Analysis of plasma treated carbon fiber reinforced polymer (CFRP) composites by portable Fourier Transform Infrared Spectroscopy (FTIR)

Application note

Materials testing

Authors

Alan Rein, Ph.D.
Pik Leung Tang, Ph.D.
Agilent Technologies, Inc., USA

Introduction

Engineering grade CFRP is widely used in commercial and military aerospace applications due to its unique combination of light weight, strength and impact resistance. Since it is an organic based material, it is susceptible to physical and chemical stresses that are different than those that affect metals used in aircraft manufacture. The Agilent 4100 ExoScan FTIR system is known to be a highly useful non-destructive analyzer for measuring the deleterious chemical changes in CFRP that occur from oxidation resulting from elevated thermal exposure. In this application note, we show that the 4100 ExoScan is equally effective in measuring how well the surface of a peel ply released CFRP structure is treated and activated via plasma treatment to support optimal bonding of CFRP parts.

Composite parts are commonly formed using pre-preg that is cured in place around molds to form the desired shape. The process consists of placing the pre-preg between layers of other materials and then subjecting the entire system to a vacuum. A peel ply (release fabric) layer is used to prevent the composite laminate from adhering to the other layers. This layer contains a chemical release agent, typically a polydimethyl silicone (PDMS) formulation or a hydrocarbon based formulation (wax). After the peel ply layer is removed from the formed CFRP part, inevitably some of the release agent is left on the part and this must be treated and the surface activated to achieve optimal bonding. Surface treatment and activation is conducted using radio frequency generated plasma. If the CFRP part is either under treated or over treated during the plasma cleaning process, the result will be an sub-optimal surface for bonding. Under treatment does not cause enough changes in the release agent while over treatment will change the release agent but additionally causes thermal damage to the CFRP. Under treatment causes the more severe adhesive failure with greatly reduced strength whereas over-treatment results in CFRP damage, but only moderate peel strength decrease. Therefore a fine balance of treatment is required to ensure that the surface is properly prepared and the degree of thermal damage in the CFRP is minimized.

The effectiveness of the plasma treatment is highly dependent on the speed at which the plasma nozzle traverses the CFRP surface as well as the distance the nozzle is from the surface. Small changes in either variable can lead to a significant diminishment in the effectiveness of the treatment. The intention of this study is to demonstrate that a handheld FTIR can non-destructively detect and measure chemical changes in CFRP surfaces induced by plasma treatment and subsequently provide an objective measurement of the effectiveness of the plasma treatment via a multivariate prediction algorithm.

Experimental

Materials, methods and instrumentation

To test the ability of portable FTIR systems such as the 4100 ExoScan and the recently introduced 4300 Handheld FTIR (see sidebar) to measure the effectiveness of the plasma treatment, an experimental protocol has been employed which uses the measured G1c values from the adhesive peel-strength testing of CFRP bonded to CFRP. Changes in the FTIR spectrum of the CFRP test strip were measured as a function of the distance of the plasma nozzle from the surface, as it traversed the coupon at a constant horizontal velocity and progressively changing vertical distance. In this manner, the full range of over-treated, optimally treated and under-treated surface was available for measurement by the FTIR system. CFRP treated surfaces contained PDMS or wax release agents and were tested with the 4100 ExoScan FTIR after the above plasma cleaning protocol. The FTIR system was equipped with the high collection efficiency diffuse reflectance sample interface (Figure 1). All FTIR spectra consist of 128 co-added interferograms, which took approximately 1 minute to acquire at 8 cm^{-1} resolution.

Figure 1. Agilent 4100 ExoScan FTIR spectrometer equipped with diffuse reflectance sample interface for measurement of composites

CFRP samples were plasma treated after removal from the mold. Several CFRP coupons were prepared that had both residual PDMS or wax based release agents on the surface. The plasma nozzle traversed each CRFP coupon at a constant speed (6 cm/sec) and the full sweep of the surface took approximately 4.5 sec. The distance of the nozzle from the coupon surface was pre-programmed to change from 20.5 mm to 5 mm (Figure 2). The largest vertical distance (greatest gap size) creates a condition in which the surface is under treated and remains well under 100 °C in temperature. The smaller gap sizes, for which the nozzle is close to the surface, creates an over-treated condition, and the transient temperature at the surface exceeds 260 °C. Twenty infrared measurements were made along the coupon and these spectra were representative of the different temperature conditions experienced at the surface. Several adhesive peel strength measurements were made on a number of sections of the coupons that were exposed to various nozzle heights.

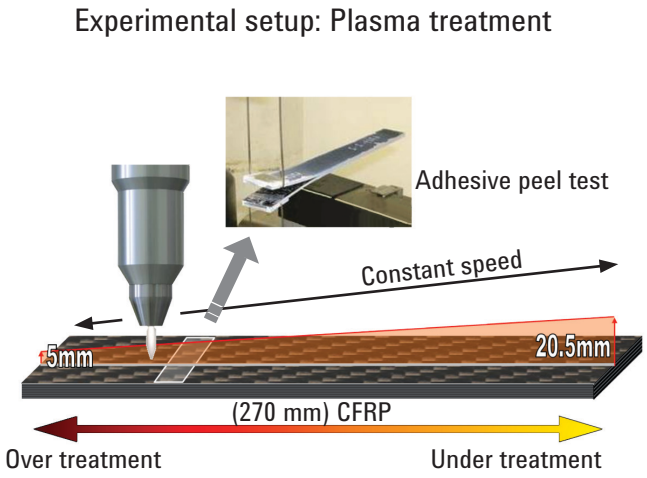

Figure 2. Plasma nozzle traverses CFRP coupon at fixed speed at continually decreasing distance from surface to induce temperature variation. Smallest plasma gap from surface creates highest temperature conditions. G1c value is collected from the adhesion peel measurements that were made with an Instron 5566 Universal Testing Machine. The CFRP laminate is 270 mm long. Two sections are bonded together with adhesive for the peel test.

Optimized Handheld FTIR Developed for Composite Analysis

Agilent has introduced the next generation handheld FTIR for the measurement of composite based products. The 4300 Handheld FTIR is a result of extensive R&D efforts in the area of non-destructive, material analysis by mid infrared spectroscopy.

Light weight. At 4.8 lbs (2.2 kg), the 4300 FTIR is the lightest handheld FTIR in existence. Make measurements for longer periods with less physical strain.

Balanced. With a center of gravity located at the handle, the system is comfortable to use. Take more accurate and precise measurements.

Rapid Scanning. With the optional MCT detector, the 4300 FTIR enables measurements to be made rapidly. Scan large surface areas in less time.

Non-destructive. The handheld spectrometer is brought to the object or surface to be measured. No need to excise a sample to be analyzed in a lab.

Immediate results. At-site analysis lets you make decisions in real-time. Focus on the measurement locations of greatest importance.

Versatile. A selection of interchangeable, no alignment sampling interfaces are available to analyze a wide range of materials and surface types.

Intuitive. Easy-to-use software guides all users to obtain great data. Preprogrammed methods, powered by advanced mathematical models, and reporting features all function automatically behind the scenes.

Temperature was independently measured as a function of the distance from the nozzle tip to the surface of the CRFP using a thermal camera with recording sensors measuring time and temperature. The measured flux is influenced both by the horizontal velocity and the nozzle height therefore as the plasma gets nearer to the surface, the temperature increases (Figure 3).

Results and discussion

The spectra of residual release agent, recorded when the plasma nozzle was at minimum and maximum distance from the coupon surface, exhibit subtle changes (Figure 4). In analyzing these spectra, certain regions are informative. For example, the broad vibrations at 3400 cm^{-1} arise from the O-H stretching modes; 3100 cm^{-1} bands are related to aromatic – H stretch; 2900 cm^{-1} from methyl/methylene stretch (alkyl), 1720 cm^{-1} from the carbonyl stretch; 1580 cm^{-1} and 1340 cm^{-1} are associated with secondary alcohols — the height of the former bands diminish with increasing temperature (i.e., bond/functional group destruction or changes) while the carbonyl band increases with rising temperatures, resulting from plasma-induced thermal damage.

These spectra indicate that for CFRP treated with either PDMS and wax release agent, there are signs of oxidative damage when the nozzle is closest to the surface (highest temperature condition) as evidenced by the increased intensity of a carbonyl peak at ca. 1720 cm^{-1}. Also, there is a noticeable drop in the O-H stretching vibration at 3300 cm^{-1} in both the PDMS and wax based release agent treated samples.

Fully cross-validated multivariate partial least squares was used to analyze the relationship between measurement position on the coupon (which in turn relates to nozzle gap and temperature to which the

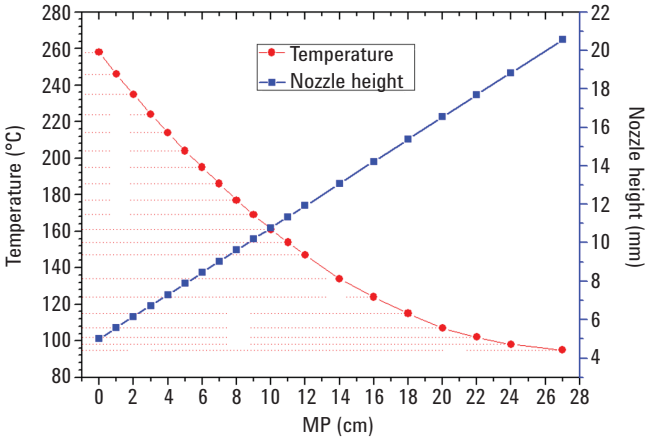

Figure 3. Nozzle height position and corresponding temperature as a function of measured positions (MP) on CFRP coupon.

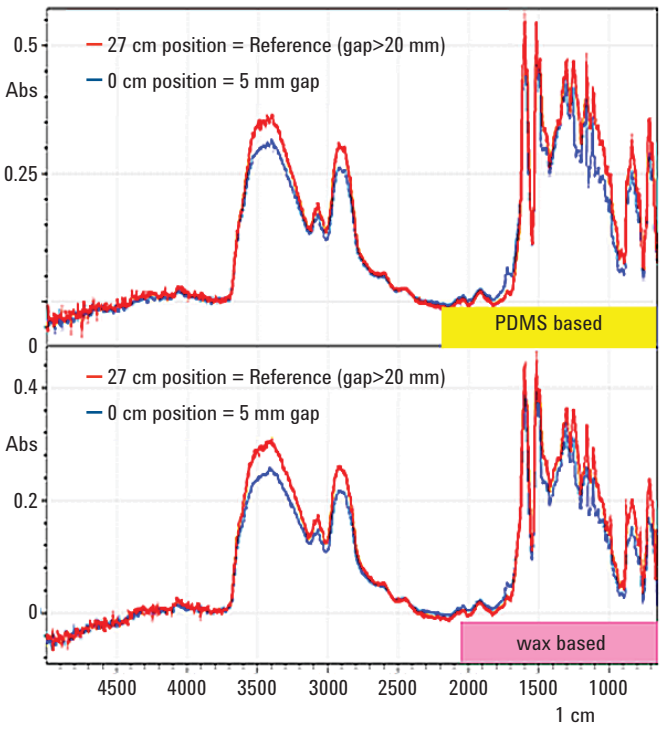

Figure 4. Infrared spectra of residual PDMS and wax release agent atop CFRP. The PDMS and wax formulations share some similarities spectrally since the PDMS formulation contains many wax-based compounds as well as PDMS.

surface is exposed) and changes in the spectra. To develop this model, 560 wavenumber points in the 780–1850 cm^{-1} region and the 2715–3700 cm^{-1} region were used. In order to optimize the model, the position on the coupon was measured via a ruler. The spectral files were recorded with the smallest nozzle gap (5 mm) corresponding to 00 cm on the coupon and the largest nozzle gap (20.5 mm) corresponding to 27 cm from the starting point. The actual versus predicted plot (Figure 5) demonstrates very good agreement and the model is able to predict within +/- 1 cm of the position on the coupon (i.e. amount of treatment) for the PDMS based release agent, as an example.

Adhesive peel strength measurements, combined with % silicon values from XPS analysis, were used to determine the under, optimal and over treatment regions of the test coupons. This information was then applied to the predicted values generated from the PLS model. The result (Figure 6) is an effective representation of the optimum plasma treatment zone, which contains only cohesive failure modes and therefore superior strength. The other zones, which demonstrate mixed or adhesive failure, were correspondingly colored yellow or red to signify warning or critical levels. The over treated region yields mixed mode failure as well as thermal oxidation of the CFRP, and is therefore in the critical zone.

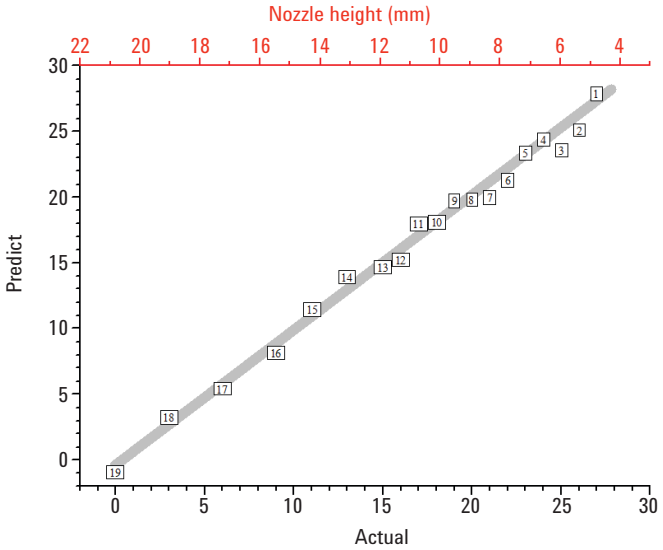

Figure 5. PLS multivariate analysis correlating infrared spectra as a function of position (i.e., nozzle height and temperature) on CFRP coupon for the PDMS based release agent. The cross-validated PLS model used three factors in the final optimized prediction model.

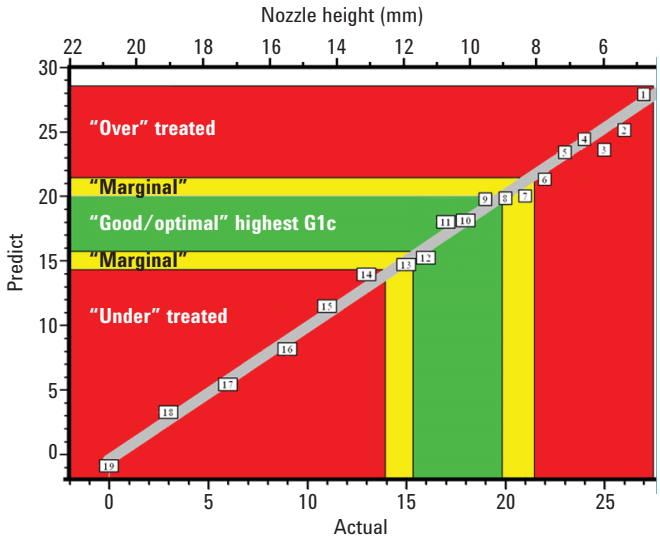

Figure 6. Independent adhesion peel tests and % silicon data were used to define the different regions of treatment and the spectra based PLS model was overlaid on these zones. The zones are readily differentiated by the PLS model, which reflect a number of subtle spectral changes. In the narrow green band, the G1c from the adhesive peel measurements is optimal for the nozzle height, velocity and type of plasma employed, as well as the region where the temperature reached does not degrade the CFRP substrate.

Conclusion

Portable FTIR systems, such as the 4100 ExoScan and the recently introduced 4300 Handheld FTIR, equipped with a diffuse reflectance interface provide valuable information for monitoring plasma treatment to ensure removal of CFRP peel layer release agent. We have demonstrated that plasma treatment of CFRP surfaces containing PDMS or wax based release agents result in spectral changes associated with partial removal of the agent, as well as chemical bond changes. A multivariate PLS model was developed that correlates spectral changes with nozzle position on the CFRP surface. Thus, this model relates to the temperature flux that the surface is experiencing and the chemical changes that result. The PLS model for plasma nozzle position (i.e., corresponding heat flux) compares quite well with the results from adhesive peel ply measurements. The information from this work also compares favorably to XPS measurements, which show the effect of increasing and decreasing silicon concentration on experimentally determined adhesive peel strength G1c values.

Acknowledgement

Agilent Technologies, Inc. gratefully acknowledges the contributions of the scientists and engineers at Airbus Group Innovations for data, information and discussion associated with this project.

www.agilent.com

Published November 23, 2015
Publication number: 5991-4033EN

Agilent Technologies