Outline

- Why this tutorial?
- Ablative TPS - early studies
- Organic resin composites
- Surface recession mechanisms/modeling
- **High fidelity model development**
- Testing approaches/requirements
- Future needs

What is a high-fidelity model?

- A *high-fidelity* model of an ablative TPS material will *accurately** predict:
  - Surface recession
  - Surface temperature
  - Bondline temperature
  - Char thickness/char depth
  - In-depth temperatures $= f(x,\theta)$
- Mathematical models of material thermal/ ablation performance are used for:
  - TPS design
  - Materials trade studies
  - TPS mass estimates for systems analysis studies
  - etc.

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* ± 10% on temperature; ± 20% on surface recession and char thickness

Why do we need high-fidelity models?

- Typically, TPS design sizes the material thickness to limit bondline temperature to a predefined maximum (adhesive limit)
- If bondline temperature is the design criterion, why isn't a model that accurately predicts maximum bondline temperature adequate?
  - The flight environment cannot be accurately simulated in ground test $\Rightarrow$ requirement to use mathematical models for ground-flight connectivity
  - Maximum bondline temperature is of limited value unless *time* of max bondline temperature is predicted accurately (flight events)
- Mathematical models that adequately represent materials physics and chemistry can be extrapolated to flight with some confidence
  - Performance assessment at conditions beyond range of ground tests
  - Basis for assessment of design margin requirements

$$\rho c_p \frac{\partial T}{\partial \theta}\bigg)_x = \frac{1}{A}\frac{\partial}{\partial x}\left(kA\frac{\partial T}{\partial x}\right)_y + \left(h_g - \bar{h}\right)\frac{\partial \rho}{\partial \theta}\bigg)_y + \dot{s}\rho c_p \frac{\partial T}{\partial x}\bigg)_\theta + \frac{\dot{m}_g}{A}\frac{\partial h_g}{\partial x}\bigg)_\theta$$

where the individual terms have physical meanings which may be interpreted (from left to right) as: rate of storage of sensible energy, net rate of thermal conduction, energy associated with decomposition, convection of sensible energy due to coordinate system movement, and energy associated with the convection of pyrolysis gases through the material.

Density

Note that the material density can be written in terms of three components, i.e.,

$$\rho = \Gamma\left(\rho_A + \rho_B\right) + \left(1 - \Gamma\right)\rho_C$$

where

Γ = Resin volume fraction

A and B represent components of the resin

C represents the reinforcing material

Each of the three components can decompose according to the Arrhenius relation:

$$\frac{\partial \rho_i}{\partial \theta} = -B_i \exp\left(-E_{a_i}/RT\right)\rho_{0_i}\left(\frac{\rho_i - \rho_{r_i}}{\rho_{0_i}}\right)^{\psi_i} \qquad i = A,B,C$$

where

ρ_{0_i}	=	the initial density of component i
ρ_{r_i}	=	The residual or terminal density of component i
B_i	=	The pre-exponential factor for the pyrolysis reaction of component i
E_{a_i}	=	the activation energy for the pyrolysis reaction of component i
ψ_i	=	The reaction order for the pyrolysis reaction of component i

Thermophysical Properties

Thermophysical properties (i.e., thermal conductivity and specific heat) are required for both virgin and fully charred material. In the pyrolysis region, thermophysical properties of partially pyrolyzed material are assumed to be a simple mixture of pure virgin and pure char material properties. Thus, the properties are mass weighted using the instantaneous predicted density, i.e.,

$$c_p = x\, c_{p_v} + (1-x)\, c_{p_c}$$

where the weighting variable x is based on the convenient fiction that partially pyrolyzed material is a simple mixture of pure virgin material and pure char. The quantity x is defined as the mass fraction of pure virgin material in this imaginary mixture that yields the correct local density:

$$x = \frac{\rho_v}{\rho_v - \rho_c}\left(1 - \frac{\rho_c}{\rho}\right)$$

The thermal conductivity k will be weighted in the same manner unless more complex x-weighting information is provided. That is, the user may input functions of x for the following equation for the thermal conductivity of partially degraded material:

$$k = f_1(x)\, k_v + f_2(x)\, k_c$$

Pyrolysis Gas Enthalpy

The *traditional* procedure for calculating the enthalpy of the pyrolysis gases h_g is to estimate the elemental composition of the gas and assume that the gas is in thermochemical equilibrium throughout the temperature range of interest. This approach has proved successful in applications at very high heating rates since: (1) the equilibrium assumption is probably valid at the surface temperatures typical of such heating rates, and (2) the steep temperature gradients typical of these applications confine the pyrolysis zone to a narrow region where modeling inaccuracies have a small influence on overall material thermal response predictions.

The elemental composition of the pyrolysis gas is usually estimated from

$$\mathcal{K}_{pg_i} = \frac{\mathcal{K}_{v_i} - r\,\mathcal{K}_{c_i}}{1 - r}$$

where

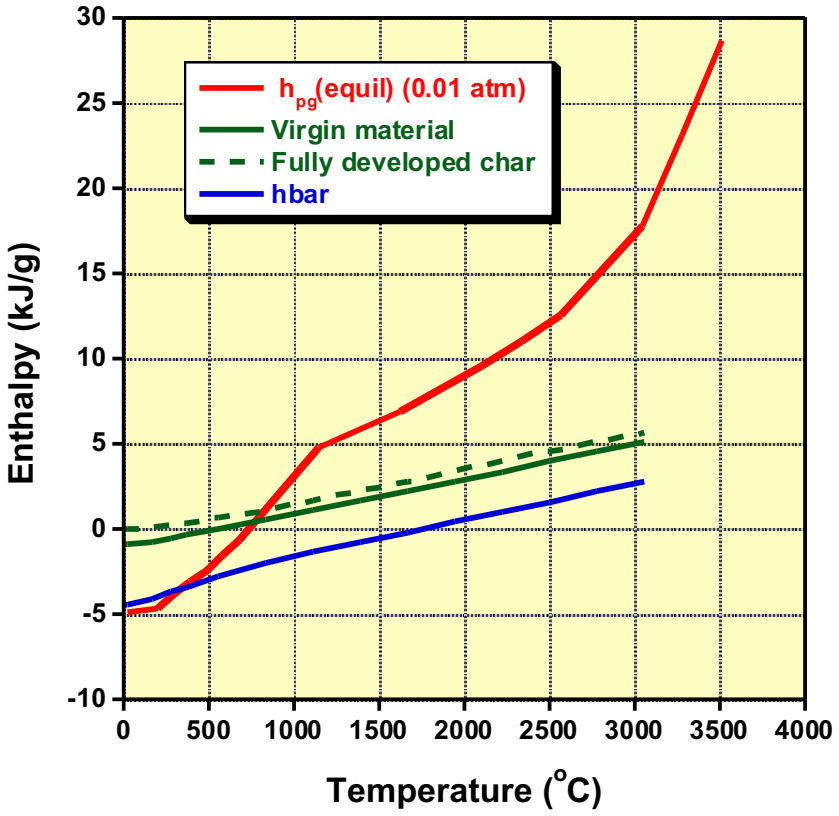
$\mathcal{K}_{pg_i}$ = Elemental mass fraction in the pyrolysis gas

$\mathcal{K}_{v_i}$ = Elemental mass fraction in the virgin material

$\mathcal{K}_{c_i}$ = Elemental mass fraction in the charred (residual) material

r = Residual mass fraction (ρ_c / ρ_0)

- A thermochemical equilibrium calculation made with the ACE code using the resultant pyrolysis gas chemical composition for a carbon phenolic is illustrated as $h_{pg}(equil)$ in the figure. This calculation was done at a pressure of 0.01 atm. The curve would be different at other pressures, particularly at the higher temperatures.



Also shown in the figure is the enthalpy of the virgin and char materials with respect to a standard state of 298 K. These terms are calculated by the following equations:

$$H_v = \int_{298K}^{T} c_{p_v} dT + \Delta H_{f_v}^0$$

and

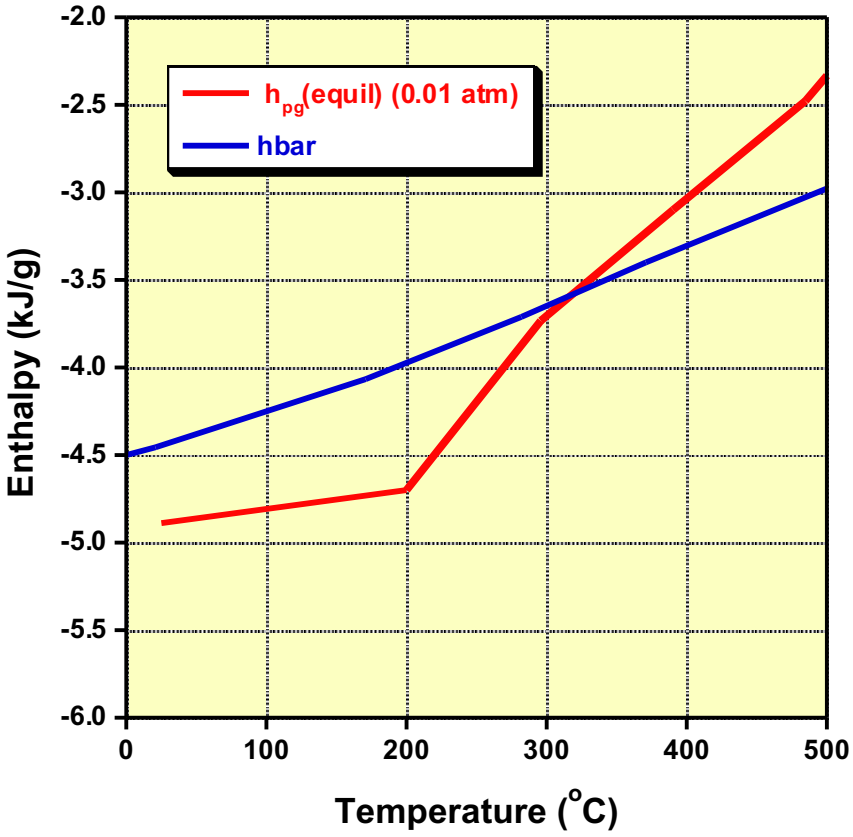
$$H_c = \int_{298K}^{T} c_{p_c} dT + \Delta H_{f_c}^0$$

The line labeled $\bar{h}$ in the figure represents the sensible energy of partially pyrolyzed material. It is calculated by the equation

$$\bar{h} = \frac{\rho_v H_v - \rho_c H_c}{\rho_v - \rho_c}$$

Fundamentals - 8

- The term $\left(h_g - \bar{h}\right)$, where h_g is the pyrolysis gas enthalpy, is interpreted as the "heat of decomposition" and in order for the pyrolysis reactions to be endothermic, that term should be positive. The figure illustrates that this term can be negative in the lower temperature range (the range where the major pyrolysis reactions occur) when the equilibrium assumption for pyrolysis gas enthalpy is used. This results in exothermic pyrolysis reactions.



Ladacki et al presented data for the pyrolysis of phenolic resin that definitely indicates endothermic decomposition. Ladacki's data provided values for the "heat of pyrolysis" at three temperatures, as summarized in the table below.

Temperature (°F)	Temperature (°C)	Heat of pyrolysis (Btu/lbm of resin)	Heat of pyrolysis (kJ/g of resin)
750	399	371	0.86
1110	599	506	1.18
1620	882	742	1.73

The values in the table were curve fit such that the heat of pyrolysis versus temperature can be represented by the equation:

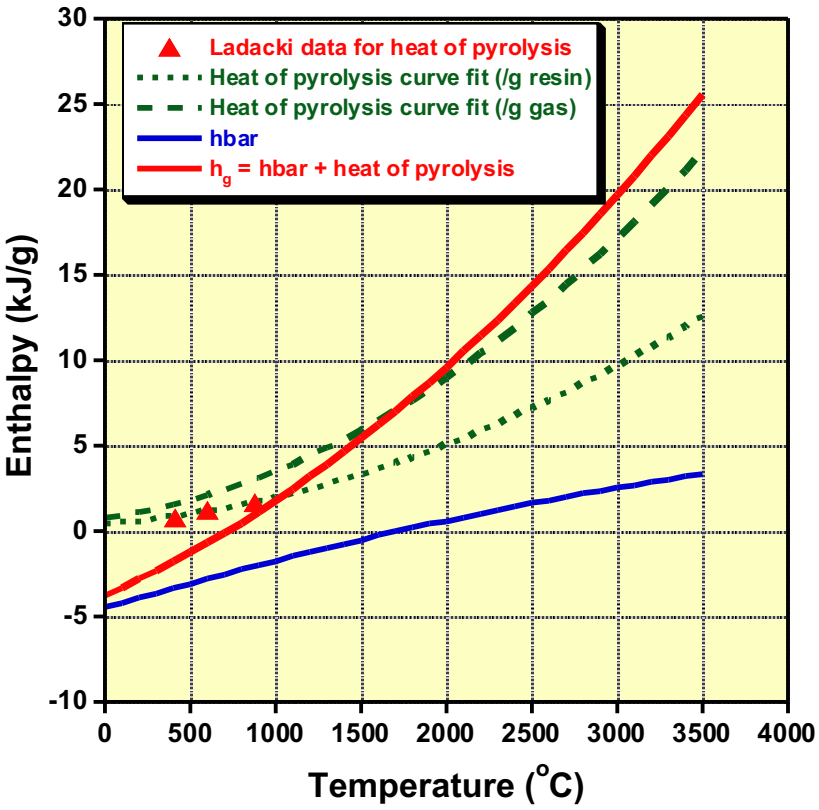
$$\Delta H_p = h_g(T) - \bar{h}(T) = 0.25305 + 3.9621 \times 10^{-4}\, T + 7.5977 \times 10^{-7}\, T^2$$

where

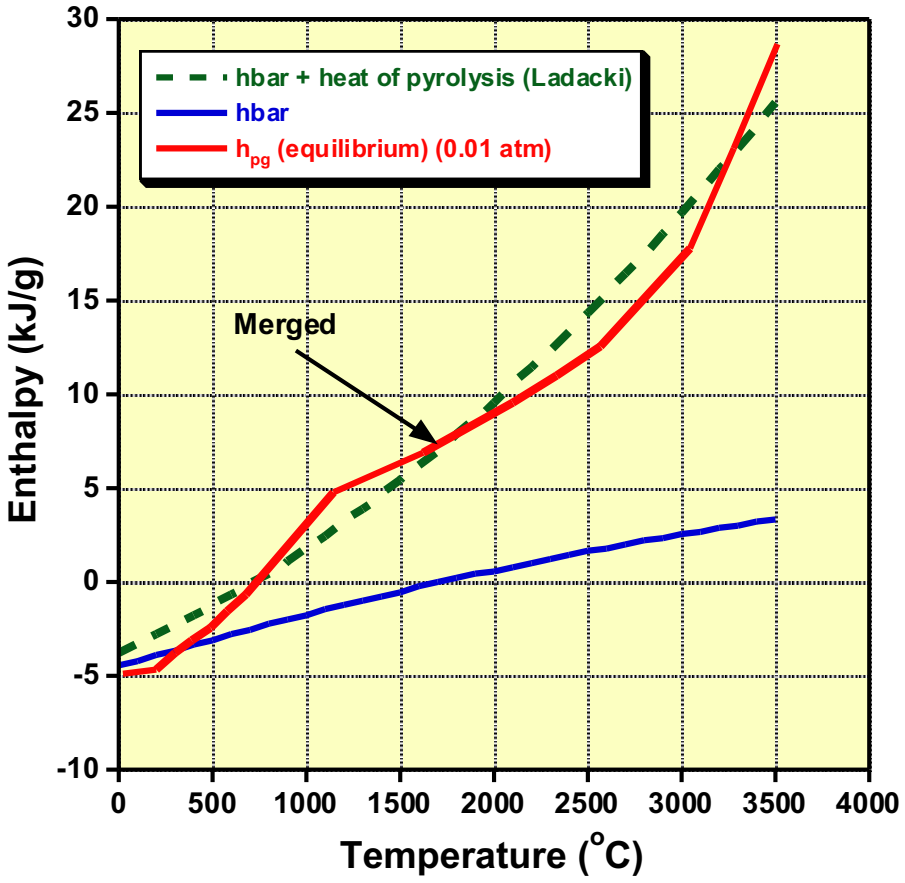
ΔH_p = Heat of pyrolysis (kJ/g of resin)

T = Temperature (K)

According to Ladacki, the pyrolysis gas enthalpy should be represented by $\left(\overline{h} + \Delta H_p\right)$ and in order to combine the $\overline{h}$ and ΔH_p terms, the ΔH_p must be converted from (kJ/g of resin) to (kJ/g of gas). This conversion is accomplished by multiplying by the resin mass fraction and dividing by the mass of pyrolysis gas generated per mass of virgin composite, namely $(1-r)$, where r is the residual mass fraction. The figure illustrates how the Ladacki data is utilized to develop a model for the pyrolysis gas enthalpy in the temperature range where resin pyrolysis occurs.



The assumption of equilibrium behavior of the pyrolysis gas is still acceptable at higher temperatures. However, the equilibrium composition and enthalpy of the pyrolysis gases is a function of pressure as well as temperature. Consequently, the equilibrium pyrolysis gas enthalpy should be calculated for a range of pressures that covers the range of interest for the particular problem. The low temperature Ladacki-based pyrolysis gas enthalpy should then be "merged" with the high temperature equilibrium enthalpy at each pressure to finalize the pyrolysis gas enthalpy model



Approach to Model Development - 1

Thermochemical Properties:

1. Conduct TGA experiments (inert gas, low temperature rise rates). Residual mass fraction defines *char yield*. Data fits provide decomposition kinetic constants.
2. Conduct DSC experiments (inert gas, low temperature rise rates). Data provides heat of reaction for pyrolysis reactions as function of temperature.
3. Measure elemental composition of virgin material.
4. Measure heat of combustion of virgin material and derive heat of formation (unless known).
5. Derive elemental composition of char from known constituents and char yield data. Can be problematic to measure (explained later).
6. Derive heat of formation of char from known constituents and existing data
7. Derive elemental composition of pyrolysis gases. Develop model(s) for pyrolysis gas enthalpy using combination of thermochemical equilibrium calculations and measured heat of pyrolysis data.

Approach to Model Development - 2

Thermophysical properties:

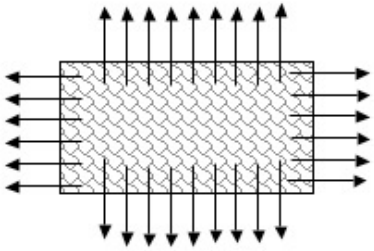
1. Measure specific heat of virgin material as function of temperature.
2. Measure thermal conductivity of virgin material as function of temperature (and orientation, if appropriate).
3. Derive specific heat of char from known (or derived) composition using method of mixtures.
4. Measure optical properties of virgin material
5. Derive optical properties of char from known composition and properties of similar materials (or determine experimentally)
6. Measure thermal conductivity of char as function of temperature (and orientation, if appropriate).

Assertion: the thermal conductivity of the char cannot be measured in standard lab facilities!

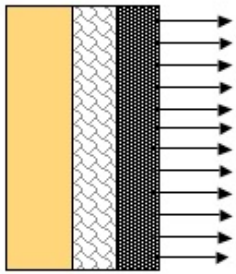
Approach to Model Development - 3

Traditional practice has been to bake the material in an oven and measure the thermal properties of the resulting “char.” Studies conducted under the Apollo heat shield program (and re-validated in other programs) demonstrated that the cellular structure of “oven chars” was different than the cellular structure of chars formed in ground test or flight.

OVEN CHAR



IN-SITU CHAR



Given that finding, why would one expect the thermal conductivity of oven chars to be representative of actual material properties?

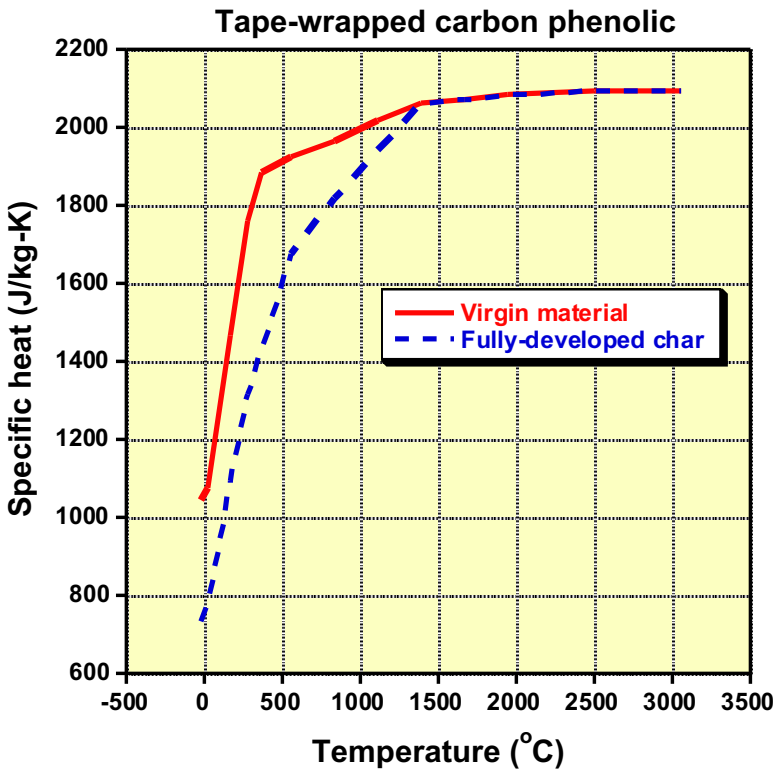
Approach to Model Development - 4

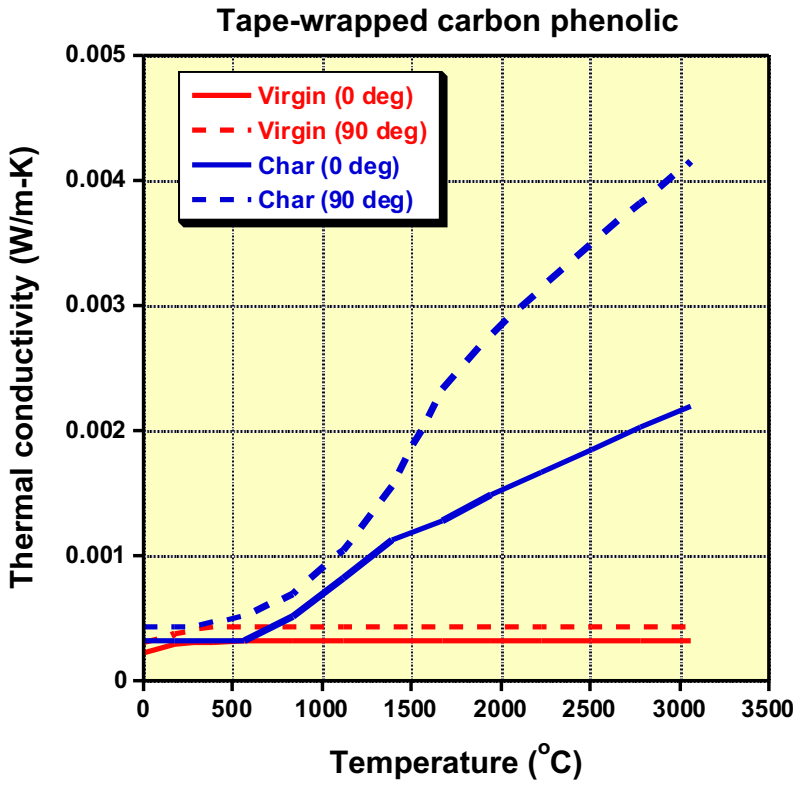
1. Assemble all measured/derived thermophysical and thermochemical properties (with exception of char thermal conductivity)
2. Conduct ground tests over range of conditions of interest
3. Instrument each ground test material sample with multiple in-depth thermocouples (ensuring data capture over full range of anticipated temperatures)
4. Derive the "char thermal conductivity" $\left[k_c = f(T, \phi)\right]$ through iterative correlation of the in-depth thermocouple data

This approach has been used successfully for many materials and TPS applications for over 30 years and repeatedly validated with flight data.

WARNING: The char thermal conductivity derived in this manner should not be treated as a material property as it compensates for the uncertainties in all of the other properties/parameters in the material thermal model.

Approach to Model Development - 5





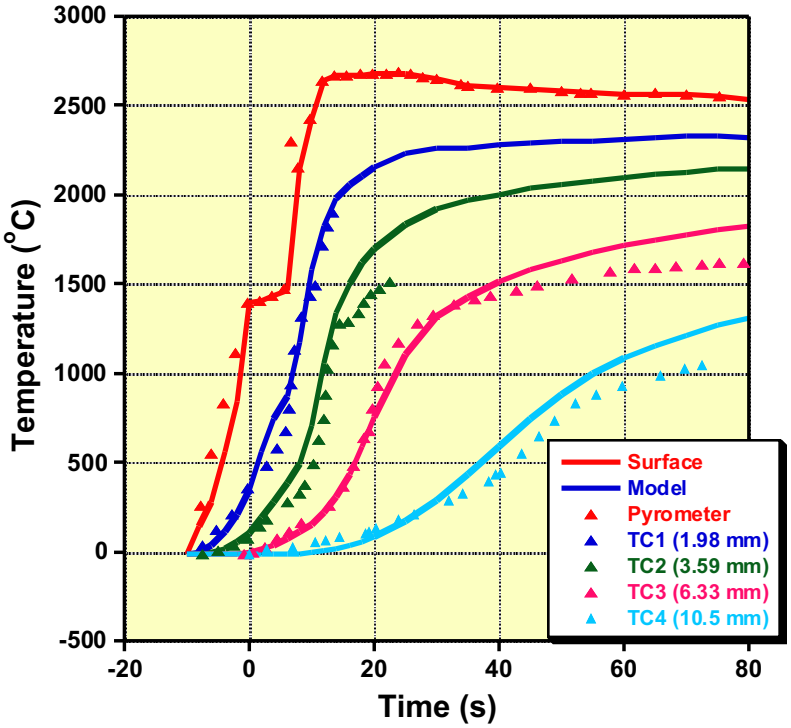
$$k_\theta = k_0\left\{1+\left[\frac{k_{90}}{k_0}-1\right]\sin^2\theta\right\}$$

where θ is the angle between the ply and the heated surface.

Example

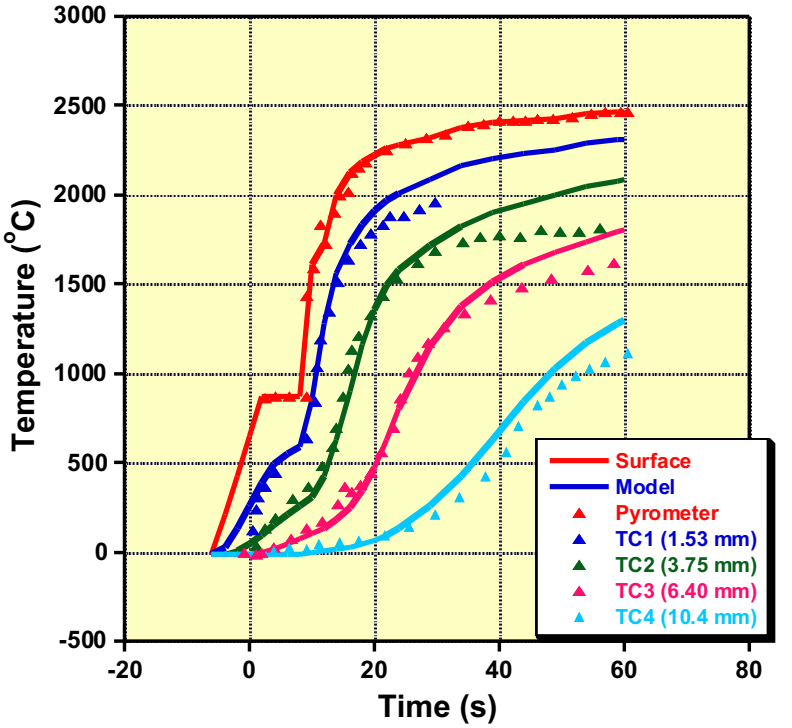
Tape-wrapped carbon phenolic
Arc jet test in N_2/He mixture

900 W/cm^2 10° ply orientation



Tape-wrapped carbon phenolic
Arc jet test in N_2/He mixture

900 W/cm^2 90° ply orientation



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