

Fire Characteristics of Polyester FRP Composites with Different Glass Contents

by

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Abstract

For the composites industry to “design for fire” more thorough understanding of how typical FRPs decompose under fire conditions is needed. Under fire conditions the role played by the glass and the resin (and additives) for FRPs are keys to understanding the fire behavior. To that end, this study continues work presented at Composites 2006. A polyester resin system and three glass contents will be considered. This set of polyester FRPs has been carefully fabricated and documented so as to provide “transparency” as to the system compositions. The polyester FRP of this study have been evaluated in modern bench scale fire test apparatuses (Cone and FPA) with additional instrumentation to allow surface and internal temperatures to be measured as well as surface heat fluxes. Additionally, thermal analysis of the polyester polymer resin is conducted using Thermalgravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). This study provides complete data sets for pyrolysis modeling for the polyester FRP composite. Development of simplified pyrolysis models will allow the composites industry to “design for fire” via virtual simulations of fire behavior. For typical fire thermal insults, it is found that the internal temperatures for typical fire heat flux levels are more than ade-

quate to decompose the polyester resin. The temperature distributions are also insensitive to the glass content indicating that for flammability the base characteristics of the polyester FRP are controlled by the surface glass layers.

1. Introduction

Traditionally, the manufacture of composites is largely a guess and check operation with regards to fire characteristics. The original design composite is tested via standard fire tests but the composite would need to be re-tested if the resin type or glass content was changed, possibly without knowing if the change will positively affect the test results. The testing cycle can be time consuming and expensive. However, if the manufacturer had an idea of how changing the resin type or glass content would affect the results, this would provide a guideline to ease the time and financial commitment of manufacturing fire-safe composites. The current work aims to provide a beginning to systematic research into how the thermal decomposition characteristics of a polyester resin and different glass contents affect the overall fire behavior of typical fiber reinforced polymer (FRP) composites.

Bench-scale apparatuses such as the Fire Propagation Apparatus (FPA, ASTM E 2058[1]), the Cone Calorimeter (ASTM E 1354[2]) and thermal analysis instruments - Thermalgravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) - are used in this study to provide useful data which can be used in a fire model to simulate burning. In the fire community, using data similar to that which will be developed in this study as parameters in a fire model in order to simulate the end use of the material is the long-term goal [3]. Significant steps were taken toward this goal with the development of the Fire Dynamics Simulator (FDS) developed at the National Institute for Standards and Technology [4] and other computational fluid dynamics (CFD) based fire models [5][6]. A subset of these more comprehensive models is the pyrolysis model, which describes the heating and decomposition of the material. A good review of pyrolysis models is available in the literature [7]. From the composites literature [8][9][10][11], there is a significant amount of work on the temperature profile of composites with regards to thermo-mechanical stability. These studies incorporate a comprehensive pyrolysis model but focus more on temperatures at depth instead of temperatures at or close to the surface, which are more important for reaction to fire characteristics.

The current work aims to obtain data from bench-scale test apparatuses that can be used to study the thermal behavior of the polyester FRP as well as the effect of the fiber glass contents within the FRPs on its fire characteristics. In addition to the bench-scale testing, a simple thermal analysis of the polymer resins is performed to better understand its thermal behaviours. The minimum heat flux for proper ignition, a common fire

engineering “property,” was determined for the polyester composites by varying the applied heat flux to the material. A simple parameter estimation to determine the thermal diffusivity, thermal conductivity and specific heat was completed in an attempt to further differentiate the composites. Additionally, a more sophisticated pyrolysis model developed by Lautenberger at University of California, Berkeley [12] was used to model the polyester composites. The results from these exercises will be presented in the later part of this study. While traditional bench-scale measurements such as heat release rate and mass loss rate will be used, measuring surface and in-depth temperatures as well as changing the environment to which the sample is exposed to give additional insight into the behavior of the polyester composites and provide the beginning of a data set useful for modelling purposes.

2. Testing Equipment and Materials

2.1. Composite Systems

In the following discussion, the term “system” will be used to indicate the resin type. Hence, instead of polyester resin based FRP composite, System1 will be used to designate the polyester FRP. The term “sample” will be used to differentiate between glass contents (e.g. sample 1A has a lower glass content than sample 1B). Lastly, the term “specimen” will be used to represent one individual composite from the sample that will be tested.

Three different polyester fiber reinforced polymer (FRP) samples are being tested for the current work. Table 1 shows the different glass content for the three polyester (System 1) FRP composites that were tested in the current study. From the table, it can be seen that there was a variability of 6-10mm in thickness over all of the composite systems used. The polyester (System 1) resin used in this study was brominated for its fire receptivity and antimony trioxide was added as an additive. The antimony trioxide acts as a synergist that assists the flame retardancy of the polymer resin. Among the various effects of adding antimony trioxide, the major role of this additive is reacting with the halogen such as bromine and removing the radicals that are essential for combustion chemical reactions to proceed. This additive is also known to delay the escape of halogen from the flame, which increases its concentration and diluting effect [13]. The polyester resin used in this study is listed as Class 1 or A with regards to ASTM E 84 [14].

There are three different types of fiberglass used in each of the composites: Owens Corning chopped strand mat (67.8g/m^2), Fiber Glass Industries (FGI) 2-end satin roving (882g/m^2) and St. Gobain plain cloth (332g/m^2). The pattern of fiberglass, which has properties similar to E-glass, repeats 3, 4 and 5 times to create the lowest, medium and highest glass contents. The layers of glass, which are a special tight weave, are fully wetted with the resin and held together with a very thin 15 mil phenolic binder veil by Schmelzer, Inc.. The ability of the individual layers of glass to fully wet with the

resin is unknown and the glass/resin ratio will be assumed to be constant throughout the cross section of the composite. A prominent glass layer which is thought to be the FGI 2-end satin roving layer can be seen from the cross section of the composite and thus allows for a measurement of the distance between repeats of the fiberglass pattern. The FGI fiberglass has a 5 by 7mm weave and a 5-7mm stitch can be seen on the cross section of the composites so the assumption of the prominent glass layer is thought to be valid. From the measurements, the fiberglass pattern repeats every 1-2mm.

2.2. The FPA and the Cone Calorimeter

The FPA [1] is a bench-scale fire test apparatus in which the sample is heated by four radiant lamps. Each IR lamp consists of 6 bulbs with a tungsten wire in argon gas, which provides a uniform heat flux (to within 5kW/m^2 , determined from testing) over the specimen surface of up to 60kW/m^2 . The lamps emit with spectral energy peaks of 1.15 and 0.89 microns [15]. A long quartz tube can be used to create an atmosphere for the test that is different than the ambient (i.e. from pure nitrogen to 40% enhanced oxygen). A flow rate of air at 200 lpm is run through the bottom of the air chamber so that the sample is in a flow field during the test. The ignition source is a 10mm long blue pilot flame located 10mm above the center of the sample. The FPA can be used to measure useful engineering data such as heat release rate, mass loss rate, smoke yield and smoke extinction coefficient. The standard specifies a carbon dioxide generation based heat release rate, which will be used for the FPA in this study [1].

The Cone Calorimeter [2] is similar to the FPA but it also has some important differences. The heater in the Cone is an electrically heated rod in the shape of a cone, instead of the IR lamps in the FPA. The sample in the Cone is exposed to the ambient environment and is not in a flow field so the apparatus can only perform tests under ambient conditions. The ignition source is an intermittent sparker instead of the pilot flame used by the FPA. The Cone standard specifies an oxygen consumption based heat release rate, which will be used for the Cone in this study [2].

The difference in the radiant source between the Cone and the FPA is noteworthy because the FPA radiation apparently tends to absorb at depth into the composites evaluated in this study while the Cone does not. This difference causes a discrepancy in the time to ignition between results obtained from the Cone and the FPA. Testing performed with thermocouples to demonstrate differences between FPA and Cone test results were inconclusive. The temperature begins to rise a bit slower in the Cone; after the initial period however, the thermocouple traces for identical tests performed on the two apparatuses match each other fairly well. An attempt was also made to resolve the absorption issue by applying carbon black powder to the surface of the specimen in the FPA to prevent in-depth absorption. The carbon

black decreased the time to ignition in the FPA to match that of the Cone, indicating that the FPA does experience some in-depth absorption.

2.2.1. *Sample Holder*

Instead of the non-insulated aluminium dish that is specified in ASTM E 2058 [1], an insulated sample dish described by de Ris and Khan [16] is used. The sample is surrounded by Cotronics[®] paper insulation on the back and sides, as shown in Figure 1, to provide a barrier to heat loss. The assumptions that can be made based on the presence of the insulation (e.g. no heat loss from the back face or sides of the sample) are very useful in modelling the sample's reaction to the applied heat flux. The sample holder is also beneficial for installing embedded and back face thermocouples as well as embedding a heat flux gage to lie flush with the sample surface.

2.2.2. *Instrumentation Installation*

In order to install the thermocouples at depth, 1.25mm diameter holes were drilled at appropriate depths from the surface. The holes were drilled 38-50mm (1.5-2 inches) into the edge of the sample. From testing with both thermocouples at different radii as well as with the heat flux gage, it was found that there is a zone of uniformity with regards to temperature and heat flux within a 32mm (1.25inch) radius from the center of the specimen. Since the specimens have a diameter of approximately 102mm (4 inches) diameter, the thermocouple bead was located within this zone of uniformity. In order to eliminate air gaps in the holes drilled for the thermocouples, thermal grease (OmegaTherm Thermally Conductive Silicone Paste, Model OT-201 from Omega Engineering) was inserted along with the thermocouples (Omega Precision Fine Wire Thermocouples, Model 5TC-GG-K-30-36 from Omega Engineering). The back face thermocouple was affixed to the middle of the back surface with Krazy glue, which is inexpensive, dries very fast and has proven to be consistent and repeatable for back face temperature measurements. The surface thermocouple was attached with a thin layer of high temperature adhesive (Resbond 907 Industrial Strength Fireproof Adhesive from Cotronics Corp.). The surface thermocouple was located one inch from the edge of the sample so that the bead was in the zone of uniformity but not affected by the pilot flame (the ignition source used in the FPA).

Originally, an infrared thermometer was used to measure sample surface temperature. In the FPA, the IR thermometer is mounted on a bracket and has a spot size that is 2.3cm (0.9inch) in diameter whose center is located approximately one inch from the edge of the sample to avoid the pilot flame. In the Cone, the infrared thermometer is closer to the sample surface, resulting in a spot size of 1.3cm (0.5inch) and is situated to view the center of the sample. Unfortunately, the infrared thermometer did not provide repeatable results for the poly-

ester composites and did not provide results consistent with the surface thermocouple for any of the composites. The reason for this is not known but there are a number of theories in the literature including absorption of the emitted radiation by gases coming from the sample such as CO, CO₂ and H₂O [17][18] or the transmissive properties of the resin material [19]. Due to issues with results from the infrared thermometer, the surface thermocouple will be used for surface temperature measurements and the IR thermometer will not be further discussed.

A heat flux gage was also embedded in the sample to lie flush with the surface. The dual heat flux gage (MedTherm model number 32-15TKS-15R(S)-21846) that was used was able to partition the heat flux into both convective and radiative fractions. However, a resin condensate layer formed on the gage just before ignition or after a prolonged period of non-flaming decomposition. The formation of this layer caused the radiometer to read essentially zero heat flux and caused a change in the reading of the total heat flux gage. Even though the reading from the total heat flux gage after the condensate formation is still being interpreted, the information obtained before this time from both the total and radiative heat flux gage can be used to partition the heat flux from the FPA and Cone into its radiative and convective portions.

2.2.3. *Uncertainties*

The uncertainty for the different variables was determined via statistical analysis performed on data from tests with identical conditions. All uncertainties listed in this study are full scale (as opposed to \pm half scale). The uncertainty in the heat release rate (45kW/m²) was determined from calibration tests done with PMMA, acetone, methane and propylene in the FPA; it is an average value. The analysis for the uncertainty in the time to ignition, burn duration and mass loss rate for the FPA is based on three PMMA tests performed at 50kW/m². A sample set of three is believed to be sufficient in this case because the FPA standard calls for three identical tests to be performed to correctly determine other properties [1]. From these tests, the maximum uncertainty in the time to ignition and the burn duration were found to be 9s and 101s, respectively. The uncertainty in the mass loss rate was found to be 17mg/s (2.4g/sm²). The uncertainty in the critical mass flux at proper ignition was found to have a maximum uncertainty of 6.5g/sm² from population statistics on PMMA and composite samples.

The uncertainty in the thermocouple measurements was determined from comparing the traces from identical tests, including PMMA and composite testing. Population statistics were calculated based on this comparison for a number of tests and the average, across all tests, of the maximum deviation between two traces was found. The thermocouple measurements have, on average, a maximum deviation of 27°C with a standard deviation of 18°C; the maximum deviation will be used to

evaluate significant differences in the thermocouple traces.

The uncertainties calculated above for the FPA will also be used for evaluating significant differences in Cone tests. The heat release rate uncertainty in the Cone is governed by the C factor, which is determined by calculating the heat release rate of a methane fire at different mass flow rate steps and inserting the subsequent values into an equation for the C factor that is provided in ASTM E 1354 [2]. The required uncertainty from the standard is 5% and it is known that the Cone meets this requirement. Therefore, no additional calibration testing was required on the Cone for the purposes of this study.

2.3. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The instruments used in this study were manufactured from PerkinElmer: Thermalgravimetric Analysis 7 (TGA7) and the Differential Scanning Calorimetry 7 (DSC7). Throughout this study, TGA and DSC were used for a non-isothermal test purposes and the tests were conducted in an air environment. Using TGA7, 4 different heating rates of 5°C/min., 10°C/min., 30°C/min. and 50°C/min. were applied to measure the mass loss history of each resin sample. For each test, a sample amount of 7.5 mg ~ 10.5 mg was used. TGA7 was calibrated using 4 different standard reference materials over the temperature range of ambient to 850°C: Alumel, Nickel, Perkalloy and Iron. Each reference was checked for its magnetic transition temperatures, which should be within +/- 5°C of its reported values. For DSC7, constant heating rates of 10°C/min., 30°C/min., 50°C/min. and 70°C/min. were used to measure the heat flow through the sample during its thermal decomposition. A sample amount of 7.5 mg ~ 9.5 mg was used for each test. This instrument was calibrated using the standard indium and zinc references for a temperature range of ambient to the maximum temperature available from the instrument, 500°C. The melting points of these references were checked to be within +/- 10% of its reported values. The energy check was performed using indium. The heat of fusion for indium was calibrated to be within 20% ~ 30% of its reference value. A simple baseline subtraction was conducted to eliminate the unnecessary curvatures within the heat flow curve.

3. Proper Ignition Concept and Testing Matrix

3.1. Proper and Improper Ignition

The concept of proper ignition that was used in this study is an extension of the concept of “sustained flaming” that was developed in ASTM E 2058 [1]. The standard defines sustained flaming as the “existence of flame on or over most of the specimen surface for at least a 4s duration” [1]. Since one of the goals of this study is to produce useful data for the development of pyrolysis models, a fully developed flame cone is necessary to make the simplifying assumption of one-dimensional

burning. Another benefit to this definition is that it does not count edge burning as significant burning because the end use of this product (i.e. a wall, ceiling, floor) would usually be so large that edge effects would be very minor. A flame is considered to be effectively one-dimensional if it is even over the entire sample surface and is unified into a single flame cone (not necessarily axisymmetric). A distinction was made between cellular burning (flamelets over most or all of the surface) and edge burning. If a sample started to burn with cellular flaming and then progressed into a flame cone, it was still called proper ignition for the purposes of this study. Visual observations were made as to the time of the beginning and end of the flame cone so that data could be properly truncated for modelling purposes.

The concept of a critical mass flux is used by modellers as an ignition criterion and sometimes as an extinction criterion. When the mass flux reaches a critical value, the sample is assumed to have ignited and when it decreases past this value near the end of the test, the flame is assumed to have gone out [20]. The critical mass flux at proper ignition was determined for the samples studied and the results are displayed also in Table 1. As can be seen from the table, there is a high degree of uncertainty in the critical mass flux. The critical mass flux is based on the time to ignition (uncertainty of 9s) and on the mass loss rate (uncertainty of 17mg/s or 2.4g/sm²) and therefore has a high degree of variability (6g/sm²). Also, all tests that experienced proper ignition, including FPA and Cone tests at a variety of heat fluxes, were included to obtain the statistics displayed in the table. Despite the high degree of uncertainty, there is a downward trend in the critical mass flux at proper ignition with increasing glass content for System 1 composites (polyester). The PMMA is included as a reference from the literature to ensure consistency. PMMA has a critical mass flux at ignition of 4-5g/sm [2][20] which matches with the value obtained with the FPA (within the uncertainty). Another interesting note with regards to the table is that the critical mass flux at proper ignition is approximately 10g/sm² for all of the materials studied, including the PMMA and all of the composite systems.

3.2. Testing Matrix

Tests were performed on the composite systems to determine the minimum heat flux for proper ignition. The minimum heat flux for proper ignition represents the condition under which the material will experience ignition but not necessarily fire spread and will help to rank the materials according to resin type and glass content. If the value of the minimum heat flux is low, the resin is less thermally stable and the probability that it will experience fire spread are increased over those materials that have a higher minimum heat flux. With regards to fire modeling, the idea of minimum heat flux for proper ignition as defined in this study is important since it represents the heat flux at which the concept of one-dimensional burning is applicable. The results for these

minimum heat flux tests were reported in the 2006 Composite and Polycon paper [21] as well as in Table 1.

A testing matrix was created in an effort to compile a good set of data for modeling purposes. The matrix consisted of tests to fully develop potential differences with glass content for polyester (System 1) composites, perform non-flaming tests, study environmental effects and compare results between the Cone and the FPA. The difference between results from the Cone and the FPA is discussed above. All tests had instrumentation including embedded and back face thermocouples; some later tests also had a surface thermocouple to measure sample surface temperature. Separate tests were performed with an embedded heat flux gage. The added instrumentation provides good data for both boundary conditions (surface temperature and surface heat flux up to the development of condensate on the gage) and parameter estimation (temperature profile in the specimen). Non-flaming tests are important because the decomposition kinetics of the sample can be tested without the added complexity of the flame. Tests were performed under different environments (with no pilot flame in order to lengthen the non-flaming condition) to determine if the decomposition kinetics would significantly change.

In order to better determine differences with glass content, tests were done with the polyester composites at all three glass contents in the FPA at 50kW/m^2 ; all of these tests experienced proper ignition. Tests were also done at 50kW/m^2 in the FPA under nitrogen, air and 40% oxygen enhanced air atmospheres as well as at 50kW/m^2 in the Cone. A heat flux of 50kW/m^2 was chosen as a representative heat flux for the tests because it is a common heat flux in the literature and it represents a mid-range value for the two testing apparatuses used in this study.

4. Results

Many aspects of the composites were studied through the use of this testing matrix geared toward calibration of a pyrolysis model and comparing glass content for polyester (System 1) composites. As discussed in the previous section, tests were also done under air, nitrogen and 40% oxygen enhanced air. Since no difference in the temperature profile was determined and this is not the main focus of the current study, these results will not be further discussed below.

4.1. Effect of Glass Content

Figure 2 is a graph of the heat release rate traces from FPA tests done at 50kW/m^2 for the polyester (System 1) composites. The end of the trace is truncated based on visual observations of the loss of the fully developed flame cone although data was collected throughout the entire test. Recalling that the heat release rate uncertainty for the FPA is 45kW/m^2 , it can be seen that the top layer has a significantly higher heat release rate than the rest of the layers for 1A and 1B but 1C does not have a significant initial peak. Considering the differ-

ence in the initial peak with changing glass content, it can be seen that the magnitude of the initial peak is significantly different between 1A and 1B as well as between 1A and 1C but there is not a significant difference between the initial peaks of 1B and 1C. However, the graph shows a trend that as the glass content is increased, the magnitude of the initial peak decreases. These differences are believed to be related to the surface texture. The surface texture of 1A and 1B is smooth and 1A is highly glossy, which seems to indicate that there is a resin film on the surface. However, 1C has a very bumpy surface due to the weave from the glass layers, which may indicate that there is much less resin near the surface than for 1A or 1B and thus a less significant initial peak in the heat release rate trace.

Given the accuracy with which the heat release rate can be determined in the FPA, the difference in the plateau region of the curve is insignificant (see Figure 2) across all of the System 1 samples. Once the top layer of resin is burnt off, the glass layers block the heat transfer into and the mass transfer out of the specimen, slowing the decomposition of the resin. This effect appears to be present irregardless of the glass content for the range of glass contents studied.

From the test data, the time to ignition for samples 1A, 1B and 1C are 124s, 145s and 159s, respectively. Given that the uncertainty in the time to ignition is 9s, there is a significant increase in the time to ignition with glass content for all of the polyester composites. In Figure 2, the test is truncated at the loss of flame cone, which is approximately the same for all three glass contents if the time axis is normalized with the thickness of the specimen, as it appears in the graph. This result apparently indicates that the three different glass contents reach the same sort of condition at the loss of the flame cone but more work is needed to understand the results.

A comparison of surface and in-depth temperatures for the specimen can further demonstrate differences with glass content for the polyester composites, as shown in Figure 3 and Figure 4. Since the samples are different thicknesses, the time axis is normalized by the thickness of the sample. The normalization uses a non-dimensional Fourier number, assuming that all of the samples have the same thermal diffusivity. The temperature axis is a temperature rise to eliminate any differences in initial temperature between the thermocouples. The temperatures at a depth of one-third from the surface as well as the back face were also recorded but are not shown in the graph to reduce clutter; they follow a similar trend. From Figure 3, it can be seen that there is not a significant difference in the in-depth temperature with glass content for the polyester composites. Referring to Figure 4 for the surface temperatures, there is a significant difference with glass content for all of the polyester composites before ignition but all of the traces plateau within the uncertainty shortly after ignition. From the composites literature [22], the thermal conductivity of the E-glass is an order of magnitude higher than that of

the composite. The materials being studied are layered composites so if there is more glass closer to the surface, there will be a higher local thermal conductivity at the surface. The local thermal conductivity at the surface is thought to be higher for the higher glass content due to the surface texture (as discussed above), resulting in a lower surface temperature. As the test progresses and the resin is consumed, the temperatures for all of the different glass contents plateau to a similar surface temperature. In Figure 4, one of the 1A samples is with a pilot flame and the other is not. However, the test with no pilot flame autoignites and exhibits the same surface temperature behavior as the test with the pilot flame.

4.2. Thermal Decomposition of Polyester Resin

To understand the effect of the polyester resin on the overall fire behaviour of the FRP composite, the thermal decomposition of the resin sample was tested using TGA7 and DSC7. This resin sample was produced with the same procedure as the resins found in the FRP composites that were tested earlier in this study. Using these instruments, the polyester resin was tested to study its thermal behaviour in detail. The analysis results shows that the polyester resin starts to degrade from 200°C to 500°C, which is a wider thermal decomposition temperature range compared to that of resins such as phenolic resins (see (a) and (b) in Figure 5). The degradation process for the polyester resin initiates with a small amount of mass loss, in the order of 10% of the total sample weight. This is followed by a large mass loss within the next 100°C of temperature increase. At this stage, the sample releases energy as it degrades resulting in an exothermic degradation reaction, which is shown in (c) in Figure 5. Depending on the heating rate, approximately 90% of the total weight loss of the polyester resin is completed around 420°C to 500°C. Beyond this temperature, there is less than 5% of mass loss.

5. Analysis

The data was separated into two distinct phases: the initial heating phase without any decomposition of the resin and the later phase where the actual thermal decomposition occurs. For the initial heating phase, a simple inert homogenous solid solution for the temperature equation was used to estimate the unknown thermal properties - thermal diffusivity, thermal conductivity and specific heat. For the entire process including the later phase, a more advanced model developed by Lautenberger [7][12] was used to initially model the pyrolysis of polyester FRP composites with different glass contents.

5.1. Parameter Estimation for Initial Heating Phase

The thermal diffusivity, thermal conductivity and specific heat can be estimated using an inert homogenous solid solution for the temperature profile with no absorption at depth. The assumption of no absorption at depth was investigated with PMMA in the FPA by comparing actual temperature profiles to the analytical

solution for absorption at depth into an inert homogeneous solid, as solved for in the literature [12], up to half the time to ignition. This cut-off point was used since the equation assumes that the material is inert. It is considered that within this time interval, the temperature increase of the sample is insufficient for chemical decomposition to occur. It was found from the analysis that 33% of the incident heat flux is absorbed 0.75mm into the sample while the remainder is absorbed at the surface. Since the uncertainty in the location measurements for the thermocouples is on the order of 1mm, it is assumed that this absorption depth is negligible since it is within the location uncertainty of the instrument being used to determine the temperature profile.

The absorption at depth for the composites could not be determined the same way as PMMA since there are too many unknown parameters in the equation (i.e. absorption coefficient and thermal properties). As discussed in previous sections, it is known from experimentation that the ignition time is slightly longer in the FPA than it is in the Cone for the same material and that applying carbon black to the sample surface in the FPA lowers the ignition time to that of the Cone. This indicates that there is some absorption at depth in the FPA but not in the Cone, since it matches the ignition time for the test with the carbon black. However, the temperature profiles observed in the same sample tested in the Cone and the FPA are the same, within the uncertainty, indicating that the absorption at depth in the FPA is insignificant.

Therefore, the thermal properties can be estimated using an inert homogenous solid solution for the temperature profile with no absorption at depth. The equation is available in the literature [23] and is repeated below.

$$T = T_0 + \frac{\dot{q}''_{absorbed}}{H} \left[\operatorname{erfc}\left(\frac{x}{2\sqrt{\delta t}}\right) - \exp\left(\frac{Hx}{k} + \frac{\delta H^2 t}{k^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{\delta t}} + \sqrt{\frac{\delta H^2 t}{k^2}}\right) \right]$$

In the equation, T is the temperature (K), T_0 is the initial temperature (K), $\dot{q}''_{absorbed}$ is the absorbed heat flux (W/m^2), H is the linearized heat transfer coefficient (W/m^2K), x is the depth from the surface (m), δ is the thermal diffusivity (m^2/s), t is time (s) and k is the thermal conductivity (W/mK). The absorbed heat flux is assumed to be equal to the applied heat flux.

The heat transfer coefficient is an important parameter in the equation but it is inherently difficult to calculate. From tests performed with the embedded heat flux gage, it was found that convection does not play a significant role in heating or cooling of the embedded gage in the period before formation of the condensate layer (i.e. before the radiometer reads a value of zero). It is interesting to note that there appeared to be convective heating in the FPA (possibly due to the forced air flow causing a stagnant area above the sample surface) and convective cooling in the Cone (which is natural convec-

tion). However, the difference was a maximum of 6kW/m^2 , which is the uncertainty of the heat flux gage.

Beaulieu [24] determined an average heat transfer coefficient, H , of $30\text{W/m}^2\text{K}$ considering a temperature range of $20\text{-}350^\circ\text{C}$ in an apparatus similar to the FPA. The same temperature range is found for the tests performed in this study, up to the cutoff point of half the time to ignition. Since the convective portion of the heat flux is insignificant, it is assumed that the radiation emitted from the surface dominates the heat loss. Therefore, it is assumed that the heat transfer coefficient from Beaulieu can be used to analyze both Cone and FPA test results. Beaulieu found that the deviation between the actual and predicted temperature profiles was 20°C using this value of H .

In order to estimate thermal properties, the actual temperature data was compared to the theoretical temperature derived from the analytical solution given above up to half the time to ignition. At half the time to ignition, there is no significant visual decomposition and the temperature rise at the back face is no more than 100°C (as measured by a back face thermocouple) for all of the composites considered in the parameter estimation exercise. Since the thermal diffusivity is the controlling parameter in the equation, it was changed until the global residual between the actual and the analytical temperature profiles was at a minimum. The thermal conductivity was then changed until the same condition was achieved and the values were reported. The residual was defined as the sum of the difference between the actual and predicted values at each time step for each of the temperature measurements; all of these sums were then summed to obtain an overall global residual. The value of the specific heat (c) is directly related to the thermal diffusivity (δ), thermal conductivity (k) and density (ρ) by $\delta=k/\rho c$. The value of the density was measured prior to the test while the thermal conductivity and thermal diffusivity were found from the procedure above, so the specific heat of the material was also found indirectly and is reported in the results. For the tests performed without the surface thermocouple, the surface temperature is not included in the optimization procedure. After the addition of the surface thermocouple late in the testing regime (see discussion in Instrumentation section above), additional tests were performed using the same method including the surface temperature measurement.

The initial values that were used for the PMMA and the composites were taken from the literature over the temperature range $300\text{-}475\text{K}$. This temperature range was used since PMMA begins to decompose at 475K [24]. The literature values for PMMA [25] in the temperature range considered are shown in Table 2; they do not change significantly over the given temperature range. Since only the thermal conductivity, specific heat and density were given in the literature [25], the diffusivity was found by the equation used above to determine specific heat from the optimized thermal parameters (i.e. $\delta=k/\rho c$).

The initial values for the polyester composites were taken from an average of the values reported in the literature for the thermal conductivity and specific heat of similar virgin composites [8][9][10], assuming that a vinylester resin is essentially equivalent to a polyester resin. The initial values used for the polyester composites are listed in Table 3. From the literature, the thermal conductivity does not change more than 0.02W/mK in the temperature range $300\text{-}475\text{K}$ and the specific heat in this temperature range was $1081\text{-}1098\text{J/kgK}$ [22] and $1221\text{-}1361\text{J/kgK}$ [9]. The thermal conductivity of E-glass, which is similar to the glass used in the current study, alone was found to have a much higher value than the composite and was equal to 1.09W/mK [22]. The value of the global residual was mapped versus the thermal diffusivity and then the thermal conductivity by a range of plus and minus one order of magnitude, which covers a wide range of materials [26], in order to ensure that the residual was a global minimum.

The method was attempted first on the PMMA tests to determine how well the parameters could be estimated using the method described above; the results are shown in Table 2. Although the method is a bit crude, the results are decent when compared to the published literature values for PMMA.

Since the method was determined to produce proper values for PMMA, it was then used on the polyester composite materials to estimate the thermal properties to further determine differences with glass content. The results are shown in Table 3. The results in the table are average optimal thermal parameters from multiple tests and the surface temperature is not included. A typical graph of the actual temperature curves versus the average predicted temperature profile with optimized values of thermal diffusivity and thermal conductivity is shown in Figure 6 for the polyester composite. From the graph, it can be seen that the model uncertainty is larger than the 20°C found from Beaulieu [24] which is to be expected since the uncertainty of the thermocouples alone is 27°C . From Table 3, it can be seen that there is no significant difference with glass content with regards to the estimated thermal properties. Since the temperature profile in the composites was found to be similar with glass content (see Figure 3), the similarity in the estimated thermal properties is expected.

Tests were performed with surface thermocouples and the surface temperature was then included in the optimization procedure; the results are shown in Table 4. From the table, there is not a significant difference in the effective thermal properties with glass content. Graphs of actual versus average predicted values for the polyester composites are shown in Figures 6 and 7. From the graph, it can be seen that the theory matches the surface temperature and the $1/3$ depth thermocouple to within the uncertainty from Beaulieu [24], indicating that the surface thermocouple is providing reasonable and consistent results. The $2/3$ depth thermocouple is under-predicted, which may be due to the temperature at the back face

(less than 100°C as discussed above) and the resultant thermal wave affecting the results for the deeper thermo-couple.

5.2. *Pyrolysis Modeling of Polyester FRP Composite*

The pyrolysis model developed by Lautenberger is a generalized model, which can be applied to most solid fuels. The model solves the conservation equations for different phases – mass, species and energy for both gaseous and condensed-phase and momentum for gaseous phase. The model may account for the kinetics of the thermal degradation of the polymer resin by a single or a multi-step reaction mechanism. This information will be provided by the thermal analysis results that were performed earlier in this study.

As a first approach to model the polyester (System 1) FRP composite using this pyrolysis model, the composite was modelled as a homogeneous material. The polyester resin and the fiber glass are lumped to represent “pseudo” species. The effective thermo-physical properties are calculated using the mass fraction of each component of System 1. The modelling results show that the heat release rate (HRR) of System 1 sample increased gradually instead of demonstrating the initial peak observed from the actual bench-scale tests (see Figure 2). One of the possible explanations for this discrepancy between the modelling and the experimental results is that there are limitations due to the homogenous approximation. Therefore, next step is designed to incorporate the microstructure of the composite cross-section and modelling a heterogeneous material. This part of the research is still on-going and the results will be presented in the future work.

6. **Conclusions and Future Work**

The results of this study are important to the composites industry because it is the beginning of a systematic research into how the polyester resin decomposes under fire conditions and how the glass content affects the overall fire performance of polyester (System 1) FRP composites. The effect of glass content of polyester composite is found to be less significant. For example, there is a difference in the peak heat release rate (see Figure 2) with glass content for the polyester composites but there is no significant difference in the average heat release rate in the plateau region of the trace. There is an increase in the time to ignition and a decrease in the burning time with glass content for the System 1 composites (see Figure 2).

The surface temperature significantly decreased with glass content for the polyester composites, which may be related to the conductivity of the glass as compared to the composite (see Figure 4). However, there is only a slight change with glass content for the in-depth thermal profile (see Figure 3). Before the composite resin decomposes, the heating is controlled by the resin as it has a lower conductivity than the glass. After the

composite resin decomposes, the heating is controlled by the glass as it builds up a blocking layer.

From the parameter estimation exercise (before decomposition of the composites), it was found that the thermal properties are invariant with regards to glass content; further testing with the surface thermocouple is needed to verify this result. The results from the initial pyrolysis modelling (homogeneous approximation) conducted with Lautenberger’s model showed that the model was not capable of capturing the actual phenomena due to over-simplification of the problem. More work will be carried out to incorporate the microstructure of the polyester (System 1) composite to upgrade the modelling performance in the future.

This work is also very important to the fire industry because it provides data specifically useful for calibration of fire models, including surface temperature, in-depth temperatures and radiative and convective portions of the heat flux prior to ignition. Tests were also completed with extended periods of a non-flaming condition, which is useful for pyrolysis models because there is no added complexity due to the flame. Currently, the heat flux data is only applicable up to the formation of the resin condensate on the gage face (i.e. when the radiometer reads zero) even though the gage is left in the sample and provides a reading for the entire test. It would be beneficial to determine if the reading from the total heat flux gage could be used after the formation of this condensate. More tests with the surface thermocouple would also be very beneficial.

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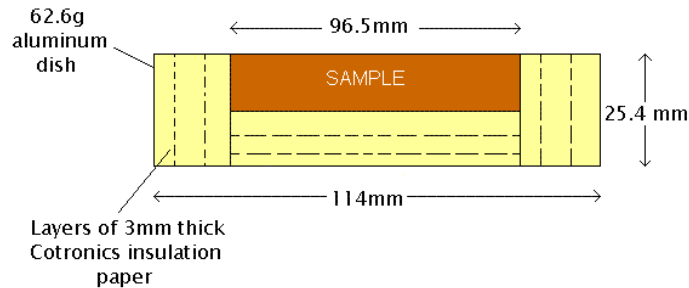


Figure – 1: Insulated Sample Holder Designed by de Ris and Khan [15]

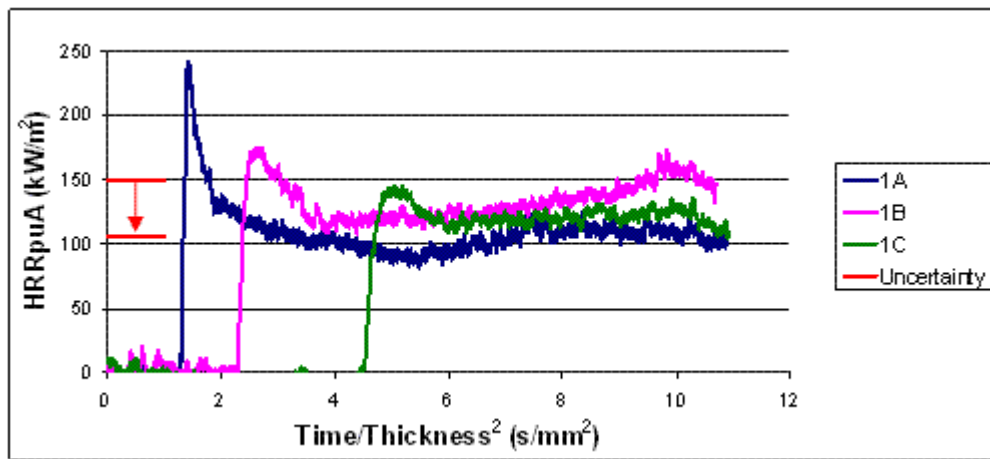


Figure – 2: Comparison of the Generic CO₂ Based Heat Release Rate per Unit Area (HRRpuA) for System 1 (Polyester) Composites at Three Different Glass Contents. All tests were performed in the FPA [1] at an applied heat flux of 50kW/m², truncated at loss of flame cone. Time zero is start of exposure. The thicknesses of the samples are (in mm): 1A 10, 1B 8 and 1C 6.

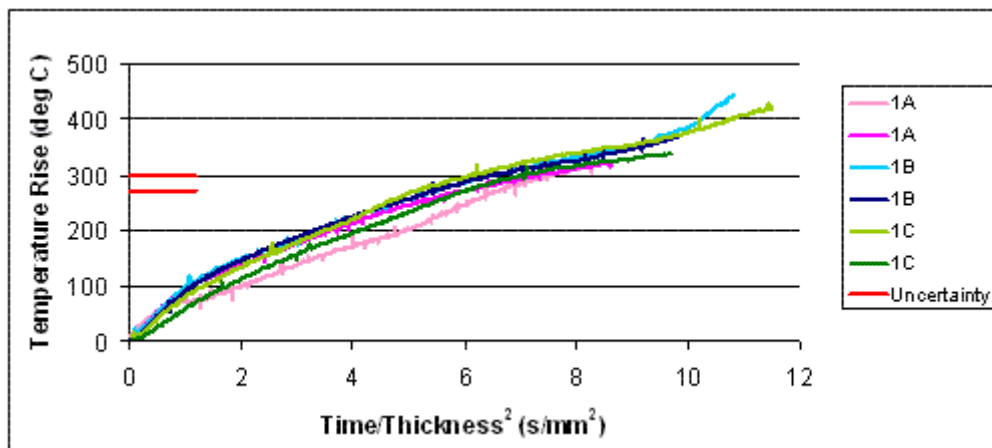


Figure – 3: Comparison of 2/3 In-Depth Temperatures for the System 1 (Polyester) Composites at Three Different Glass Contents. All tests were performed in the FPA [1] at an applied heat flux of 50kW/m², truncated at loss of flame cone. Time zero is start of exposure. The thicknesses of the samples are (in mm): 1A 10, 1B 8 and 1C 6.

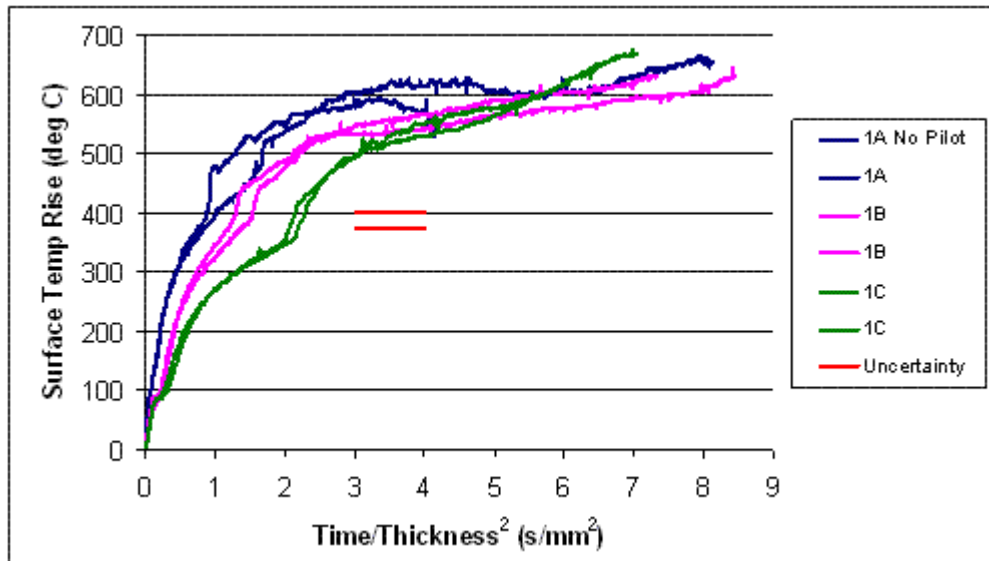


Figure – 4: Comparison of Surface Temperatures for the System 1 (Polyester) Composites at Three Different Glass Contents. All tests were performed in the FPA [1] at an applied heat flux of 50kW/m², truncated at loss of flame cone. Time zero is start of exposure. The thicknesses of the samples are (in mm): 1A 10, 1B 8 and 1C 6. Ignition occurs when there is a discontinuous jump in the surface temperature.

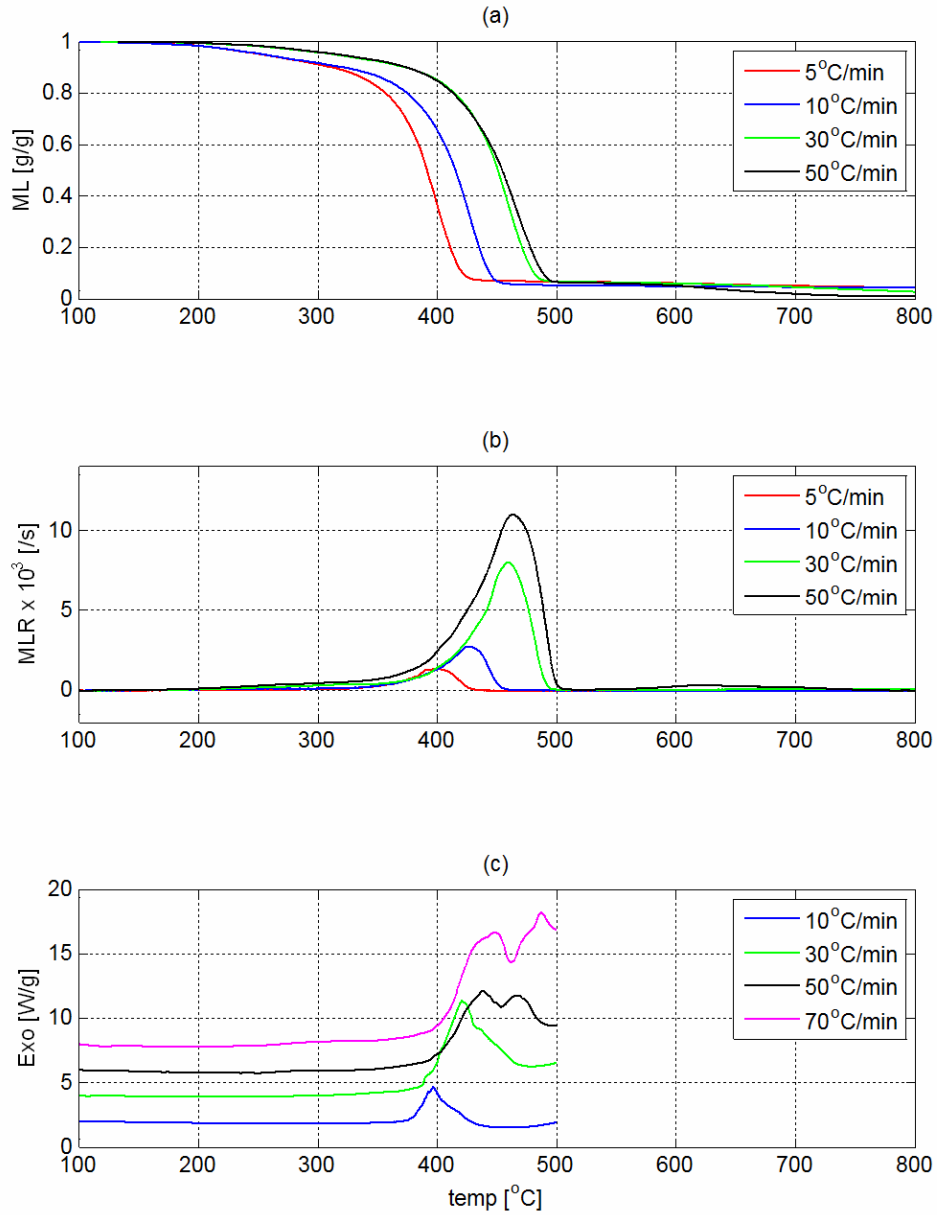


Figure – 5: TGA and DSC Analysis Results for Polyester Resin Tested under Air Environment: (a) mass loss [g/g] (i.e., TGA curves); (b) mass loss rate [1/s] (i.e., DTG curves); (c) exothermic heat flow [W/g].

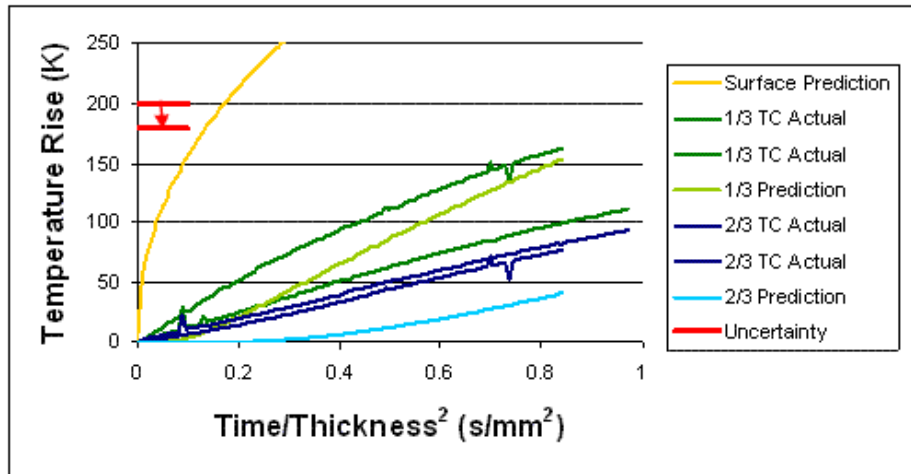


Figure – 6: Comparison of Actual and Predicted Temperatures Using Average Estimated Values for 1B (Polyester). The tests were performed in the FPA [1] at an applied heat flux of 50kW/m^2 , truncated at half the time to visual ignition. The 20°C uncertainty is from Beaulieu [22].

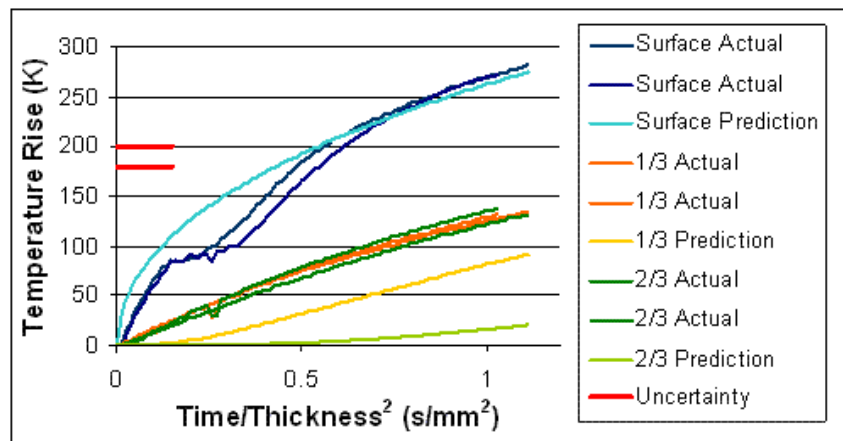


Figure – 7: Comparison of Actual and Predicted Temperatures Using Average Estimated Values for 1C (Polyester), including surface thermocouple data. The tests were performed in the FPA [1] at an applied heat flux of 50kW/m^2 , truncated at half the time to visual ignition. The 20°C uncertainty is from Beaulieu [22].

Table – 1: Description of the FRP Composites, the Minimum Heat Flux for Proper Ignition Range for the polyester composites (System1) and the Critical Mass Flux at Proper Ignition and its Standard Deviation. The Sample Thickness and the Minimum Heat Flux for Proper Ignition (determined in the FPA [1] for System 1 and in the Cone [2] for all others) are listed as ranges. %RFG =%Refined Glass Content.

Sample	Resin System	Glass (%RFG)	Thickness (mm)	Min. HF (kW/m ²)	Avg. Critical MF at Proper Ignition (g/sm ²)	Standard Deviation (g/sm ²)
1A	Brominated Polyester	33.0	8.5-10	25-30	13	2.9
1B	Brominated Polyester	46.5	8.0-9.0	20-25	10	4.1
1C	Brominated Polyester	73.3	6.0	20-25	8	1.5
PMMA	-	-	-	-	9	6.5

Table – 2: Parameter Estimation Values for PMMA, not including surface temperature data. The actual literature values are shown in the last row [23].

Heat Flux (kW/m ²)	Diffusivity (m ² /s)	Conductivity (W/mK)	Specific Heat (J/kgK)
15	1.7E-07	0.24	1300
15	1.3E-07	0.22	1600
28	2.5E-07	0.22	840
60	1.4E-07	0.22	1500
Average	1.7E-07	0.23	1300
Standard Deviation	5.1E-08	0.01	350
Difference From Actual	6.2E-08	0.00	440
Literature Values	1.1E-07	0.22	1700

Table – 3: Parameter Estimation Values for the Polyester Composite Materials, not including surface temperature data. The values shown are average values from multiple tests. The literature values are shown in the last two rows [8]-[10]. k=thermal conductivity, c=specific heat and δ=thermal diffusivity.

Sample	δ Avg (m ² /s)	δ Std Dev (m ² /s)	k Avg (W/mK)	k Std Dev (W/mK)	c Avg (J/kgK)	c Std Dev (J/kgK)
1A	1.8E-07	7.0E-08	0.33	0.01	1400	440
1B	1.4E-07	4.2E-08	0.35	0.01	1600	550
1C	1.4E-07	1.0E-08	0.34	0.02	1400	34
Lit. Polyester	1.8E-07	N/A	0.32	N/A	1155	N/A

Table – 4: Parameter Estimation Values for the Polyester Composite Materials, including the surface thermocouple data. k=thermal conductivity, c=specific heat and δ=thermal diffusivity.

Sample	δ (m ² /s)	k (W/mK)	c (J/kgK)	ρ (kg/m ³)
1A	1.0E-07	0.32	1900	1600
1B	6.1E-08	0.33	3500	1600
1B	5.4E-08	0.32	3800	1600
1C	7.5E-08	0.32	2300	1900
1C	7.6E-08	0.33	2300	1900