Application Note

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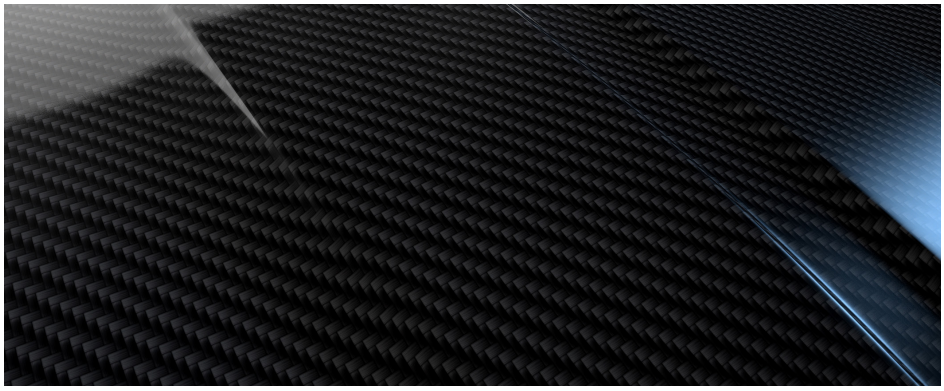
Quantification of Release Agent on a Carbon-Fiber-Reinforced Polymer using a Hand-Held FTIR

Non-destructive, in-situ analysis completed in less than one minute



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Introduction

Release agents are applied as a liquid to form a thin film coating, aiding removal of carbon-fiber-reinforced polymer (CFRP) parts from a mold or peel ply. This process can lead to inevitable contact transfer, causing release agent to remain on the part. Before painting or bonding of the CFRP component to other structures, proper post-treatment to remove vaporizable components of the release agent is required. Inadequate post-treatment leads to reduction of bond strength of joined parts or poor topcoat paint adhesion.

The complexity of CFRP systems require the use of technologies such as FTIR spectroscopy, for the analysis of the surface matrix of the material. This study aims to demonstrate that FTIR spectroscopy can nondestructively measure the level of release agent on a carbon fiber epoxy system before bonding.

This work was part of a joint project commissioned by the European Union entitled ENCOMB (extended nondestructive testing of composite bonds) [1].

Experimental

The CFRP system was a T700 carbon fiber incorporating M21 epoxy with resultant coupons of six unidirectional layers. This fiber/polymer combination is an advanced formulation designed for extreme aeronautical performance. The release agent was a Henkel Frekote 700NC formulation. The release agent formulation contains 1 to 3% polydimethylsiloxane (PDMS) with the remaining consisting of various volatile and nonvolatile hydrocarbons.

Further details of the treatment scheme and the mechanical testing of bond strength are reported in research articles by ENCOMB consortium members [2,3,4]. The project examined the effects of four contamination scenarios on bonding CFRP with Cytec FM300 K.05 film adhesive by mechanical and instrumental measurement. The contamination scenarios were release agent [5], moisture uptake, aqueous acidic extract of a fire-resistant, phosphate-ester hydraulic fluid, and thermal damage. Bonded CFRP coupons were mechanically tested for bond strength by calculation of the critical strain-energy release rate (GIc). This parameter was calculated from analysis of the stress-strain curve. The GIc is directly related to the energy required to fracture the bonded CFRP, and is, therefore, often seen informally as the bond strength.

Mechanical tests were performed using an MTS Universal Testing Machine in compliance with ISO 15024 and 25217.

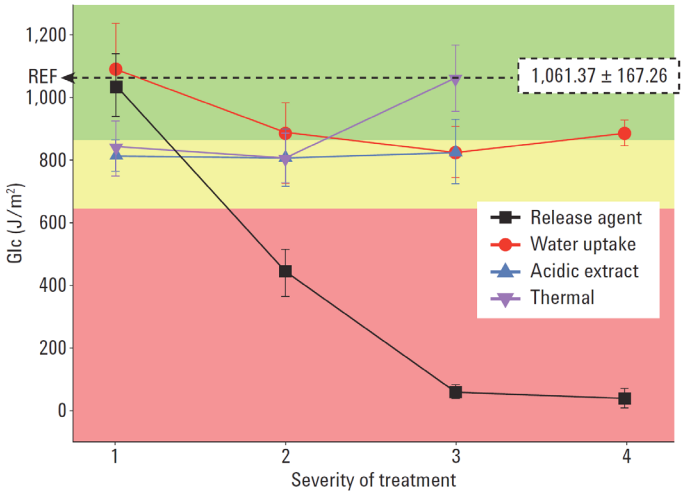
For FTIR measurements, an Agilent 4100* Handheld ExoScan equipped with a diffuse reflectance sample interface was used. The 4100 ExoScan handheld FTIR spectrometer has been used extensively for the measurement of composites and polymers, as well as in surface analysis applications.

Each CFRP coupon was measured at a minimum of 16 discrete sampling points resulting in 71 spectra. The spectra consisted of 128 coadded interferograms measured at 8 cm–1 resolution giving a measurement time of 40 seconds for each point. The complexity of the release agent formulation [5], treatment, and CFRP system required the use of multivariate analysis (MVA) to develop a model based on the FTIR spectra. FTIR spectra of the release agent on the CFRP coupons' spectra were split into two groupings for processing by MVA. Fifty-five spectra were used to develop a cross validated model, and 16 were used as validation spectra. The results of the FTIR analysis were compared to measurement of percentage silicon present on the surface, as determined by X-ray photoelectron spectroscopy, the accepted consortia reference method.

Results and Discussion

The ENCOMB project measured the effect of four treatment scenarios with various levels on the GIc critical energy of fracture. These included the amount of residual release agent, water/moisture uptake, pH of acidic extract, and thermal damage. Figure 1 is a graph of GIc versus treatment severity for the four contamination scenarios. Treatment severity is defined by increasing levels of the respective treatment scenario. For release agent, the increasing severity value reflects increasing levels of surface contamination, from 1 (2.2% silicon) lowest, to 4 (10.5% silicon) highest. The highest severity level has a resultant GIc value of 40 J/m^2. This represents a significant drop of the GIc value at the lowest severity level 1 of 1,036 J/m^2. Of the four different treatments, the graph clearly shows that bond strength is most affected by the level of residual release agent present. The color-coding in Figure 1 is based on current best practice for acceptable strength ranges and includes mechanical error and guideline bond strength.

A



B.

	Treatment severity level			
Treatment scenario	1	2	3	4
Release agent (% Si)	2.2 ± 0.3	6.7 ± 0.2	8.4 ± 0.8	10.5 ± 0.3
H_2O uptake (% mass increase)	0.46	1.84	1.19	1.29
Acidic extract of FRHF (pH)	4	3	2	
Thermal degradation (°C)	190	200	210	

Figure 1. GIc bond strength versus release agent, water/moisture uptake, pH of acidic extract, thermal damage, and treatment severity, where 1 is the lowest severity and 4 is the highest severity (A). The dotted line represents a GIc value of 1,061.37 J/m^2, which is the reference bond strength of an optimally treated bonded carbon-fiber-reinforced polymer. The table (B) shows the four treatment scenarios versus their severity levels and the individual treatment values.

**The 4100 Exoscan FTIR instrument has been superceded by the Agilent 4300 model, which has superior performance characteristics, as well as being lighter in weight and ergonomically improved.*

The measurement of the percentage silicon present on the surface of CFRP by X-ray photon spectroscopy (XPS) is a commonly used method for determining the amount of residual PDMS release agent. The relationship between that value and the GIc is well characterized and, as the percentage silicon increases on the composite surface, the mechanical strength of the bond decreases (Figure 2B). In this study, four levels of treatment were applied to provide a range of residual percentage silicon on the CFRP coupon, from 2.2 to 10.5%, as determined by XPS. Figure 2 shows the average FTIR spectra that result from the four treatment levels, and the effect on bond strength with increasing residual release agent on the CFRP surface.

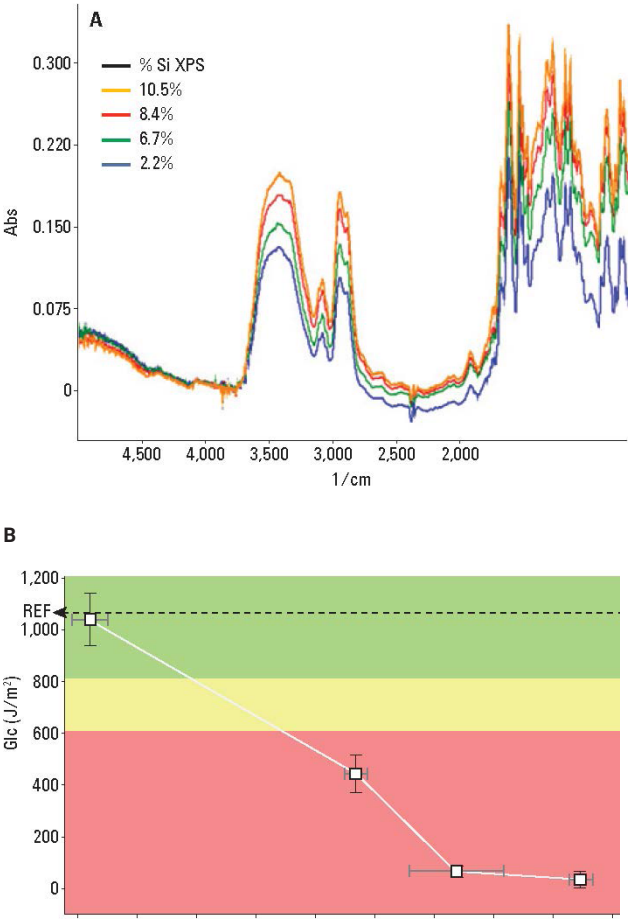


Figure 2. Averaged FTIR spectra of four release agent treatment levels (A) and the percentage silicon determined by X-ray photoelectron spectroscopy. The resultant effect on the (GIc) bond strength and the associated errors from multiple measurements are shown in B.

To correlate the FTIR spectra for the different levels of treatment with the percentage silicon, as determined by XPS, a partial least squares (PLS) model was implemented that required several preprocessing steps. Multivariate modeling of FTIR [6,7] spectra was effective for measuring several CFRP-related chemical changes, such as those resulting from thermal damage, and proving the efficacy of plasma treatment for surface preparation of CFRP before bonding. In this release agent study, the resultant cross-cross validated PLS model was optimal using four factors, as shown in a graph of the standard error of cross validation versus number of factors (Figure 3A). The percentage silicon predicted by the PLS model calibration and validation spectra for the four treatment levels is shown in Figure 3B at approximately ¾:¼.

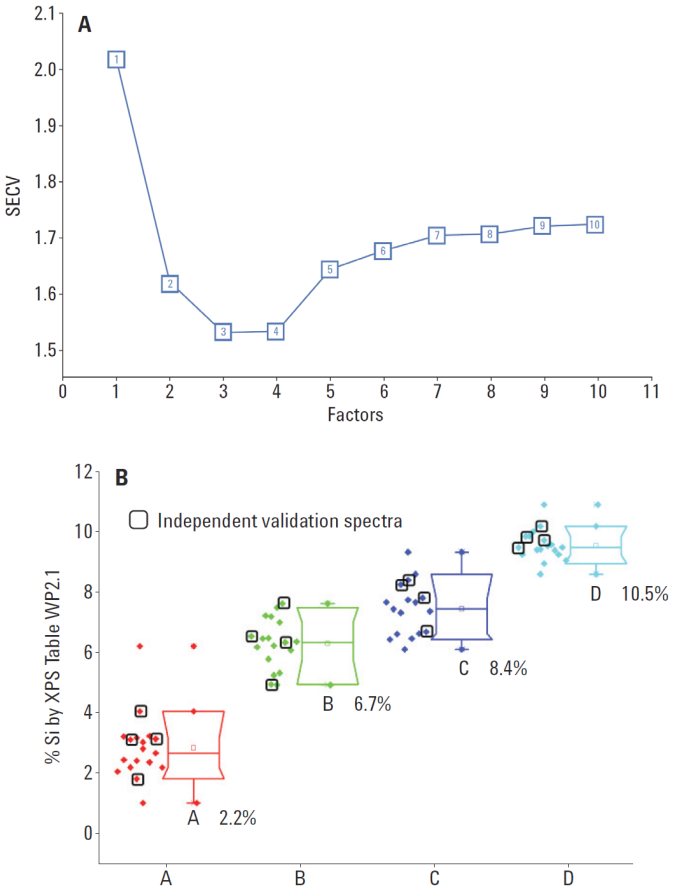


Figure 3. Standard error of cross validation versus number of factors (A), four treatment levels, and their partial least squares predicted values (B). The boxed black values are the validation spectra set aside to independently test the partial least squares model.

Table 1. Percentage silicon on a carbon-fiber-reinforced polymer coupon as determined by X-ray photoelectron spectroscopy and percentage silicon as predicted from FTIR spectra using a multivariate method with the Agilent Handheld FTIR.

Treatment level/severity	% Si XPS	% Si XPS and Agilent Handheld FTIR
1 (A)	2.2 ± 0.3	2.5 ± 1.07
2 (B)	6.7 ± 0.2	6.3 ± 0.81
3 (C)	8.4 ± 0.8	8.3 ± 0.87
4 (D)	10.5 ± 0.3	10.1 ± 0.51

The MVA model PLS regression has an R = 0.96, which is very encouraging for such a complex system. The 4100 ExoScan results yielded a strong correlation between multivariate spectral changes and the percentage of silicon, when cross referenced with XPS results (Table 1).

Conclusions

Of the identified treatment scenarios, the residual release agent had the most deleterious effect on bonding strength. If CFRP components are left untreated, or partially/poorly treated and then bonded, there is often a drastic loss in the tensile strength of the bond. If the CFRP part is coated, rather than bonded, then the peel strength/adhesion strength of the coating will be adversely affected. The importance of ensuring that surfaces are properly prepared before further manufacturing operations cannot be overstated, as witnessed by the dramatic drop in GIc bond strength caused by increasing amounts of remnant release agent.

In this study, we successfully demonstrated the ability of an Agilent Handheld FTIR analyzer to measure accurately the amount of release agent remaining on the surface of a CFRP panel in a fully nondestructive manner. We 'trained' the FTIR analyzer with a model to predict the percentage Frekote 700NC on an advanced CFRP T700/M21 system to within 1 to 2% silicon as correlated to XPS results. The PLS-calibrated model can be incorporated into a "pass/fail" method that quantifies and categorizes the result to indicate the severity level in a color-coded manner. This enables the direct determination of whether the removal of release agent from the surface of a CFRP component is complete, independent of other physical, chemical, or mechanical criteria.

The Agilent handheld FTIR instrument enabled in-situ measurements, with the analysis accomplished in less than 1 minute, without any sample preparation.

Due to the onboard method, the instrument can be used by individuals with varied experience levels to get accurate results. This allows the system to be used in manufacturing quality assurance and maintenance applications for rapid, direct measurement of a CFRP component. In addition, as demonstrated in previous studies, the FTIR analyzer can ascertain that surface areas are properly treated by plasma cleaning, and detect and measure thermal damage in CFRP.

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New and appropriate methods of nondestructive quality assurance, such as the portable FTIR and interface system, are vital as carbon fiber composite technology becomes more common in vehicles of all types, aerospace, and consumer products.

Acknowledgement

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