)	6.83	8.73	7.86
Tensile Mod. (Mpsi)	1.20	1.30	1.27
Perp. Shear (kpsi)	12.4	11.3	11.8
Short Beam Shear (kpsi)	2.85	3.91	3.58
Water Absorp. (%)	.34	.25	.27
Density (lb/in3)	.063	.063	.063

COMPOSITES 2006

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