

Evaluation of the Thermal Degradation of Polymer Matrix Composites via Ultrasonic Spectroscopy and Fracture Toughness

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Research Objective: Investigate the potential of ultrasonic spectroscopy to detect subtle changes in the mechanical behavior of polymer matrix composites exposed to high heat fluxes.

Approach: Construct polymer matrix laminate composites from commercially available prepregs, which are utilized in industrial applications. Conduct traditional ultrasonic image scanning of the composites before and after exposure to realistic thermal loads. Extract waveforms from the ultrasonic images and transform appropriate portions into the frequency domain via fast Fourier transformation. Details are described below:

Materials: Laminates were fabricated from 3501-6 prepreg provided to us by Hexcel Corporation. The 3501-6 prepreg consists of IM6G carbon fiber and partially amine cured epoxy. Unidirectional panels of 30 plies were fabricated in a hand lay-up fashion with a 0.02 mm aluminum spacer inserted midway through the lay-up sequence along one edge of the panel. The panels were cured in an autoclave according to manufacture's specifications. Double cantilever beam (DCB) tests specimens were then machined from each panel to a total length of 20 cm and a width of 2.5 cm. The notch produced from the spacer measured approximately 12 mm.

Ultrasonic Spectroscopy: Selected DCB specimens were submerged in water and scanned in a back scatter (pulse/echo) mode with a Panametrics model V316 20 MHz focused transducer. The transducer used had a 3 mm diameter element and a focal point 19 mm from its face. A Panametrics model 5601A/TT pulser/receiver was used to drive the transducer. The signal from the pulser/receiver was digitized at a rate of 1 GHz with a Sonix STR81G PC based digitizer. Panametrics Inc. Multiscan software was used to set the trigger threshold and gate the echoes returning from the sample. The software controlled two stepper motors that scanned the transducer in the X - Y plane via a Panametrics P1399 position match generator and MEI motion controller.

Specimens were held by an aluminum fixture designed such that they could repeatably be placed in the same location before and after heat exposure. The height of the transducer above the sample was calibrated for each sample by recording a waveform from a rectangular piece of epoxy of known composition. Five A-scans were collected and averaged every 0.25 mm along the length of the sample and digitally stored as a B-scan. B-scans were collected every 2.5 mm along the width of the sample. The B-scans were collected to form a three-dimensional data array for each DCB specimen. The 3D array could be separated into A-scans at selected

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points in the specimen, B-scans along the specimen length or width of the specimen, and C-scans to map specific depths across the entire sample.

Thermal Exposure: Thermogravimetric analysis (TGA) was conducted on a sample of the epoxy matrix with a heating rate of 10°C/min in a nitrogen atmosphere. The onset of degradation was observed to occur at 325°C. Thus, short term – high intensity exposures were conducted at temperatures above this degradation temperature and long term – low intensity exposures at temperatures below it. The untabbed ends of the DCB specimens were exposed to extreme temperatures (350, 400, and 450°C) for one hour, short term – high intensity. The exposure apparatus consisted of a steel two liter beaker containing about 100 ml of sand. This was placed on a hot plate and wrapped with glass wool for insulation. Thermocouples were placed on the ends and at 5 cm increments along the length of each sample. Samples were inserted into the apparatus such that 12 mm of the untabbed end was immersed in the sand. The average thermal gradients after 20 minutes of exposure were determined for samples exposed at 350, 400, and 450°C. The thermal gradient induced in the long term – low intensity specimens was produced in a similar manner using silicone oil at 205°C for four weeks.

Mode I Energy Release Rate Measurement: The Mode I tests were conducted at a cross head speed of 2 mm/min. Crack lengths were measured optically during the testing and verified/corrected after inspection of the fracture surfaces after the testing was complete. The energy release rates were determined using the compliance method. In this approach, the measured compliance is used to calculate the energy release rates.

Fourier Transform Infrared Spectroscopy (FTIR): Spectra were collected at 2.5 cm intervals along the length of the fracture surfaces of each specimen. These measurements were conducted by Cristiane Rodriguez of Nicolet using a Nicolet Magna 760 spectrometer interfaced to an InspectIR microsampling accessory with a silicon ATR (attenuated total reflectance) crystal producing an IR spot size of approximately 70 µm. 200 scans were collected and averaged per spectrum.

Simultaneous Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC): After fracture toughness was measured, a lengthwise section of each sample was removed and samples, approximately 10 mg each, were cut from this section at 2.5 cm intervals. Each sample was heated at a rate of 10°C/min in nitrogen (flow rate = 50 ml/min) using a Rheometrics STA Model 1500 TGA/DSC. Weight loss and heat flow were recorded for each sample from 30 to 900°C.

Accomplishment Description: This research illustrates ultrasonic spectroscopy's remarkable sensitivity to changes in material properties and chemical transformation upon thermal degradation. Thus, ultrasonic spectroscopy may be useful as a means of detecting incipient damage prior to the formation of delaminations and the detection and monitoring of thermal degradation of PMCs. Short term – high intensity thermal loads induced an increase in Mode I fracture toughness with a sharp increase occurring prior to

catastrophic failure. Observation of the fracture surfaces indicated that one mechanism of increased toughening may include fiber bridging in the regime just prior to the rapid decrease in fracture toughness. The dependence of the ultrasonic spectral amplitude on thermal degradation correlated with the observed changes in Mode I fracture toughness. A sharp rise in amplitude occurred just prior to the location of the sharp rise in toughness. This behavior was most pronounced for the specimen exposed to 450°C and incrementally decreased in magnitude for the specimens exposed to 400 and 350°C. FTIR, TGA/DSC, and fracture toughness correlated with ultrasound indicating that 250°C is a critical temperature at which thermally induced damage greatly increases. Also, it is intriguing that with long term – low intensity thermal loads there is a resultant decrease in fracture toughness and ultrasonic signal amplitude.

Significance: Once perfected, this method may assist in the non-destructive evaluation aircraft components indirectly exposed in fire situations. This would enable engineers and inspectors to ascertain whether or not to remove components from service in controlled fire situations.

Expected Results: Short term – high intensity: After thermal exposure the intensity of the frequency spectra are increased with a distinct increase occurring just before the intensity drops off sharply. The location of the sharp drop off is adjacent to delaminations. In this area and beyond (moving closer to the heated end) no back wall reflections were detected. Similar behavior was observed for the specimens exposed to 400 and 350°C for one hour. However, the magnitude of this behavior decreased with exposure temperature. This evidence clearly illustrates a direct correlation between the severity of thermal exposure/damage and the ultrasonic frequency spectrum. Under normal conditions, the critical energy release rate is independent of crack length and is ascribed a value of G_{IC} . The unaged (control) specimens have G_{IC} values of 240 J/m². The specimen exposed to 450°C has greater toughness values than the control and there is a jump in toughness prior to failure near the heated end. Again similar effects are seen for the specimens exposed to 400 and 350°C specimens except the toughness is only slightly greater or similar to the control specimens prior to a jump in toughness just before failure. A remarkable similarity is noted in the shape of the ultrasonic amplitude and G_{IC} curves. Both figures show an increase in magnitude over the unaged specimen with a sharp increase occurring just before delamination and failure respectively. Several consistent trends are noted between the ultrasonic amplitude and G_{IC} curves; 1) sharp drop in amplitude occurs just before a sharp increase in toughness, 2) the location of these sharp changes shifts to the right (closer to the heated end) with decreasing exposure temperature, and 3) the intensity of the amplitude jump sequentially decreases as the severity of the thermal gradient was reduced. Thus, there is a strong correlation between the ultrasonic spectra and fracture toughness responses to thermal degradation. The sharp increase in ultrasonic amplitude prior to this region may be evidence of incipient damage prior to delamination. Plotting the data versus exposure temperature collapses all of the data together with the sharp drop off in frequency spectra and sharp rise in fracture toughness occurring at 250°C. This clearly indicates evidence of a critical temperature at which severe thermal degradation and/or composite delamination takes place. FTIR and TGA/DSC analysis confirms 250°C as a critical temperature for this composite system.

Long term – low intensity: A progressive decrease in signal intensity occurred as one moved closer to the heated end. Thus, the attenuation coefficient as a function of frequency and clearly illustrate that the loss in signal intensity began with the highest frequencies and then progressed to the lower frequencies as damage increased. The unexposed specimens had a G_{IC} value of 260 J/mm^2 . The exposed specimens incurred a significant decrease in G_{IC} to a value of 120 J/mm^2 near the heated end. As the crack propagated away from the heated end a gradual increase in toughness occurred obtaining a value of 160 J/mm^2 14 cm from the heated end. Again we observe a correlation between the ultrasonic frequency spectrum and the fracture toughness.

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