SUPERSONIC RETROPULSION SURFACE PREPARATION OF CARBON FIBER REINFORCED EPOXY COMPOSITES FOR ADHESIVE BONDING

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ABSTRACT

Surface preparation is widely recognized as a key step to producing robust and predictable bonds in a precise and reproducible manner. Standard surface preparation techniques, including grit blasting, manual abrasion, and peel ply, can lack precision and reproducibility, which can lead to variation in surface properties and subsequent bonding performance. The use of a laser to ablate composite surface resin can provide an efficient, precise, and reproducible means of preparing composite surfaces for adhesive bonding. Advantages include elimination of physical waste (i.e., grit media and sacrificial peel ply layers that ultimately require disposal), reduction in process variability due to increased precision (e.g. increased reproducibility), and automation of surface preparation, all of which improve reliability and process control. This paper describes a Nd:YAG laser surface preparation technique for composite substrates and the mechanical performance and failure modes of bonded laminates thus prepared. Additionally, bonded specimens were aged in a hot, wet environment for approximately one year and subsequently mechanically tested. The results of a one year hygrothermal aging study will be presented.

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1. INTRODUCTION

There is currently a focus among aircraft manufacturers to advance aspects of adhesive bonding technology necessary to improve airframe design and simplify fabrication methods while simultaneously improving aircraft performance. Adhesive bonding technology requires advancement in several areas such as process control for surface treatments, bonding, real time, in-line characterization methodologies for quality control, and non-destructive assessment of bond strength and quality to achieve Federal Aviation Administration (FAA) certification [1,2]. However, current techniques for surface preparation of composites such as grit blasting and peel-ply lack the reproducibility likely necessary to achieve the level of quality control required for said certification. As part of a continued effort to improve surface preparation for composite to composite bonding, the use of laser ablation as a means of creating surface topography is under investigation [3]. In this work, a frequency tripled Nd:YAG laser has been used to controllably and selectively remove resin from the surface of a composite to a depth of several microns, ideally such that exposure and damage of carbon fibers on the surface are minimal. The use of a laser to achieve the surface treatment provides a high degree of controllability leading to high precision and reproducibility of the surface topography created. Also, the laser surface treatment

is rapid, lends itself to scale-up and automation, and is practical for use in a variety of settings such as an industrial production facility or repair depot. It is intended to replace the use of peel-plies and grit blasting surface preparation techniques, both of which create waste byproducts. The laser technique has also been applied to metals, such as titanium, and has the potential to replace one or more environmentally unfriendly chemical treatment steps currently in use [4].

The premature or unexpected failure of an adhesive bond can usually be traced to defects in the preparation of the faying surface [5,6]. Current surface treatment techniques based on mechanical abrasion such as grit blasting or sanding and peel ply have limited repeatability and can leave contamination that reduces bond performance.

Non-standard techniques such as atmospheric pressure plasma, arc discharge, and laser ablation have been demonstrated but are still undergoing evaluation by the aerospace industry [7,8,9]. Laser ablation is a subtractive process which relies upon highly-focused laser radiation to remove and redistribute material on a surface [10,11,12,13]. Ultra-violet laser systems are commonly used for high precision work such as medical procedures, the machining of fine parts, and printing microelectronic circuit patterns. The ablation process has been demonstrated to generate high precision surface topography simultaneously with the removal of surface contaminants and modification of surface chemistry [3, 14].

In this study, composite lap shear specimens were fabricated from T800/3900-2 prepreg, laser ablation patterned using a frequency tripled Nd-YAG laser, and then bonded using AF-555M structural adhesive film. Specimens were placed in an environmental chamber at 71 $^{\circ}$C (160 $^{\circ}$F) and 85% relative humidity (RH) and removed periodically to measure apparent shear strengths and determine failure modes. These results were compared to specimens tested prior to aging and control specimens that were aged in a desiccator. Comparisons were made with specimens fabricated from the same materials using a peel ply surface treatment [15].

2. EXPERIMENTAL

2.1 Materials

Composite panels (CFRP, 30.5 cm x 30.5 cm) were fabricated in a vacuum press from 16 plies of unidirectional Torayca P2302-19 prepreg (T800H/3900-2 carbon fiber-toughened epoxy resin system). The panels were made by placing the prepreg in a stainless steel mold and heating under vacuum at 690 KPa. The mold was lined with a high temperature polyimide film in order to produce a smooth surface. The laminates were trimmed around the edges and cut into two panels that were each 10.2 cm x 20.3 cm. Scotch-Weld AF 555M structural adhesive film (areal weight: 244 g/m^2; 3M Company) was used as received.

2.2 Laser Ablation

Laser etching of CFRP panels (10.2 cm x 20.3 cm) was performed using a PhotoMachining, Inc. laser ablation system with a Coherent Avia® frequency tripled Nd:YAG laser (7-watt output at 355 nm). The following parameters can be adjusted: laser power, frequency, beam width, beam spacing, scan speed, and number of passes. Prior to bonding, composite surfaces were laser

ablated in a crosshatch pattern with 51 μm line spacing. The laser was operated at 80% current, 80 kHz frequency, 25.4 cm/sec, with 1 pass and had a beam width of 25 μm. A thermopile type laser power meter was used to measure the laser beam power at the substrate surface.

2.3 Microscopy

Material surfaces were imaged using a Zeiss LSM 5 Exciter confocal microscope and an Olympus BH-2 optical microscope equipped with a Hitachi KP-D50 digital color camera.

2.4 Adhesive Bonding

After surface preparation via laser ablation, two CFRP panels (10.2 cm x 20.3 cm) were bonded using a strip of AF-555M adhesive (dimensions: 1.59 cm x 20.3 cm) shimmed to a final bondline thickness of 203 μm. The adhesive was laid down on one exposed composite panel surface and a roller applied to manually remove entrapped air. The adhesive was then sandwiched by laying down the second composite panel on top of the previous panel such that there was a 1.27 cm overlap. Shims were used to align and control the final bondline thickness. The assembly was then placed in a vacuum bag and cured in an autoclave at 177 °C (350 °F) for 2 h. The autoclave operated at a heating rate of 1.1 °C/minute and a cool down rate of 5.5 °C/min. Vacuum (101.6 KPa, 30 in Hg) was applied during the first 30 minutes prior to and during early-stage heat-up. After the autoclave reached 54 °C (130 °F), the vacuum was turned off for the remaining process cycle.

2.5 Specimen Preparation

Bonded panel sets from the autoclave were trimmed to minimize edge effects and subsequently machined into seven 2.54 cm by 19 cm specimens. After all specimens were obtained, groups of specimens were selected based on panel origin, void content, and measured bondline thickness to maximize group-to-group uniformity. All specimens were dried in a vacuum oven at 50 °C and 760 mmHg for 24 h followed by drying at 66 °C and 760 mm Hg for 24 h before recording the dry mass for each specimen. Two groups of dried specimens were used to establish baseline lap shear properties of unaged specimens by testing at RT and 71 °C. The remainder of the specimens was divided into control and experimental lots.

2.6 X-Ray Computerized Tomography (CT)

X-ray CT images of bonded coupons were obtained using a Hytec imaging system. The x-ray system consists of a micro focus x-ray source, a flat panel detector, a rotational stage, and a computer to control data acquisition. The bonded coupons were scanned at a magnification of 7.6 times resulting in a resolution of 16.7 μm per pixel.

2.7 Hygrothermal Aging

The aging conditions selected for this study were 71 °C (160 °F)/85 % RH and based in part on Composite Materials Handbook 17, CMH-17 [16]. A MicroClimate™ model MCB-1.2 environmental chamber manufactured by Cincinnati Sub-Zero was used. Control specimens were sealed in a plastic bag and stored under low humidity (~20% RH) in desiccators at room temperature. Control specimens were removed and tested at the same time intervals as those in the aging chamber.

2.8 Mechanical Testing and Failure Mode Analysis

Single lap shear specimens (2.54 cm wide with a 1.27 cm overlap) were tested according to a slight modification of ASTM D3165-00 (ASTM, 2000) using an MTS 810 Test Frame with an MTS 661.20 Force Transducer (25 to 100 kN) and MTS 647 Hydraulic Wedge Grips (100 kN capacity; 21 MPa maximum pressure) using a minimum of five specimens per set of conditions. The modification to ASTM D3165-00 (ASTM, 2000) regarded how the bonded test specimens were gripped. All other significant portions of the standard (i.e., adhesive overlap, adherend thickness, gripped portion of the specimen, crosshead speed, etc.) remained the same. This modification allowed for a considerably simpler bonding configuration as well as an overall materials savings in that less CFRP had to be produced and less adhesive was used. Specimens were tested at room temperature and 71 $^{\circ}$C. A set of at least five specimens were tested per condition and the average apparent shear strength reported. After testing, failure modes were analyzed by visual inspection and categorized according to ASTM D5573-99 and ASTM D5573-ADJ as cohesion (C), thin layer cohesion (TLC), adhesion (A), light fiber tear (LFT), and fiber tear (FT) [17]. For the purposes of discussion in this paper, cohesion failure has been used to capture all failure modes (e.g. C, TLC, LFT and FT) except adhesion.

3. RESULTS AND DISCUSSION

3.1 Materials

The composite adherends were fabricated from T800H/3900-2 prepreg as described in the experimental section. After fabrication, all panels were characterized for quality and void content by ultrasonic inspection, microscopic examination and acid digestion. In general, no significant problems were encountered in panel fabrication and all panels had void contents well below 2% by volume.

3.2 Laser Ablation

The composite panels were laser ablated across one end of each panel at a width of 1.6 cm, which corresponds to the overlap bond area. The laser was operated at a speed of 25.4 cm/sec and 1 pass was used for each line. The laser operating parameters are presented in section 2.2. A crosshatch pattern was generated as represented in Figure 1. The laser ablation process was rapid and the surface topography very reproducible. A variety of patterns and topographical features could be generated or alternatively, the entire surface could be ablated. The pattern and laser operational parameters selected for this study were based on prior experimental investigations [3]. It is of interest to note that laser ablation produces a flat surface whereas peel ply surface treatment generates a degree of curvature on the surface [3,13].

Approximately 40 composite panels were laser ablated over multiple weeks to produce the 138 individual lap shear specimens needed for the three-year aging study. During this time, the laser ablation system had some operational issues and several parts had to be replaced including the focusing lens. As a consequence, some of the laser ablated panels differed from the rest in terms of their dimensional features, particularly those fabricated first in the series. There were some inconsistencies observed in the laser ablation depth, particularly in the middle of the panels, but

the panels were deemed acceptable for use in this study. From these "first generation" laser ablated panels, 42 lap shear specimens were produced. The heritage of each lap shear specimen was tracked in terms of the specific composite panel it was fabricated from as well as the complete history of the composite panels including the specific prepreg batch. One lesson learned from this work was that the ability to measure the energy delivered by the laser at the substrate surface was an effective means of quality control. A device for performing this measurement was integrated into the laser ablation process about half way through the panel fabrication (i.e., after the first generation panels were laser ablated).

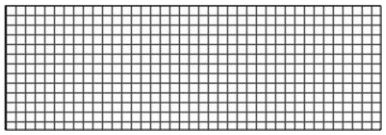


Figure 1. Illustration of the crosshatch pattern generated on the bonding surfaces of the CFRPs.

3.3 Microscopy

After laser ablation panels were characterized using optical and confocal microscopy to measure dimensional features created by the laser. A representative confocal microscope image is shown in Figure 2. Under the laser conditions used for this work, the dimensional features of the "pillars" were on the order of 10-12 μm high, 23-25 μm wide, and spaced apart by around 50 μm. The ability to reproduce these features from panel to panel was excellent provided the energy delivered by the laser at the substrate surface was kept constant.

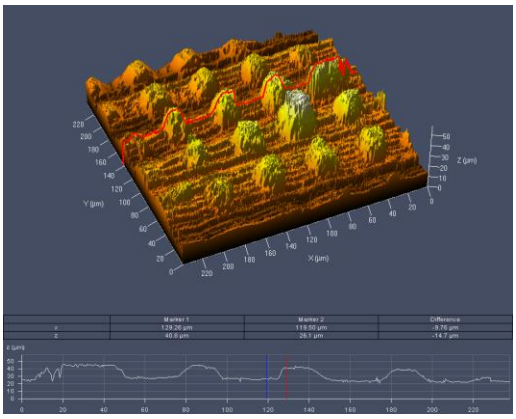


Figure 2. Confocal microscope image of laser ablated composite surface.

3.4 Adhesive Bonding

Although there were no significant problems encountered in the bonding process, some minor variations in bondline thickness were experienced. Bondlines were measured using an optical microscope to view the cross-section of each bond and also calculated from the CT imaging data. These measurement techniques yielded different thicknesses but the scatter within any one technique was reasonable. For example, via CT imaging the bondline thickness averaged 0.16 mm (6.4 mils) with values ranging from 0.14 mm (5.4 mils) to 0.2 mm (7.7 mils). In comparison,

the optical microscope gave an average of 0.11 mm (4.3 mils) with a range from 0.08 mm (3.3 mils) to 0.16 mm (6.4 mils). Average void content within adhesive bondlines was 5.7% as determined by CT imaging.

3.5 Specimen Fabrication

Once the composite panels were bonded, they were cut into individual specimens using a wet saw. Single lap shear specimens were dried by heating under vacuum at 50 °C for 24 h. The temperature was then increased to 66 °C for an additional 24 h under vacuum. Specimens were allowed to cool under vacuum and weighed immediately after exposing to atmosphere. Specimens were arranged in groups of five and selected so that a good representation of specimens from different bonded panels and varying void content were mixed together.

3.6 X-Ray Computerized Tomography

X-ray radiographs were generated by extracting the bondline from CT images of the coupons and displaying the average intensity as an image. Voids in the image appeared as darker areas and darker shades corresponded to voids occupying more of the bondline thickness. During this process of generating radiographs bondline thickness and total void fraction in the bond were determined by measuring the image amplitude difference at the bond-coupon interface and the bond-void interface and using the amplitude differences to determine the values. Representative radiographs are presented in Figure 3 for bondlines with 1.2, 5.0 and 9.9% void contents.

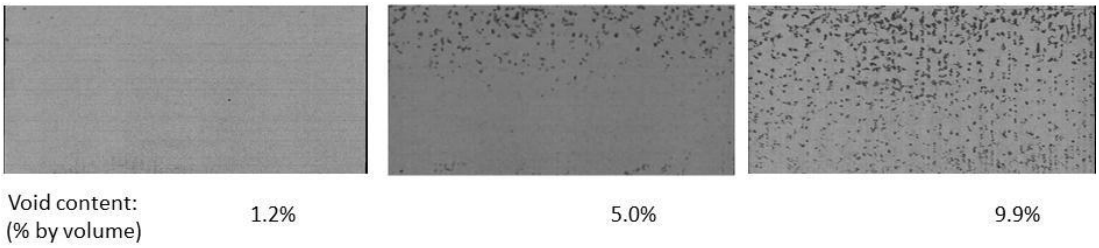


Figure 3. Representative radiographs of lap shear specimen bond areas.

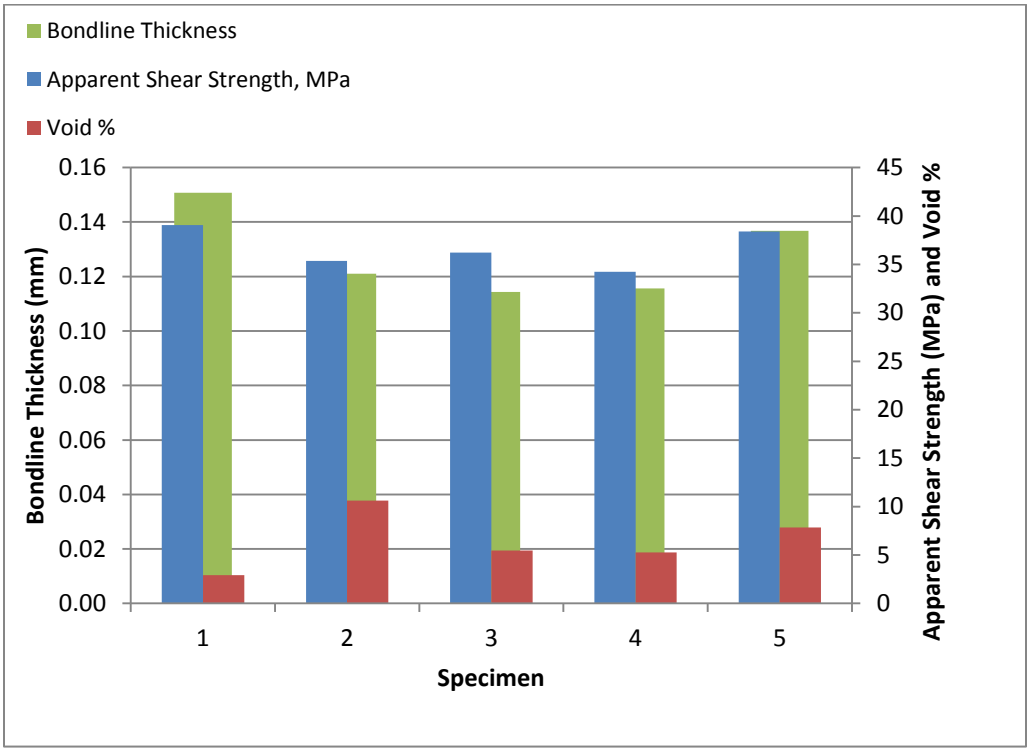
3.7 Hygrothermal Aging

To conduct the three-year aging study, a total of 138 single lap shear specimens were required. The specimens were aged at 71 °C and 85% RH, and control specimens were stored in a low humidity chamber (20% RH) at room temperature. The temperature and humidity was monitored using a portable recording device that allowed the data to be stored and downloaded to a computer via a USB interface.

3.8 Mechanical Testing and Failure Mode Analysis

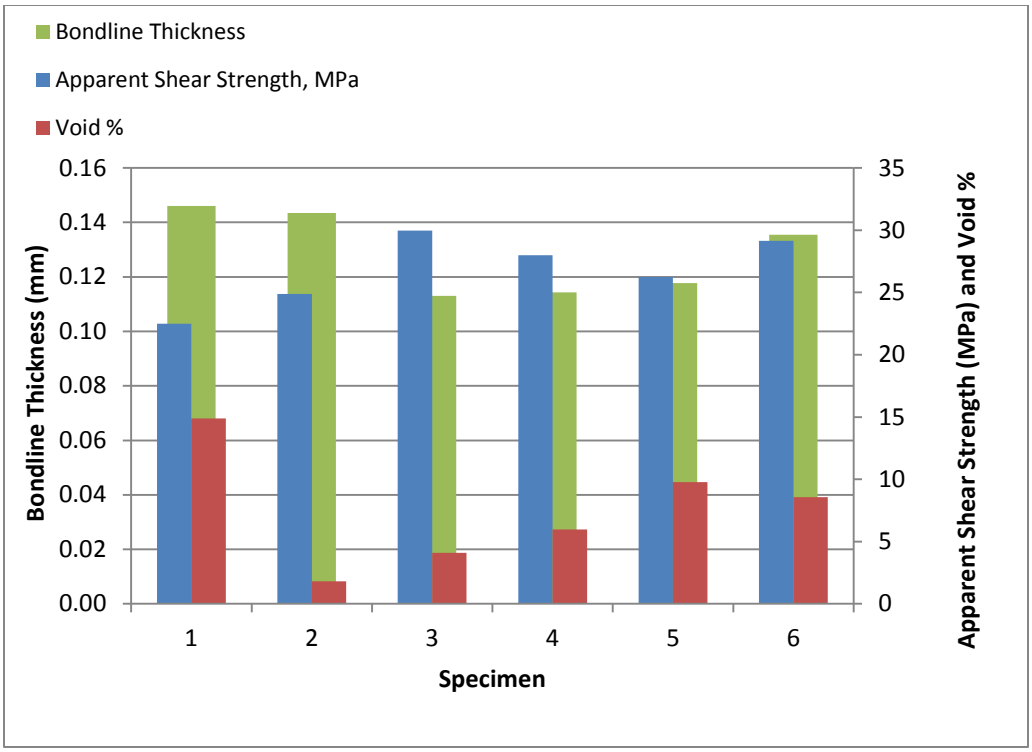
Lap shear testing was conducted on a series of specimens prior to beginning the hygrothermal aging process at both room temperature and 71 °C (160 °F) and the average apparent shear strengths were 35 and 33 MPa, respectively, with nearly 100% cohesion failure. In comparison,

lap shear specimens fabricated from the same materials using a wet peel ply surface treatment (Hysol EA-9895) exhibited apparent shear strengths of 38 MPa at room temperature and 30 MPa at 82 °C (180 °F) [15]. The unaged lap shear strengths and failure modes for the two different surface treatments were quite comparable. At the time of this writing, the lap shear specimens had been hygrothermally aged for 360 days. Aged samples were removed at about 100, 184, 272, and 360 days. Control specimens were also removed and tested but at less frequent intervals. The aged specimens were weighed and mechanically tested within 1-2 h of removal from the chamber to minimize drying. After 360 days of aging, the specimens gained about 0.75% weight due to water uptake whereas the control samples exhibited little to no weight change. The apparent shear strength values obtained at RT for control and aged specimens after 360 days is presented in Figures 4 and 5, respectively.



* Bondline thickness measurement obtained using optical microscopy

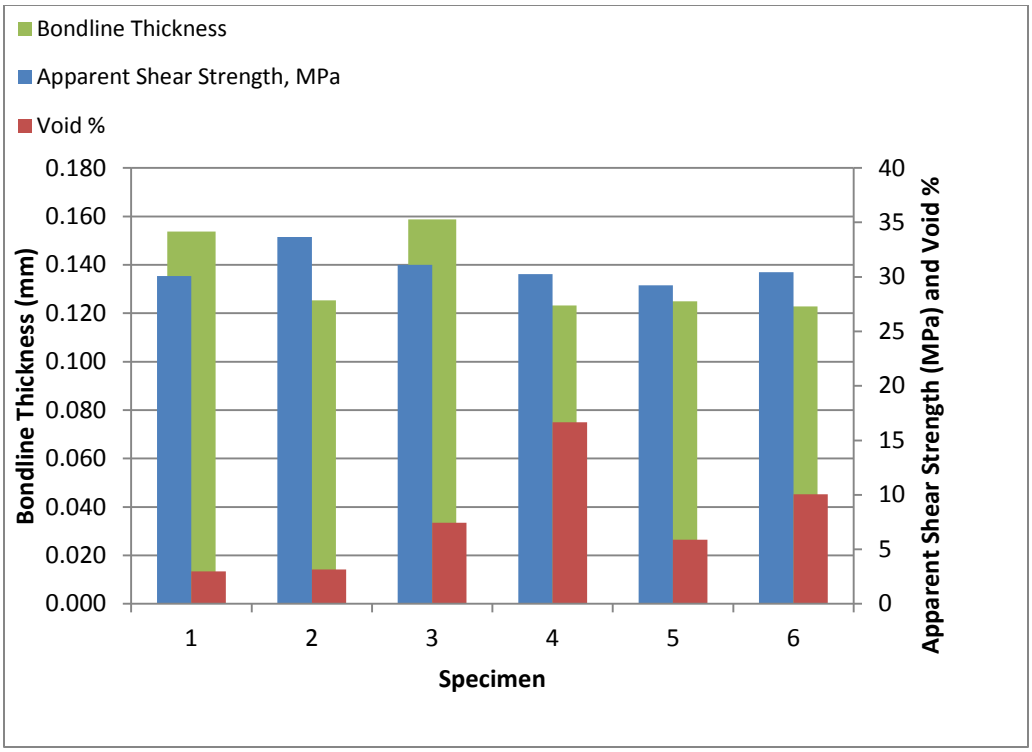
Figure 4. Control lap shear test results after 360 days, tested at room temperature.



* Bondline thickness measurement obtained using optical microscopy

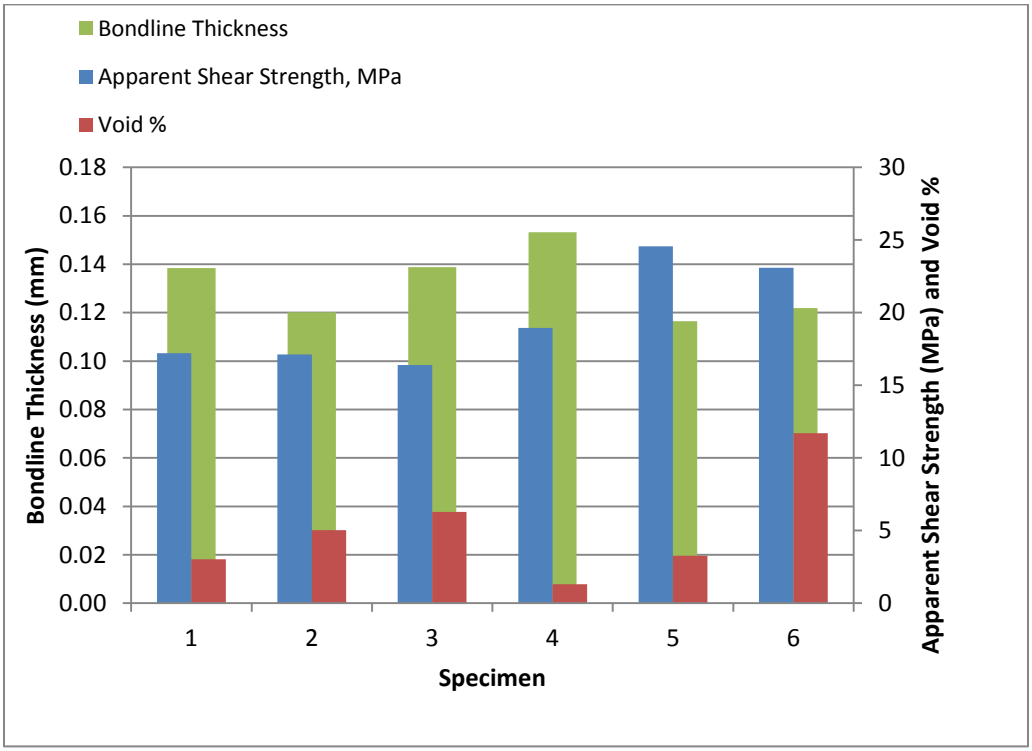
Figure 5. Aged lap shear test results after 360 days, tested at room temperature.

Also included is the void content and bondline thickness for each specimen. After 360 days of aging the apparent shear strengths were 27.0 ± 2 MPa whereas the control specimens exhibited values of 36.6 MPa ± 2 MPa. This represents a reduction in apparent shear strength of about 27% with both the aged and control specimens exhibiting nearly 100% cohesion failures. In comparison to the previous study with aging data at 82 °C (180 °F) and 85% RH from lap shear specimens fabricated using a wet peel ply surface treatment, after 320 days aging the apparent shear strength was 27.0 ± 6.3 MPa (29% reduction) with predominantly cohesion failures observed [15]. The similarity of the results from these two tests is notable despite the difference in aging temperatures. The apparent shear strength values for control and aged specimens obtained at 71 °C after 360 days aging are presented in Figures 6 and 7, respectively.



* Bondline thickness measurement obtained using optical microscopy

Figure 6. Control lap shear test results after 360 days, tested at 71 °C.



* Bondline thickness measurement obtained using optical microscopy

Figure 7. Aged lap shear test results after 360 days, tested at 71 °C.

After 360 days and testing at 71 °C, the apparent shear strengths averaged 30.8 ± 1.5 MPa for the control specimens and 19.5 ± 3.4 MPa for the hygrothermally aged specimens. In comparison to the 82°C/85% RH data from the same materials using a wet peel ply surface treatment, after 320 days aging the apparent shear strength when tested at 82°C was 29.5 ± 2.7 MPa for the control specimens and 23.1 ± 2.0 MPa for the aged specimens with predominantly cohesion failures observed [15]. The larger drop in apparent shear strength for the specimens that received the laser ablation surface treatment was of concern, so further investigation into the heritage of those samples was initiated.

The data is presented graphically in Figures 8 and 9 for specimens tested at room temperature and 71 °C, respectively. Also included in Figures 8 and 9 is the water uptake, which had nearly reached equilibrium at about 200 days aging. The average water uptake for the aged lap shear specimens was about 0.75%. The failure mode as a function of aging time was also plotted. The control specimens after 360 days and testing at 71 °C exhibited exclusively cohesion failure modes. In contrast, for hygrothermally aged specimens, the amount of cohesion failure decreased after 200 days and was evident at 360 days as well. Detailed investigation of the failure modes of specimens at 200 and 360 days revealed that a few specimens exhibited high adhesion failures. For example, of the 6 specimens aged 200 days, 3 exhibited predominantly adhesion failures (90%) while the other 3 specimens exhibited >95% cohesion failures. For the 6 samples aged 360 days, 2 exhibited predominantly adhesion failures (95%), while the other 4 specimens exhibited >95% cohesion failures. All of the specimens that exhibited adhesion failures also had the lowest apparent shear strengths within their respective sample set. The impact of the adhesion failures on the data is evident in Figure 9 as a notable reduction in cohesion failure mode as a function of aging time and the large error bars associated with that batch of specimens. The heritage of all specimens that exhibited adhesion failure was traced through their fabrication steps and it was determined that they emanated from laser ablated panels that were part of the first generation of panels fabricated. Thus, the laser processing conditions are directly linked to the loss of mechanical properties observed after hygrothermal aging.

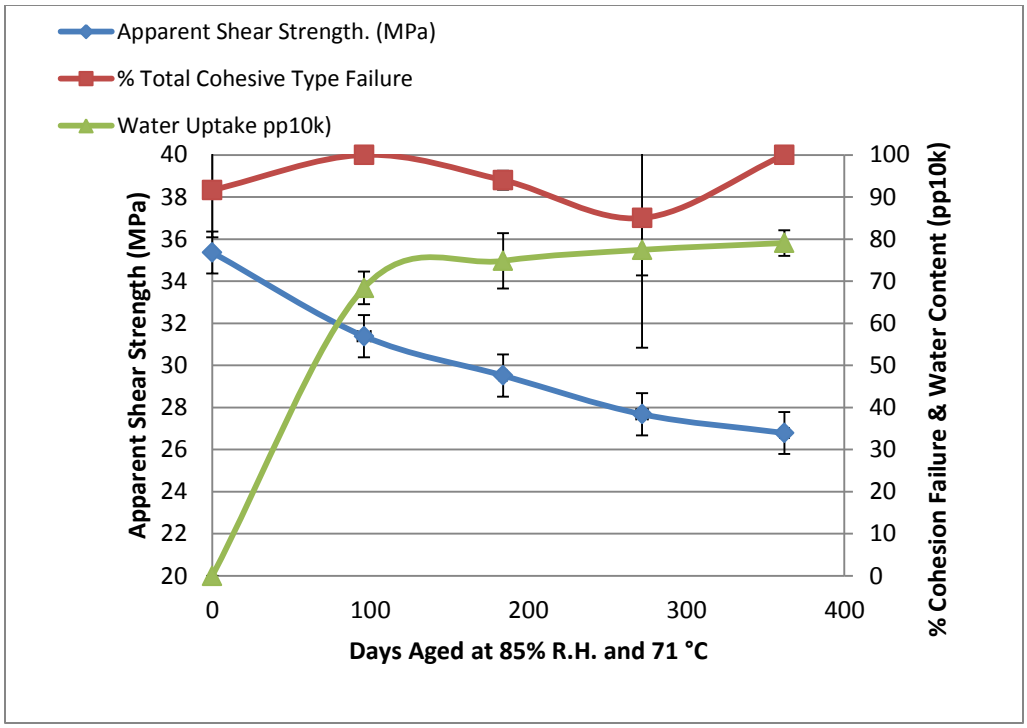


Figure 8. Apparent shear strength (RT), water uptake and % cohesion failure as a function of hygrothermal aging time.

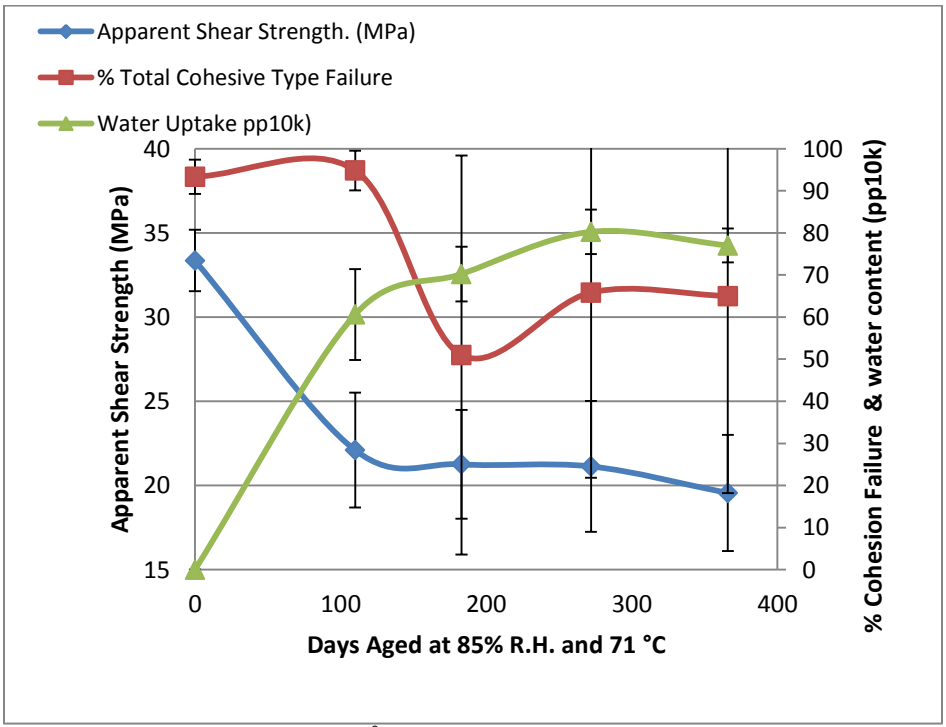


Figure 9. Apparent shear strength (71 °C), water uptake and cohesion failure as a function of hygrothermal aging time.

Further analysis of all lap shear specimens fabricated from first generation panels showed some interesting trends. Of the 42 individual first generation specimens, 25 have been tested thus far. Those in the unaged lot as well as those in the control lots did not exhibit any adhesion failures and the apparent shear strengths were comparable to the rest of the samples within their respective batch. However, first generation laser ablated specimens that underwent hygrothermal aging exhibited statistically lower apparent shear strengths within their respective batches and began to exhibit adhesion failures after around 200 days of aging. Specimens from all subsequent laser processing generations exhibited predominantly cohesive type failure modes and high apparent shear strengths. This clearly indicates that the first generation laser ablated panels, due to improper function of the laser, did not receive uniform surface treatment over the entire bond area. Although the difference in surface treatment for the first generation specimens was evident in the reduction in ablation depth, the effect on mechanical properties and failure mode was not apparent until after hygrothermal aging for at least 200 days. This observation further emphasizes the importance of monitoring the laser pulse energy at the substrate surface to ensure consistent ablation as well as the importance of process control for surface preparation of adhesively bonded joints. As a result of this work, and during the course of fabricating the lap shear specimens, protocols were developed to better verify that the laser ablation process was being conducted in a repeatable, traceable manner, and any malfunction of the laser could be readily detected. Surface preparation is acknowledged as the most important and critical aspect of bonding, because it affects the final texture and chemistry at the interface [1]. FAA certification methodology for primary bonded structure consistently calls for strict in-process control and post bond inspections [1]. The state-of-the-art surface treatment for composites is currently peel-ply which provides excellent performance in bonded structures. However as the desire to achieve FAA certification intensifies, the laser ablation method can offer an improved level of process control for the surface treatment of composites.

4. SUMMARY

A 355 nm laser was used to ablate patterns into the surface of CFRP adherends to a depth of around 10-12 μm without damaging or exposing carbon fiber. The adherends were characterized via microscopy and subsequently used to fabricate single lap shear specimens using AF-555M adhesive. The single lap shear specimens were hygrothermally aged at 71°C and 85% RH for 360 days. The apparent shear strengths were reduced with increasing hygrothermal aging time and exhibited predominantly cohesion failure. In the case of aged specimens that exhibited adhesion failure, causality was traced back to improper laser surface treatment in which a significant portion of the faying surface received either reduced or no ablation. It was found that measuring laser pulse energy at the substrate provided an effective means of quality control for the preparation of highly uniform faying surfaces. Overall, the results of this study relative to stability of the surface to hygrothermal aging compare well with that published using the same substrates but with a wet peel ply surface treatment. The advantage of laser ablation as pre-bonding treatment is that it can provide a more precise and reproducible surface preparation that is amenable to scale-up and could afford better reproducibility and robustness in a production

environment. Due to these inherent traits, laser ablation offers the potential to be an integral part of an adhesive bonding methodology that may ultimately lead to FAA certification.

5. ACKNOWLEDGEMENTS

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