The Effect of Surface Coatings on Fire Growth Over Composite Materials

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T. J. Ohlemiller and J. R. Shields

Abstract

Structural composites are vulnerable to fire in two respects: 1) their resin content may ignite and enable the spread of flames over the surface of the structure; 2) the resin may degrade from the heat of a localized fire exposure thus weakening the composite structure. The present study focuses mainly on the first issue, in particular, on the ability of various commercial coatings to prevent flame spread. The second issue is examined briefly by applying thermocouples to the back surface of test specimens. Four commercial coatings have been tested over an unretarded vinyl ester/glass composite. In addition an uncoated phenolic/glass composite and a polyester/glass composite coated with a fire retarded resin were tested. In all cases the configuration was a 3.3 m high corner with a 53 cm square propane gas burner at its base, operated at 250 kW as the fire exposure. The results show that, with the proper choice of coating and coating thickness, fire growth can be suppressed quite effectively. Two of the coatings, applied at a substantial thickness, were reasonably effective at slowing the penetration of heat to the back of the composite panels. The other coatings, much thinner in application, were notably less effective at slowing heat penetration.

1) Introduction

The types of composite materials of interest here are composed of an organic polymer resin and long, oriented fibers, usually inorganic in nature (glass in the present study). Structural elements are usually built-up from multiple plies of such oriented fiber-in-resin layers. The fibers provide the majority of the strength in their direction(s) of orientation. The binder serves to protect the fibers, hold them together and transfer mechanical loads between them.

Such composites are very attractive materials of construction due to their strength, relatively light weight and evident weather resistance. They are being considered for various infrastructure uses such as building reinforcement to enhance earthquake resistance, highway overpass reinforcement

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1 An alternative means of producing certain types of composite structural elements such as beams is pultrusion which is somewhat analogous to extrusion and has all fibers oriented along the long axis of the beam. Such materials are not examined here.
and repair, as well as foot and highway bridge construction. These materials are also of great interest for ship and off-shore oil drilling platform construction. Both of these latter areas of application pose some unique problems not addressed in the present study the focus of which is on infrastructure.

A significant concern in any infrastructure application of composites is the possibility that an accidental (or deliberate) fire may impinge on the structure. This is potentially problematical for two reasons. First, heat weakens the polymer binder. Thermoplastic binders begin to creep and then to flow as the impinging flames raise their local temperature past the glass transition temperature. Thermoset binders degrade to a char or a flowing melt. The functioning of the binder is thus diminished and the composite loses its strength, particularly with regard to forces which tend to separate the fibers. If this local, heat-induced loss penetrates deeply enough in a critical portion of the structure, it may collapse. The second aspect of the problem can greatly magnify the first. The binder may ignite and support the spread of flame on the composite surface. Thus the localized, external fire may cause a larger structural fire involving the composite. This clearly increases the chance of structural collapse.

The present study is focused principally on the question of fire growth on the surface of a composite. We seek to achieve an understanding of the controlling factors of this phenomenon first. Thus all of the work done here is with composites in a non-loaded condition. Ultimately it may be necessary to address the possible interaction between loading and fire response which may come about through load-induced movements in the composite. Such effects have been seen in small-scale tests of fire endurance [1], analogous to ASTM E-119.

All polymeric binders are not equally prone to ignition and fire growth involvement. This depends strongly on the thermal stability of the polymer. Most polymers which are very good in this regard are rendered impractical for infrastructure use by virtue of their cost. An exception is phenolic resin which is both relatively inexpensive and relatively fire resistant. An example of this type of binder is examined briefly in this study. Polyester binders have the longest history of usage and thus the largest data base on longterm durability. One example of this type is included here. Vinyl ester resins are a major contender for infrastructure applications (and ship construction) because of a good balance of cost and physical properties. They are a major focus here.

Previous work [2, 3, 4] has demonstrated that polyester and vinyl ester composites are not very resistant to fire growth. Brominated vinyl ester resins are a distinct improvement but still exhibit significant fire growth potential [4]. This has prompted an examination of a different technology for fire growth suppression in the present study, intumescent coatings.

Intumescent coatings are not a new technology. The basic formulations originated decades ago [5]. The technology continues to evolve and improve in ways necessary to make a practical and effective product for challenging new applications such as composites.
Such coatings incorporate an organic material to contribute carbon to a char, a compound such as a polyphosphate which can reduce the organic to char when heated and a material which can evolve gases at just the right temperature so as to foam the developing char. A properly foamed char serves as an effective thermal insulation layer, protecting the underlying material from the fire. The basic intumescent ingredients are contained within additional components which provide coherence and adhesion to the substrate much like an ordinary paint, mechanical and weathering resistance and the ability to remain an effective insulating structure in the presence of a fire. It should be noted that the durability of a coating (in terms of long term adhesion and weather resistance) is a key factor in its viability for infrastructure usage. These issues are not examined in this study. Such issues need clarification only after it is established that a freshly applied coating can achieve the desired fire protection.

An intumescent layer can serve two fire protection functions by virtue of its insulating properties. First, by reducing the heat flux seen by the underlying polymer resin, the coating delays the onset of degradation and then slows its rate when it finally does occur. This reduces the rate at which the resin contributes fuel vapors to the adjacent, external fire. In turn, this reduces the local rate of heat release (or prevents it from increasing as it normally would as the polymer resin gets involved in the initiating fire). It is heat release which causes flame extension upward on a vertical surface. Flame extension and fire growth can be prevented if the heat release rate suppression is sufficient.

The second function of the intumescent is to slow the rate of heat flow deeper into the underlying material. As noted above, this heat effectively reduces the load bearing cross section of the composite as an increasing fraction of the cross section is pushed above the glass transition temperature of the resin.

The present study is directed primarily at the first function of intumescent coatings, i.e., suppression of fire growth on the surface of composites. We have taken the opportunity to gather some data relevant to the second function, as well, by following the temperature rise on the rear surface of our exposed samples, albeit in a worst case condition (insulated rear surface).

There is a lack of consensus on appropriate tests for fire growth potential on composites to be used in infrastructure applications, probably because likely fire-exposure conditions are not well-defined. A composite bridge, for example, may be exposed to fire on its road surface due to an accident that causes a gasoline spill. The road surface will likely be a non-composite substance designed to provide wear resistance. Any fire threat to the composite materials below the road deck could depend strongly on where the burning gasoline flows, how long it burns and the details of the bridge support structure. Such a bridge is also vulnerable to debris (or arson) fires at the base of its abutments. Here the main threat is most likely upward flame spread. It is this type of threat that is behind the choice of test configuration in the present study. Good fire growth control in this configuration should also lead to good behavior in the variety of more complex configurations that may ensue from a fuel spill, for example, on the bridge deck or other structural surfaces.
2) Background: Related Work on Composites and Fire

The bulk of previous work on composite flammability has been aimed at applications to aircraft, ship structures or off-shore oil-drilling platforms. Aircraft composites are usually based on a honeycomb core for weight minimization. This gives them rather unique physical properties; such materials are not included in the present summary. Here the more pertinent work is briefly surveyed to put the present study into a broader context.

Compared to many flammable materials, composites have a built-in advantage that helps resist the worst consequences (extensive fire involvement). This is a result of their (usually) inert fiber content. The fibers displace polymer resin, making less fuel available to the fire. When the outermost layers of a composite lose their resin due to heat-induced gasification, they act as an insulating layer, slowing heat penetration into and evolution of gases from the depth of the composite. In this sense, the fibers function similarly to the foamed char left by an intumescent coating. One consequence is that the heat available from unit volume of a composite falls sharply with increasing thickness [6]. This is a consequence of the fiber layer protecting deeper layers of resin.

Recognition of the insulating properties of the fiber layer has lead to the development of composite fire barriers for some applications such as equipment shielding on off-shore oil platforms [6, 7, 8]. The evident paradox of using a flammable material as a fire barrier is usually lessened by the use of a strongly charring resin such as a phenolic, which is widely recognized as having substantially lesser flammability than other common resins such as polyester, vinyl ester or epoxy [6, 9].

The insulating quality of a thick, intact fiber layer is also touted as a major benefit of the use of composites in certain warships, such as minehunters [10]. A four hour engine room fire aboard such a ship was contained by the composite wall structure (polyester/glass), though it evidently gutted the engine room itself. This containment behavior is notably superior to that which steel or aluminum might give since these metals transmit enough heat to cause ignition in adjacent compartments. However, these observations miss the point of the fire growth issue raised above. If the composite resin were carefully chosen and/or properly protected, a fire such as this might be contained and suppressed without threatening the compartment of origin. Of course, on warships the fire within a given compartment may in some cases be a result of an overwhelming source, such as a large fuel leak; in such a case internal fire spread is moot and containment by the compartment walls becomes paramount [11].

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2This is not to say that phenolic composites will not burn. Their lesser rate of heat release as a consequence of charring means that they can resist larger external fire insults before yielding to fire involvement. Their water content can evidently lead to loss of structural integrity under some circumstances.
For most applications of composites, fire growth potential should be the first issue addressed and overcome. Rather surprisingly, this issue has received relatively little attention, except for a limited number of compartment fire growth studies [11, 12]. Much of the sparse work on fire spread on the surface of a composite has employed tests for lateral or downward flamespread [6, 13, 14]. These are relatively slow modes of fire growth and they differ mechanistically from upward flamespread, which tends to be much faster. Good performance in the lateral/downward mode does not necessarily imply good performance in upward spread. The converse, however, is likely to hold true, i.e., resistance to upward spread should carry over to yield resistance to lateral or downward spread.

At present there are no small scale tests for upward flamespread potential. The closest pertinent test is full-scale and it involves both lateral and concurrent flamespread (an analog of upward flamespread). This is ISO 9705 which has been recommended for interior surface materials (including composites) in high speed passenger ships [15]. This is a full room test and can be quite expensive for assessing composites. As an enclosure test, it may be unnecessarily severe for composites which are utilized in open spaces, such as in bridges or piers.

Ideally, expensive, large scale tests would be unnecessary; one would be able to predict susceptibility to fire growth by upward flamespread from appropriate tests on small samples of the composite of interest. This sort of prediction requires a verified flamespread model or, at least, a well-tested empirical correlation. NIST has conducted limited testing of three available models for fire growth upward on a flat wall against experimental data for a vinyl ester/glass composite [3]. None of the models was capable of highly quantitative predictions of the observed behavior but all were sufficiently so as to provide a clear, semi-quantitative indication of a substantial potential for fire growth on this composite.

A flat wall is less susceptible to fire growth than is a configuration which permits radiative interchange among burning surfaces. In general, composite structures should not be assumed to be flat since this could lead to an overly optimistic assessment of fire growth potential. NIST has used a 2.4 m open corner test to look at the effects of exposure fire size on the potential for upward flame spread on composites [4]. The results confirm a strong sensitivity to initiating fire size, as implied by models for the simpler, flat wall configuration. Models for fire growth in a corner are in a more tentative state than those for single, flat vertical surfaces. A future goal of the present study is to extend and test available models for this configuration.

Suppression of fire growth potential calls for measures which either preclude the heat from an external fire getting to the surface of a composite or which dampen the inherent response of the resin to this heat. At one extreme is total insulation of the composite [17, 18]. This has been suggested as a solution for both the hazard of fire involvement and for the threat of structural

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3 ASTM E-84 is a somewhat comparable full-scale test which is commonly included in building codes for interior finish materials. Evidently this test could be expected to rank composites similarly, though no comparisons to ISO 9705 behavior per se have been reported [16].
collapse [17]. A sufficiently thick layer (e.g., 5 cm) of ceramic fiber insulation can keep the temperature of the composite not only below its ignition temperature but also below its glass transition temperature for periods of thirty minutes or more. The practicality of this as a solution to the fire problem is not resolved; there are issues of durability and lost space.

Flame retarded resins are the most readily implemented potential solution to fire growth problems but they only lessen the flammability of a composite. This translates into resistance to a bigger external fire source before fire growth ensues [4].\(^4\) Whether this is sufficient depends on the use of the composite and the ignition sources it is likely to experience. Choice of a strongly charring resin such as a phenolic can provide greater benefits if other properties are compatible with the application.

As noted previously, intumescent coatings are an established fire protection technology for non-composite applications. Limited work has been done on their ability to protect composites [18, 19, 20, 21, 22]. Sorathia looked at the ability of various coatings, including certain intumescents, to delay or suppress ignition and to lower the rate of heat release during burning in small-scale tests (Cone Calorimeter) [19, 20]. Grand [18, 21] tested the ability of several commercial coatings to suppress lateral flame spread (ASTM E1317) and to extend the duration of fire resistance of composites in a standard temperature-time exposure (ISO 834) which does not call for mechanical loading of the test specimen. These studies revealed that only a limited minority of commercial coatings have the needed ability to remain in place during intense heat exposures characteristic of large fires.\(^5\) In general, the coatings examined were not nearly as effective as a layer of ceramic insulation in suppressing heat flow through a composite.

There appear to be no previous studies in the literature of the ability of coatings to suppress upward fire growth on composites. The current work helps to rectify this void.

3) Experimental Details

Test Configuration. Figure 1 is a schematic of the 90° corner configuration used in the present study, showing the burner placement at its base. This is a minor modification of the configuration used in Ref. 4. The corner here was 3.35 m (11 ft.) high, as opposed to 2.7 m (9 ft.) high in the previous study. Also the ceiling segment at the top of the corner in the previous

\(^4\)In unpublished NIST tests of the same type as is reported in Ref. 3, brominated vinyl ester/glass composites exhibited essentially unchanged ignition behavior but required somewhat stronger external heat fluxes to sustain full height flame spread (1.2 m); the increase was from 3-5 kW/m\(^2\) to approximately 10 kW/m\(^2\).

\(^5\)Early tests in the present study indicated the same types of non-adherence problems with some coatings; this helped limit the present work to coatings that do adhere to the surface of a vinyl ester/glass composite during a fire.
study has been removed since we are focussing here more on external structures rather than compartments. The test sample consisted of four composite panels, arranged as shown; their total exposed surface area was 4.6 m². To minimize the cost of the composite materials, the test samples occupied only that portion of the corner likely to be involved in upward or lateral flame spread. Note that there was a juncture between separate panels at the line where they abut at mid-height that was an artifact of this particular test arrangement. The panel junctures at the corner vertex (where one panel overlaps the other by one panel thickness) were also test artifacts. In an actual application, it is probable that all of these junctures would be smoothly bridged by the same composite material. Any gaps around the periphery of the panels greater than about 2 mm were filled with ceramic felt to minimize the tendency for air or fire gases to pass through them. The sample panels were held in place by peripheral, spring-loaded clips attached to a metal framework that touched the panels only along their outer edges and along the corner vertex. The only vertical load on the panels was due to their own weight. The panels were insulated on the back with R-11 fiberglass batts. The calcium silicate boards to either side of the test panels assured a smooth inflow of air to the corner fire plume and helped keep the plume vertical by providing some isolation from any lateral flow disturbances in the test facility.

A square propane gas burner was used as the fire initiation source. Its top lip was 30 cm above the floor and even with the bottom of the test panels. Its width, 0.53 m, was chosen as the largest size consistent with the constraints on available sample size and the need to allow some space for lateral flame spread. Greater burner width means a greater radiative component and thus a higher total flux to the sample surface. The burner was filled with gravel and sand in the manner of the source specified in ISO 9705. Note that the wide burner yields a relatively short flame height for a given burner power [23], especially as compared to the 0.17 m burner specified in ISO 9705. This allows a substantial vertical height over which to observe upward fire growth. In all tests the burner was placed immediately adjacent to the vertex of the corner with no air gap.

Propane flow was measured with a dry test meter and corrected for deviations from normal temperature and pressure conditions. All tests were run with a nominal burner power of approximately 250 kW; this varied up to 260 kW for some tests but was always constant during a given test. This power level was chosen to provide a serious, full-scale challenge to the coated test samples while still allowing vertical and lateral space on the sample faces on which to observe fire growth.

Figure 2 is a diagram of the propane flow system. Two cylinders of liquified propane were used to obtain and maintain sufficient flow for a 250 kW fire for up to one hour. Two 160 liter tanks

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6The test fire here is probably as intense, or more so, than any arson-like or vandal-caused fire is likely to be for an exposed composite structure. It may not be as intense as the worst case ignition scenarios for a building interior where soft furnishings could be the fire source and it certainly is not as intense an exposure as would be caused by a large scale fuel spill, e.g., a tank truck fire.
of water were used to maintain the propane tanks near room temperature, approximately 24 °C, (to avoid any pressure loss in the propane tanks via evaporative cooling). A third tub was used to bring the propane gas to near room temperature using two 9 m copper coils immersed in water. Flow was monitored using a Singer AL-800 dry test meter (DTM)\(^7\) for repeated checks during the course of a fire exposure. Also, a Cole-Palmer 10262 by-pass flow meter was used as a quick reference flow indicator.

The fire exposures were run under a flow collection hood (height 4 m, duct opening 1 m by 1 m) equipped with oxygen and mass flow sensors to allow rate of heat release measurements from the fires. The system was designed for much higher heat release rate fires but by running at reduced flow rates and calibrating it with a propane fire of known heat release rate before each test, adequate measurements were possible. The raw data were corrected both for zero drift of the oxygen sensor and for system response by normalizing with the known heat release rate of the propane test fire; the residual uncertainty in the heat release rate measurements due to system noise and certain ambiguities in the zero drift for some cases is approximately ± 5-7%. The known heat release rate calculation was based on the measured propane flow rate and the assumption of complete combustion.

Prior to the first fire test, the heat fluxes from the burner to one side wall were measured at sixteen points using a set of four Medtherm Schmidt-Boelter total heat flux gages (see Fig.3). These 6 mm diameter gages were inserted through holes from the back so that their sensor surface was flush (within an estimated error of ± 1/2 mm) with that of the 1.27 cm thick calcium silicate board used in place of the test panels. These gages measure the total heat flux to the sensor surface, which in this case was kept at 80 to 85 °C to prevent water condensation. Because soot deposition on the sensor surface was a problem during the flux measurements, the gages were pulled just prior to each measurement and dusted off to avoid a calibration shift. The measurements were made after the burner had been running at a nominal power level of 250 kW for more than 35 minutes. The combination of positional uncertainty, noise due to flame fluctuations and rapid soot accumulation in some locations lead to an estimated uncertainty of ± 10-15% for the flux values.

**Test Materials.** The three types of composites tested were as follows:

- vinyl ester epoxy resin/glass fiber
- polyester resin/glass fiber
- phenolic resin/glass fiber

\(^7\)Specific brand names are mentioned for clarity only. No endorsement by NIST is implied nor is it implied that these are the best for the application.
In all cases, 14 plies of woven roving (plain weave) E-glass fiber, weighing 815 g/m² (24 oz/yd²) were used. This gave a nominal thickness of 9-10 mm for all of the panels. The three types of composites were made by three different commercial manufacturers. The majority of the work focused on coated vinyl ester composites; one fire test each was done with the polyester and one with the phenolic composites.

The coatings tested are listed in Table 1 below. Note that the applied thicknesses vary, being determined in some cases by the coating manufacturer who applied them. For one coating (B) the effect of varying the thickness was examined. The two thick coatings (A and C) are based on two-part epoxy resins which required special spray equipment for application; each was applied by its respective manufacturer at a thickness they felt was best for this type of exploratory application. Both of these coatings are in current use in industrial applications such as for protection of storage tanks filled with flammable fluids or for off-shore oil platform equipment protection applications.

Coating B is a commercial product intended for light industrial and residential use. Exterior application requires a protective overcoat for weathering resistance which was not applied here. It is this coating which was tested briefly in Reference 4 using a smaller fire and a thicker layer. This coating was applied in our laboratory using a paint roller. The lesser thickness case required four successive coats; the greater thickness required eight coats. While this much labor is not practical in a realistic application, it is assumed that this problem could be overcome with modifications to the product viscosity and/or the application technique. The uniformity of the coating thickness on the sample face was somewhat technique dependent and was better in the replicate tests reported below.

![Table 1. Coating Materials](image)

<table>
<thead>
<tr>
<th>Designation</th>
<th>Type</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Intumescent, epoxy-based</td>
<td>7-8</td>
</tr>
<tr>
<td>B</td>
<td>Intumescent, water-based latex, includes ceramic fibers</td>
<td>0.5, 0.9</td>
</tr>
<tr>
<td>C</td>
<td>Intumescent, epoxy-based</td>
<td>6-7</td>
</tr>
<tr>
<td>D</td>
<td>Intumescent, water-based latex includes ceramic fibers</td>
<td>1</td>
</tr>
<tr>
<td>FRPE</td>
<td>Flame-retarded polyester resin</td>
<td>0.3-1.0</td>
</tr>
</tbody>
</table>

Coating D is a modified version of a commercially available product; the addition of ceramic fibers is not normally done. Ceramic fibers were present in this coating (and in B above) as an
aid in keeping the intumesced layer intact on the sample surface in spite of thermal stresses and fire-induced flows. It should be noted that this coating did not have good resistance to mechanical damage; it remained fairly soft over the few day period between application and fire testing.

The coating designated as FRPE is simply a flame retarded version of the same polyester resin from which the bulk of the composite was made (i.e., only the coating contained a flame retardant). The coating has no intumescent properties. The indicated thickness range is due to uneven application. This is reported to be the combination currently used in U. S. Navy minehunter construction.

4) Discussion of Results

Imposed Heat Flux. Figure 4 shows the contours of constant incident heat flux level obtained by linear interpolation from the sixteen measured locations of Figure 3. Note that the ordinate and abscissa scales are not equal; in effect, the flux distribution is stretched laterally in Figure 4 for greater clarity. It is apparent that, on average, the burner flame contracts laterally as it moves up the corner.

The flame from this burner pulsates strongly, as does any pool-like fire, with the flame tips here occasionally reaching 1/2 m or more above the top of the corner. The pulsation frequency is approximately 1.4 Hz; the flux values in Figure 4 are averaged over many pulsation periods. The mean flame height range indicated in Figure 4 is for flames continually attached to the burner; the mean of the maximum flame tip height (not necessarily attached to the lower flame volume) was about 15% higher on average. Both results were obtained by averaging the instantaneous behavior seen in three video segments, three seconds long, at one minute intervals. The center of the mean flame height range in Figure 4 is about 25% greater than the value predicted by Kokkala’s corner flame height correlation [23]; he does not specify which definition of instantaneous flame height he used in his correlation.

Note that the flux level in the corner area just above the burner is quite high. This is presumably largely a consequence of the thickness of the flame zone in this region - nearly that of the 53 cm burner width. Kokkala [23] found a roughly linear dependence of peak flux on burner size for a similar corner configuration; he also attributed this effect to increasing radiative path length with burner size. This high flux region helps to make this test more severe than the nominal 250 kW burner power level might imply. It imposes a more challenging test on the adhesiveness of the coatings than would be obtained with a smaller burner run at the same power level.8

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8A smaller width burner produces a taller flame but Kokkala’s correlation for flame height suggests that the wall area affected by the burner shrinks slightly. When this is combined with the lower heat flux, which yields a lower heat release rate upon ignition, one anticipates that the smaller burner also is less likely to yield upward flame spread.
There are two caveats that should be noted regarding the heat flux results in Figure 4. First, the flux gage surface is cooler than the surrounding wall. The convective component is thus over-estimated for any condition other than for early times in the burner exposure period when the wall itself is also cool.

The second caveat concerns the fact that a portion of the total heat flux, especially near the vertex of the corner, is radiation from the opposite wall. The data in Figure 4 are for an inert, calcium silicate wall which has essentially reached its steady-state temperature distribution. The local surface temperature will be highest where the incident heat flux is highest. The contribution from wall-to-wall radiation will be highest in the same region (lower left of Figure 4). The limiting value of the radiative view factor in this region is 1/4, as the vertex is approached. If the wall were totally adiabatic and thus it had to re-radiate all of its incident flux to achieve a steady-state surface temperature (an upper limit estimate), then 1/4 of the measured flux near the lower vertex would be radiation from the opposite wall. This proportion will drop higher in the flame and as one moves away from the corner vertex. In an actual test where the wall is a coated composite, endothermic reactions in the outer layers of the coating (and in the underlying composite) will keep the wall surface temperature down for some time, lowering the wall-to-wall radiative interchange. Then, depending on the insulating effectiveness of the intumesced coating layer, the surface temperature could rise higher than it did on the calcium silicate wall, boosting the radiative interchange flux contribution and yielding a somewhat higher total incident heat flux, especially in the lower left region of Figure 4.

**Fire Growth.** In previous work with composite materials, we took advantage of a peculiar aspect of the behavior of woven roving-based materials to discern the position of the attached flame front during fire growth on the composite surface. The attached flame front is the upward moving ignition front and is the dividing line between material which is burning and material which is not burning. With most materials, the position of the attached flame front in upward fire spread is largely obscured by the flames playing on the sample face from lower ignited regions of the sample or from the ignition source. For woven roving composites, the permeability and/or the thermal properties exhibit a periodic variation across the composite face that corresponds to the periodicity of the weave in the glass ply. As a consequence, subsequent to ignition, the gases evolved from the composite surface tend to occur in small jets (2-3 mm diameter) that emerge from this periodic structure. These small, regularly patterned jets are relatively easy to discern. The highest position where these jets occur is taken as the position of the attached flame front at any instant as it spreads up the face of the material.

When the composite surface is coated, as it was for all tests in this study, all ability to discern such a regular pattern of jets is lost. Instead one relies on observation of much coarser and less well-defined irregularities in the appearance of the flickering flames as the coating begins to strongly emit gases. Typically the coating could not be discerned at all in the video tapes below about 1.2 m because of the opacity of the burner flames. Consequently, we are unable to report detailed data on the position of the attached flame front as it moved up the corner, when such movement occurred at all. We have tried to give an accurate indication of when the attached
flames reached the top of the corner, for cases where that occurred. That is more discernible because the flames there appear against the dark space behind the top of the corner.

As it happens, the attached flame height was not a very good indicator of the fire intensity, especially for cases where the flames seemed to spread upward slowly. In some of those cases this apparent slow spread may have been due to progressive involvement of gases emitted from the inner edges of the composite panels in the corner vertex area. This sort of effect may be sensitive to the details of the structure in the corner and might not occur if the corner vertex region was constructed of a non-broken layer of composite plies.

The most pertinent measure of the intensity of the fire is the rate of heat release. This is the true measure of the potential for spread to other surfaces beyond the area of origin and the true measure of the driving force behind the movement of heat and toxic gases. Figures 5 to 13 show the measured rate of heat release curves for the nine corner tests performed in this study.

Figure 5 shows what was, by far, the most intense fire seen; this occurred with the FRPE coating on the polyester/glass composite. We do not have a comparable test with no surface coating as a reference case but it appears that this coating had very little protective effect against fire growth. The flames reached the top of the corner somewhat more slowly than was the case for some of the coated vinyl ester samples below (Figures 7 and 8) but the subsequent fire seemed essentially unchecked. This is the one case in which a wider sample would have yielded a still more intense fire since the flame spread all the way to the lateral edges of the panels over most of the corner height. This fire, like others, was stopped by cutting off the gas supply to the burner and then applying water when the fire began to show a significant threat of spreading onto the backs of the panels. There seems little doubt that a structure built from this material combination would be vulnerable to unchecked surface flame spread.

Figure 6 shows one of the least intense fires seen; this occurred with the uncoated phenolic composite. The extent of upward flame spread seen was the least for any materials combination tested here. The small heat release rate contribution from the sample (20-30 kW) was a result of burning the resin out mainly from the lower regions of the sample where the heat flux was highest (Figure 4). This sample experienced the worst delamination seen in this test series, both down low in the high flux region and at the inner corners of the lowest portions of the upper panels. This last effect is presumably a consequence of the joint in the sample faces at mid-height. The delamination occurred erratically (in time and location) and with explosive force which caused gas jets to sometimes shoot several feet outward. This presumably was a result of the release of steam pressure build-up between plies.

Figure 7 shows the heat release behavior for one of the thick, heavy duty industrial coatings (Coating A) applied to vinyl ester/glass. It is apparent that the coating itself is somewhat flammable and exhibited, in the first few minutes, rapid flame spread yielding a substantial heat release peak. The fire intensity died back rapidly as the intumescent properties of the coating were further activated and then reached a steady low level (ca. 80 kW above the burner power level), driven by the gas burner heat flux input. The visible portions of the continuing heat
release (outside the lower area where the burner flame is opaque) came from a combination of periodic flare-ups in lateral-spreading flames, a few cracks in the coating and from the vertical joint at the corner vertex. The real threat here appears to be the initial peak in heat release rate. In the absence of a modeling study (planned for the future), we cannot confirm the potential for substantial further spread (on a larger structure). However, some further spread beyond the 3 m height used here is very likely and, had this been an enclosure with a ceiling of the same materials, the result would likely have been a significantly larger fire.

Figure 8 shows the results from the other thick, heavy duty industrial coating (Coating C) applied, again, to vinyl ester/glass. The overall behavior was quite similar to that seen above (Figure 7) except that the initial peak here is considerably less. The light green flame coloration noted with both of these coatings suggests that they share a common flame retardant. The post-peak lateral spread flare-ups were stronger here and can be discerned through the noise in the data. Other sources of a continuing heat release contribution from the sample appear to be comparable to those noted for Figure 7. The lower initial peak here would be expected to yield a much lesser propensity for further spread. It should be noted that these two coatings are being compared on the basis of one test of each so the reproducibilities of these peaks are not known. (Other tests were replicated; see below.)

Figure 9 shows the heat release results for Coating B, applied quite thinly compared to Coatings A and C (though rather thick according to the manufacturer’s guidelines). The protection it provided against flame spread lasted about 3-4 minutes. (The finite heat release rate contribution during this period is likely due to the organic content of the coating burning off in the area behind the opaque region of the burner flame.) Subsequently, the ignited area began to spread. This did not appear to be due to the coating flaking off. Rather, it was due to its inability, at this thickness, to sufficiently limit the heat flux penetrating to the vinyl ester resin. The resin began to gasify at a rate sufficient to sustain a flame. Attached flames reached the top of the corner when the total heat release rate was about 400 kW. Lateral flame spread caused further increase in the sample’s contribution to total heat output before the test was stopped by shutting down the burner.

Figures 10 and 11 show the results of duplicate tests of a thicker application of the same coating (B) to vinyl ester/glass. The result is a somewhat longer period (six to seven minutes) of no attached flame spread (beyond the region obscured by the opaque burner flames). The subsequent growth of the heat release contribution from the sample is slower than in Figure 9 and the sample contribution may be levelling off at about 100 kW by the time the tests were stopped. If this low level contribution were sustained, it would probably assure little threat of fire growth beyond the area burning here. The reproducibility of the overall behavior is good though this is somewhat obscured by the higher level of system noise in Figure 11.

Figures 12 and 13 show duplicate tests of Coating D applied at a thickness slightly greater than that of Coating B above. It should be noted that this coating (D) has an exceptional ability to intumesce, increasing in thickness in the highest flux regions by a factor of about 100 and thus reaching a thickness of approximately 10 centimeters. All of the other coatings increased in
thickness by a factor of the order of ten. While this extraordinary intumescence did not lead to exceptional behavior in retarding the increase in temperature on the back side of the composite (see below), it did result in very good resistance to fire growth. Here again one sees a brief initial heat release peak, presumably due to the organic content of the coating burning in the highest heat flux regions of the sample face. This is minimal and signifies no threat to regions beyond the test area. This initial peak quickly dies back to a negligible level in Figure 12 and a low level (ca. 30 kW) in Figure 13. There is no indication of true flame spread beyond the area masked by the opaque burner flame. Any heat release seen comes from a few cracks in the coating, the vertical joint area and whatever forced flaming is occurring behind the opaque region of the burner flame. One prominent source of the increase seen near the end of the burner exposure in Figure 12 is the loss of a roughly 30 cm square chunk of the coating from just above the mid-height joint on one panel. The extent to which the joint may have contributed to this loss cannot be determined. The tests were stopped primarily because the back surface temperatures were well past the point at which the composite would have been able to bear a load.

**Heat Penetration.** As noted above, thermocouples were placed on the back of both lower panels in each fire test. Figure 4 shows the locations used in all but the test with Coating A (where they were somewhat lower and closer to the corner, on average).

Recall that the back surface of the panels was insulated with R-11 fiberglass to provide an essentially adiabatic rear surface boundary condition and, more importantly, to preclude rapid fire growth on the back of the panels. This rear boundary condition is, of course, only one of many that may be pertinent in structural uses of composite materials. For a given thickness of material, it is probably a worst case with regard to the time to a structural failure condition since it does not allow any cooling of the back layers of the composite. Note that the rear surface conditions begin to be felt after a time interval that depends on the thickness of the material and its thermal diffusivity. This thermal relaxation time is of the order [24]

\[ t_{tr} = (0.1) \left[ \frac{l^2}{\alpha} \right] \]

where \( l \) is the material thickness and \( \alpha \) is its thermal diffusivity. For the vinyl ester composite (uncoated), using a measured value of thermal conductivity and density plus an estimated heat capacity, one obtains a thermal diffusivity of 0.001 cm\(^2\)/s. For a 1 cm thick composite this yields a thermal relaxation time of the order of 100 seconds. This suggests that the rear surface condition did not appreciably affect the upward flame spread for those tests where rapid spread was seen, i.e., those tests where the flames reached the top of the corner in 100-200 seconds or so. All of the fire exposures were appreciably longer than this and so all were ultimately influenced, with regard to interior heat build-up, by this rear boundary condition.

It is of interest to estimate how much difference an alternative rear boundary condition might make in the time for the rear surface of the composite to reach some benchmark temperature
value. An accurate estimate of this would require an extensive model of both the behavior of the coating and the behavior of the composite as heat penetrates and induces extensive chemical changes and gasification. In the absence of such a model we have used instead a model for the penetration of heat in an inert solid with the same thickness and thermal properties as the vinyl ester/glass composite. This is a one-dimensional, non-linear, numerical model which includes both convective and radiative terms in the boundary conditions. We have compared the time for the rear surface to reach 100 °C above ambient for two rear boundary conditions. The first is an adiabatic rear surface. The second case is that in which the rear boundary can lose heat by convection and radiation to room temperature surroundings. The front boundary in both cases is subject to a constant radiative flux and can also lose heat by natural convection. At a flux of 50 kW/m², the adiabatic rear reaches 100°C above ambient 20% faster than the condition allowing rear surface heat losses. At a flux of 100 kW/m², the time difference is only 11%. While this is not a definitive assessment of the effect of the rear surface condition, it suggests that the effect is fairly small and almost certainly less than a factor of two.

Figure 14 shows the measured temperature by the lowest thermocouple on the back side of a test panel (usually the left panel). The data have been edited to remove points obtained beyond the time at which the thermocouple junction had obviously opened up in two cases. In fact the data are not necessarily an accurate measure of the back surface temperature beyond 200-250 °C or so because in several cases the glass tape holding the thermocouple against the surface permitted a loss of tight contact (though heat sinking compound was always present). These data are representative but do not give a measure of the scatter in individual tests. Table 2 indicates the data spread for a given test; it gives the average and standard deviation for the times at which two fixed temperatures were reached, 100 and 150 °C, based on the six thermocouples on the backs of the samples. It should be noted that the time to reach a given temperature was not necessarily shorter for the lower thermocouples where Figure 4 would indicate that the incident flux was higher. The inert heat conduction model mentioned above indicates that the time to a fixed back temperature is a fairly weak function of incident heat flux (a 300% flux change gave a 50% time change to reach 100°C). The variations here may have thus been influenced more by local non-ideal behavior of the composites, such as interply bubble formation, than by local heat flux.

Inspection of Figure 14 and Table 2 shows that only the two thick, heavy-duty industrial coatings (A and C) substantially slowed the heat flow into the composites. Their much greater original thickness (as compared to the other coatings) was undoubtedly an advantage in this regard; it allows, for example, for the inclusion of much more endothermic material per unit area. Table 2 implies that Coating A is somewhat more effective as a heat barrier than Coating C for the conditions of this test. (Recall that Coating A was also more prone to fire growth, however.)

Among the other materials combinations there do appear to be significant differences in the retarding of heat flow to the back of the panels, though none were nearly so effective as Coatings A and C. Coating B appears to be rather ineffective, regardless of thickness. Surprisingly, Coating D and the FRPE Coat would seem to be equally effective. Recall that Coating D expanded by a factor of 100 by the end of the test whereas the FRPE coating was non-insulating.
in character (i.e., its sole intended role is as a flame retardant). This conclusion is perhaps not warranted since we do not know the thermal conductivity of the PE/Glass composite as compared to the VE/Glass composite; this could account for the results though it seems unlikely to do so fully. Alternatively, one might argue that the flame retardant in the FRPE coating kept the local flame temperature adjacent to the outer panel surface lower for some time; there is no direct evidence of such an effect, however. Coating D may, in fact, expand too much. Excessive porosity allows radiative transfer in porous insulations; the high flame fluxes lead to high temperature in the coatings and thus the possibility of substantial transfer of heat by radiation. The back surface temperature of the uncoated phenolic showed a plateau like that in Figure 14 for all six thermocouples. This may reflect an enhanced insulative effect brought on by the extensive delamination noted for this type of panel.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Time (sec) to 100 °C (± s.d.)</th>
<th>Time (sec) to 150 °C (± s.d.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE/Gl + Coating A</td>
<td>804 ± 62</td>
<td>1882 ± 116</td>
</tr>
<tr>
<td>VE/Gl + Coating B (1 mm)</td>
<td>189 ± 20</td>
<td>284 ± 30</td>
</tr>
<tr>
<td></td>
<td>186 ± 24</td>
<td>288 ± 38</td>
</tr>
<tr>
<td>VE/GL + Coating B (1/2 mm)</td>
<td>184 ± 22</td>
<td>272 ± 32</td>
</tr>
<tr>
<td>VE/Gl + Coating C</td>
<td>731 ± 93</td>
<td>1457 ± 153</td>
</tr>
<tr>
<td>VE/Gl + Coating D</td>
<td>240 ± 30</td>
<td>407 ± 61</td>
</tr>
<tr>
<td></td>
<td>229 ± 24</td>
<td>390 ± 54</td>
</tr>
<tr>
<td>Uncoated Phenolic/Gl</td>
<td>199 ± 23</td>
<td>287 ± 36</td>
</tr>
<tr>
<td>FRPE Coat on PE/Gl</td>
<td>262 ± 32</td>
<td>403 ± 33</td>
</tr>
</tbody>
</table>

For the vinyl ester resin that was the main focus here, available data [17, 25] indicate that the flexural strength drops by a factor of two at 120°C and by a factor of 4 at 150°C. The tensile strength, derived mainly from the fibers, does not decline at these temperatures [17]. Compressive strength data are not reported but one would expect that a compressive load in the plane of the fiber plies could not be supported for long above the temperatures just noted. Reference 25 in fact states that a vinyl ester/glass composite is not suitable for a load bearing application above 130-140°C. This same reference indicates that a phenolic/glass composite loses about 25% of its flexural strength at 150°C; higher temperature data are not available.

In light of these data, Table 2 would seem to imply that the fire endurance of the coated vinyl ester composites tested here is rather poor; only Coating A extended the time to reach 150°C.
(and almost certain structural failure) past 30 minutes. Many material applications require resistance to standard fire curves (e.g., ASTM E-119) of 30 or 60 minutes. In fact the picture is not quite so negative as this might imply. Standard fire curves require several minutes to elevate the heat exposure whereas here the exposure was essentially full force instantaneously. Also, the standard exposure situations do not normally include thermal insulation of the unexposed side, as was done here. It was noted above that the uninsulated case would heat up somewhat more slowly. Furthermore, the results here are for a composite that is 1 cm thick. Equation (1) for thermal relaxation time of an inert material is dependent on the square of the material thickness. This implies that a 2 cm thick composite would require four times as long to reach the back surface temperatures seen in Table 2. Of course, one must also bear in mind that, depending on the specific design, a composite structural element may fail when the "no-strength isotherm" (taken above to be in the range 130-140°C for vinyl ester/glass) has penetrated to some finite fraction (less than one) of the full depth of the element's cross section.

Gibson and Hume [7] found a plateau in the rear surface temperature rise of various composites during a furnace test exposure. In a one-dimensional model of the heat flow through their composites, they found that the endotherm and convection caused by resin gasification was the source of this extended protection of the unexposed side of the composite. We did not see a comparable plateau here (except with the phenolic/glass composite), but such a mechanism is plausible and could provide some added time to resist a fire exposure.

5) Summary and Conclusions

The results here indicate that intumescent coatings can control the potential for fire growth on vinyl ester composites. There is, however, considerable variation in the efficacy of the four commercial coatings examined. Coating A was effective in protecting the composite from involvement in the fire but itself contributed substantial fuel initially, yielding a potentially threatening, early surge in heat release rate. Coating B was tested at two thicknesses. The lesser thickness (0.5 mm) provided only a few minutes of protection against involvement of the composite. The subsequent fire growth was slowed but not checked. At the greater thickness (0.9 mm), this coating was more effective but fire growth still began in 6 to 7 minutes. The test data suggest (but do not prove) that this fire was limited to a non-threatening size. Thus there are indications that this coating might suffice, at this thickness, to control fire growth. A still greater thickness (ca. 1.5 mm) might be the most effective choice. Coating C, like A, was exceptionally thick, having been applied by the manufacturer. Unlike A, it contributed a relatively small amount of fuel initially then proceeded to good job of protecting the composite from fire growth. Coating D was exceptionally intumescent and it contributed a minimal amount of fuel to the burner fire. It was quite effective at preventing fire growth. The fire-retarded polyester resin painted on the outside of an unretarded polyester/glass composite provided about one minute of protection against fire growth. The subsequent fire was the most intense seen here. The uncoated phenolic/glass composite was excellent in regard to resistance to fire growth but it showed a disconcerting tendency to delaminate explosively. In any event, it is clear that several of the materials combinations examined here have the potential to yield a composite
structure that is highly resistant to the threat of uncontrolled fire growth subsequent to an accidental fire exposure.

The ability of these material combinations to resist heat penetration did not correlate well with their ability to resist fire growth. Coating A was most effective in slowing the rate of rise of the rear surface temperature. Coating C was nearly as good. The other materials combinations were all substantially worse in this regard. Coating D and the FRPE resin coat were about equally effective, providing a 50% longer time to a back surface temperature of 150°C than did the remaining combinations.

The adequacy of the fire resistance performance of any of these material combinations is dependent on both the design of the structure in which they might be employed and the fire scenario in which they might be exposed. If the fire exposure occurred on a non-critical part of the composite (with respect to load bearing), any coating or material which precluded fire growth would be adequate. If the fire occurred on a critical portion of the composite, the time to failure depends on the thickness of the composite and any load safety factor, in addition to the nature and thickness of any protective coating. The adequacy of a coating in this situation also depends on the maximum time which the exposure fire could persist and the minimum time needed to impose fire suppression measures. Thus to carry the study of the effectiveness of coatings to the next, more practical level, it is necessary to define the actual structural application. Then too one can begin to examine the other practical issues that are pertinent to real world applications, such as weather, UV light and mechanical abrasion resistance.

The present study was based on a single, fairly severe fire exposure condition. It is of interest to know what might be the impact of other fire exposures. It is of equal interest to be able to estimate the effect of such changes in exposure conditions or in coating properties on the basis of less expensive tests. The next step planned in this program involves the development and assessment of a model of fire growth in a corner configuration which uses as input data on the coated composite obtained in bench scale tests. A verified model of this sort will satisfy this need.

6) Acknowledgement

The authors would like to gratefully acknowledge the considerable assistance of Eric Greene who was instrumental in obtaining the sample materials.

7) References


22) Greene, E., Private communication regarding tests performed at VTEC Laboratories, New York, NY.


FIGURE 1. Schematic of Corner Burn Configuration (10 ft. Panels)
FIGURE 2. Schematic of 250 kW Propane Burner set-up
FIGURE 3. Schematic of Flux Gage Positions
Figure 4
Flux Contours Based on Measured Fluxes
53 cm Burner at 250 kW

Corner Height is 305 cm

Mean Flame Height +/- Std. Dev.

Position of Rear Surface Thermocouples

Flux Units are kW/m²
Figure 5

Corrected Rate of Heat Release
Polyester/ Glass with FRPE Coat

- Nearly 100% of Sample Face Flaming
- Burner Power Output
- Attached Flames To Top of Corner At 105 - 115 Seconds
Figure 6
Corrected Rate of Heat Release
Phenolic/ Glass with No Coating

Corrected Rate of Heat Release (kW)

Burner Power Output

Attached Flame Spread Less Than Half Corner Height

Time From Start of Test (sec)
Figure 7
Corrected Rate of Heat Release
Vinyl Ester Glass with Coating A

Corrected Rate of Heat Release (kW)

Time From Start of Test (sec)

Persisting Flaming
Mainly in Corner Vertex

Burner Power Output

Attached Flames Reach Top of Corner
Before 60 Seconds
Figure 8
Corrected Rate of Heat Release
Vinyl Ester/ Glass with Coating C

Attached Flames Reach Top of Corner
At 60-80 Seconds
Figure 9
Corrected Rate of Heat Release
Vinyl Ester/ Glass with Coating B
(0.5 mm Thick)

Corrected Rate of Heat Release (kW)

Time From Start of Test (sec)

Burner Power Output

Attached Flame Area Growing;
Reaches Top at About 400-450 Seconds
Figure 10
Corrected Rate of Heat Release
Vinyl Ester/ Glass with Coating B
(0.9 mm Thick)

Burner Power Output

Attached Flames to Top of Corner
At About 600 Seconds
Figure 11
Corrected Rate of Heat Release
Vinyl Ester/ Glass with Coating B
(0.9 mm Thick, Replicate)

Attached Flames to Top of Corner
About 550-575 Seconds
Figure 12
Corrected Rate of Heat Release
Vinyl Ester/ Glass with Coating D

Time From Start of Test (sec)

Corrected Rate of Heat Release (kW)

Increasing Flames at Sample Joints (Primarily)
And Coating Cracks (Secondarily)

Burner Power Output
Figure 13
Corrected Rate of Heat Release
Vinyl Ester/ Glass with Coating D
(Replicate)

Burner Power Output
Gradual Increase in Flaming at Joints and on Cracks in Coating

Corrected Rate of Heat Release (kW)
Time From Start of Test (sec)
Figure 14. Output From Lowest Thermocouple In All Tests

Time From Start of Burner (sec)

Rear Surface Temperature (°C)

- Coating A
- Coating B, 0.9 mm
- Coating B, 0.5 mm
- Coating C
- Coating D
- Uncoated Phenolic
- FRPE Coating on PE
The Effect of Surface Coatings on Fire Growth over Composite Materials

Structural composites are vulnerable to fire in two respects: 1) their resin content may ignite and enable the spread of flames over the surface of the structure; (2) the resin may degrade from the heat of a localized fire exposure thus weakening the composite structure. The present study focuses mainly on the first issue, in particular, on the ability of various commercial coatings to prevent flame spread. The second issue is examined briefly by applying thermocouples to the back surface of test specimens. Four commercial coatings have been tested over an unretarded vinyl ester/glass composite. In addition an uncoated phenolic/glass composite and polyester/glass composite coated with a fire retarded resin were tested. In all cases the configuration was a 3.3 m high corner with 53 cm square propane gas burner at its base, operated at 250 kW as the fire exposure. The results show that, with the proper choice of coating and coating thickness, fire growth can be suppressed quite effectively. Two of the coatings, applied at a substantial thickness, were reasonably effective at slowing the penetration of heat to the back of the composite panels. The other coatings, much thinner in application, were notably less effective at slowing heat penetration.

KEY WORDS (MAXIMUM OF 9; 28 CHARACTERS AND SPACES EACH; SEPARATE WITH SEMICOLONS; ALPHABETIC ORDER; CAPITALIZE ONLY PROPER NAMES)

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