

ATMOSPHERIC PLASMA TREATMENT OF FIBER REINFORCED COMPOSITES FOR ADHESIVE BONDING

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Keywords: atmospheric plasma treatment, composites, bonding, surface preparation

ABSTRACT

There is a growing interest in the use of atmospheric plasma treatment techniques for the surface preparation of graphite-epoxy composite hardware prior to bonding. In this paper, we will discuss the effects of atmospheric plasma treatment on the microstructural, chemical and resultant mechanical properties of the treated composites as well as compare them to similar composites prepared by conventional methods. Atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) were used to investigate the surface chemistry and morphology of the treated composites and were correlated to lap shear bond strengths. The results allow us to separate the mechanical contributions caused by ablation-induced surface roughness from chemical contributions due to formation of specific reactive surface functional groups. The mechanical and chemical mechanisms that govern surface properties and contribute to the observed enhanced bonding will be discussed.

1 Introduction

The surface preparation of fiber-reinforced composites prior to adhesive bonding is a critical process in the manufacturing of satellite and launch vehicle composite hardware. Current standards for preparing the surface of composites for bonding utilize either mechanical roughening or peel ply techniques. As suggested by the name, mechanical roughening utilizes abrasion to remove surface contaminants and increase roughness. Matienzo et al. [1] have suggested that the relatively high level of surface roughness induced by some abrasion treatments leads to mechanical interlocking and thus increases intrinsic adhesion. Other work [2] has discounted this mechanism, and concludes that ensuring a contamination free surface is the critical factor for successful bonding. Abrasion techniques have also been shown to negatively affect the bond performance of higher modulus fiber composites due to subsurface fiber-matrix decoupling damage caused during the surface preparation procedure [3]. Two additional areas of

concern with abrasion are the generation of dust and the inconsistency in the surface prep related to operator variability. The peel ply technique is also used extensively for bonding aircraft, satellite, and launch vehicle composite parts. A peel ply is typically a woven material that is cured onto the surface of the laminate. The function of the peel ply is to protect the surface until just prior to bonding, at which time the peel ply is stripped away leaving a fresh surface for bonding. However, peel ply contamination has been shown to negatively impact bond performance. The peel ply fiber coatings, as well as the peel ply fibers themselves, can detach and have been shown to contaminate the bond area. Peel plies are also typically moisture-absorbing materials that if not carefully controlled and dried can negatively impact moisture sensitive matrix materials during cure and further erode composite bond properties.

Recently, there have been a number of articles that have evaluated the use of atmospheric plasma treatment as an alternate method over currently accepted surface preparation techniques [4, 5]. The recent availability of plasma sources that operate at atmospheric pressure and at relatively low temperatures has made atmospheric plasmas a promising alternative to vacuum plasmas. The atmospheric plasma treatment process uses a capacitive discharge at atmospheric pressure to produce a uniform high density of mix of ions, electrons, and free radicals. The reactive species impinge on the surface of the composite resulting in both microstructural and surface chemistry modifications that may improve adhesive bonding. Atmospheric plasma activation is currently considered a viable pretreatment for bonding surfaces to address known variability concerns associated with other alternative surface preparation methods.

In this study, the impact of atmospheric plasma treatment on the bonding behavior of several composite systems will be investigated. Understanding how plasma treatment affects the chemical and microstructural features of this composite material as well as the mechanical behavior of the resultant bond will allow an assessment of the suitability of incorporating this technique into the industry practices.

2 Materials and testing methods

2.1 Processing of Composites

The composite materials investigated in this study were Nelcote E765 epoxy with AS4 PAN-based carbon fiber. The laminates consisted of 8 prepreg plies laid up in a unidirectional configuration. The laminates were cured in an autoclave at 121°C under a pressure of 0.69 MPa (100 psi) and subsequently post-cured in an oven at 177°C for 2 hr. Further details are described in a previous publication [4].

2.2 Plasma Treatment

A Surfex Technologies AtomFlo-400 atmospheric plasma unit was used to treat all samples investigated in this study. The control unit uses helium gas as the carrier and oxygen as the active

gas. All gases are of 99.9% purity. The plasma wand (Surfx PS02129) utilized a 25 mm linear beam. Plasma conditions were fixed at 96W of radio frequency (13.56 MHz) power, 0.450 L/min of oxygen as the active gas, and 30 L/min. of helium was used as the carrier gas. During treatment, the samples were placed on a stationary stage and a robotic arm holding the plasma head was scanned at a constant rate across the specimen face. A scan rate of 24.5 mm/sec was used for all specimen treatments. The working distance was held fixed at 1.0 mm from the source. Samples were typically evaluated within 2 hr of treatment unless otherwise stated. The plasma exposure is defined in terms of the number of passes by the plasma head over the test surface. The plasma exposures used in this study were 0, 1, 3, 6, 12, 24, and 48 passes. Emission spectroscopy was used to verify active species in the plasma after glow.

2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) system (SSI) using Al K α source was used for surface chemical analysis as a function of plasma treatment of the composite samples. Analyzer pass energies of 150 and 50 eV were used for wide scans and high-resolution spectra respectively. The XPS analysis chamber was pumped by an ion pump and had a base pressure of 1×10^{-10} Torr.

2.6 Atomic Force Microscopy

An AGILENT 5500LS Atomic Force Microscope (AFM) was used for analysis of the surface morphology of the composite specimens. A number of $10 \times 10 \mu\text{m}$ scans were obtained and compared as a function of plasma treatment condition. The RMS and surface area difference were also measured as a function of treatment condition. A separate set of composite specimens were mounted edgewise in epoxy and polished to a 1- μm finish.

2.7 Mechanical Testing

2.7.1 Lap Shear testing

Composite-to-composite single lap shear testing was performed per ASTM D 3165 [6] to assess the effectiveness of plasma treatments for enhancing bond strength. All composite adherends tested in this investigation were post-cured at 177°C. E-glass/epoxy doublers having the same thickness as the AS4/E765 laminates (1.5 mm) were bonded to one side of the 150 x 150-mm laminates.

2.7.2 Fracture Toughness testing

Mode I, crack opening, interlaminar fracture toughness was measured by the double cantilever beam technique following test procedures specified in ASTM D 5528 [7]. A unidirectional composite having a built-in delamination was loaded across the delamination in tension.

Samples were prepared by bonding two 8-ply laminates together using Hysol EA9394 adhesive with a bond line gap of 0.13 mm. A PTFE insert 63mm long was placed at one end of the 127

mm long assembly to form the built-in delamination. Further details are described in a previous publication.

3 Results

Composite samples were treated using our robotic stage controlled atmospheric plasma treatment (APT) unit shown in Figure 1. Specimens were treated from 1 to 48 passes using an oxygen plasma to evaluate wetting, microstructural, surface chemical changes, and mechanical performance for two types of composites. We will discuss only the epoxy treated specimens in this limited format of the manuscript. All of the test parameters have been optimized when using oxygen as the active gas as discussed in a previous publication [5]. The test parameters have been chosen to promote the optimum environment for the interaction of oxygen free radicals in the after glow with the composite surfaces, while limiting damage to the composite material.

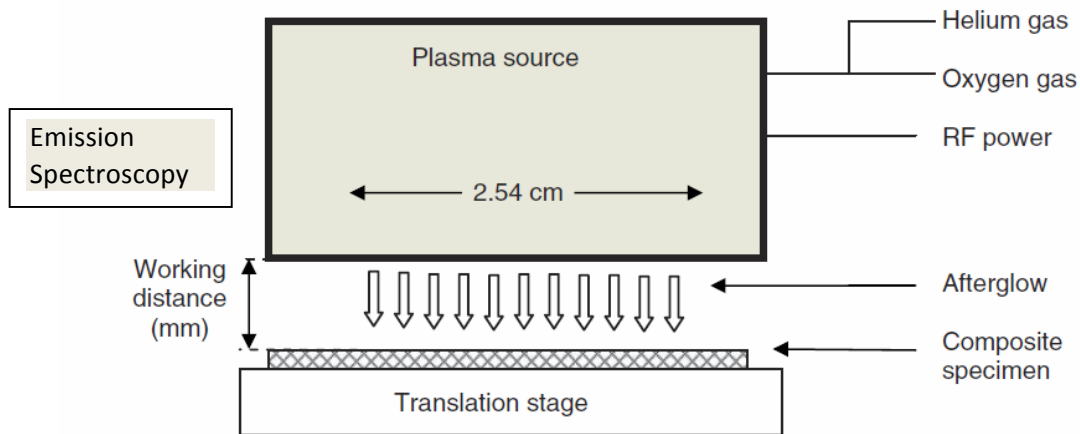


Figure 1. Schematic showing the test set-up for the surface preparation of composites using the SurFx atmospheric plasma treatment unit

Figure 2a shows the effect of plasma treatment on the lap shear strength (LSS) of our composite system adhesively bonded using a room temperature cured epoxy (Henkel 9394). The control, solvent wiped specimen yields a LSS of approximately 16.4 MPa. The data shows a sharp increase in bond strength with initial treatment, with a continued gradual improvement as the number of passes is increased. An improvement of approximately 50% in strength was observed after 48 passes, with a 30 % increase in strength occurring with only 6 passes. If one compares the APT samples to the conventional abrasion treated specimen, the improvements are even more substantial. An analysis of the fracture surfaces shows that solvent-treated specimens exhibit a fair degree of adhesive failure. The APT treated specimens on the other hand, show a greater fraction of failure occurring deeper within the first ply as the number of passes increases. The failure for the abrasion treated is almost exclusively within the first ply despite the low LSS. We believe this to be a result of subsurface damage caused by the abrasion treatment.

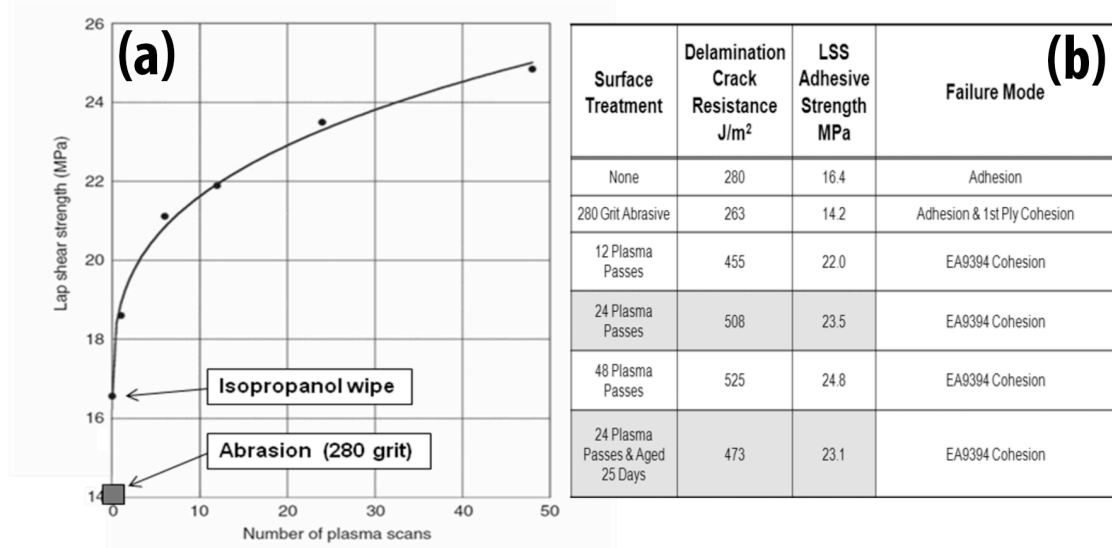


Figure 2. Example of (a) Lap Shear strength and (b) fracture toughness of a graphite/epoxy as a function of plasma scans (duration)

Figure 2b also shows the fracture toughness values for our composite as a function of treatment. As shown, there is a significant improvement after 12 passes from 280 to 508 J/m². The failure mode also changes dramatically from being purely adhesive in nature to entirely cohesive. Further treatment passes show only a gradual added improvement. Figure 2b also shows that the fracture toughness and strength of these bonded composites remain quite stable and retain most of their improved properties even though they were not bonded shortly after treatment. 25 days of exposure after APT only had a minor effect of strength and delamination resistance.

Contact angle measurements showed that treatment significantly improves wetting most likely due to the incorporation of oxygen functional groups. However, this effect is saturated after 6 passes and would not alone explain the continued improvement in mechanical performance. Microstructural analysis using atomic force microscopy (AFM) also indicates that the morphology of the surface of the resin changes in roughness as function of treatment as shown in Figure 3a. Figure 3b shows these periodicity surface changes in morphology when comparing the control specimen to one with 12 passes of treatment. Even though there are notable changes in surface roughness from 13 nm to 110 nm over our test conditions, this degree of surface roughness change only translates in a minor increase in surface area (12 passes - 4% change). This increases roughness alone cannot adequately explain the observed strength improvements.

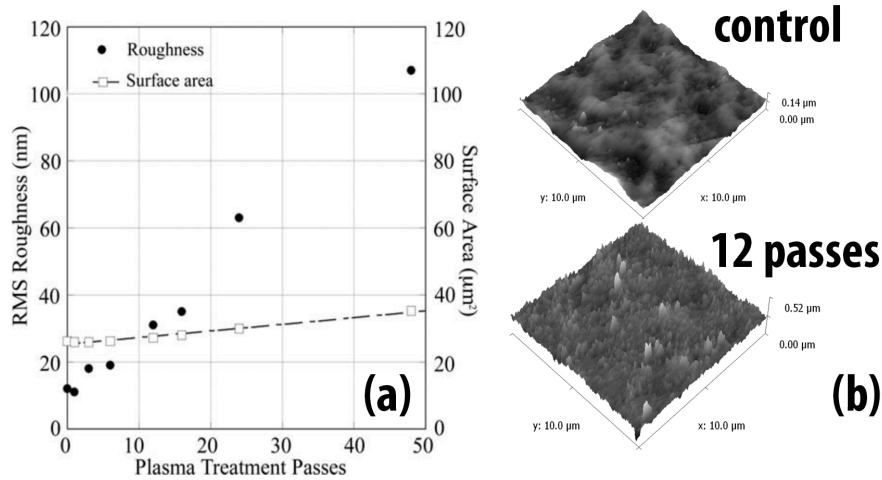


Figure 3. The effect of plasma treatment passes on (a) surface roughness and surface area by AFM and (b) morphological changes

Figure 4 shows the deconvoluted photoelectron high resolution C 1s spectra for our APT treated composite specimens. Each peak can be associated with a specific functional group. The peak at 284.6 eV is the hydrocarbon peak (-C_xH_y-). Subsequent plasma treatments of the surface create new peaks at the shoulder of the original hydrocarbon peak related to binding energies for the functional groups created. The peak at 286.2 has been attributed to alkoxy groups (C-O); the peak at 288.2 eV to carbonyl groups (C=O), and the peak at 289.2 eV is representative of carboxyl groups (O-C=O). Extended details are described in a previous publication [4]. Even though oxygen uptake concentrations rapidly reach a maximum after a few passes, the carboxyl concentration increases as shown in the associated Table in Figure 4, similarly to increases observed earlier in LSS with treatment.

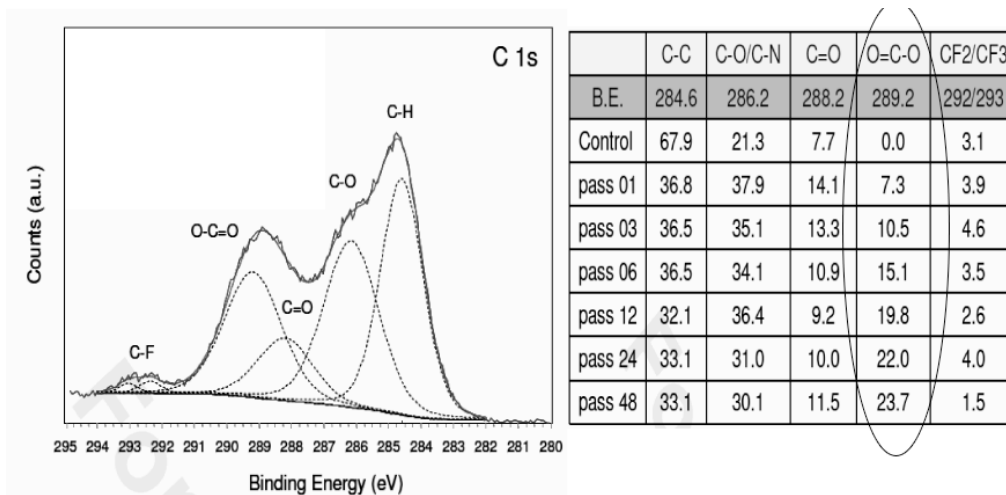


Figure 4. High resolution XPS Spectra of composite samples as a function of APT with associated functional group concentrations shown.

Figure 5a illustrates the similar trends in both adhesive strength and carboxyl group concentration as a function of passes. Figure 5b shows the correlation between adhesive strength and concentration of active carboxyl sites on the surface of the treated composites. Covalent bonding between carboxyl groups and epoxides has been reported in the literature as a utilized crosslinking mechanism [8]. A portion of unreacted epoxide groups in the adhesive could chemically react with the carbonyl groups on the composite surface, and therefore enhance bond strength as observed. Reactions between amine and carboxyl groups are also possible. Even though this proposed mechanism and data explain observed increases in strength, one cannot exclude possible morphological contributions from plasma treatment.

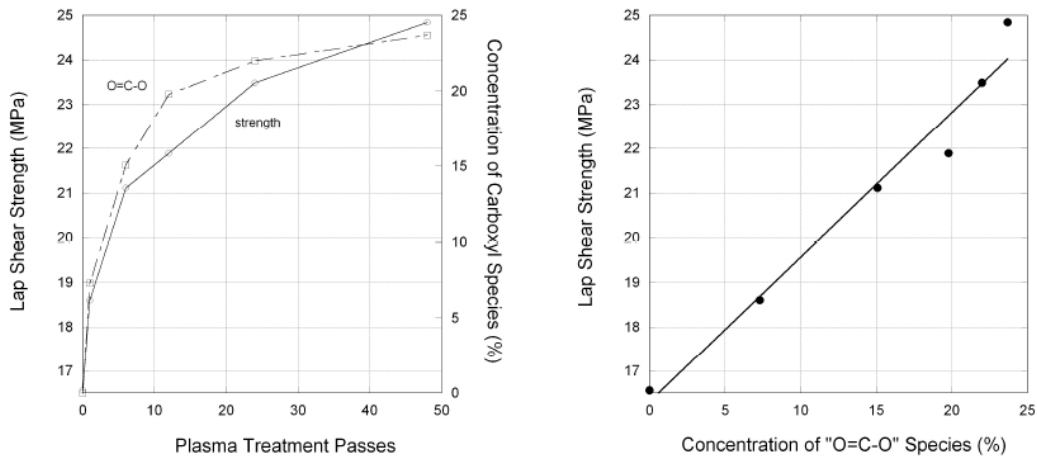


Figure 5. (a) LSS and carboxyl concentration as a function of treatment passes (b) correlation between O=C-O chemical groups formed and LSS after APT

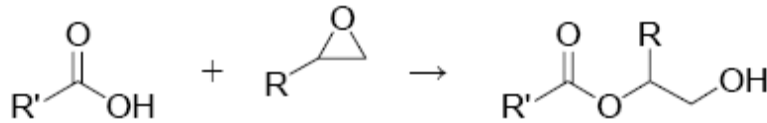


Figure 6. Possible bonding between the carboxyl groups on the composite surface and epoxide groups in the adhesive

Conclusions

Plasma treatment of composite specimens is a suitable treatment for surface preparation of composite hardware. The procedure is simple, non-operator dependent, and exhibits no damage to the reinforcement for the conditions chosen in this study. The adhesive bond strength was shown to increase as a function of passes. In creases in bond strength of approximately 50% over control specimens were realized after 48 passes, and increases by 30% were obtained with as little as 6 passes. XPS showed that even though oxygen content is maximized after 1 pass, the carboxyl content continued to increase with APT. The carboxyl content was shown to correlate well to increases in LSS. It is believed these improvements are due to improved bonding at the interface between carboxyl groups and the epoxide functionality in the adhesive. Contributions to the strength of bonded composites from microstructural changes such as surface area contributions due to increases in roughness appear minor. Chemical changes to the surface of treated specimens appear to be primary mechanism for mechanical improvements, however since microstructural and chemical changes occur simultaneously, they cannot be studied completely independent of each other.

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