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PROPERTIES AND PROCESSING CHARACTERISTICS OF LOW DENSITY CARBON CLOTH PHENOLIC COMPOSITES

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I. INTRODUCTION

Ply-lift and pocketing are two critical anomalies of carbon cloth phenolic composites (CCPC) in rocket nozzle applications [1]. Ply lift occurs at low temperatures when the A/P and in-plane permeabilities of the composite materials are still very low and in-plane porous paths are blocked. Pocketing occurs at elevated temperatures when in-plane permeability is reduced by the A/P compressive stress. The thermostructural response of CCPC in a rapid heating environment involves simultaneous heat, mass, and momentum transfers along with the degradation of phenolic resin in a multiphase system with temperature- and time-dependent material properties as well as dynamic processing conditions [2]. Three temperature regions represent the consequent chemical reactions, material transformations, and property transitions, and provide a quick qualitative method for characterizing the thermostructural behavior of a CCPC.

In order to optimize the FM5939 LDCCP (low density carbon cloth phenolic) for the nozzle performance required in the Advanced Solid Rocket Motor (ASRM) program, a fundamental study on LDCCP materials has been conducted [3]. The cured composite has a density of 1.0±0.5 gm/cc which includes 10 to 25 % void volume. The weight percent of carbon microballoon is low (7-15 %). However, they account for approximately one third of the volume and historically their percentages have not been controlled very tightly. In addition, the composite properties show no correlation with microballoon weight % or fiber properties (e.g. fiber density or fiber moisture adsorption capacity. Test results concerning the ply-lift anomaly in the MNASA motor firings were [3]:

- Steeper ply angle (shorter path length) designs minimized/eliminated ply lifting
- Material with higher void volume ply lifted less frequently
- Materials with high (>9%) microballoon content had a higher rate of ply lifting
- LDCCP materials failed at microballoon-resin interfaces.

The objectives of this project are:

1. To investigate the effects of carbon microballoon and cabosil fillers as well as fiber heat treatment on plylift-related mechanical properties.
2. To develop a science-based thermostructural process model for the carbon phenolics. The model can be used in the future for the selection of the improved ASRM materials.
3. To develop the micro-failure mechanisms for the ply-lift initiation and propagation processes during the thermoelastic region of phenolic degradation, i.e. postcuring and devolatilization.

II. FILLER-RESIN INTERACTION AND FIBER HEAT TREATMENT

Six lots of LDCCP (Table 1) were fabricated by varying the fiber heat treatment condition, type of carbon microballoon, and the use of silica filler. Parameters governing the across-ply tensile properties, interlaminar shear strength, and plylift failure modes will be examined. The effects of the resin-filler interaction on gas permeability and thermal expansion behavior will also be investigated.

Table 1. Material Description

Prepreg Material	Fabric	Resin	Microballoon	Cabosil
FM5939 LDC 1722	BP CCA-8+	Ironsides 91LD	T	No
FM5939 LDC-X1 1723	BP CCA-8+	Ironsides 91LD	T	Yes
FM5055 LDC 1724	BP CCA-8	Ironsides 91LD	A	Yes
FM5055 LDC-X2 1725	BP CCA-8	Ironsides 91LD	T	Yes
FM5055 LDC-X3 1726	BP CCA-8	Ironsides 91LD	T	No
FM5939 LDC-X1 1727	BP CCA-8+	Ironsides 91LD	T	Yes

The FM5055 LDC material, fabricated with a carbon microballoon type A, is a "historical" LDCCP material, and FM5939 LDC, with a CCA-8+ carbon fabric and carbon microballoon type T, is under development for the ASRM program. The effects of microballoon type and the presence of cabosil on the specific gravity and volatile content are shown in Table 2.

Table 2. Composite density and volatile content, preliminary data

Prepreg material	Specific gravity[1]	Residual volatile, %[2]
FM 5939 LDC 1722	1.076	1.684
FM 5939 LDC X1 1723	1.071	1.850
FM 5939 LDC X1 1727	1.063	1.834
FM 5055 LDC 1724	1.034	2.405
FM 5055 LDC X2 1725	1.064	2.387
FM 5055 LDC X3 1726	1.073	2.260

1. - ASTM D 792: Standard Test Methods for Specific Gravity (Relative Density) and Density of Plastics by Displacement
2. - Thiokol Specification for RSRM, STW 5-2845E: Nozzle Reinforced Plastic Component Testing and Accepting Criteria

III. Polymer Degradation Model: An Initial Model Framework

Following the work published in wood pyrolysis [4], a one-dimensional material balance equation for the gases generated in the composite is given as:

$$\frac{\partial(\epsilon \rho z_g)}{\partial t} + \frac{\partial(\rho_g u)}{\partial x} = R_g \qquad (1)$$

where ρ_g = density of gas, u = superficial gas velocity, ϵ = porosity, and R_g = gas generation rate. Using Darcy's law for a porous medium, the momentum balance equation on gases permeation can be expressed as:

$$u + \frac{K}{\mu}\frac{\partial p}{\partial x} = o \qquad (2)$$

where K = permeability, μ = viscosity of gas. By defining an effective thermal conductivity, the energy balance equation on the solid phase is:

$$(1-\epsilon)\rho_s C_s \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[k^* \frac{\partial T}{\partial x}\right] - \rho_s u C_g \frac{\partial T}{\partial x} + h_R R_s \qquad (3)$$

where $k^* = (1-\epsilon)k_s + k_g$, C_s = heat capacity of solid, C_g = heat capacity of gas, h_R = heat of reaction, R_s = solid generation rate ($=-R_g$). In the material balance equation, the rate of polymer degradation is defined as:

$$R_s = -R_s = \frac{\partial}{\partial t}[(1-\epsilon)\rho] = \frac{\Delta M_R}{V}\frac{d\alpha}{dt} \qquad (4)$$

$$\frac{d\alpha}{dt} = \Sigma w_i \frac{d\alpha_i}{dt} \qquad (5)$$

where R_s = solid generation rate, w_i = weight fraction of volatile, pyrolysis gases, and carbon char, respectively, and α_i = degree of degradation for devolatilization, pyrolysis, and charring, respectively.

In the above equations, the material properties, e.g. thermal conductivity, heat capacity, and permeability, have to be estimated as functions of temperature, degree of degradation, and fiber or resin volume fraction. The rate of degree of degradation, $d\alpha/dt$, will be determined from the experimental data.

IV. Microscopic Analysis of Residual Thermal Stress in a Single Fiber-Matrix System

Efforts have been made to develop analytical tools for predicting stresses and internal pressure created when the composite is heated rapidly [1]. These models provide good insight into the thermal and mechanical responses of composites. However, the fracture mechanics of these models was based on macro-mechanics. In this section, a model framework for polymer thermal degradation and composite micro-mechanics will be presented.

Consider a single fiber embedded in a matrix, and the system is cooled by ΔT. Due to the differential thermal contraction a contact pressure, p, is developed at the fiber-matrix interface. The fiber is subjected to an external pressure, p, at r_f (radius of fiber) and resin is subjected to an internal pressure, p. Based on this thick cylinder model, the radial displacements and residual thermal stress can be calculated by the following equations [4].

$$u_f = \frac{(1-v_f)}{E_f} r_f P \tag{6}$$

$$u_m = \frac{r_f p}{E_m} \left(\frac{r_f^2 + r_m^2}{r_m^2 - r_f^2} + v_m \right) \tag{7}$$

where u_f, u_m are radial displacements of fiber and matrix, E_f, E_m are elastic modulus of fiber and matrix, r_m is the radius of matrix, and v_f, v_m are volume fraction of fiber and matrix. Compatibility at the fiber-matrix interface requires that

$$u_m - u_f = (\alpha_m - \alpha_f)\, r_f\, \Delta T \tag{8}$$

Combining Eqs. (6)-(8), the residual thermal stress at the microscopic level is:

$$P/\Delta T = \frac{(\alpha_m - \alpha_f)}{\frac{1}{E_m} \left(\frac{r_f^2 + r_m^2}{r_m^2 - r_f^2} + v_m \right) + \frac{1-v_f}{E_f}} \tag{9}$$

The typical values of E_m and α_m for phenolic resin are 5 GPa and 70 x 10^{-6}/°C, and E_f and α_f for medium-modulus carbon fibers are 270 GPa and 3.5 x 10^{-6}/°C, respectively. In the case of $v_f=0.6$ and $r_f^2/r_m^2=0.6$, the value of $P/\Delta T$ in Eq. (9) will be equal to around 70 KPa/°C. When the phenolic composite is cooled from a curing temperature of 160°C to a room temperature of 25°C, the micro-level residual thermal stress is -9.4 MPa.

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