SURFACE ACTIVATION METHODS FOR BONDING TO THERMOPLASTICS: PLASMA AND A NEW TAILORED UV BASED METHOD

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ABSTRACT

The constant trend to optimize the costs of raw materials and related processing costs has accelerated the use of thermoplastic composites as alternatives to traditional thermoset composites in the Aerospace Industry. While thermoplastics can be easily fused together above their melting temperatures, it is difficult to bond them to dissimilar substrates, including thermosets and aluminum. The high melting temperatures of engineered thermoplastics like Polyarylether Ketone family (350 – 430 °C) limit their process. Therefore, lower temperature bonding systems would be desirable.

This paper discusses the development of a new and rapid UV pretreatment method for thermoplastic composites allowing improved bonding to dissimilar substrates. In addition, plasma pretreatment is also investigated as a common method since it can have good proficiency in some cases depending upon the chemistry of adhesives. Contact angle measurement was done for surface analysis of treated substrates where regarding to the new tailored UV method, complementary analysis such as XPS and TOF-SIMS was conducted. To evaluate the bond strength, mechanical tests including fracture toughness (G_{1C}) and tensile lap shear tests were conducted.

Contact angle measurements, XPS, and TOF-SIMS analysis revealed an increase in polarity and wettability of the thermoplastic surface after pretreatments due to the formation of new oxygen-containing functional groups. This rapid UV surface treatment method led to a significant improvement in bonding of PAEK thermoplastic composites with both low and elevated temperature-cure adhesives verified by mechanical test results. This method offers new opportunities for fast and safe bonding to the thermoplastic materials resulting in excellent bond strength comparable with plasma pretreatment.

1. INTRODUCTION

In aerospace industry, the need to develop high-performance structural materials has been continuously growing where the unrelenting passion of the industry demands more replacement of metals with light weight composite materials in primary structures like fuselages and wings [1]. Composite materials typically consist of strong fibers in a tough resin matrix which have been traditionally thermosetting resins. However, the constant trend to optimize the costs of raw materials and related processing expenses has accelerated the application of thermoplastic

composites as alternatives to thermoset composites in the aerospace industry. Unlike thermosets, thermoplastics do not need chemical crosslinking for solidification and can be easily formed under sufficient heat and simply solidified by cooling to maintain their shapes at speeds much faster than curing of thermosets. Therefore, high-performance engineering thermoplastics have attracted a lot of attention in composite industries for aerospace applications where polyaryletherketones (PAEKs) represent the most promising class of materials for this purpose.

Polyaryletherketones (PAEKs) are semi-crystalline thermoplastic resins with outstanding thermal and mechanical properties where the ratio of keto- and ether- groups defines different families within this class. Polyetheretherketone (PEEK) with two ether groups in its repeat unit (Figure 1) has a growing interest in manufacturing of carbon fiber reinforced plastics (CRFP) due to its outstanding properties such as good dimensional stability at high temperature due to its high melting point (about 335 °C), high yield strength (about 90 MPa) with an elongation at break of 120-170% [2]. However, high-performance engineered thermoplastic polymers especially PEEK show poor wettability and adhesive bonding strength due to the low surface energy. These characteristics do not allow satisfactory adhesion of surface finishes such as paints or effective adhesion in structural bonding of thermoplastic composite structures.

As a solution, surface treatment of the thermoplastic substrate is required to modify their surface chemistry and improve their wetting characteristic [3]. For this purpose, various chemical and physical surface treatments have been developed including solvent cleaning, etchants such as chromic acid, corona discharges, flame and plasma pretreatment [4,5]. However, physical pretreatment methods are preferred in the industry. Plasma surface treatment is often one of the preferred methods as it can provide stronger and more stable surface energy enhancement. Low pressure plasma (LPP) can result in a higher quality of surface treatment, but it has a limiting factor for the size of parts due to the restricted size of the vacuum chambers [5]. To eliminate the expensive limiting vacuum systems, many research studies have been done on atmospheric-pressure plasma (APP) leading to significant improvement in adhesion strength of the thermoplastic composite parts, but still it calls for more investigations [2,5-8].

Another physical method for surface treatment of the thermoplastics is ultraviolet (UV) irradiation technique. UV excimer lamps allow the surface treatment at low surface temperature. In addition, the relative simplicity in using and building a continuous treatment system makes it appropriate for industrial applications [2].

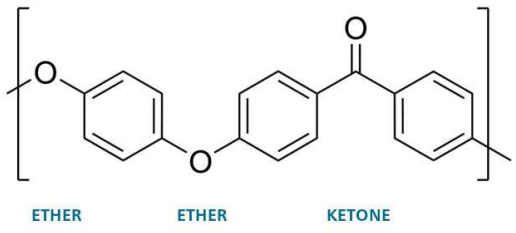

Figure 1. Chemical structure of PEEK.

A recent UV surface treatment technique developed at Henkel Aerospace offers a significant improvement in the adhesion strength to the PAEK family represented by PEEK with the advantage that a very short processing time is sufficient. The emitted photons by UV irradiation can activate or break chemical bonds at the surface of the polymeric substrates. Additionally, the UV irradiation can generate highly reactive ozone formed from oxygen through photolysis. Consequently, the treatment results in the formation of new functional groups at the surface of the thermoplastic substrates increasing the polarity and wettability where many of the new formed functional groups are able to form covalent bonds with the epoxy adhesive leading to very strong bonds.

2. EXPERIMENTATION

2.1 Materials

Adhesives with different curative classes designed for distinct service temperatures were used in this study. Three films adhesives with high temperature cure system which are commercially available including LOCTITE EA 9696, EA 9695, and EA 9658 and two paste adhesives including a room temperature cure adhesive, LOCTITE EA 9394, and an elevated temperature cure paste adhesive, LOCTITE EA 9394/C-2 were used as bonding adhesives for preparing mechanical test specimens including fracture toughness and tensile lap shear specimens. All film adhesives are unsupported (no scrim) with a specific mass of 0.29 kg/m^2. Proprietary customer prepregs for preparing thermoset composite panels with unidirectional fiber orientation as well as PEEK composite panels (carbon reinforced with 5HS fiber pattern) were used to prepare the test specimens for mechanical testing. All thermoset and thermoplastic composite panels had a thickness of 0.16 cm (0.063 in). For secondary bonding trials, LOCTITE EA 9895 WPP was used as a wet peel ply.

A surfacing Film LOCTITE EA 9845 LC with cupper mesh was used to evaluate the effect of the pretreatments on bonding strength of PEEK substrates and epoxy-based surfacing films.

2.2 Treatment Methods

Plasma treatment was done with an Open-air Plasma system with a rotation jet at atmospheric pressure. The treatment was done with a 14-degree nozzle with the following conditions: a travel speed of 6.5 mm/s, a pressure of 10 psi, and a specimen distance of 10 mm.

UV surface treatment was done by using a specific UV excimer lamp and variation in UV intensity was done by adjusting the distance to the lamp and exposure time. Equation 1 shows the relation between UV intensity, lamp-specimen distance and exposure time. UV intensity has a linear correlation with exposure time where it exponentially reduces by increasing the distance to the excimer lamp mainly due to absorption of UV radiation in the ambient atmosphere [2].

$$I_{treatment} = I\,(d).\,t\,\left[\frac{mJ}{cm^2}\right] \qquad [1]$$

Where $I_{treatment}$ is indicating intensity, d is representing the distance between the lamp and specimen and t is time in seconds.

2.3 Test Methods

Double cantilever testing (DCB) was done with rectangular laminated specimens consisting of one carbon-reinforced PEEK panel and one carbon-reinforced epoxy panel bonded by the adhesives. First, a large thermoplastic panel (15.24 cm x 30.48 cm) was treated by UV or plasma pretreatment method. The specimens layup consists of thermoplastic panel, adhesive film, and thermosetting prepregs with UD alignment where bonding was done by co-curing of the adhesive and prepregs mainly in an autoclave at 177 °C (350 °F) under a pressure of 0.6 MPa (90 psi) for 2 h. The large bonded panels were cut into 1.27 cm (0.5 in) wide strips with a length of 30.48 cm (12 in). The test was conducted according to a customer specification to measure mode I fracture toughness energy (G_{1C}). The testing was done with a crosshead speed of 2.54 cm/min where loading was applied to reach a crack with a length of about 10 cm. During the test, each crack arrest position was marked on the edge of the specimen. The area in the load deflection curve between two known crack length positions were measured to calculate the fracture energy.

Tensile Lap Shear tests were done according to ASTM D1002 [9]. First the PEEK panels were abraded in overlap area by a sandpaper with a grit size of 400 and then treated by UV or plasma pretreatment method. To make the specimens, 2 large panels of PEEK with a size about 23 cm x 10 cm where bonded with adhesives along their length with an overlap of 1.27 cm and bond-line of about 0.127 mm. Curing was done in an oven at a specific curing temperature recommended for each adhesive under a pressure of 0.3 MPa provided by clamps. Then the large bonded panels were cut into 2.54 cm wide strips. In the case of notched lap shear specimens, two large pretreated panels with dimensions of 20.3 cm x 20.3 cm where bonded by the film adhesives where curing was done in an autoclave at 177 °C (350 °F) under a pressure of 0.6 MPa (90 psi) for 2 h. The bonded panels were cut into 2.54 cm wide strips notched to give a 1.27 cm overlap at the end.

3. RESULTS

3.1 Surface Analysis

Many studies have been done on surface analysis of PAEK thermoplastic family treated by atmospheric plasma method. Techniques such as contact angle measurement and XPS showed that plasma treatment increases wettability and polarity of the surface of PEEK thermoplastics and composites by forming some oxygen-containing polar functional groups [5-8]. In this study, several surface analysis techniques including XPS, TOF-SIMS, and contact angle measurements have been used to investigate the effect of this new tailored UV method on the surface characteristics.

3.1.1 X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) was conducted to obtain a quantitative and chemical composition analysis of the surface of the thermoplastic composite substrates before and after UV treatment. The information provided by XPS analysis is displayed in Table 1.

Table 1. Elemental analysis of PEEK panels surface with different UV irradiation time.

Treatment method	Treatment time (s)	Average Carbon (%)	Average Nitrogen (%)	Average Oxygen (%)
No treatment	0	78.5	0.9	17.5
UV method	10	66.8	1.6	26.7
UV method	90	64.5	1.0	28.1

Table 1 shows content changes of three elements on the substrate surface due to UV treatment. A very short UV exposure time (10 sec) resulted in a significant increase of oxygen content by about 52% where the longer exposure time resulted in an increase by about 60%. Similar observations have been reported regarding plasma treatment of PEEK substrates in the literature whereas the oxygen content increase by plasma activation is greater (about 75%) [7] suggesting higher proficiency of plasma treatment in increasing surface polarity. These pretreatments lead to the formation of new oxygen-containing functional groups such as carbonyl, carboxyl and hydroxyl groups which significantly increase the polarity and wettability of the surface. In addition, many of these new functional groups are able to form covalent bonds with reactants in adhesives such as epoxy adhesive leading to robust bond lines.

Contact angle measurement was conducted to evaluate the change of wettability after both UV and plasma treatment (Figure 2). As expected, the test showed both activation methods resulted in a significant reduction in water contact angle indicting an increase in polarity and consequently wettability of the surface. Interestingly, plasma activation resulted in lower contact angle values confirming XPS analysis observation where correlation between the level of surface polarity and adhesion strength will be evaluated in the next section.

Figure 2. Contact angle (θ) of a water droplet on PEEK panel surface before and after surface pretreatment.

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an extremely sensitive analytical technique providing elemental, chemical state, and molecular information from the surface of solid materials. In this work, TOF-SIMS was conducted to evaluate and identify the effect of UV irradiation on the chemical structure and composition of the surface of PEEK composite panels. This analytical test confirmed the formation of various new functional groups such as alcohols, aldehydes, ketones and carboxyl groups.

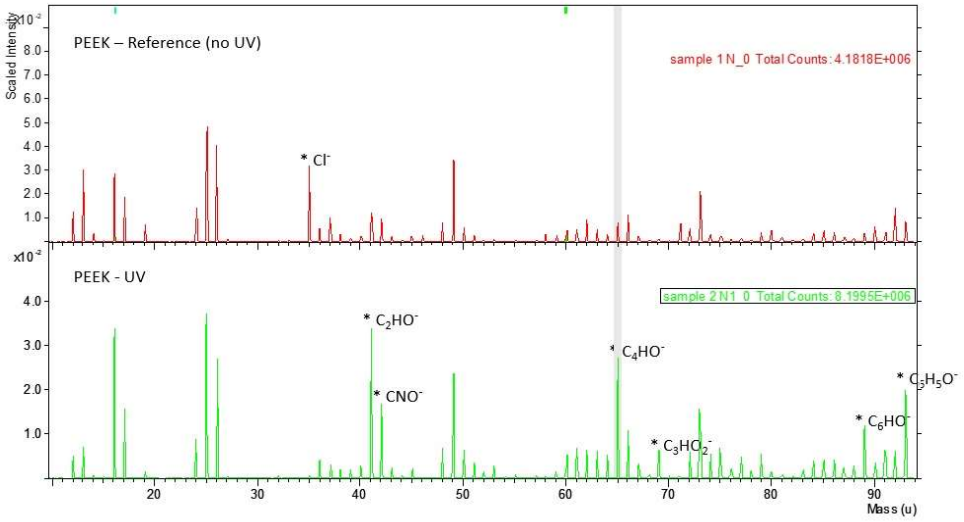

Figure 3. TOF-SIMS spectrum diagrams of PEEK panels before and after UV pretreatment.

The multiple surface analytical techniques demonstrated the efficiency of the UV and plasma pretreatment methods in improving the polarity and wettability of the composite surface by the formation of new functional groups which allow to form covalent bonds with the epoxy adhesives.

3.2 Mechanical properties

3.2.1 Fracture toughness

Fracture toughness was chosen as the key test method to evaluate the bonding capability of the treated thermoplastic PAEK substrates, represented by PEEK, with high temperature-cure film adhesives. This test method measures the toughness of the adhesive captured in G_{1C} value and the adhesive bond failure mode allows for an excellent evaluation of the adhesion performance between adhesive and substrate. For this purpose, LOCTITE EA 9696, EA 9695 and EA 9658 were selected to prepare double cantilever beam (DCB) test specimens for G_{1C} fracture toughness measurements.

Figure 4 shows the effect of surface treatment methods on fracture toughness energy (G_{1C}) of DCB specimens bonded with different epoxy-based film adhesives. The figure illustrates an improvement in adhesive bonding of CF-PEEK to CF-Epoxy substrates by conducting the surface pretreatments; however, the efficiency of each activation method is different. This discrepancy in the performance of UV and plasma activation was confirmed by surface analysis. Plasma treatment results in a greater increase in polarity and wettability of PEEK substrate, but it does not necessarily mean a better performance in improving adhesive bonding of the thermoplastic. In fact, the chemistry of the adhesive also plays an important role on the proficiency of each treatment method. For instance, in the case of PEEK bonding with LOCTITE EA 9658, UV irradiation has a better performance whereas plasma activation is more efficient in PEEK bonding with LOCTITE EA 9695.

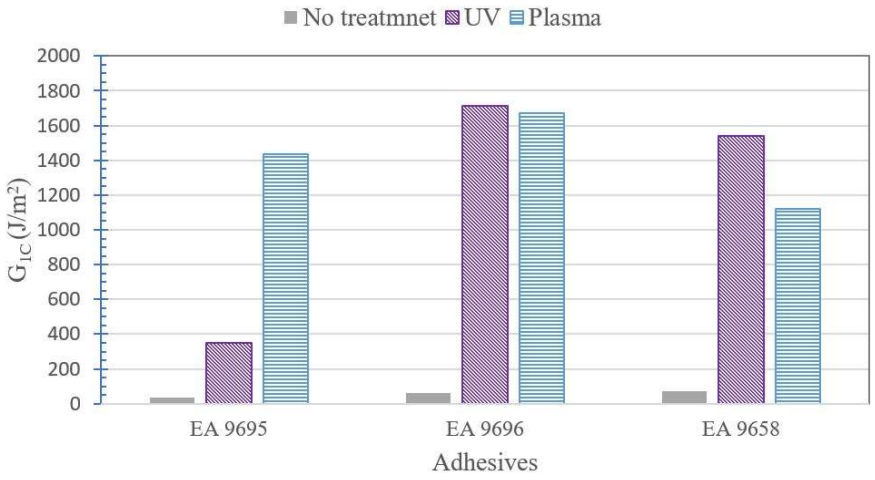

Figure 4. Fracture toughness (G_{1C}) measurements of PEEK samples bonded with EA 9696, EA 9695, and EA 9658 with and without UV and plasma pretreatment.

Adhesive bond failure mode as illustrated in Figure 5 clearly indicate the effect of the both treatments on improving adhesion strength. The failure mode for all untreated substrates was 100% adhesion failure to the PEEK substrate. In contrast, UV and plasma activation directed the fracture failure mode to mainly substrate failure except in case of bonding UV treated substrate with EA 9695 where the main failure is adhesion failure with some level of cohesion failure of the adhesive.

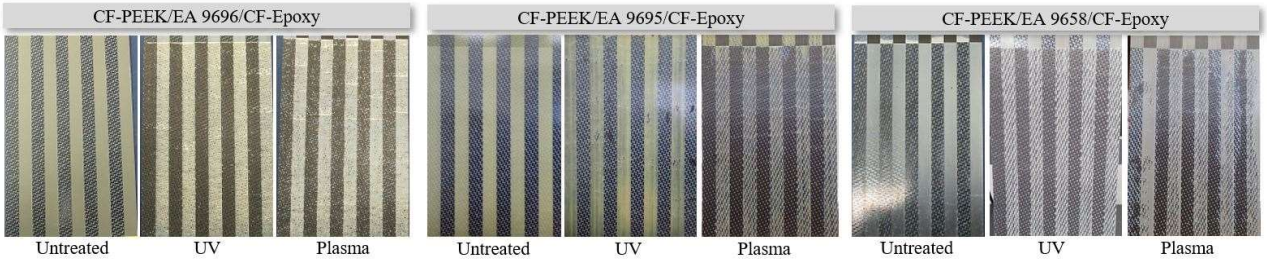

Figure 5. Adhesive bond failure mode of DCB specimens with and without UV and plasma pretreatment. The thermoplastic and thermoset strip from each DCB specimen are paired where the black 5HS woven pattern strip is PEEK.

A deeper study in the chemistry and formulation of LOCTITE EA 9695 was done for better understanding the cause of the substantial discrepancy in the performance of UV and plasma activation in PEEK bonding. Theoretically, the adhesion strength of bonding with a specific adhesive depends upon rheological behavior, polarity and surface tension, as well as chemistry and reactive functional groups of the adhesive. In this study, we found out the curing mechanism and rate of the adhesive plays a very important role in bonding of UV treated PEEK substrates. In this regard, slight modification in curative formulation was done to change the reactivity of EA 9695. The results suggested that an optimization in the adhesive curing rate is favorable to achieve strong adhesion strength likely by controlling chemical bonding between adhesive and new functional groups formed on the activated substrate. Figure 6 shows how the curing rate

modification strongly enhanced bonding of UV treated PEEK and improved failure mode from adhesion failure to mainly substrate failure.

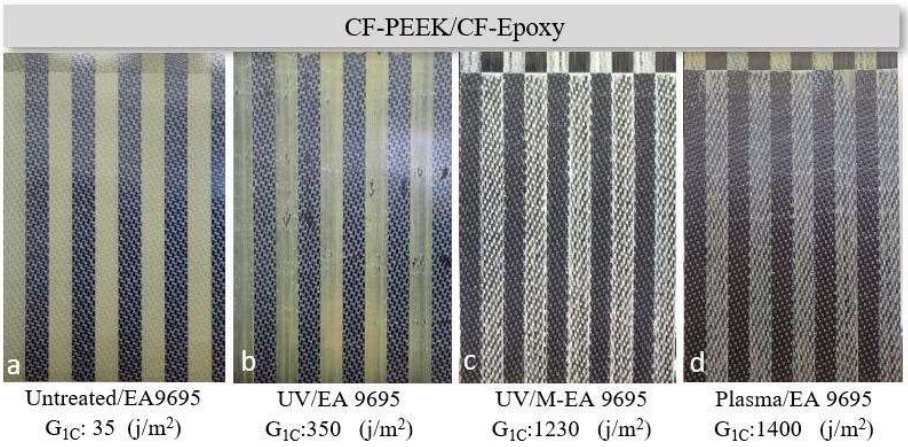

Figure 6. Adhesive bond failure mode of DCB specimen a) untreated/EA 9695, b) UV/EA9695, C) UV/Modified (M)-EA 9695, d) Plasma/EA9695. The thermoplastic and thermoset strip from each DCB specimen are paired where the black 5HS woven pattern strip is PEEK.

Although UV and plasma treatment have almost similar performance in adhesive bonding of PEEK substrates in most cases, it is noteworthy that the areal activation rate (m^2/s) of UV method is about 10 times faster than that of plasma activation which favors the UV treatment with regard to high throughput applications especially for large parts and substrates. For instance, required treatment time for a DCB size panel (20 cm x 35cm) by a UV bulb with a size of 10 cm is about 20 - 40 sec, but by one plasma jet is about 5-7 min.

3.2.2 Bonding Types: Co-Bonding and Secondary bonding

To determine the scope of application opportunities that the newly developed UV based method provides, the fracture toughness samples prepared with multiple bonding methods including co-bonding inside autoclave, co-bonding Out of Autoclave (OoA), and secondary bonding have been evaluated. LOCTITE EA 9696 adhesive was selected for this side by side comparison. In Figure 7, for both co-bond inside and out of autoclave, G_{1C} values (≈1600 J/m^2) are nearly identical and mainly substrate failure was observed. The lower G_{1C} values (1170 J/m^2) for the secondary bonding can be explained by the observed peel ply failures on the thermoset composite panel and no adhesion failure to the thermoplastic PEEK substrate was noticed.

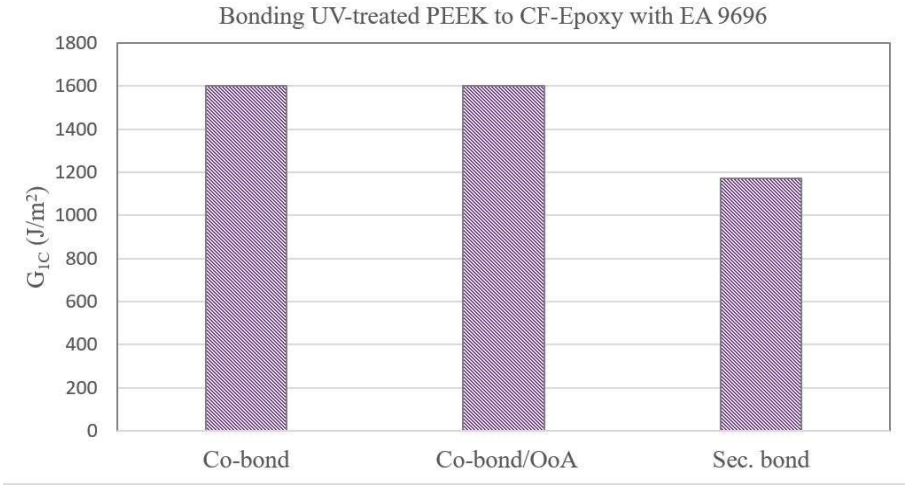

Figure 7. Comparing different bonding of UV treated PEEK to CF-Epoxy

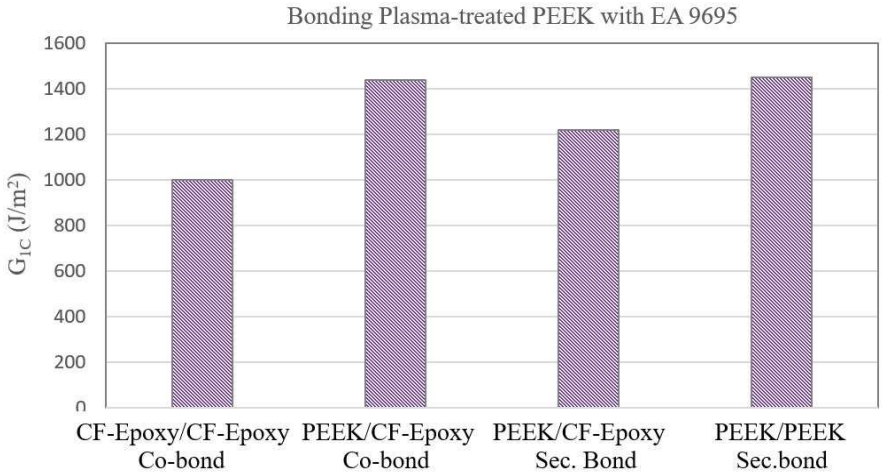

Figure 8. Comparing different bonding of Plasma treated PEEK to CF-Epoxy

The performance of plasma treatment for secondary bonding of PEEK substrate with EA 9695 has been evaluated. Figure 8 shows DCB results for co-bonding and secondary bonding of PEEK which demonstrates the high efficiency of the activation for different bonding types. In other words, the treatment leads to almost identical strength for co-bonding and secondary bonding. It is noteworthy that the flexibility of the substrate affects G_{1C} values via affecting stress distribution during running the test. G_{1C} values of co-bonded PEEK/CF epoxy is higher than that of co-bonded thermoset CF-epoxy since PEEK composite (5HS) has less rigidity compared to CF-Epoxy (UD).

3.2.3 Tensile lap shear

Tensile lap shear is a common test method to evaluate the adhesion strength of adhesive bonding of various substrates in Aerospace industry. In this section, single tensile lap shear and notched tensile lap shear were used to evaluate the effect of UV and plasma treatment on improving PEEK

substrates bonding with room and elevated temperature-cure paste adhesives and high temperature-cure film adhesives respectively.

Figure 9 shows tensile lap shear strength of PEEK specimens treated by UV or plasma and bonded with LOCTITE EA 9394 and EA 9394/C-2 which are room-temperature and elevated temperature cure (>93 °C) adhesives respectively. The results proved a significant improvement in PEEK bonding with UV and plasma activation almost with the same performance. However, the failure mode was mainly adhesion failure with some level of substrate failure.

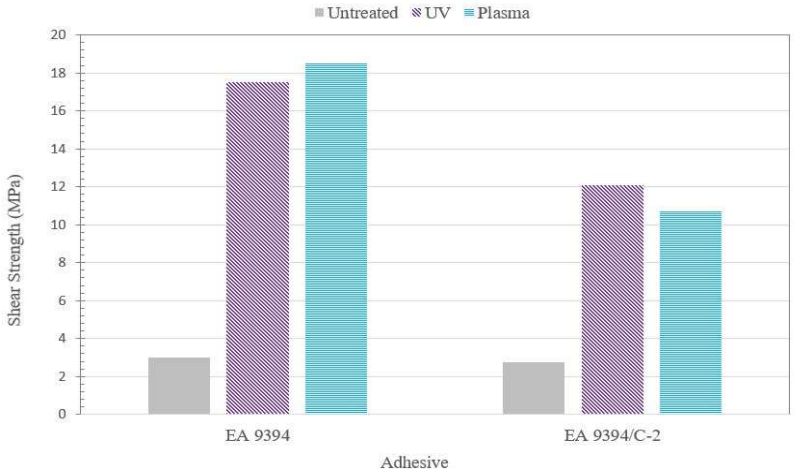

Figure 9. Tensile lap shear of PEEK substrates bonded with a room-temperature cure (EA 9394) and an elevated-temperature cure (EA 9394/C-2) paste adhesive with and without pretreatments

To further study this new tailored UV treatment effect on PEEK bonding with film adhesives, notched tensile lap shear test has been used to validate DCB test results. Table 2 and Figure 10 show shear strength values and failure mode of PEEK specimens bonded with LOCTITE EA9696 and EA9658. High shear strength and substrate failure mode confirmed that UV treatment significantly enhances the bonding strength.

Table 2. Shear streangth and failure mode of UV treated PEEK specimens bonded with film adhesives.

Specimen	Surface treatment	Shear strength (MPa)	*CV (%)	Failure mode
CF-PEEK/EA 9658	Untreated	3.5	18	Adhesion failure
CF-PEEK/EA 9658	UV treated	25.3	5	Mainly substrate failure
CF-PEEK/EA 9696	Untreated	3.2	12	Adhesion failure
CF-PEEK/EA 9696	UV treated	26.7	2	Mainly substrate failure

*CV: Coefficient of variation

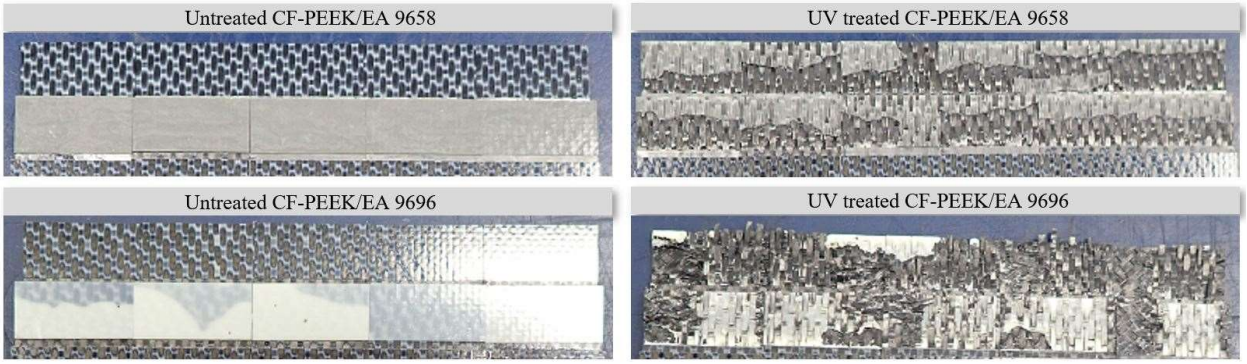

Figure 10. Adhesive bond failure mode of notched tensile lap shear specimens with and without UV treatment.

Overall the mechanical tests including fracture toughness and tensile lap shear tests conclude that the new tailored UV pretreatment method allows for forming very strong bonds to the thermoplastic PEEK substrate comparable with plasma activation. However, the efficiency of each pretreatment on improving adhesive bonding of PEEK substrates strongly depends upon the chemistry and characteristics of the adhesive as well.

3.4 Surfacing film application

Surface pretreatment of thermoplastic composites is not only essential for adhesive bonding, but it is also required for cosmetic applications and painting. Thermoplastic and thermoset composite structures that are exposed to environmental conditions or need to meet certain aesthetic requirements typically include a surfacing film with or without lightning strike protection to provide the required surface properties to the composite structures prior painting.

To demonstrate the efficiency of UV and plasma pretreatment on adhesion strength between a surfacing film and a PEEK composite panel, the epoxy-based LOCTITE EA 9845 LC (with cupper mesh as lightning strike protector) was used as a surfacing film. The adhesion strength evaluation of the surfacing film cured at 177 °C inside autoclave (0.62 MPa pressure) and out of autoclave (vacuum pressure) was done by Cross Hatch test method (Figure 11). Untreated substrate has very poor adhesion to the surfacing film whereas pretreated samples (Figure 11b and c) showed excellent crosshatch rating of 10/10 indicating strong adhesion. It is noteworthy that the test showed similar efficiency of the both pretreatment methods for improving bonding of the surfacing film to PEEK substrate. In addition, similar results were observed for specimens cured at a lower temperature (121 °C).
This example indicates that the UV and plasma pretreatment methods can be used for bonding a wide range of epoxy-based thermosetting materials and are not exclusively limited to epoxy adhesives.

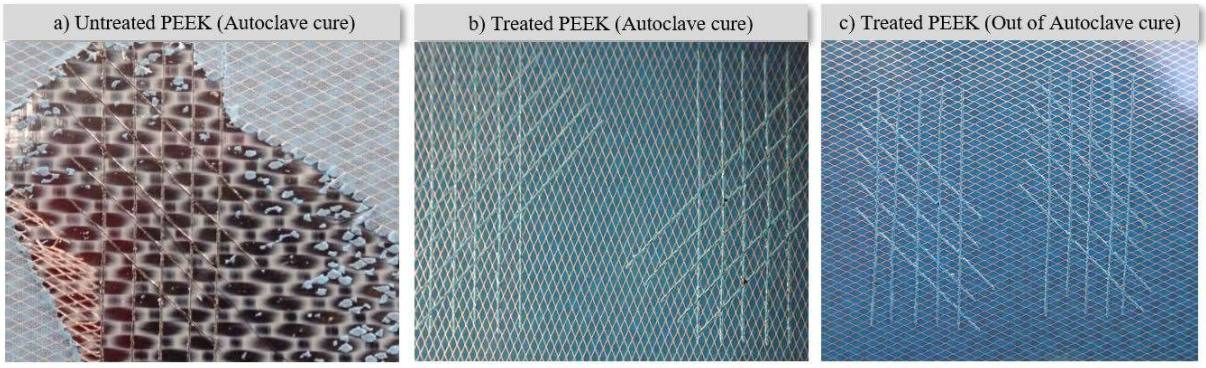

Figure 11. Effect of pretreatment on bonding of surfacing film to PEEK composite panels: Inside and out of autoclave cured at 177 °C.

4. CONCLUSIONS

In a side by side comparison, the effect of a new tailored UV surface pretreatment versus plasma activation on adhesive bonding strength of PEEK thermoplastic composite substrate was evaluated. In this regard, analytical techniques were used to learn the effect of the treatments on surface characteristics of the substrate and mechanical tests including double cantilever beam and tensile lap shear test were conducted to examine bonding strength.

After only 10 seconds of UV irradiation, surface analysis by XPS and TOF-SIMS revealed a significant increase in oxygen content (17% to 26.7%) due to the formation of new polar groups such as carboxylate, carbonyl, hydroxyl, aldehyde, and ketone groups at the surface. Similar observation related to plasma treatment of PEEK have been reported in the literature except with a higher oxygen elemental increase. Water contact angle measurements showed a substantial reduction in the values after treatment where plasma activation resulted in much lower contact angle values indicating higher efficiency of plasma activation in increasing wettability and polarity of PEEK surface. These chemical modifications at the surface overcome the low surface energy of the thermoplastic and lead to a much better wettability of the surface. In addition, the new formed chemical groups allow for covalent bonding to the epoxy-based adhesives resulting in dramatically improved bonding strength (G_{1C}: 1600 J/m^2) with mainly substrate failure. Plasma treatment results in a greater increase in polarity and wettability of PEEK substrate, but it does not necessarily mean a better performance in improving adhesive bonding of the thermoplastic, as the mechanical results showed that the performance of each treatment is not only defined by surface characteristics of the pretreated substrates, but also depends upon the chemistry, curing rate and mechanism of the adhesive.

The capability of UV and plasma activation was evaluated for different bonding types. The results showed high efficiency of UV treatment for co-bonding inside and outside of autoclave and secondary bonding in autoclave. Similar results were observed regarding the proficiency of plasma activation in improving different bonding types such as co-bonding and secondary bonding of PEEK substrates. Tensile lap shear tests showed high efficiency of the both treatment techniques for improving bonding of the thermoplastic composite with epoxy-based adhesives containing

different curatives including high temperature cure (121 and 177 °C), elevated temperature cure (93 °C), and room temperature cure (25 °C) formulation.

UV and plasma pretreatment methods can be used for bonding a wide range of epoxy-based thermosetting materials and are not exclusively limited to epoxy adhesives. In regard to a cosmetic application, the adhesion strength of an epoxy-based surfacing film to a thermoplastic PEEK substrate by using the both treatment methods was evaluated where the surfacing film was cured as different conditions including inside and out of autoclave at 121 and 177 °C. In a side by side comparison, the crosshatch testing showed nearly perfect adhesion of the treated samples with both activation methods whereas the untreated specimens displayed adhesion failure to the PEEK surface.

In conclusion, the new UV treatment method offers new opportunities for fast and safe bonding to thermoplastic materials resulting in excellent bond strength comparable with plasma activation with the advantage of a much shorter activation time. However, the efficiency of each pretreatment method strongly depends on the chemistry of the bonding adhesive as well.

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