

FT-IR PHOTOACOUSTIC SPECTROSCOPY APPLIED TO THE CURING AND AGING OF COMPOSITES

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ABSTRACT. Fourier-transform infrared photoacoustic spectroscopy has been applied to carbon-fiber composites to test whether bulk physical properties of the composites could be determined using the near-surface-sensitive photoacoustic approach. Both the cure levels of carbon fiber/cyanate ester composites and the interlaminar shear strengths of artificially aged carbon fiber/epoxy composites were successfully measured. Standard errors of cross validation were 3.46% cure for a sample set ranging from 8% to 95% cured and 1.60 MPa for aged samples with strengths ranging from 22 to 77 MPa.

INTRODUCTION

Carbon-fiber composites are often used where strength-to-weight ratios are critical, so their strength must be maintained during production and service. Numerous factors that affect the chemical composition of a composite can result in significant shortfalls in mechanical performance. These chemical changes are reflected in the mid-infrared spectra of the material, but carbon-fiber-based composites are normally difficult to probe by optical spectroscopy because they are both opaque and nonreflective. Photoacoustic spectroscopy (PAS) is insensitive to opacity and nonreflectivity because it senses the heat deposited near the surface of a sample when it absorbs light [1]. Fourier-transform infrared (FT-IR) PAS can therefore acquire mid-infrared spectra from conventionally intractable materials, such as carbon-fiber composites, but the measurement probes only a few micrometers to a few tens of micrometers into the material. This probe depth is too shallow to directly characterize the material bulk, which defines the mechanical properties of the matrix. Nevertheless, the near-surface chemical changes that PAS can probe may be predictive of bulk chemistry changes and could therefore be used to predict, using partial-least-squares (PLS) chemometrics [2], mechanical and other properties of the bulk.

We report two studies examining whether FT-IR PAS can be used to determine bulk properties of composites. Specifically, we have correlated FT-IR PAS spectra of carbon fiber/cyanate ester composites with cure level and the spectra of carbon fiber/epoxy composites with loss of strength from accelerated aging by heat treatment. A more detailed discussion of the accelerated-aging study is provided elsewhere [3].

In these studies we have used a conventional, commercial photoacoustic detector cell, in which a small sample is sealed while being tested. Open-ended cells, which are pressed against a large body to interrogate it, have been developed [4, 5], so the approach discussed here could be performed in a truly nondestructive manner.

EXPERIMENTAL

All photoacoustic spectra for both the cure-level and accelerated-aging studies were acquired using Digilab FTS 7000 FT-IR spectrometers with Win-IR Pro (Version 3.2) software and MTEC Photoacoustics photoacoustic detectors. The spectrometers scanned at 2.5 kHz (0.158 cm/s retardation velocity) and 8 cm⁻¹ resolution. The photoacoustic detectors were purged with helium and a small amount of magnesium perchlorate desiccant was placed in each sample chamber. A metal ring was placed atop the samples to block infrared radiation from reaching the cut sides of the samples and contributing to the photoacoustic signal. The spectra were normalized by ratioing against the photoacoustic spectrum of a carbon-black-coated membrane (MTEC Photoacoustics).

Composites of M55J carbon fiber and Hexcel 954-6 cyanate ester resin were used for the cure-level study. Both individual plies of prepregged unidirectional tape (prepreg) and 2.9 mm thick laminates were used as test samples. The laminates had a [45/0₃/-45/0₂]_{S3} layup. Different cure profiles were used for the various samples, but all were ramped at 1 to 2 °C/min up to a first cure temperature, where they were held for a set length of time, followed in some cases by a second ramp at 1 to 2 °C/min up to a higher, second cure temperature where they were held for another set time. The individual plies of prepreg were cured in air at ambient pressure in an oven. Low-cure samples were cured at 121 °C (250 °F) for 0 to 240 min with no second, higher temperature period. High-cure samples were cured at 121 °C for 180 minutes, and then ramped to 177 °C (350 °F) and held for 30 to 120 min. The laminates were cured in an autoclave at 100 psi, which was applied during the first upward temperature ramp and released during the final downward temperature ramp. Some laminates underwent only a single cure period at 124 °C (255 °F) of 120 or 180 min. Others were cured for 180 min at 124 °C, followed by a second cure period of 120 min at either 149 °C (300 °F) or 177 °C (350 °F).

Cure levels were determined with a TA Instruments Model 2910 differential scanning calorimeter, using unbaked prepreg as a 100% uncured reference. The samples were ramped from room temperature at 20 °C/min with a nitrogen purge up to either 400 °C for prepreps or 375 °C for laminates. Prepreps were tested using hermetic pans, but the laminates were tested using open pans because of their size. The data was normalized using fiber volume. Each sample was tested in triplicate and the three results averaged.

Both Model 200 and Model 300 MTEC Photoacoustics detectors were used for spectrum acquisition during the cure-level study. Some low-cure prepreg samples initially evolved substantial moisture when placed in the detector, so they were stored in a desiccator for several days before being analyzed. Partial least squares (PLS) correlation between the spectra and the calorimetry measurements was performed using the PLSplus/IQ (Version 5.10) module of GRAMS/AI (Thermo Galactic). A four-out cross validation was used during the analysis because the laminates tested consisted of four-sample sets, each set taken from the same cured plate.

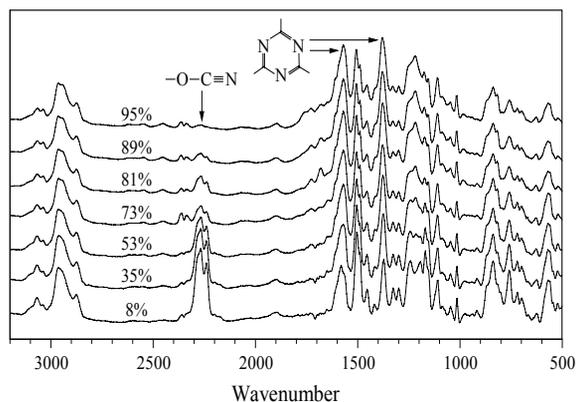


FIGURE 1. Spectra of carbon fiber/cyanate ester composite material at the cure levels marked. The spectra have been scaled so that the peak at 1111 cm^{-1} relative to the valley at 1138 cm^{-1} is the same size in all.

Carbon/epoxy laminate samples used for the accelerated-aging study were all cut from a single panel of IM7 polyacrylonitrile-based carbon fibers and 997-3 epoxy resin. The panel was manufactured by Boeing using advanced fiber tow placement [6] and consisted of 25 plies of prepreg with a layup of $[(-45/45/0_2)_3, 90, (0_2/45/-45)_3]$. The panel was 6.59 mm thick. A total of 120 rectangular bars 12 mm by 38 mm were cut from the panel for interlaminar shear strength measurements. In addition, a 6 mm by 6 mm square was cut from the panel at the end of each bar for photoacoustic spectroscopy examination. The bars and squares were artificially aged by baking for four hours in air at ambient pressure at selected temperatures. Eleven equally spaced temperatures ranging from 149°C to 288°C were used. Ten bars and ten squares were prepared at each temperature, and ten pairs of unbaked bars and squares were retained as baseline samples.

Short-beam shear tests were performed on an Instron 1000 Universal Electro-mechanical Testing System according to the ASTM method for interlaminar shear strength [7]. The Instron 1000 was equipped with a 44 kN load cell. The interlaminar shear strength for each sample was determined from the equation

$$S_H = 0.75P_B / (bd) \quad (1)$$

where S_H is the shear strength, P_B is the breaking load measured with the Instron unit, and b and d are the width and thickness of the sample, respectively [7].

An MTEC Photoacoustics Model 200 photoacoustic detector was used to collect the spectra during the accelerated-aging study, and 256 scans were co-added for each spectrum. Spectra were acquired from the smooth, tool side of each intact 6 mm square. Partial least squares correlation of the spectra with the mechanical data was performed with Pirouette (Version 3.02; Infometrix, Inc.), using a one-out cross validation.

RESULTS AND DISCUSSION

Cure Level

As detailed in the Experimental section, both single-ply material and laminates were cured using a variety of cure profiles so as to produce a diverse sample set. This was to test whether a robust correlation between the near-surface spectra provided by PAS and bulk cure level could be developed. Figure 1 shows spectra of the carbon fiber/cyanate ester composites at various cure levels. The 8% through 73% cure spectra are from single-ply

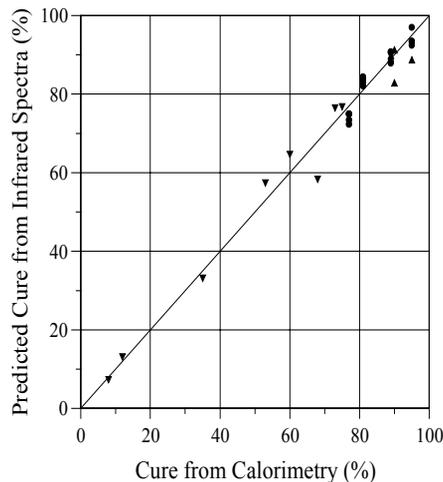


FIGURE 2. Cross validation of the PLS model for cure level of carbon fiber/cyanate ester composites predicted from their photoacoustic spectra. (▼) Single-ply prepreps with a single low-temperature cure period, (▲) single-ply prepreps with both low- and high-temperature cure periods, (●) laminates.

prepreg tapes, and the 81% through 95% cure spectra are from laminates. Despite the diverse nature of the sample set, there are numerous spectral trends associated with increasing cure that are consistent over the whole data set. The most obvious are the disappearance of the bands at 2268 and 2237 cm^{-1} from the cyanate monomer ($-\text{O}-\text{C}\equiv\text{N}$) and the growth of the 1570 and 1377 cm^{-1} bands from the triazine ring of the cured resin [8]. Although not evident in Figure 1, the baselines of the spectra are not near zero signal. Photoacoustic spectroscopy acquires useful spectra from carbon-fiber composites, but the carbon fibers, which absorb at all mid-infrared wavelengths, do contribute to the photoacoustic signal by raising the baselines of the spectra. For the prepreg samples, the photoacoustic signal at the baseline was typically about three-quarters of the total (baseline plus peak) signal at the top of the strongest peak. For the laminates, the baseline signal was about half the total signal at the top of the strongest absorption peak. In addition, the prepreg spectra as observed had sloping baselines, indicating substantial light scattering, which have been corrected in Figure 1. The laminate spectra did not have this artifact.

The cross validation for the best PLS correlation found between the photoacoustic spectra and the calorimetric cure-level determinations is shown in Figure 2. The standard error of cross validation (SECV) for this model is 3.47% of cure. The model used the full 4000 to 498 cm^{-1} range of the spectra; applied mean centering, multiplicative scatter correction (MSC) [9], and second derivative (23-point Savitsky-Golay) preprocessing to the spectra; and required 3 factors. The spectra were not baseline corrected before being used in the PLS modeling. As Figure 2 implies, the photoacoustic spectra are able to track the cure level accurately despite the variety of cure profiles used and the inclusion of both prepreg and laminate samples.

Accelerated Aging

The carbon fiber/epoxy laminates showed little change in shear strength for baking temperatures up through 177 $^{\circ}\text{C}$, but above that point their strength dropped with increasing rapidity as the baking temperature rose, as described in more detail elsewhere [3]. Figure 3 shows typical spectra for selected temperatures. Even at aging temperatures of 177 $^{\circ}\text{C}$ and less, definite spectral changes from the unbaked material are evident, despite

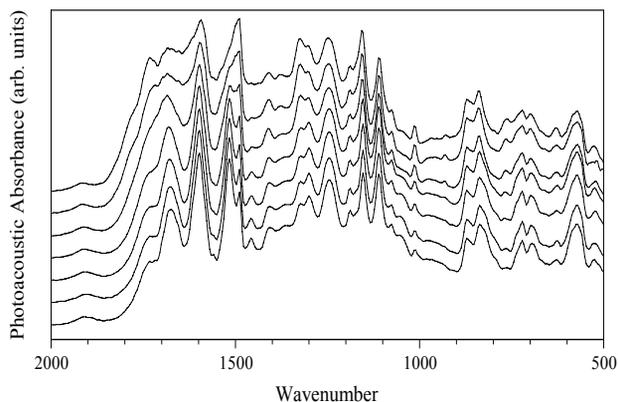


FIGURE 3. Spectra of carbon fiber/epoxy laminates after accelerated aging at various temperatures. The temperatures are (from top to bottom) 288 °C, 260 °C, 232 °C, 204 °C, 177 °C, 149 °C, and unbaked. The spectra have been scaled so that the 1597 cm^{-1} peak is the same size in all.

there being no loss in shear strength. Above 177 °C, however, spectral changes grow more rapidly with increasing temperature. Oxidation of the resin is a major degradation pathway, and the growth of the carbonyl peak at 1732 cm^{-1} is indicative of this process. In addition, increased temperature reduces the spectral contrast, as indicated by the filling in of the valleys between peaks. This may come from the less uniform structure of the material after heat treatment, which produces a variety of micro-environments, each of which shifts the absorption peaks slightly, broadening the observed bands. As noted for the curing-study spectra, absorption from the carbon fiber raises the baseline of the spectra, although this is not evident in Figure 3. For these composites, the photoacoustic signal at the baseline is approximately half the total signal at the top of the strongest peak.

The initial chemometric analysis was performed using a PLS training set in which the measured interlaminar shear strength for each test bar was paired with the photoacoustic spectrum of the square cut out by the end of the bar. The optimum result for this training set achieved a SECV of 3.65 MPa. It used the 544 to 1937 cm^{-1} range and four factors, with MSC and mean-centering preprocessing. Figure 4A shows the single-elimination cross validation for this model.

In the interlaminar shear strength test, there can be considerable randomness in the exact breaking load, so error in the individual measured strengths may be the major contributor to the SECV of the model described above. We therefore also performed PLS modeling where the interlaminar shear strengths for the ten samples at each temperature were averaged and this averaged strength was paired with each of the ten spectra for a given temperature in the PLS training set. For this averaged-strength modeling, the best result used 544 to 1937 cm^{-1} and six factors, with MSC and variance-scaling preprocessing applied to the spectra. Figure 4B shows the single-elimination cross validation for this model, which has a SECV of 1.60 MPa, less than half that of the individual-strength model. Given that the sample set covers a 54.8 MPa strength range, this is very good accuracy. Photoacoustic spectroscopy has no difficulty measuring bulk properties of carbon-fiber composites, as long as those properties are reflected in the infrared spectra.

We have also tested a minimally destructive method of sampling composites for FT-IR PAS analysis. A small amount (< 1 mg) of powder is sanded from the surface of a composite, and then the powder is analyzed. For the same sample set used above, the optimum PLS model based on the averaged-strength values gave a SECV of 2.02 MPa. This powder-sampling study is discussed in more detail in Reference 3.

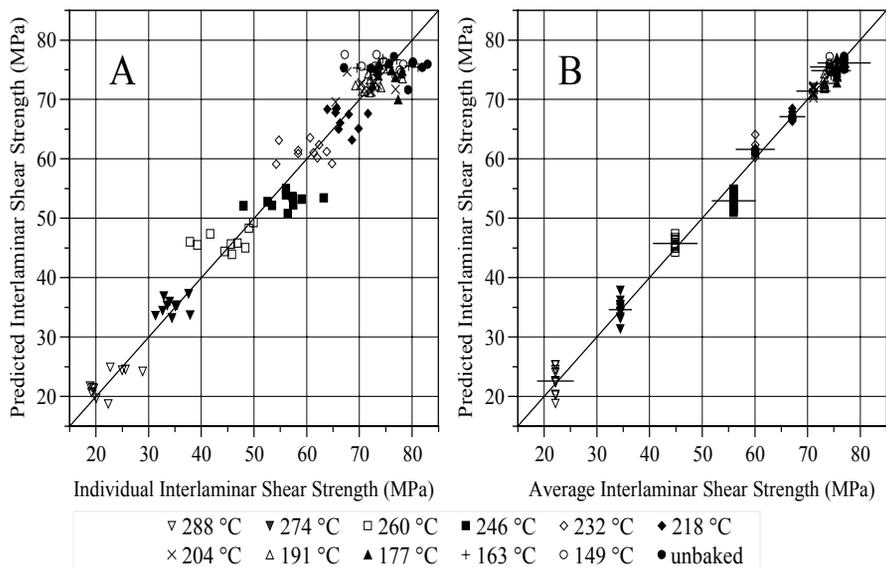


FIGURE 4. Cross validations for PLS models for interlaminar shear strength of carbon fiber/epoxy laminates predicted from their photoacoustic spectra. (A) Model based on pairing individual shear-strength measurements with individual spectra in the PLS training set. (B) Model based on pairing the average shear-strength measurement at a specific temperature with each spectrum in the training set. The horizontal bars are $\pm\sigma$ of the shear-strength measurements. Plot B is adapted from Reference 3 by permission of the Society for Applied Spectroscopy.

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