Prediction of Interlaminar Shear Strength of a Thermally Aged Carbon/Epoxy Composite Material by Fourier Transform Infrared Photoacoustic Spectroscopy

Jeffrey J. Sweterlitsch
Iowa State University

Roger W. Jones
Iowa State University, jonesrw@ameslab.gov

David K. Hsu
Iowa State University

John F. McClelland
Iowa State University, mcclelland@ameslab.gov

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Abstract
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Keywords
Biochemistry Biophysics and Molecular Biology, Mechanical Engineering, Center for Nondestructive Evaluation, carbon/epoxy composites, interlaminar shear, photoacoustic spectroscopy, strength

Disciplines
Acoustics, Dynamics, and Controls | Biochemistry, Biophysics, and Structural Biology | Mechanical Engineering

Comments
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Prediction of Interlaminar Shear Strength of a Thermally Aged Carbon/Epoxy Composite Material by Fourier Transform Infrared Photoacoustic Spectroscopy

JEFFREY J. SWETERLITSCH,* ROGER W. JONES, DAVID K. HSU, and JOHN F. McCLELLAND†

Ames Laboratory (J.J.S., R.W.J., J.F.M.), and Center for Nondestructive Evaluation (D.K.H.), Iowa State University, Ames, Iowa 50011

Photoacoustic spectroscopy was used to predict the interlaminar shear strength of a carbon/epoxy composite. Samples were artificially aged by exposing the samples to elevated temperatures in an air environment. Short-beam shear tests were performed to determine mechanically the interlaminar shear strength of the samples. Photoacoustic spectra of the samples were also collected and compared to mechanical data. Chemometrics were performed on the spectral and mechanical data, and a good correlation was found between the near surface chemistry of the composite and overall mechanical integrity.

Index Headings: Photoacoustic spectroscopy; Interlaminar shear strength; Carbon/epoxy composites.

INTRODUCTION

Carbon/epoxy composite materials are widely used in applications where strength-to-weight ratio is critical to their performance. Significant deterioration of mechanical performance can occur due to chemical changes in the composite’s epoxy matrix related to aging. Infrared photoacoustic spectroscopy (PAS) can be used to monitor chemical changes in the epoxy matrix, but the measurement probes only approximately 1 to 10 micrometers into the material due to the high absorption of the graphite fibers. This probe depth is too shallow to characterize directly the bulk of the sample, which defines the mechanical properties of the matrix. In spite of this limitation, it is still possible that the near surface chemical changes that PAS can probe are predictive of bulk chemistry changes and can be used to predict, using chemometrics, mechanical changes within the bulk. This work is designed to explore this possibility as it applies to the interlaminar shear strength (ILSS) of a carbon/epoxy composite.

EXPERIMENTAL

The experimental work of this research involved preparing and artificially aging 120 samples of the same composite by exposing the samples to elevated temperature for a set length of time. The samples were then characterized using Fourier transform infrared (FT-IR) PAS1–6 to study the chemical changes that resulted from the heat exposure. The photoacoustic spectra were compared with mechanical experiments that measured the interlaminar shear strength of the composite samples, and chemometric analysis was performed to determine what, if any, correlation existed between the photoacoustic and mechanical measurements.

The carbon/epoxy composite samples used for this research were acquired from a solid laminate consisting of polyacrylonitrile-based carbon fibers, identified by the composite industry as “IM7” carbon fibers, and an epoxy resin, identified by the composite industry as “977-3” resin. The composite panel was manufactured by Boeing in a process called advanced fiber tow placement.7 This method of manufacturing the composite utilizes a robotic head that lays down groups of thin strips of carbon fibers, impregnated with the epoxy resin and identified as “tow-pregs”, that are oriented in the same direction, resulting in a five-centimeter-wide band called a “course.” Adjacent courses make up one ply, or layer, that is ~260 μm thick. Additional plies with fibers running in different directions are added to build up the thickness of the laminate. The laminate is then cured in a vacuum bag, under external pressure and at elevated temperature, following the manufacturing cure cycles. The arrangement of the 25-ply solid laminate composite panel used in this research was [(–45/45/0)3/90, (0/45/~45)]2, and the panel was 6.59 mm thick, where “~45,” “45,” “0,” and “90” are the orientation angles of individual plies, and the subscripts are short-hand notation for listing adjacent plies (or sets of plies) that have the same orientation angle. Upon inspection, the composite sample had two different types of flat faces, one that was shiny (the “tool side”), and an opposite face that was slightly textured (the “bag side”). The “bag side” appears textured because it was in contact with a bleeder cloth during the curing of the composite laminate. The shiny “tool side” would normally be the exterior surface of a manufactured part, and would therefore be the most easily accessible surface for PAS analysis in the context of a nondestructive evaluation. All sampling in this research took place on this shiny surface.

Two sampling methods for collecting PAS spectra were used in the experiments. In the first method, designated direct sampling (DS), small square samples were cut from the composite panel, placed in the photoacoustic detector, and analyzed with the FT-IR beam impinging directly on the sample surface. In the second method, designated surface powder sampling (SPS), powder was removed from the composite panel using an abrasive paper. The powder was then transferred to a sample cup and placed in the photoacoustic detector for analysis.
A total of 120 sample rectangular bars 12 mm wide and 44 mm long were cut from the composite panel, and from each sample bar two smaller pieces, 6 mm × 6 mm square, were cut and one was used for the DS photoacoustic measurements. The remaining 38 mm long and 12 mm wide sections were used for the interlaminar shear strength measurements using the short-beam shear test. To prepare the powdered samples for the SPS measurement, powders were removed from a surface area of 1.6 cm² using a 400-grit emery from the shiny side of each short-beam shear test specimen. The powdered samples weighed 0.64 mg ± 0.15 mg, which corresponds to a thickness of approximately 2.5 micrometers.

The samples were artificially aged prior to preparation for DS and SPS measurements by baking in an oven in air at a prescribed temperature and time. Previous unpublished work from this laboratory had demonstrated that temperature exposure was a more influential factor than time exposure, so the time exposure was kept constant at 4 hours. Eleven different temperatures were chosen that varied from 149 °C to 288 °C at intervals of 13.9 °C. Ten samples were prepared for each temperature and subsequently cooled to room temperature prior to collecting measurements. Ten additional samples were prepared as room-temperature (baseline) samples.

The short-beam shear tests were performed on an Instron 1000 Universal Electromechanical Testing System using the ASTM method for determining the interlaminar shear strength.⁸ The Instron 1000 was equipped with a 44 kN load cell. The short-beam test fixture had a pair of parallel rollers at a prescribed separation distance that supported the specimen from the bottom. A software-controlled load was applied to the center roller on top of the specimen to cause the deflection. The Instron 1000 recorded the deflection of the sample as a function of the load until the sample failed by exhibiting a series of sudden drops of the load. The results of measurements on ten different samples were averaged in order to account for the natural variability in mechanical failure measurements on composite materials.

A Digilab FTS 7000 FT-IR spectrometer and an MTEC Photoacoustic, Inc. Model 200 photoacoustic detector were used to collect the photoacoustic spectra, with WinIR Pro as the data acquisition software. The spectra were then converted into GRAMS/AI version 7 (Thermo Galactic, Salem, NH) format to perform mathematical manipulations, which were in turn converted into Pirouette 3.02 (Infometrix, Inc., Woodinville, WA) format to perform the chemometric analysis of spectra combined with the mechanical data. The spectrometer scanned in rapid-scan mode at 2.5 kHz (0.158 cm/s retardation velocity), with 256 scans averaged together to produce the final photoacoustic spectrum for each sample. The spectral resolution was 8 cm⁻¹, and the spectral range was 400–4000 cm⁻¹. The thermal diffusion length, commonly referred to as the sampling depth, depends on the thermal diffusivity of the composite material, estimated to be 10⁻³ cm²/s, and the wavelength of the infrared light. For the spectral range specified, the thermal diffusion length varied from 22.4 μm at 400 cm⁻¹ to 7.1 μm at 4000 cm⁻¹. Ultra-pure helium was used as both a purge gas to remove moisture that evolves from the sample as well as the transducer gas in the photoacoustic cell. Even after purging the cell with helium, because of the large surface area of the composite sample, moisture can still evolve from the sample over several days, so to reduce water vapor in the detector’s sample chamber during the collection of the DS (SPS) photoacoustic spectra, a small amount of desiccant was placed in a small piece of aluminum foil (in a cup), and then placed in the photoacoustic sample holder beside (under) the sample.

RESULTS AND DISCUSSION

Mechanical Results. The 120 samples were tested on an Instron 1000 using the ASTM method for determining the interlaminar shear strength of the composite samples.⁸ Typical load versus deflection curves for different temperatures are presented in Fig. 1. Theoretically, the applied load increases linearly with increasing deflection of the sample, and at the breaking load there is a sudden drop in the applied load as the sample is deflected beyond its breaking point. The samples that were at room temperature and the elevated temperatures of 149 °C and 218 °C demonstrate this, but for the highest temperature of 288 °C, after a small initial drop in applied load, the applied load remains relatively constant with increased deflection of the sample, indicating that at this temperature the sample was severely damaged and was simply flexing under the applied load.

The interlaminar shear strength for each sample was determined as follows:

\[ S_H = 0.75P_b/\beta d \]

where \( S_H \) is the shear strength in Pascals, \( P_b \) is the breaking load in Newtons, \( \beta \) is the width of the sample in m, and \( d \) is the thickness of the sample in m. Figure 2 shows the decline in average shear strength of the samples as the exposure was increased. The vertical bars indicate the range of measured shear strength for the ten samples that were exposed to a particular temperature.

Photoacoustic Spectroscopy Results. Figure 3 shows the fingerprint region of the photoacoustic spectra measured using the DS method. For the purpose of comparison, the spectra have been scaled forcing the local minima at ~1998 cm⁻¹ and the local maxima at 1593 cm⁻¹ to match. The spectra shown are the averaged spectra of the ten samples that were exposed to a particular tem-
temperature. A primary indicator of degradation of composite material is the presence of oxidation. The growth of the peak near 1720 cm$^{-1}$, where carbonyl (C=O) absorbs infrared light strongly, is due to chemical oxidation of the epoxy resin. An additional sign of degradation is that the unique spectral features of the epoxy resin are getting washed out and becoming less defined with increased exposure temperature.

**Chemometric Analysis: Direct Sampling.** The spectral data for each exposure temperature were paired with the corresponding average mechanically determined interlaminar shear strength for each exposure temperature. Although data were collected between 400–4000 cm$^{-1}$, only the region between 544–1937 cm$^{-1}$ was used for the chemometric analysis. Multiplicative scatter correction (MSC) and variance scaling preprocessing steps were applied to the spectra. Partial least squares (PLS) was used to create a regression model, using one data point for cross-validation. The best-fit model used six factors. Figure 4 shows the predicted interlaminar shear strength based on the photoacoustic spectra of the composite samples. If the model were perfect, all data points would lie on the diagonal line, which has a slope of unity. For the DS measurements, there is a standard error of cross-validation (SECV) of 1.60 MPa over the range of the interlaminar shear strength of 54.78 MPa.

**Chemometric Analysis: Surface Powder Sampling.** The chemometric procedure was repeated, but with the spectra collected using SPS. The spectral data for each exposure temperature were paired with the same corresponding average mechanically determined interlaminar shear strength for each exposure temperature as in the DS method. The same data collection range and analysis range were used for the SPS method; however, the SPS spectra were converted into 13-point second derivatives, followed by MSC preprocessing. These spectra were converted into second derivatives to remove variations in the height and slope of the baselines because the SPS spectra had a larger and more variable contribution from the carbon fiber. PLS was again used to create a regression model, and the best-fit model used six factors. Figure 5 shows the predicted interlaminar shear strength based on the photoacoustic spectra of the surface powders. This method of predicting the interlaminar shear strength produced an SECV of 2.02 MPa over the range of the interlaminar shear strength of 54.78 MPa.

**CONCLUSION**

The results of this work show that photoacoustic spectroscopy can be used as a nondestructive (DS method) or...
minimally destructive (SPS method) analytical technique for determining the thermal aging degradation of a carbon/epoxy composite. In order for the DS method to operate in a nondestructive mode on composite assemblies it would be necessary to modify the photoacoustic detector and FT-IR spectrometer so that the apparatus can directly attach to the material being analyzed rather than cutting specimens to fit into the current detector’s sample cup as was done in this study. In instances where this is not practical, the SPS method allows a minute specimen to be removed from the composite without significantly altering its mechanical strength and then analyzed in the laboratory using existing instrumentation.

Photoacoustic spectroscopy should be applied with caution for the prediction of bulk mechanical properties of carbon/epoxy composites because the method only probes a maximum of several tens of micrometers into the material’s surface. In the case of thermal aging at elevated temperatures in air, near surface PAS spectra, however, appear to be predictive of bulk chemical changes, thus allowing the prediction of bulk mechanical properties of the carbon/epoxy material.

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