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Kinetics, evolving thermal properties, and surface ignition of carbon fiber reinforced epoxy composite during laser-induced decomposition

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ABSTRACT

The decomposition kinetics, heats of reaction, evolving thermal conductivity and emissivity, and surface ignition conditions of carbon fiber reinforced polymer (CFRP) composites during laser-induced polymer matrix decomposition were investigated. Woven carbon fiber-epoxy panels of different thicknesses were irradiated with a 1.07-μm, 2-kW ytterbium fiber laser at irradiances of 5–525 W/cm^2. The changing front and backside surface temperatures were measured using a mid-wave infrared camera, adjusted using measured emissivity of irradiated and un-irradiated CFRP samples. The evolving temperature maps were fit to a 3D, explicit, finite difference, thermal model to estimate Arrhenius kinetic rate parameters, heats of reaction, and thermal conductivity during a two-step epoxy decomposition reaction and a single stage char oxidation reaction. The kinetics is not strongly dependent on heating rates of 20–700 °C/sec and parameters determined at lower laser powers extrapolate well to higher powers. Surface ignition occurs at critical surface temperatures of 1198 ± 50 °C.

1. Introduction

The use of carbon fiber reinforced polymer (CFRP) is increasing in many aerospace, military, and automotive applications [1]. Thermal damage and combustion has been studied and modeled primarily for fire science applications [2–4], at lower heating rates and often for piloted ignition. For piloted ignition of an epoxy matrix, volatile surface fluxes of approximately 7.5 g/m^{2}s [5] are required, a condition that is produced by incident heat fluxes of at least 1.3 W/cm^2. In contrast, lasers provide many times the necessary surface heating to produce volatile products but provide no ready ignition source, producing much different ignition criteria. The fielding of tactical high-energy laser (HEL) weapon systems and the proliferation of fiber lasers makes CFRPs likely target materials in future laser engagements [6–8]. We seek to develop a model for evolving material thermal and optical properties, and decomposition kinetics capable of describing ignition and mass loss under high irradiance HEL conditions. In particular, surface temperatures and hydrocarbon plume concentrations required for ignition and characterizing the rate of mass loss at high heating rates is critical for weapons applications.

At the fiber laser wavelength of 1.07 μm, the epoxy matrix is highly transmitting and carbon fiber is highly absorbing [9], resulting in laser absorption primarily into the first fiber layer followed by conduction to the surrounding epoxy [10]. Carbon fibers are thermally robust and require high irradiance to achieve CFRP burn-through, but much less to decompose the epoxy resin. Cured epoxy softens (120 °C) and dehydrates (250–300 °C) before decomposing via random chain scission (300–450 °C) to produce volatile fragments and char [11]. Resin decomposition can have damaging effects due to fouling and combustion of volatiles on both interior and exterior panel surfaces and significant reductions in CFRP compressive strength [2].

As volatile decomposition vapors accumulate in the vicinity of the laser spot, they can be detected and their relative concentrations tracked during the period leading up to ignition using an imaging Fourier Transform Spectrometer (IFTS). IFTS uses a Michelson interferometer and a detector array to generate interference spectra at every pixel in a scene. IFTS has been previous used to analyze the constituents of industrial smokestacks [12], jet engine exhaust plumes [13], chemical plumes [14], natural gas flare emissions [15], and HEL material degradation plumes (fiberglass [16], polymethyl methacrylate (PMMA) [17], and graphite [18]).

This work uses high-speed thermal imagery and a simplified thermal model to determine evolving front and back CFRP surface temperatures and to estimate unknown thermal properties and

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kinetic parameters throughout epoxy decomposition at low laser irradiance. Results are applied to the prediction of surface temperatures at higher laser powers. The necessary conditions for surface ignition under HEL irradiation are also determined using thermal and IFTS imagery.

2. Experimental

Commercially available CFRP panels were obtained from Protech Composites Inc. in thicknesses of 1.7, 2.4, 3.2 mm and contained 4,6, or 8 plies of 6K 2 × 2 twill weave carbon fiber fabric. The polymer matrix was a Bisphenol A diglycidyl ether (DGEBA) based epoxy resin blend and was injected under vacuum. The hardener identity was not released by the manufacturer.

Panels were irradiated by a 2-kW continuous wave IPG Photonics ytterbium doped fiber laser at 1.07 μm, as shown in Fig. 1. Front and back surface temperatures were simultaneously recorded with a mid infrared camera by placing a flat mirror behind the CFRP panels. A beam splitter was used to illuminate a stationary scatter plate and the spatial and temporal laser beam irradiance variation was recorded by near infrared (NIR) camera. A 30-Hz visible camera was used to witness each test. Tests were conducted on an open optical table with ceiling mounted ventilation hood (upward flow speed approximately 0.2 m/s).

Square, 10.38 cm × 10.38 cm, 3.2-mm thick panels were irradiated at 5, 10, 36, and 64 W/cm^2, with the square 1.7-and 2.4-mm thick panels irradiated at 10 and 36 W/cm^2. The laser spot diameter was 6 cm for all but the 64 W/cm^2 shot (2.3 cm diameter). Spot size was stable and measured at 1/e^2 of peak value. Reported irradiance values are the average irradiance within 0.5 cm of laser center. High irradiance (85–525 W/cm^2) experiments were conducted on 30.48 cm × 15.24 cm strips with a 2.4-cm diameter laser spot and 15.24 cm × 2.54 cm strips with a 1.65-cm diameter laser spot. Tests were run for two minutes or until surface ignition occurred. Irradiance reached peak levels in approximately 0.5 s and irradiance in a given pixel varied by ± 0.4–1.7% with the highest instability nearest laser hot spots.

Thermal imagery was recorded at 160 × 128 pixel resolution using a FLIR SC6000 MWIR camera. The camera was operated with a band pass filter from 3.8 to 4.0 μm and a neutral density filter of O.D. 1.0. On low irradiance tests, a silvered mirror was placed behind the sample and angled to allow the camera to view both the front and backside of the panel side-by-side in the same frame. The test panels were imaged at an angle of 32.6° off normal, in the same horizontal plane. Spatial resolution was 1.49 mm/pixel x 1.22 mm/pixel for the front side and 1.61 mm/pixel x 1.48 mm/pixel for the back.

The mid-infrared imagery was corrected for detector non-uniformity, non-linearity, bad pixels and detector spectral response on a pixel-by-pixel basis using an Electro-Optical Industries CES600-06 wide area blackbody at T = 50–600 °C. Images were collected sequentially at four integration times (0.1, 0.3, 2, and 4 ms for laser irradiance of 10 W/cm^2) at frame rates of 120–240 frames per second (30–60 fps per integration time). The multiple integration times extended the dynamic range to 300–2500 K.

The accuracy of the surface temperature is primarily dependent on surface emissivity at the 3.9-μm wavelength of the thermal camera. The spectral emissivity of undamaged and damaged CFRP material was measured from 2 to 25 μm with a SOC-100 Hemispherical Directional Reflectometer (HDR) manufactured by Surface Optics Corp at temperatures up to 500 °C [19]. Room temperature absorptivity (α) of undamaged material, charred material, and bare fibers at 1.07 μm were also measured using a Cary 5000 UV-Vis-NIR spectrophotometer. Absorptivity of undamaged CFRP was 0.93. Surface charring due to thermal decomposition increased α to 0.98 and char oxidation to bare fiber decreased α to 0.86.

Spatially- and temporally-resolved (~0.5 mm and ~10 Hz) infrared emission spectra (λ = 1.5–5 μm) of the decomposition plume prior to ignition were measured from the side using a Telops Hyper-Cam MWIR Imaging Fourier Transform Spectrometer (IFTS), as shown in Fig. 1(b) [20]. Many of the volatile epoxy decomposition products have IR absorption peaks at 3000 cm^{-1} resulting from C-H bond stretching and near 3700 cm^{-1} due to phenolic O-H stretching. The observed emission is used to monitor the relative concentration of volatiles prior to ignition. The Telops IFTS spectral resolution was 16 cm^{-1} with 128 × 64 pixel images acquired at 9–14 frames per second and a spatial resolution of 0.46 cm/pixel.

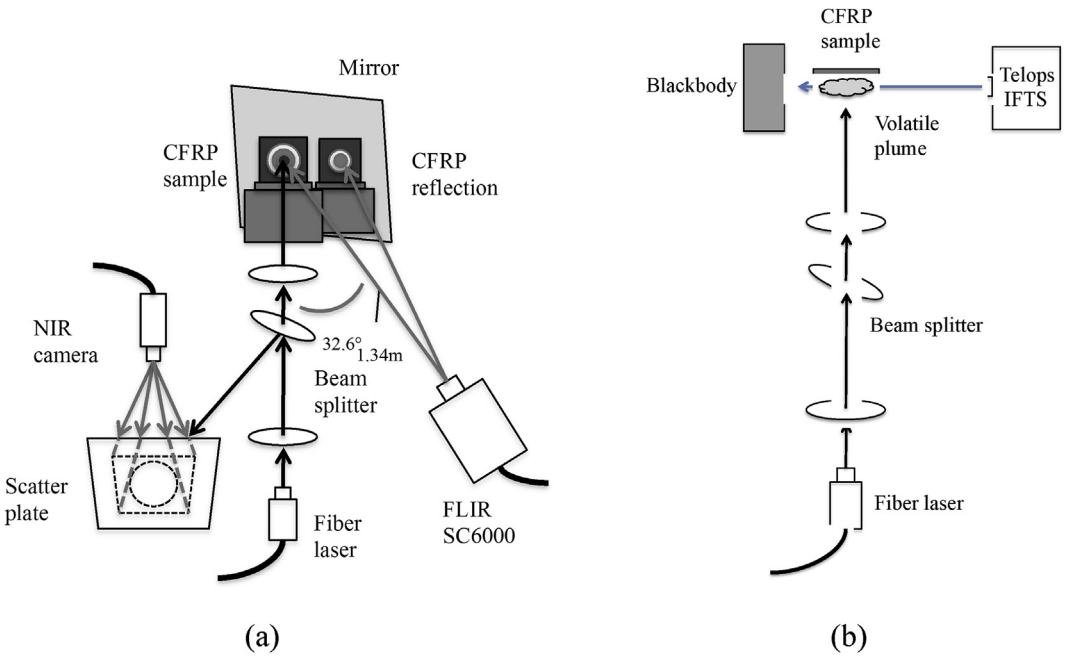

Fig. 1. Experimental Schematic for: (a) surface temperature imaging and (b) plume emission hyperspectral imaging.