MODELING OF THERMO-PHYSICAL PROPERTIES AND THERMAL RESPONSES FOR FRP COMPOSITES IN FIRE

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ABSTRACT

The decomposition process of FRP composites exposed to fire was modelled based on chemical kinetic theory. Considering that the material is combined of two different phases: undecomposed and decomposed material, the changes of thermo-physical properties, including mass transfer, thermal conductivity and specific heat capacity, were obtained as continuous functions of temperature or time. Based on these material property sub-models, a one-dimensional model was proposed to predict the thermal responses of FRP composites exposed to fire. Several sets of boundary conditions were considered in the model, including prescribed temperature or heat flow, heat convection and/or radiation. The results obtained were compared to experimental data from structural fire endurance experiments on cellular FRP panels with and without liquid-cooling. For each scenario, calculated and measured time-dependent temperature progressions at different material depths were in good agreement.

KEYWORDS

Fiber reinforced polymers; thermal properties, thermal responses, modelling.

INTRODUCTION

The increased use of Fiber Reinforced Polymer (FRP) composites in major load-bearing structures brings many challenges to material scientists and structural engineers. One of these challenges is the understanding and prediction of the behaviour of FRP composites under elevated and high temperatures. For FRP composite materials, it has been reported that the material state and properties of a polymer composite remain stable below the onset of glass transition temperature, $T_{g,\text{onset}}$, of its resin. However, when the temperature reaches $T_g$, significant changes in the material state and properties occur. When the temperature of the resin approaches the decomposition temperature, $T_{d}$, it starts decomposing and produces various other phases (smoke, liquids, incombustible and combustible gases). In structural design, both structural and non-structural members must provide enough fire ignition prevention and fire resistance to prevent fire and smoke from spreading and structural collapse. In order to understand the structural behaviour on the level of systems, the thermal response of FRP composites under elevated and high temperature needs be understood and predicted.

Griffis et al. in 1981 developed a model to predict the thermal response of graphite epoxy composites. Stepped temperature-dependent effective thermal properties were used in this model. The same thermo-physical property models was later used by Chen et al. in 1985, Fanucci in 1987, etc. Temperature-dependent true thermo-physical property models were introduced by Henderson et al. in 1985. Further development of this model can be found in Gibson et al. in 2004, Looyeh et al. in 2001, Mouritz et al. in 2004, Davies et al. in 2006, etc.

New thermo-physical property models were developed and are introduced in this paper. Furthermore, experimental comparative studies were conducted on cellular slabs of glass fiber-reinforced polyester composites (Keller et al. 2005, 2006). The property models were assembled in the final governing equation, and the thermal responses obtained from the mathematical model were compared to experimental results.

MODELING OF THERMO-PHYSICAL PROPERTIES

Decomposition and Mass Transfer Model

The mass of FRP composites shows little change until decomposition starts. The decomposition process can be described by the theory of chemical reaction rate and the Arrhenius law. Considering the decomposition process
as a one-stage chemical reaction, the rate of decomposition is determined by the temperature, $T$, and the quantity of reactants as follows:

$$
\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp \left( \frac{-E_A}{R \cdot T} \right) \cdot (1 - \alpha)^n
$$

(1)

where $\alpha$ is the degree of decomposition, $A$ is the pre-exponential factor, $E_A$ is the activation energy, $R$ is the universal gas constant (8.314 $\text{J/mol} \cdot \text{K}$), $\beta$ is a constant heating rate, $n$ is the reaction order.

To validate Eq. (1), thermogravimetric analysis (TGA) was conducted on composite materials (E-glass fiber and polyester resin) on a TA2950 TGA instrument. The experiment was run from room temperature to 550ºC in an air atmosphere. Four heating rates (2.5ºC/min., 5ºC/min., 10ºC/min., and 20ºC/min.) were used for the study. The material sample size was kept consistent for all runs: 5.3 mg ± 0.4 mg. The kinetic parameters were estimated based on Ozawa method (Ozawa 1965). The theoretical values calculated from Eq. (1) were then compared to the experimental results in Fig. 1, a good agreement can be found.

![Figure 1. Decomposition degree from TGA compared with modelling results from Ozawa method](image)

After the determination of the decomposition model, the mass transfer during decomposition can be obtained according to Eq. (2):

$$
M = (1 - \alpha) \cdot M_i + \alpha \cdot M_e
$$

(2)

where $M$ is the temperature-dependent mass, $M_i$ ($M_e$) is the initial (final) mass. Since only resin decomposes to gases when the temperature exceeds the decomposition temperature, most of $M_e$ is composed of fibers. Accordingly, Eq. (2) can be expressed as:

$$
M = (1 - \alpha) \cdot M_i \cdot (f_{i0} + f_{m0}) + \alpha \cdot M_e \cdot f_{i0} = M_i \cdot f_{i0} + M_e \cdot f_{m0} \cdot (1 - \alpha) = M_i - \alpha \cdot M_i \cdot f_{m0}
$$

(3)

where $f_{i0}$ ($f_{m0}$) is the initial fiber (resin) mass fraction. Furthermore, the temperature-dependent mass fraction, $f_b$ ($f_m$), and volume fraction, $V_b$ ($V_m$), of the undecomposed (subscript $b$) and decomposed (subscript $a$) material can be obtained from Eqs. (4) to (7):

$$
\frac{f_b}{f_0} = \frac{M_i \cdot (1 - \alpha)}{M_i \cdot (1 - \alpha) + M_e \cdot \alpha}
$$

(4)

$$
\frac{f_a}{M_e} = \frac{M_e \cdot \alpha}{M_i \cdot (1 - \alpha) + M_e \cdot \alpha}
$$

(5)

$$
V_b = \frac{f_b}{f_i/M_i + f_m/M_e} = 1 - \alpha
$$

(6)

$$
V_a = \frac{f_a}{f_i/M_i + f_m/M_e} = \alpha
$$

(7)

The temperature-dependent fiber mass fraction, $f_b$, and resin mass fraction, $f_m$, are given by Eqs. (8) and (9):

$$
f_b = \frac{M_i \cdot f_{i0}}{M}
$$

(8)

$$
f_m = \frac{M_i \cdot f_{m0} \cdot (1 - \alpha)}{M}
$$

(9)

**Thermal Conductivity Model**

At any specified temperature, the composite material can be considered as a material composed of two phases: the virgin material and the decomposed char material, which are connected in series in the heat flow (through-thickness) direction. The effective thermal conductivity of the composite materials can then be obtained as
\[
\frac{1}{k_i} = \frac{V_b}{k_b} + \frac{V_a}{k_a}
\]

where \(k_i\) denotes the thermal conductivity for the composite material over the entire temperature range, \(k_b\) \((k_a)\) is the thermal conductivity for the undecomposed (decomposed) material. The volume fraction \(V_b\) \((V_a)\) of the undecomposed (decomposed) material was obtained according to Eqs. (6) and (7).

The obtained temperature-dependent effective thermal conductivity is shown in Fig. 2. In this figure, the initial thermal conductivity, \(k_{ib}\), is verified by the experimental result at room temperature. When the temperature increases and approaches \(T_{onset}\) (approximately 255°C), the resin starts to decompose. During this process, gases are generated and fill the spaces of the decomposed resin and between delaminating fiber layers, exhibiting a rapid decrease of thermal conductivity in the temperature range from 200°C to 400°C. Thermal conductivity of the decomposed material (above 400 °C) is obtained by considering that the resin is fully replaced by the gases generated during decomposition. Similar curves to those shown in Fig. 2 were also found in (Fanucci 1987). However, the conductivity was artificially adjusted to reflect the decrease during the decomposition process. Compared with the previous model, since the volume fraction of each phase was directly obtained from the decomposition model, a continuous model for thermal conductivity is achieved in this paper, instead of a stepped function and linear interpolation process used previously.

![Figure 2. Modelling for thermal conductivity](image1)

![Figure 3. Modelling for specific heat capacity](image2)

**Specific Heat Capacity Model**

The true specific heat capacity is related to the quantity of heat required to raise the temperature of a specified mass of material by a specified temperature. For composites, it can be estimated based on the mixture approach. Considering again that the material is composed of two phases - undecomposed and decomposed material - the total heat, \(E\), required to raise the temperature by \(\Delta T\) of the material with the mass \(M\) should be equal to the sum of the heat required to raise the temperature of all its phases to the same level, as shown in Eq. (11):

\[
C_{p,c} = \frac{E}{\Delta T \cdot M} = C_{p,b} \frac{\Delta T \cdot M \cdot f_b}{\Delta T \cdot M} + C_{p,a} \frac{\Delta T \cdot M \cdot f_a}{\Delta T \cdot M} = C_{p,b} \cdot f_b + C_{p,a} \cdot f_a
\]

where \(C_{p,c}\) is the specific heat capacity of the composite material, \(C_{p,b}\) \((C_{p,a})\) is the specific heat capacity of the undecomposed (decomposed) material, and \(f_b\) \((f_a)\) is the temperature-dependent mass fraction of the undecomposed (decomposed) material according to Eqs. (4) and (5).

For the effective specific heat capacity, the energy change during decomposition (i.e. decomposition heat) must be considered. The rate of energy absorbed for decomposition (endothermic reaction) is determined by the reaction rate, i.e., the decomposition rate, which is obtained by the decomposition model (Eq. 1). Combining Eqs. (1) and (11) gives:

\[
C_{p,e} = C_{p,b} \cdot f_b + C_{p,a} \cdot f_a + \frac{d \alpha}{dT} \cdot C_d
\]

where \(C_d\) is the total decomposition heat, \(\alpha\) is the decomposition degree defined in Eq. (1). Experimental results for the effective specific heat capacity were obtained by DSC tests in (Henderson 1982). A comparison between the resulting model (Curve 1 based on Eq. 12) and DSC results (Curve 2 from experimental results) is shown in Fig. 3. The change of effective specific heat capacity can be reasonably predicted from room temperature up to about 530°C, including the increase in specific heat capacity due to decomposition represented by the peak point in Curve 1. An additional peak was found in Curve 2 at around 600°C. The nature of this second peak is not addressed in (Henderson 1982) and, therefore, cannot be further discussed. The true specific heat capacity can also be obtained by Eq. (11) as shown by Curve 3 in Fig. 3. No peaks result from the decomposition heat for the true specific heat capacity. Comparing the effective specific heat capacity from
model and DSC (Curve 1 and 2) with the true specific heat capacity (Curve 3) in Fig. 3, the area between Curves 1 and 3 compares well to that between Curves 2 and 3. This area denotes the total decomposition heat.

**MODELING OF THERMAL RESPONSES**

**Governing Equation for Heat Transfer**

Assuming a one-dimensional heat transfer, the following governing Eq. (13) is obtained by considering that the net rate of heat flow should be equal to the rate of internal energy increase and the heat flow is given by the Fourier law related to temperature gradients:

\[
\frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) = C_p \rho \frac{\partial T}{\partial t}
\]

Substituting the temperature and time dependent material properties (Eqs. 2, 10, 12) into Eq. (13), a non-linear partial differential equation is obtained. A finite difference method can be used to solve this equation considering given boundary conditions. Temperature responses can then be calculated along the time and space axis.

**Boundary Conditions**

Different kinds of boundary conditions can be considered in the thermal response model: prescribed temperature or heat flow boundary conditions as expressed in Eq. (14) and (15), respectively:

\[
T(x,t) \big|_{x=0,L} = T(t)
\]

\[
-k \frac{\partial T(x,t)}{\partial x} \big|_{x=0,L} = q(t)
\]

where \(x\) denotes the spatial coordinates in one dimension, \(x=0\) and \(L\) define the space coordinate at the boundaries, \(T(t)\) and \(q(t)\) describe the specified time-dependent temperature and heat flux at the boundaries. Compared with the boundary conditions for prescribed temperature and heat flow, heat convection and radiation are more general cases. The equation of heat convection is given by Newton’s law of cooling:

\[
-k \frac{\partial T(x,t)}{\partial x} \big|_{x=0,L} = h(T_e - T \big|_{x=0,L})
\]

where \(h\) and \(T_e\) denotes the convection coefficient and ambient temperature at the boundary. Heat transfer through radiation is calculated using the Stefan-Boltzmann law, where the net heat transfer, \(q_r\), is expressed according to Eq. (17):

\[
q_r = \varepsilon \cdot \sigma \epsilon \left( T_e^4 - T^4 \big|_{x=0,L} \right)
\]

where \(\varepsilon\) is the emissivity of the solid surface (0.75-0.95 linearly assumed from 20°C-1200°C), \(\sigma\) is the Stefan-Boltzmann constant (5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}).

**Solution of Governing Equation**

The governing equation, Eq. (13), is a partial differential equation with non-linear, time and temperature-dependent material properties, and general boundary conditions. The implicit finite difference algorithm was used to solve the governing equation. For \(n\) spatial nodes, \(n\) coupled algebraic equations are obtained (the first one \((i=1)\) and the last one \((i=N)\) are determined by boundary conditions). Based on the material properties at the previous time step \(j-1\), the temperature profile at time step \(j\) can be calculated by solving these \(n\) coupled algebraic equations. Substituting the temperature at the time step \(j\) into the material property models, the material properties are obtained and then serve as the input for the next time step \(j+1\).

**APPLICATION AND DISCUSSION**

**Description of Basic Model**

Structural fire endurance experiments were performed on cellular GFRP slabs (DuraSpan® 766 slab system from Martin Marietta Composites), as show in Fig. 4. Three full-scale specimens (SLC01, SLC02, and SLC03) were
fabricated. The specimens were subjected to serviceability limit state loads in a four-point bending configuration. Thermal loading was then applied according to the ISO-834 fire curve to the underside of the specimens. Specimens SLC01 and SLC02 were liquid-cooled during mechanical and thermal loading through slowly circulating water in the cells; specimen SLC03 was not cooled. The experiments on the liquid-cooled specimens were stopped after 90 minutes (SLC01) and 120 minutes (SLC02) without structural failure, whereas the non-cooled specimen failed after 57 minutes in the compressed upper face sheet (Keller et al. 2006).

In the modelling, an average 16.3 mm thick lower face sheet of the experimental specimen was discretized into 17 elements in the thickness direction and into 60 or 120 time steps. At the two sides of the lower face sheet, the boundary conditions of the heat transfer were defined for the hot face (exposed to fire) and the cold face (exposed to water cooling or air environment).

Non-Cooled Specimen SLC03

A comparison between experimental and computed values for the temperature progressions at different depths of the lower face sheet is shown in Fig. 5 (left). The slightly different depths between model and experiment resulted from the discretized depth in the model. The temperature is well predicted, even after 60 min of heating and at the locations near the hot face. Figure 5 (right) shows the comparison of temperature profiles at different times.

Liquid-Cooled Specimen SLC02

From the comparison of measured and computed through-thickness temperatures at different time steps a good agreement was found, as illustrated in Fig. 6 (left). The only exception was the 4.1 mm curve above 80 minutes, however, it is thought that the offset of this curve at this time is more likely linked to a measurement problem than to a significant change in the element behaviour. Figure 6 (right) shows the comparison of the temperature profiles through the thickness. Again, measured and computed curves compare well. In the curves at 60 min and 120 min (both experiment and model), a change in the slope is seen at distances of about 6-8 mm from the hot face. At those times and distances, the temperatures reached the decomposition temperature of around 300°C. Towards the hot face, decomposed gases reduced the thermal conductivity and a steeper slope of the gradients resulted. On the other hand, due to the liquid-cooling effect, the temperatures towards the cold face remained below 300°C and the observed flattening resulted due to the higher thermal conductivity.
CONCLUSIONS

Considering temperature-dependent thermo-physical properties, a one-dimensional thermal response model was developed to predict the temperature of FRP structural elements subjected to fire. Different experimental scenarios were conducted on cellular GFRP slabs with different boundary conditions. The results from the experimental scenarios were compared to the results from the models including the time-dependent temperature progression at different depths and temperature profiles at different time steps. A good agreement was found and the following conclusions were drawn:

1) The decomposition process of resin in composite materials can be modelled by chemical kinetic theory. Based on the decomposition degree calculated from the decomposition model, a temperature-dependent mass transfer model was obtained. The temperature-dependent thermal conductivity was then estimated by the series model. The effective specific heat capacity was obtained by assembling the true specific heat capacity with the decomposition heat, which was also described by the decomposition model.

2) The temperature-dependent thermo-physical properties including decomposition degree, density, thermal conductivity and specific heat capacity can be obtained in space and time domain using this model. Complex processes such as endothermic decomposition, mass loss, and shielding effects can be described based on effective material properties over the whole time and space domain.

3) The one-dimensional thermal response model can be used to predict the temperature responses of FRP composites in both time and space domain. Complex boundary conditions can be considered in this model, including prescribed temperature or heat flow, as well as heat convection and/or radiation.

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