Non-Destructive Evaluation of Composite Thermal Damage with Agilent's New Handheld 4300 FTIR

Application note

Materials

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Introduction

Carbon or graphite fiber composites are replacing metal structures and parts in many industries, such as aerospace, general transportation, high performance automotive, and sporting goods. These materials are favored for their reduced weight and greater strength relative to traditional metal parts. For example, the Airbus A350 and Boeing 787 are both made of approximately 50% composite materials, including wing and fuselage sections. Military jet fighters and naval craft also use this material to improve performance. These critical and complex composite applications require new and sophisticated analysis tools for development, maintenance, and repair purposes.

In this application note, we discuss the advantages of the 4300 Handheld FTIR for at-site, non-destructive analysis of thermal exposure and damage in aircraft composites.

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Unlike metal parts, composite materials can be irreversibly degraded by excessive heat. Heat damage can occur from many sources, such as engine or missile exhaust, electrical fires, or even lightning strikes. Severe thermal damage is often obvious by visual inspection where blistering or delamination is observed. However, in the longer term, moderate heat exposure is much more common and can be just as catastrophic. This type of heat damage is referred to as incipient thermal damage, since the part may have little or no visible damage.

Over the past decade, Agilent Technologies has led in developing and applying Fourier transform infrared spectroscopy (FTIR) as an advanced technique for measuring the molecular composition of composites, in support of manufacturing and maintenance operations. For example, FTIR spectral analysis is now a proven technique for detecting thermal damage in composites. This information can be used to define the breadth and depth of a thermally overexposed region of composite to assist in repair procedures.

Now, Agilent scientists and engineers have developed a next generation FTIR analyzer for the measurement of composites and polymers. The recently announced 4300 Handheld FTIR is the culmination of our experience in composite analysis via non-destructive mid-infrared spectroscopy.

Methods, materials and instrumentation

The Agilent 4300 Handheld FTIR was used for the measurements in this application note. This system is the next generation of handheld FTIR spectrometers and is developed to improve applications where performance, analysis speed, ease-of-use, and superior ergonomics are major factors. The 4300 FTIR has two configurations: one with a traditional deuterated triglycine sulfate (DTGS) detector, and the other using a faster scanning, thermoelectrically cooled mercury cadmium telluride (MCT) detector. The MCT version reduces the required scan time for analysis by greater than 50% relative to the DTGS version.

Advantages of the Agilent 4300 Handheld FTIR for the measurement of composites and polymers

The 4300 Handheld FTIR is the result of Agilent's extensive R&D efforts in material analysis by mid infrared spectroscopy. It is optimized for non-destructive analysis of polymers

- **Light weight.** Make measurements for longer periods with less physical strain. At 2.2 kg (4.8 lb), the 4300 Handheld FTIR is the lightest handheld FTIR in existence.
- **Balanced.** Take more accurate and precise measurements. With a center of gravity located at the handle, the system is comfortable to use.
- **Rapid Scanning.** Scan large surface areas in less time. With the optional MCT detector, the 4300 Handheld FTIR enables measurements to be made more rapidly.
- **Non-destructive.** No need to excise a sample to be analyzed in a lab. The handheld spectrometer is brought to the object or surface to be measured.
- **Immediate results.** Focus on the measurement locations of greatest importance. At-site analysis lets you make decisions in real-time.
- **Versatile.** Analyze a wide range of materials and surface types. A selection of interchangeable, no-alignment sampling interfaces are available.
- **Intuitive.** Easy-to-use software guides less experienced personnel to actionable results, faster. Preprogrammed methods, powered by advanced mathematical models, and reporting features all function automatically behind the scenes.

Agilent's mobile spectroscopy group, in conjunction with several commercial aerospace and military organizations, has developed a broad array of composite thermal damage FTIR methods. Each method is calibrated using a partial least squares (PLS) chemometric model. FTIR spectra of composite coupons exposed to a range of temperatures are used to "train" the models to detect spectral changes due to thermal damage. Eight models have been developed with data collected on the 4300 FTIR equipped with a diffuse reflectance attachment (4 MCT and 4 DTGS models). The spectra are collected at $8cm^{-1}$ resolution and 64 co-added interferograms. Each calibration set consists of composite coupons exposed to 375°F, 400°F, 425°F, 450°F, 475°F, 500°F, 525°F and 550°F temperatures for one hour. The models are tested using a validation set of composite coupons prepared under similar conditions.

Discussion and results

The analysis of composite materials is difficult, due in large part to the complexity of the thermal damage mechanism. Each resin system in a composite structure has a slightly different thermal degradation profile or behavior. Composite resin systems exhibit differences in the onset temperature and rate of thermal degradation. Another major consideration for measuring composites is the condition of the surface to be analyzed. Some composite resin formulations, such as Cytec Surface Master 905 (SM 905, Table 1), are used primarily on the surface of composite structures and require no sanding prior to measurement. Other composite resin systems are used as the interior core composite material and these may be measured in a sanded or unsanded condition. Carbon fiber parts are also made with different patterns of carbon fiber, but use the same epoxy resin matrix. Some use linear sheets of carbon fiber, referred to as "tape". Each layer of tape is oriented in a precise pattern to increase its strength. Other composite layouts use a weave pattern of carbon fibers, referred to as "fabric". These textural, chemical, and thermal profile differences introduce too many variables for a single predictive FTIR model.

Therefore, individual FTIR methods and models have been developed to account for each of these conditions and composite materials.

Application areas for the Agilent 4300 Handheld FTIR in the analysis of composites and polymers

- Detecting thermal and UV exposure of composites
- Guiding sanding, scarfing and patching repair processes for composites
- Measuring effectiveness of plasma treatment of composite surfaces to minimize the effect of release agents on bonding
- Determination of the peal ply material and its compatibility with the resin system
- Measuring hydrocarbon and silicone contaminants on metal surfaces prior to polymer coating
- Positive material identification to verify the identity and authenticity of composite and polymer parts
- Measuring thickness and uniformity of polymer coatings on surfaces
- Measuring curing processes

Infrared spectra of composites

The IR spectra of carbon fiber or graphite composites are typically composed of strong aromatic absorbance bands at 1600 cm^{-1} and 1510 cm^{-1} (Figure 1). Undamaged composites typically have several carbonyl peaks in the 1800–1600 cm^{-1} region. The band at 1670 cm^{-1} is consistent with a doubly conjugated ketone (i.e. Ar-C(=O)-Ar) or a secondary amide (R-C(=O)-NH-R), whereas, the weaker 1730 cm^{-1} carbonyl peak is consistent with a conjugated ester group (i.e. Ar-C(=O)-O-R). These functional groups are expected in the complex polyaromatic epoxy resins systems used in modern composites.

The carbonyl and aromatic region (1850–1500 cm^{-1}) of the IR spectra contains the best information to measure thermal damage of composites. Polyaromatic epoxy resins may include toughening agents such as polyetherether ketone (PEEK) or polysulfones, which all have strong absorbance features in this region of the IR spectrum. The aromatic peaks mentioned above are observed to diminish with increasing thermal damage (negative correlation, Figure 1) and an additional carbonyl absorbance is observed to rise with increased thermal damage (positive correlation). The broad oxidation carbonyl absorbance roughly centered at 1722 cm^{-1} in the high thermal damage composites (Figure 1, 550°F spectrum) is consistent with a carboxylic acid (COOH) and/or single conjugated ketone carbonyl group.

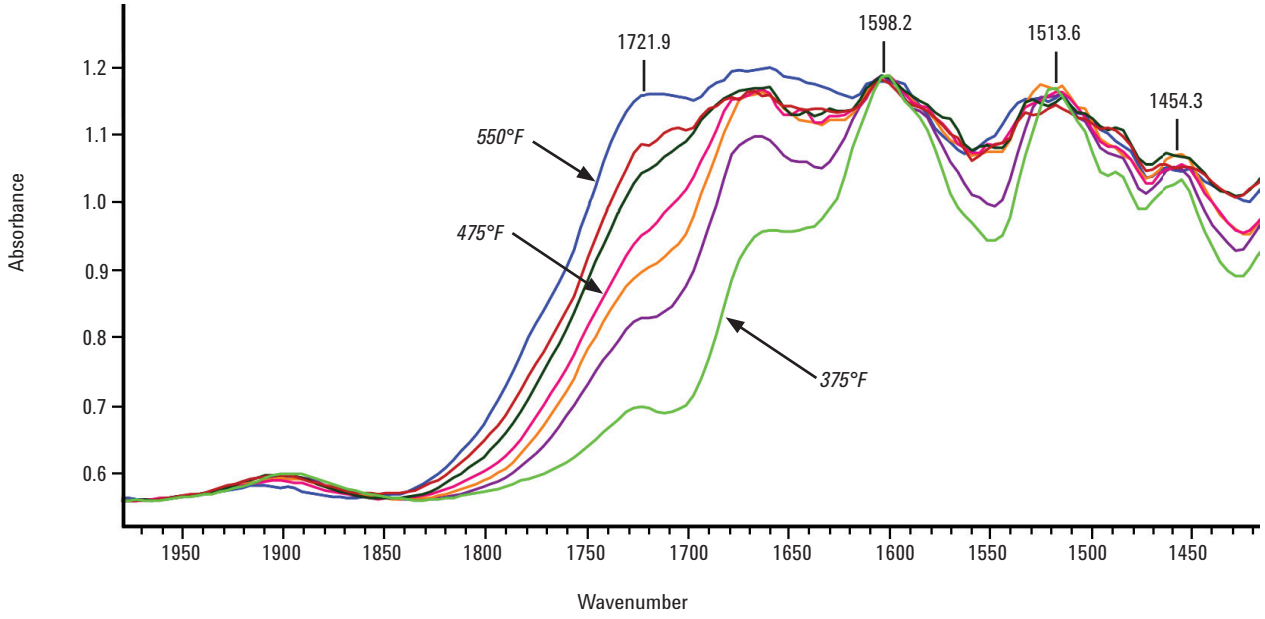

Figure 1. The IR spectra of thermally damaged epoxy composite (Epoxy 1) unsanded tape measured using the 4300 MCT FTIR. The composite coupons shown are exposed to 375°F, 425°F, 450°F, 475°F, 500°F, 525°F and 550°F temperatures for one hour. The absorbance band at 1722 cm^{-1} arises from the carbonyl stretch vibration associated with oxidation of the resin and is an indicator for thermal overexposure of the composite.

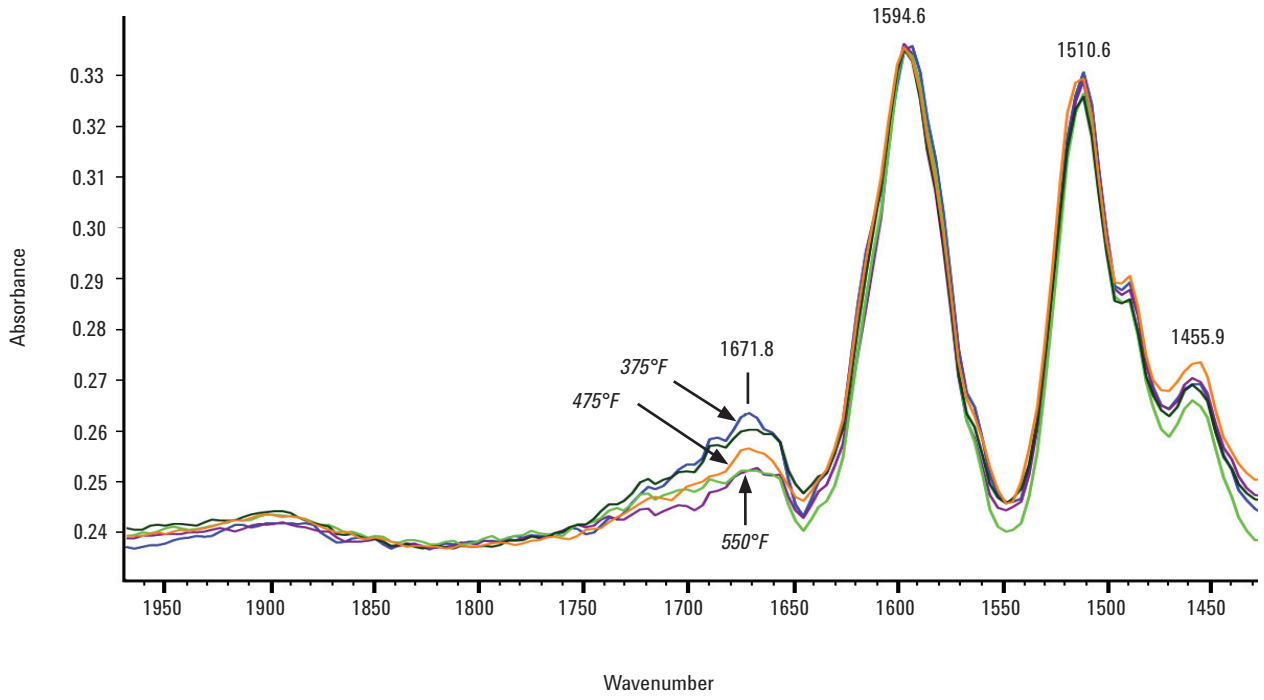

Figure 2. The IR spectra of thermally damaged Epoxy 1 sanded tape composite material measured on the 4300 MCT FTIR. The composite coupons shown are exposed to 375°F, 425°F, 475°F, 525°F and 550°F temperatures for one hour. Note the absence of the 1722 cm^{-1} vibration, since this composite damage occurs in an anaerobic environment.

The subsurface thermal damage mechanism in composites is considered primarily anaerobic, and the IR spectra of the toughened epoxy composite (Epoxy 1) sanded tape in Figure 2 support this proposed mechanism. There is no increased carbonyl absorbance in the 1700 cm^{-1} region. The main difference observed in the IR spectra of sanded composites that are thermally damaged (Figure 2) is the decrease in absorbance at 1672 cm^{-1}, which is assigned to a doubly conjugated ketone carbonyl or possibly a secondary amide carbonyl. This decrease in absorbance provides a good negative correlation to temperature exposure. Other sanded composites indicate the depletion of aromatic groups without the increase in oxidation absorbance at 1720 cm^{-1} observed in the unsanded composite material.

Performance of calibration model for composite analysis

The composite types and statistical results of the measurements are shown in Table 1. The R^2 value is the correlation coefficient of the PLS calibration, 1.000 being a perfect correlation to the spectral data. The standard error of cross-validation (SECV) is a good predictor for the amount of error in the model results and the unit for the SECV is temperature (°F). Both the R^2 and the SECV are only calculated based on the calibrations set of data. The root mean square error of prediction (RMSEP) and relative % error (Rel. % error) are both calculated based on the model's prediction results from the validation set of composite coupons. The RMSEP is an estimation of the average error that an unknown real world sample will have using the calibration model expressed in units of temperature (°F).

Table 1. The PLS calibration and validation performance results of four composite materials as measured using the 4300 FTIR MCT and DTGS configurations.

Instrument	Model statistic	SM905 unsanded	Epoxy 1 tape unsanded	Epoxy 2 fabric unsanded	Epoxy 1 tape sanded
4300 MCT	R^2	0.96	0.98	0.97	0.92
	SECV	12	8	9	13
	RMSEP	12	14	12	19
	Rel. % error	1.9	3.1	3.0	3.4
4300 DTGS	R^2	0.98	0.98	0.97	0.88
	SECV	8	8	10	20
	RMSEP	10	10	16	23
	Rel. % error	1.9	1.8	4.3	4.2

The relative percent error (Table 1) is an average of the relative percent error for the 425–525°F results in the validation set. For example, a 475°F validation coupon at 3% relative error (+/- 14°F) would be expected to predict between 461–489°F.

The results indicate similar performance of the calibrations for either 4300 FTIR configurations and all the results provide less than 5% relative error on the validation set. The target performance is less than 10% relative error on the validation set. The MCT configuration indicates slightly better calibrations for the Epoxy 1 unsanded fabric and Epoxy 1 tape sanded. The calibration performance for the SM 905 and Epoxy 1 unsanded tape are nearly the same for both 4300 configurations. The 4300 MCT system collected the spectra in 7 seconds, compared to 17 seconds for the 4300 DTGS instrument, with equivalent amount of co-added scans. Both 4300 configurations are ergonomically identical, however, the faster scanning MCT 4300 may be preferred for applications requiring repetitive analysis of samples over larger surface areas or in more physically constrained positions.

The calibrations shown above were imported into the Microlab software package to produce a method specific for the analysis of thermal exposure on each specific resin. The 4300 Handheld FTIR has an integrated computer which runs a mobile version of the Microlab software. It displays measurement results, predicting the thermal exposure; thresholds are provided to color code the result, either green for low thermal exposure or red for exposure sufficient to cause damage to the composite. In addition to the thermal exposure prediction, methods can contain other components which measure other aspects of the sample chemistry or provide information about the validity of the result. The thermal damage method also contains a component to identify whether hydrocarbon contamination is present (oil contamination index) and to determine if the sample measurement statistically matches the calibration set (M-distance). As with the main thermal exposure component, these quality measures are assigned a critical threshold and color coded accordingly. An example of the software output for the measurement of a damage sample is shown (Figure 3).

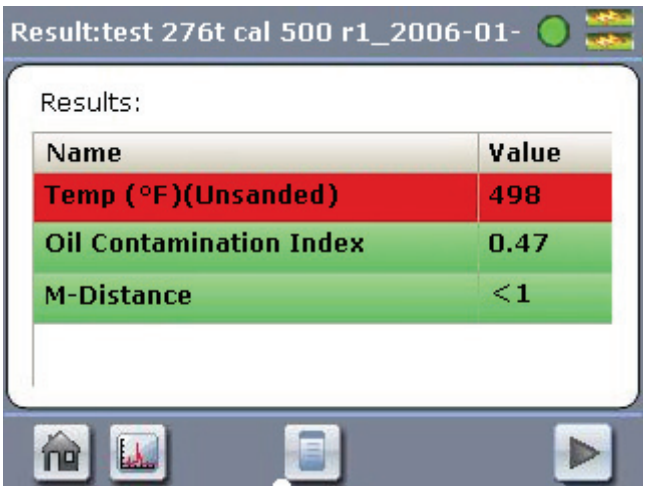

Figure 3: 4300 Handheld FTIR results screen from a measurement of a sample of Epoxy 1 Tape unsanded exposed to 500 °F for 60 minutes. The result is color coded in red to show that this sample exceeds the critical threshold indicating thermal damage.

Conclusions

We have shown that the 4300 Handheld FTIR is very effective for measuring thermal overexposure and damage in carbon fiber composites. The diffuse reflectance spectra of unsanded composites indicate increased oxidation carbonyl absorbance as the temperature of exposure increases. The spectra of sanded composites indicate the loss of ketone or amide absorbance from the polymer resin in the composite.

Both versions of the 4300 (MCT and DTGS) perform similarly in both calibration and validation sets for thermally damaged composite coupons. The MCT 4300 features a faster scan time and may be preferred for applications that require measurements to be made over larger surface areas, or for objects that require the user to be in more physically demanding locations or positions.

The increasing use of composites to replace metal components demands more sophisticated diagnostic tools to detect problems and confirm the chemical composition of the material. The Agilent 4300 Handheld FTIR is optimized for this task. The capability of at-site, non-destructive measurement of composite and polymer based products, objects and parts enables users to make real-time decisions about the quality, performance, damage and degradation of these materials.

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