ATMOSPHERIC PLASMA TREATMENT OF POLYETHERETHERKETONE COMPOSITES FOR IMPROVED ADHESION

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ABSTRACT

A handheld atmospheric plasma has been developed to treat polyetheretherketone (PEEK) composites. The instrument produces a plasma beam that covers a circular area 2.5 cm in diameter. The plasma is fed with 30 L/min of helium and 0.45 L/min of oxygen, and is supplied with 80 W of radio frequency power (13.56 MHz). The plasma beam was swept over the composite surface to activate it for bonding. Following treatment, 3M AF-563 adhesive film was applied to 2.5 x 17.8 cm² strips of PEEK. The strips were joined together and cured, and a series of lap shear tests (ASTM D-3165) were performed. Plasma treated samples failed cohesively and showed average lap shear strengths of 43.2±0.6 MPa, whereas the untreated samples failed adhesively at much lower shear strengths. Environmental testing revealed that the plasma-exposed surfaces could sit for at least 8 hours at 49 °C and 90% relative humidity prior to applying the adhesive with no loss of bond strength. The handheld plasma tool is safe, easy to use, environmentally friendly, and well suited for treating large, 3-dimensional PEEK panels.

KEY WORDS: plasma treatment, thermoplastics, carbon fiber composites
1. INTRODUCTION

Polyetheretherketone (PEEK) is a thermoplastic material used in the aerospace, automotive, and medical industries. It is attractive because of its excellent mechanical strength and high resistance to fatigue, impact, and abrasion (1). Composites made from PEEK, such as those reinforced with carbon fiber, are fire resistant, insulating, and chemically and thermally stable (2). However, this material does not adhere well to other surfaces, or form strong bonds to epoxy resins without specialized surface treatment. Methods used to treat PEEK prior to adhesive bonding include wet chemical etching (3), ion-beam irradiation (4), UV ozone oxidization (5), and oxygen plasma etching (6,7). Of these treatment methods, oxygen plasma treatment yields surfaces with the best adhesion. Plasma surface treatment has other advantages as well: it is environmentally friendly, and only exposes the polymer surface to the reactive gas, leaving the bulk structure unaffected.

In this paper, we present data on the treatment of carbon-fiber-reinforced PEEK with a handheld atmospheric pressure plasma. The atmospheric plasma tool operates at low power and voltage levels (below 100 W and 120 V), does not pose a risk of electrical shock, and is safe for use in flammable environments. In addition, the plasma source may be scanned over the sample surface, so there is no limit to the size of the object that may be treated. The results presented below provide insight into the mechanism of activating the composite with the atmospheric plasma. In addition, it is shown that high lap-shear strengths and cohesive failure are achieved after a short treatment time.

2. EXPERIMENTAL METHODS

2.1 Materials The composite materials used in this study were AS4 carbon fibers reinforcing polyetheretherketone thermoplastic. The panels consisted of 16 plies of PEEK/carbon stacked in a unidirectional manner. The prepreg plies were placed in an autoclave underneath a pressure plate to obtain a uniform, flat surface. The entire part was vacuum bagged and heated to 382 °C at 2.8 °C/min and 0.7 MPa. Then it was held at 382 °C for one hour. After cooling to room temperature, the panels were sectioned as needed for the experiments.

2.2 Plasma Treatment System Surfx Technologies’ Atomflo™-250 and -500R atmospheric pressure plasma tools were used to treat the PEEK composites. Shown in Fig. 1 is the Atomflo™-250 control unit and plasma applicator. The control unit is connected to bottles of pressurized helium and oxygen (industrial grade), and to a 120 V electrical outlet. The applicator is seen resting on top of the control unit. It is 2.5 cm in diameter by 15 cm long. The plasma gas flows out of the applicator through a showerhead. In the picture, one can see the bluish white glow of the plasma emanating from the holes in the head. Conditions for operation of the atmospheric plasma are 80 W of radio frequency power (13.56 MHz), 0.45 L/min of oxygen, and 30 L/min of helium. The gas temperature exiting the plasma is less than 66 °C. During surface treatment, the PEEK panel is moved underneath the plasma beam at a distance 2 mm from the source. Plasma exposure time is 4.7 s/cm², unless noted otherwise.
In Figure 2, a picture is shown of the Atomflo™-250 and 500R plasma applicators. Both devices run off of the same control unit. The latter device produces a linear plasma beam 5.0 cm wide by 1.5 mm across. The conditions used to operate the 500R plasma are 225 W of radio frequency power (27.12 MHz), 1.5 L/min of oxygen, and 30 L/min of helium. The PEEK samples are translated under the beam at an exposure time of 100 seconds per meter processed, with a stand off distance of 1.0 cm. The gas temperature exiting the plasma is 65 or 115 °C, depending on whether the plasma source is cooled with circulating water or not. The data presented in this report were obtained with the Atomflo™-250 atmospheric plasma tool.

### 2.3 Surface Treatment and Testing

**2.3.1 Treatment Conditions** Panels of 16-ply, unidirectional PEEK composites were cut from the pressed panels. For each treatment condition, two panels with dimensions of 15.2 cm x 17.8 cm were prepared. The surface of the panels were cleaned with acetone by wiping with a dust-free cloth then dried at room temperature for 5 minutes. Next, the samples were placed beneath the oxygen plasma beam at 2 mm distance, and treated for 10, 20, 30 and 60 seconds at the conditions indicated above.

In some cases, a fixed delay period was added between surface treatment and application of the adhesive. This was done in order to assess how long the plasma activation lasts before one observes a loss of adhesion. Pairs of panels were treated with the oxygen plasma for 30 seconds.
Then, the panels were kept at ambient conditions for time intervals of 0.5, 1.0, 2.0, 3.0 and 8.0 hours. The temperature and humidity for these dwell times were 21 °C and 50% RH, respectively. In addition, a pair of plasma-treated panels was exposed to 50 °C and 90% RH for 8 hours. After each dwell time, adhesive was applied to the panels, and then the panels were joined together and cured.

2.3.2 Lap Shear Tests The PEEK panels were made into single-lap-joint laminated assemblies according to ASTM D-3165. A sandwich structure was formed using two plasma-treated panels and 3M AF-563 film adhesive placed in between. This structure was cured in an autoclave at 135 °C and 0.24 MPa for 30 minutes. The ramp rate to the curing temperature was 2.8 °C/min. After curing, the panels were cut into 5 coupons with dimensions of 2.5 cm x 17.8 cm and notched on both sides forming a 1.25 cm x 2.5 cm overlap according to the ASTM standard.

The lap shear strength of each coupon was tested using an Instron 8562 in tension, measuring the load and displacement of the coupons until failure. The reproducibility of the strength measurement was assessed by shearing 5 coupons for every plasma treatment condition.

2.3.3 Environmental Aging The effect of environmental conditions on adhesion was assessed by aging the bonded coupons for one month prior to mechanical testing. One set of coupons was submerged in water heated to 50 °C, while the other set was kept at 24 °C and 50% RH. These samples were compared to determine the change in mechanical properties over time and when exposed to severe environmental conditions after bonding.

3. RESULTS

3.1 Surface Modification

3.1.1 Surface Roughness The samples were examined using a scanning electron microscope (SEM) to determine if there were any physical changes to the surface following treatment. For exposure times less than 30 seconds, it was found that the oxygen plasma uniformly eroded the PEEK matrix, but did not significantly alter the surface morphology. A further assessment of the surface roughness was made using scanning white light interferometry (SWLI). These measurements are capable of detecting changes in elevation of only 4.0 nm. Interferograms were recorded for samples treated with the oxygen plasma for 0, 10, 30 and 60 seconds. Figure 3 shows a plot of the RMS roughness as a function of exposure time. For the control surface, and surfaces treated up to 30 seconds, the average roughness was 110 microns. By contrast, the sample treated for 60 seconds had an average roughness of 170 micron.

A SWLI image of the PEEK composite treated for 60 seconds is presented in Figure 4. The field of view is 50 x 70 microns. One sees 4 to 5 stripes running horizontally across the image that are 5.0 to 8.0 microns in diameter and protrude out of the surface plane about 1.0 micron. These stripes are the outlines of carbon fibers that are beginning to be exposed as a result of the oxygen plasma etching of the polymer. Based on the SEM and SWLI data, it may be concluded that treatment times of 30 seconds or less do not cause significant roughening of the PEEK composite surface.
3.1.2 Contact Angle

Presented in Figure 5 are contact angle measurements for different exposure times of the PEEK composites to the atmospheric pressure plasma. In this test, a drop of distilled water was placed on the sample surface, and the static contact angle of the sessile drop measured using digital image capture and analysis software. Contact angles are related to the free energy of the surface through the equation 1:

\[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos(\theta) \]  

Where \( \gamma \) is the free energy, \( \theta \) is the contact angle, and the subscripts \( sv \), \( sl \) and \( lv \) refer to the solid-vapor, solid-liquid, and liquid-solid interfaces, respectively. Referring to Figure 5, the
untreated surface had a contact angle of 63°. Oxygen plasma treatment caused a rapid drop in the contact angle to 20° after a 10 second exposure, and a final value of 13° after a 30 second exposure. Figures 6 shows pictures of the wetting behavior before and after atmospheric plasma treatment for 60 seconds. The increased surface energy of the PEEK is clearly evident in these images.

![Figure 6: Contact angle image (a) before and (b) after plasma treatment of the PEEK surface for 60 seconds.](image)

### 3.2 Shear Strength Measurements

#### 3.2.1 Effect of Plasma Treatment
Carbon-fiber-reinforced PEEK coupons were treated with the Atomflo™-250 atmospheric pressure oxygen plasma for 30 seconds at a power level of 80 W and a distance of 2.0 mm from the showerhead. Then the samples were bonded with the AF563 film adhesive, and subjected to double-notch lap shear in the Instron machine. The average shear strength for the plasma-treated panels was 43.2±0.6 MPa (1 MPa = 145 psi). This may be compared to the untreated control panel, which had a lap shear strength of 35.0±1.2 MPa. The strength of the plasma-treated panel was comparable to the value reported by the manufacturer for the AF-563 adhesive.
Pictures of the control and the plasma-treated coupons after shearing them apart with a wedge are shown in Figure 7. Examination of the control reveals that adhesive failure has occurred in this specimen with nearly all of the epoxy material peeling off at the surface of the PEEK. By contrast, the samples treated with the atmospheric plasma exhibit cohesive failure with shear occurring within the epoxy material. This is evident by the uniform pink coating present on both sample surfaces. 

The carbon-fiber-reinforced PEEK composites were treated with the Atomflo™-500R linear beam plasma at a rate of 2.6 cm² per second. The operating conditions were 225 W RF power, 1.5 L/min of oxygen, 30 L/min of helium, and a sample-to-source distance of 1.0 cm. Afterward plasma treatment, the samples were bonded with the AF563 adhesive, cured, and then forced apart with a wedge. It was found that bond failure was 100% cohesive, yielding a failure surface identical to that shown in Figure 7b. Note that the treatment time with the 500R is 12x faster than the Atomflo-250, and the standoff distance is 1.0 cm instead of 0.2 cm in the latter case.

3.2.2 Effect of Dwell Time It was found that letting the plasma-treated samples sit for up to 8.0 hours prior to bonding did not affect the strength of the bond. Figure 8 shows the shear strength of panels with different “dwell” times under ambient conditions (21 °C and 50% RH), and at
3.2.3 Environmental Aging

Two sets of samples were aged for one month after bonding and then subjected to the double-notch lap shear test (ASTM D-3165). The aging conditions were 24 °C and 50% RH, and immersion in water at 50 °C. For these two tests, the average shear strengths were 37.9±1.0 MPa and 37.3±1.0 MPa, respectively. These values are slightly lower than samples tested immediately after bonding. Although great care was taken to prepare samples in a reproducible manner, it is possible that this small difference is due to variability in the lay up and cure of the bonded part. Nevertheless, the fact that there is little difference in shear strength between samples conditioned at normal temperature and humidity and samples conditioned under more aggressive circumstances, indicates that the bonds formed after plasma treatment are robust and resistant to the effects of harsh environments.

3.2.4 Elevated Temperature Testing

Plasma treated and bonded coupons were placed in the Instron 8562 and then wrapped with a heating element that was set to 120 °C. The samples were heated for 15 minutes to allow the entire structure to reach the set point. Once at temperature, samples were tested mechanically to determine the shear strength. The average shear strength was 28.5±2.0 MPa. Examination of the sample surfaces revealed that the failure mechanism was 100% cohesive. The shear strength measured at 120 °C is lower than that recorded at 24 °C. However, the former value is higher than that expected for the AF-563 adhesive, which according to the manufacturer, 3M, is 21.0 MPa at 120 °C.
4. CONCLUSIONS

Atmospheric plasma treatment has been examined as a method of activating carbon-fiber-reinforced polyetheretherketone for adhesive bonding. Films treated with the Atomflo™-250 and –500R RF plasma systems exhibit excellent adhesion to 3M AF563 epoxy. Double-notch lap shear tests yield bond strengths of 43.2±0.6 MPa, and the failure mechanism is 100% cohesive. The plasma treatment survives for at least 8 hours in hot, humid environments, and the bond strength does not degrade significantly during aging in water at 50 °C for 1 month. Furthermore, the decline in lap shear strength at 120 °C is as expected for the epoxy adhesive, indicating that plasma activation allows for strong, permanent bonds to be made between the composite and the glue. In conclusion, handheld atmospheric plasmas are a safe, environmentally benign and effective method of preparing PEEK surfaces for adhesive bonding, and should be especially attractive for the repair of thermoplastic composites used in aerospace and other industries.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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