Numerical Simulation of Decomposition and Combustion of an Epoxy-Carbon-Fiber Composite

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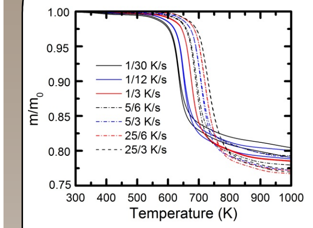
Overview

In fire environments, composite materials behave differently from conventional fuel sources and have the potential to smolder and burn for extended time periods. As the amount of composite materials on modern aircraft continues to increase, understanding the response of composites in fire environments becomes increasingly important. Thermal decomposition and oxidation of carbon-fiber composite materials were investigated to obtain data for developing thermal property and chemical reaction rate expressions that are suitable for use in numerical simulations of the fire behavior of such materials in large structures in a variety of hazard scenarios. Results from experiments with epoxy-carbon-fiber composites (Cytec Industries 977-3 unidirectional and 977-3 woven) are presented.

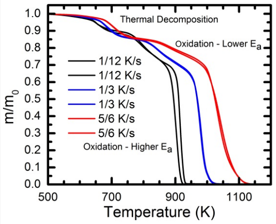
Results from Most experimental data were obtained by thermal gravimetric analysis (TGA) using open platinum pans. Simultaneous TGA-FTIR was used to examine evolved gases. Samples were thin square sheets about 2 mm on a side. The TGA purge gas was UHP N_2, high purity air, 95%N_2-5%O_2, or 98%N_2-2%O_2 flowing at 35 ml/min. Multiple heating programs were used and included: (1) constant heating rate of 1/30 K/s to 25/3 K/s (2 to 500 K/min) and (2) constant heating rate followed by isothermal heating at temperatures from 723 K to 923 K. Simultaneous TGA-DSC (SDT) with samples in open ceramic pans and air or 95%N_2-5%O_2 purge was used to evaluate enthalpy changes resulting from oxidation at temperatures from 473 K to 1273 K. Differential scanning calorimetry (DSC) with N_2 purge and samples in open gold pans was used to obtain data for evaluating specific heat and heat of gasification at temperatures from ambient to 973 K.

Thermal Gravimetric Analysis (TGA)

TGA: constant heating rate, N_2 purge



TGA: constant heating rate, air purge



Thermal decomposition of the epoxy binder (in N_2) was 22% to 24% of the initial sample mass. Rate constants were determined for thermal degradation of epoxy using TGA at a range of heating rates in nitrogen.

In air, depending on heating rate:

- The mass loss that occurred between temperatures of 600 K and 800 K was 10% to 14 % of the original sample mass and was due to decomposition of the epoxy binder
- Additional mass loss then occurred slowly between temperatures of 700 K and 850 K
- Between temperatures of 850 K and 1000 K, the rate of mass loss increased and the mass loss curves shifted substantially with heating rate
- At temperatures of about 875 K and higher (at mass loss between 30% and 40%) the rate of mass loss greatly increased.

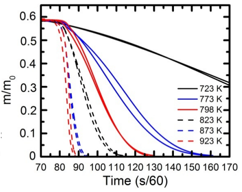
Decomposition mechanism:

(1) Thermal decomposition of the epoxy binder with concurrent formation of char, which decomposed (or oxidized) slowly until temperatures exceeded 850 K (E_a/R=27,200 K)
(2) Subsequent oxidation of the char formed from the epoxy (E_a/R=10,000 K)
(3) Oxidation of the carbon fibers (two mechanisms having significantly different temperature dependence) (E_a/R=12,100 K and E_a/R=38,000 K)

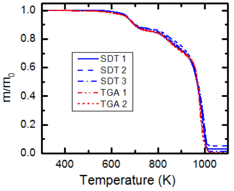
Rate constants determined using TGA in air data and data from a series of two-step experiments:

(1) Constant heating (1/3 K/s to 873 K, then isothermal until mass m/m_0 = 0.60, followed by cooling to ambient
(2) Heating (1/3 K/s) to temp from 723 K to 923 K, then isothermal until samples were consumed

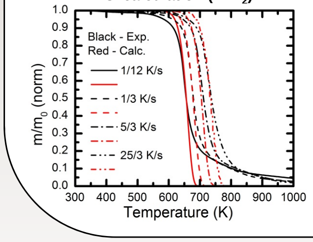
Isothermal Experiments



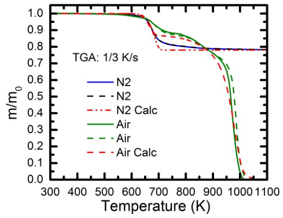
TGA compared to Simultaneous TGA-DSC (SDT)



Epoxy decomposition: exp. vs. calculation (in N_2)

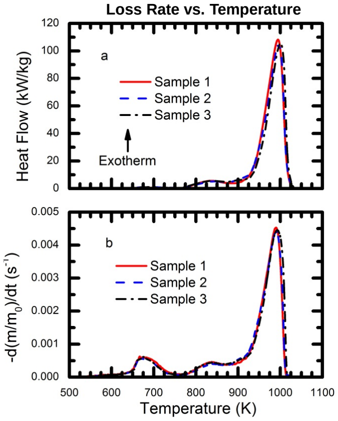


Composite Decomposition in air: exp. vs. calculation.

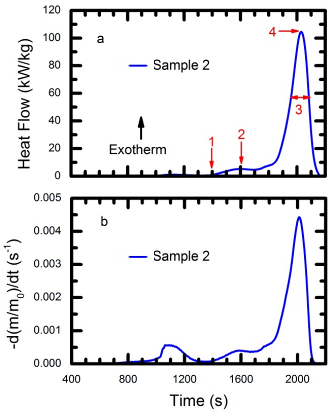


Differential Scanning Calorimetry (DSC)

Simultaneous TGA-DSC heated at 1/3 K/s in air(a) Heat flow (b) Mass Loss Rate vs. Temperature



Simultaneous TGA-DSC heated at 1/3 K/s in air (a) Heat Flow (b) Mass Loss Rate vs. time



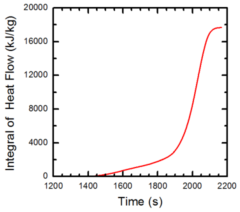
Net exothermic heat flow is not significant until temperatures above 775 K and corresponds to the two carbon fiber oxidation reactions.

The smaller peak labeled “2” corresponds to the lower-activation-energy reaction which produces mostly CO. The much larger peak labeled “4” corresponds to the higher-activation-energy reaction that produces mostly CO_2.

Calculated ΔH_1 and ΔH_2 Values

	ΔH_1 (kJ/kg)		ΔH_2 (kJ/kg)	
Sample	Method 1	Method 2	Method 1	Method 2
1	12,230	12,630	24,910	24,930
2	13,270	12,770	25,000	24,730
3	12,710	12,760	24,860	24,190
Avg.	12,740	12,720	24,920	24,620
Avg.	12,730		24,770	

For ΔH_1 (smaller peak in above figures), the time interval corresponds to the time between labels “1” and “2”. For ΔH_2 (larger peak in above figures), the time interval corresponds to the interval labeled “3.”

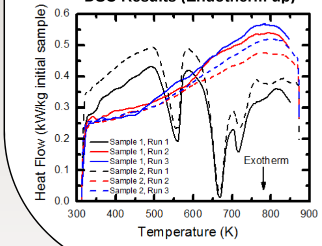


Heat of reaction ΔH_i for CF reactions was estimated using two methods:

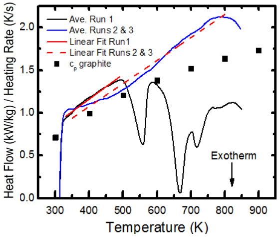
(1) Ratio of maximum heat flow Q_{max} at each peak to the corresponding rate of mass loss $d(m/m_0)/dt$
(2) Ratio of the integral of heat flow Q over a selected time interval $\int_{t_i}^{t_{i+1}} Q dt$ to the corresponding change in mass $[(m/m_0)_{i+1} - (m/m_0)_i]$

Differential Scanning Calorimetry (DSC)

DSC Results (Endotherm up)



Heat Capacity (Endotherm up)

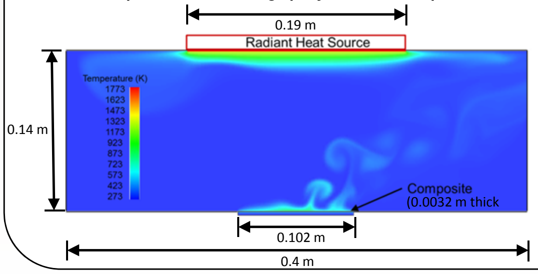


Two samples heated at 1/3 K/s then cooled to ambient temp. three times

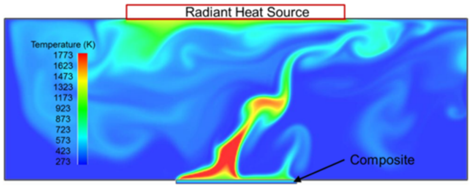
- Run 1: Decomposition of the epoxy binder: Net heat flow above 500 K is endothermic, c_p of initial composite is determined by linear fit below 490 K ($c_p = aT$, where $a = 0.00291$ kJ/kgK)
- Run 2 and Run 3 represent c_p values of remaining residue (epoxy char and carbon fibers) between 330 K and 890 K($c_p = aT$, where $a = 0.00269$ kJ/kgK)

Numerical Modeling

Temperature field during epoxy binder decomposition



Temperature field after gas-phase ignition has occurred



Preliminary implementation of epoxy carbon fiber decomposition model in Gpyro[1] coupled to Fire Dynamics Simulator (FDS)[2].

Gpyro is a generalize pyrolysis model that solves conservation equations for heat, mass, and species in a chemically reacting porous medium.

FDS provides the solution to the fluid domain solving transient low Mach number, reactive, buoyant Navier stokes equations

The surface of the composite is heated by a radiant heater, as the composite heats it begins to decompose and off gases into the fluid region. The gases in the fluid region ignite by an gas-phase 1-step Arrhenius reaction.

Additional effort quantifying comparisons to experimental data will be focus of future work.

1. http://reaxengineering.com/trac/gpyro
2. McGrattan, K., McDermott, R., Hostikka, S., Floyd, J. Fire Dynamics Simulator (Version 5) User’s Guide, NIST Special Publication 1019-5, 2010

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