THE EFFECT OF SURFACE TREATMENTS ON THE BEHAVIOUR OF ADHESIVELY BONDED, THERMOPLASTIC COMPOSITE LAP JOINTS

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Keywords: Thermoplastic composite, surface treatment, lap joint, adhesive bonding, degree of cure

Abstract

Adhesive bonding of composite materials reduces the requirement for penetrating fixtures that add weight and influence the geometry of the structure. Thermoplastic resin composites are currently of great interest, as they possess greater fracture toughness, are potentially recyclable and form imperishable prepregs, in comparison to their more commonly used thermosetting resin counterparts. However, thermoplastic resin composites present challenges when they are adhesively bonded. They have relatively low surface energies and do not adhere to adhesives as readily as their thermosets [1]. It is therefore desirable to improve the adhesive properties of thermoplastic composites to improve the adhesive bonded strength. Improvement of the adhesive properties through enhancement of surface energies has been previously demonstrated to increase the peel strength of adhesively bonded thermoplastics, demonstrating the efficacy of surface modification in affecting the behaviour of the adhesive substrate bonds strength for this load case [2]. This work will determine the effect of surface modification methods on lap shear strength.

The following study describes the behaviour of adhesively bonded single lap joints, with and without surface treatments. The effect of UV/Ozone (UV/O_3) and atmospheric plasma discharge surface treatments, on the static behaviour and strength of thermoplastic composite single lap joints (SLJs), is characterised. All SLJs in this study were sandblasted and degreased (using a non-linting solvent wipe) prior to adhesive bonding.

An improvement in joint lap shear strength (LSS) occurred after surface treatments, using both UV/O_3 and atmospheric plasma. When compared with SLJs that had been sandblasted only, the UV/O_3 LSS improved by 18.2% and the atmospheric plasma discharge LSS improved by 22.2%.

1. Introduction

Thermoplastic matrix composites possess excellent resistance to chemical attack and are anhygroscopic. The thermodynamic stability of the thermoplastic, which is responsible for these properties, also yields low adhesive properties due to relatively low surface energy. This low surface energy means that adhesively bonded joints perform relatively poorly when compared to thermosetting counterparts. The creation of large composite structures necessitates the use of joints and consequently, the issue of poorly performing adhesively bonded joints needs to be addressed. More specifically, to prevent disbond of the adhesive from the thermoplastic substrate during loading, the interfacial strength of the adhesive and thermoplastic composite must be improved. This can be achieved through surface modification methods that can potentially improve adhesive properties.

This paper examines the effects of UV/O_3 and atmospheric plasma discharge surface modification methods on the lap shear strength of thermoplastic composite single lap joints. The composite material that is the subject of this investigation, is Poly(ether ketone ketone) (PEKK) resin with a uni-directional carbon fibre reinforcement. The effect of both UV/O_3 and plasma treatments on the surface of the PEKK/carbon is examined using attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR). The wettability response, surface energy analysis +along with topographical analysis of the plasma discharge surface treated material, are also presented. The effect

of these surface treatments on the degree of cure of the epoxy adhesive, used to bond the SLJs, was determined using differential scanning calorimetry (DSC).

2. Materials

The composite laminate used in this study had a quasi-isotropic lay-up of $[0^o, 45^o, 90^o, -45^o]_{2s}$. This lay-up is not quite representative of the type of lay-up commonly used in composite structures, as it has 0^o surface plies rather than a 45^o ply (to improve damage tolerance [3]). The adhesive used was FM300k, an epoxy resin with a wide-knit carrier weave that is commonly used in many industrial practices.

3. Experimental method

A design of experiment methodology (DOE) using a Taguchi array was implemented to examine the influence of, and interaction between, surface treatment parameters. The surface treatments used were UV/O_3 and atmospheric plasma discharge. For the UV/O_3, the parameters were exposure time, UV/O_3 chamber temperature during exposure and post-exposure hold time (aging). The atmospheric plasma parameters were proximity of plasma jet to sample surface, speed of traversing plasma nozzle and number of passes over the sample surface during treatment. Five samples were used for each experimental condition, twenty in total for each DOE study. All samples were sandblasted and cleaned prior to application of the adhesive. The SLJs were statically loaded in tension to find the LSS, in accordance with ASTM D5868 (Standard Test Method for Lap Shear Adhesion for Fibre Reinforced Plastic Bonding) [4,5].

The UV/O_3 surface treatment was performed using a Novascan PSD Pro Series UV/Ozone system.

The atmospheric discharge plasma surface treatment was performed using a PlasmaTreat^{TM} system shown in figure 1.

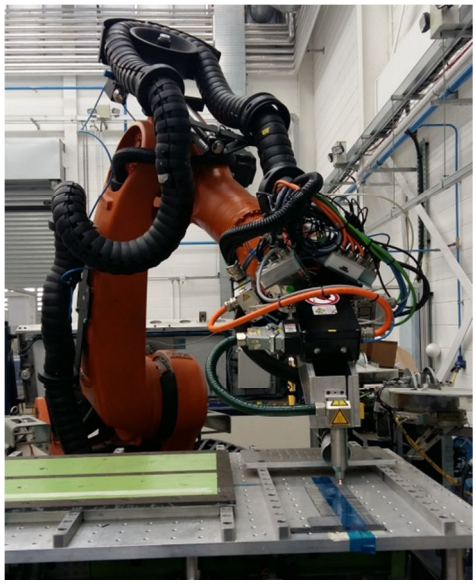

Figure 1: PlasmaTreat^{TM} system mounted on 5-axis robotic arm

The PlasmaTreat^{TM} unit was mounted on a 5-axis robotic arm which controlled all movements. Since plasma is a dynamic surface treatment method, both the effect on surface topography and surface energy have been quantified in this work.

The surface energy was quantified using a Krüss mobile drop analyser. This method uses three fluids, of known surface energies, to ascertain the surface energy of the substrate through contact angle measurement and the Owen-Wendt method [6]. In order to characterise the effect of UV/O_3 on

the adhesive properties of the composite, a wettability study was conducted, with five samples for each condition. The contact angle of a drop of distilled water was measured to show changes in the surface hydrophobic properties [7].

The surface chemistry of the PEKK/carbon was analysed using attenuated total reflection Fourier transform infra-red spectroscopy (ATR-FTIR) and the topographical changes were quantified using scanning electron microscopy (SEM), optical profilometry and atomic force microscopy (AFM).

4. Single lap joint tensile tests

4.1 Sample preparation

The LSS of the adhesively bonded SLJs, statically loaded in tension, was measured. Three types of adhesively bonded SLJs were included in this study, no surface treatment, UV/O_3 surface treated and atmospheric plasma discharge surface treated. The geometry of the joints were in accordance with test standards ASTM D5868 (lap joint geometry) and ASTM D3165 (end tab specification), figure 2.

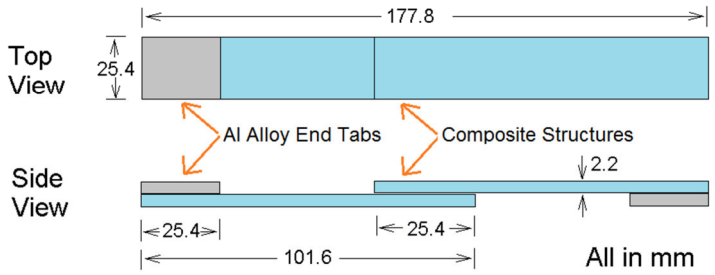

Figure 2: Single lap joint geometry

The use of end tabs is not specified by the ASTM D5868 standard, but they have been included in the geometry in this study to ensure the joint is loaded centrally through the joint interface and reduce any applied eccentric forces during tensile loading. The SLJ end tabs have been bonded to the sample using a high stretch, two-part epoxy resin as recommended by ASTM D3165.

4.2 Results

4.2.1 Influence of UV/O_3 and plasma surface treatment variables on LSS

Initial work characterising the strength and behaviour of PEKK/carbon adhesively bonded SLJs without surface treatment was performed. All of the untreated, adhesively bonded SLJs failed primarily through of cohesive failure of the adhesive layer with a small amount of adhesive/substrate disbond. All the SLJs that were subjected to UV/O_3 and atmospheric plasma discharge surface treatments, failed cohesively in the adhesive layer. A Taguchi orthogonal array was used to formulate an investigation into the effect of UV/O_3 and atmospheric plasma discharge on the LSS and mode of failure. The variables considered for UV/O_3 treatment were exposure time, temperature during exposure (chamber temperature) and post-exposure hold time. The percentage contribution to the result, i.e. the LSS, is shown below in figure 3.

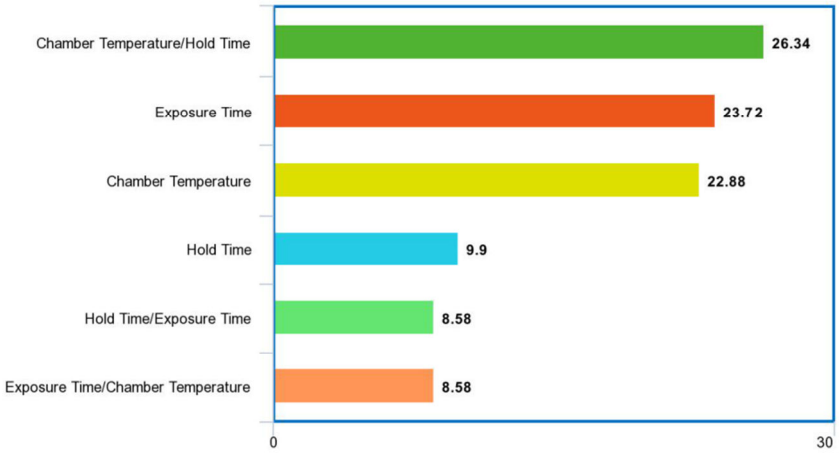

Figure 3: UV/O_3 surface treatment variables percentage contribution to variation (LSS)

Statistical analysis of UV/O_3 the results showed that exposure time was the most influential single factor in improving SLJ lap shear strength. This experiment also showed that retention of joint strength during post-exposure hold time could only be influenced by increasing chamber temperature. The variables considered for plasma treatment were plasma nozzle travelling speed, nozzle distance from surface and the number of passes over the same treatment area. Statistical analysis of the atmospheric plasma discharge surface treatment results showed that the greatest influencing single factor on lap joint strength was the plasma nozzle distance from the substrate surface, indicating that plasma intensity is the dominating factor in plasma surface treatment efficacy when considering LSS.

4.2.2 Lap shear strength (LSS)

The LSS results for the SLJs, that received optimised surface treatment, for both UV/O_3 and plasma discharge, according to the DOE analysis for each method, are shown in figure 4. The atmospheric plasma discharge and the UV/O_3 surface treated SLJs demonstrated an improvement of 18.2 ± 6 % and 22.2 ± 1.9 % respectively.

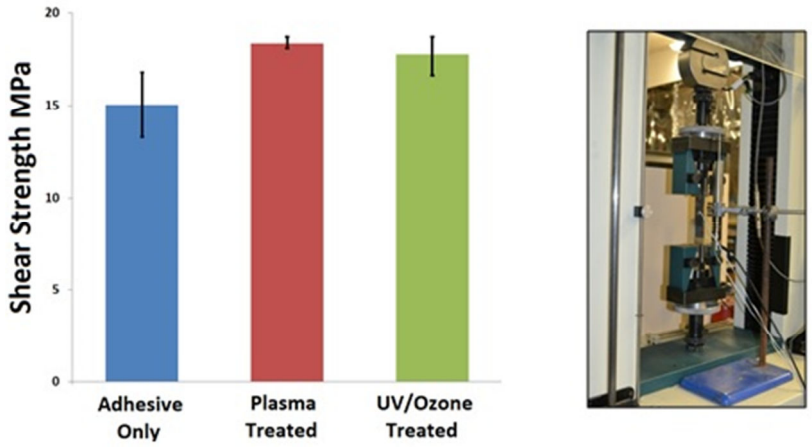

Figure 4: SLJ shear strengths with experimental set-up

5. Surface modification characterisation

5.1 ATR-FTIR analysis

An investigation using ATR-FTIR analysis could not ascertain any changes in the surface chemistry of the PEKK/carbon for either UV/O_3 or atmospheric plasma discharge treatments, figure 5.

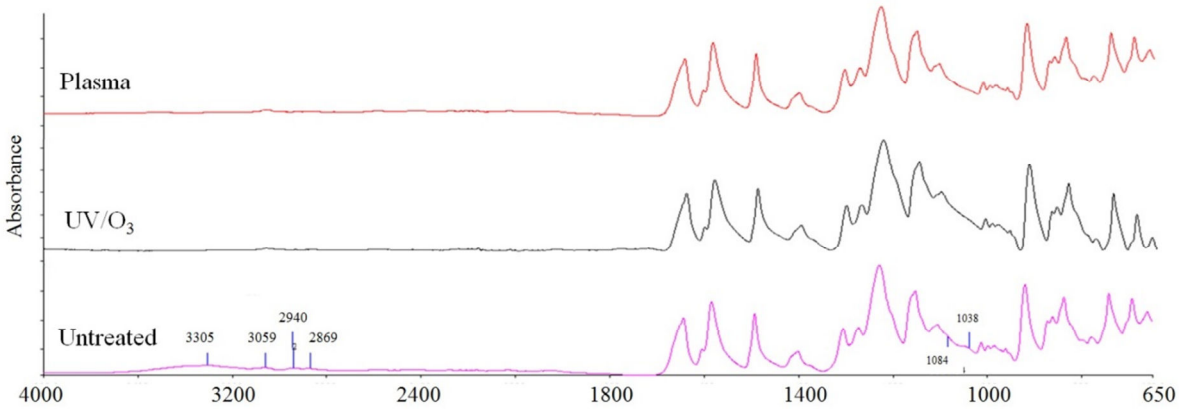

Figure 5: ATR-FTIR surface analysis of surface modified PEKK/carbon

However, the removal of both water (at 3305cm^{-1}) and mould release agent, polydimethylsiloxane (PDMS) (at 1084cm^{-1} and 1039cm^{-1}), can be established. The wavelength of the absorption peaks for both water and PDMS were confirmed through separate ATR-FTIR analysis of these materials. This shows that both UV/O_3 and plasma discharge can be used as effective cleaning and bonding preparation methods. It is possible that the ATR-FTIR analysis method includes too great a proportion of the bulk material to distinguish any changes in the surface chemistry. In the case of UV/O_3 surface treatment, it is possible that the O_3 has been physisorbed by the substrate. However, since no chemical changes would have taken place during physisorption, this cannot be detected using ATR-FTIR.

5.2 Surface wettability after UV/O_3 treatment

A wettability study, using the sessile drop method, was conducted to characterise the changes in surface energy due to UV/O_3 surface treatment [7]. The UV/O_3 surface modification was performed using a UV ozone system (Novascan PSD Pro Series), figure 2. This system uses a mercury-vapour grid lamp, with rear reflector, to generate ultra-violet light, at 185nm, within an enclosed chamber to create ozone to which the samples are exposed. The contact angle was measured at intervals of both exposure time and post-exposure hold time (aging), with five measurements for each condition to ensure a statistically reliable result. All measurements were made at a constant temperature of 24^{o}C. The contact angle was measured using digital imaging of the droplet on the material surface and analysed using *ImageJ* software. The contact angle as a function of UV/ozone exposure time and post-exposure hold time is shown in figure 6.

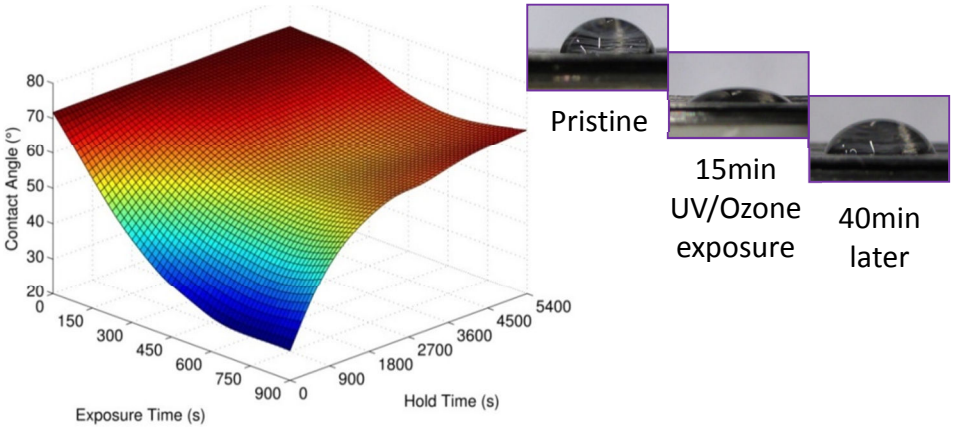

Figure 6: Contact angle response to UV/O_3 surface treatment

The wettability of the composite surface to UV/O_3 exposure and post-exposure hold time (aging), shows that the thermoplastic composite surface achieved maximum wettability/reduction in hydrophilicity after 10 minutes exposure and that nearly full hydrophobic recovery was observed after 2700 seconds (45 minutes), figure 5. The contact angle response to UV/O_3 exposure reaches a minimum value of 27.7° after 600 seconds and does not reduce further with additional exposure. After 2700 seconds (45 minutes), near full hydrophobic recovery of the PEKK/carbon was observed, as the contact angle increases to 58° close to the untreated contact angle of 71.7°. However, since the effect of the UV/O_3 surface treatment decays exponentially, some evidence of a reduction in contact angle can be seen 5400 seconds (90 minutes). No topographical analysis was performed on the UV/O_3 treated PEKK/carbon surface as no changes in the topography were expected to occur. This is because UV/O_3 surface treatment is not performed using a dynamic discharge stream; it occurs in an atmosphere partly composed of ozone gas and no force is applied to the substrate surface during treatment.

5.3 Surface energy after atmospheric plasma treatment

There is a positive correlation between total surface energy and an increase in the lap shear strength, figure 7. The surface energy is comprised of two parts: polar energy, which originates from the thermodynamic properties; and dispersive energy, which is a characteristic of the individual molecule (Van der Waal force). An increase in polar energy can improve the adhesive properties of a surface and thus increase bond strength.

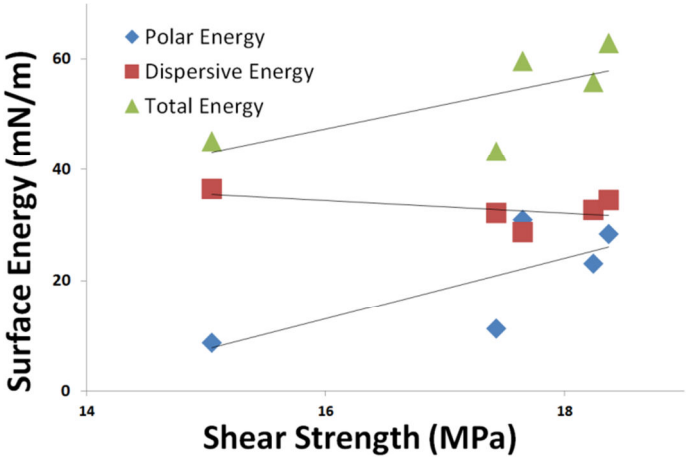

Figure 7: Surface energies of atmospheric plasma discharge treated PEKK/carbon

However, polar energy changes can occur due to both changes in the surface chemistry and the physisorption of molecules with active sites. The above investigation contributes evidence supporting changes in the surface chemistry since the dispersive energy, which is a characteristic of the specific material molecule, is seen to change with changing polar energy.

5.4 Topographical analysis of plasma treated surface

5.4.1 SEM analysis

Initially, the surface was examined using scanning electron microscopy, figure 8. In order to better characterise the effect of the plasma on the surface topography, the plasma discharge was applied to a sample that had not been sandblasted i.e. an untreated surface. The SEM images below of the plasma (only) treated surface show no clear evidence of ablation. The effect of the abrasion (sandblasting) however, is very clear, with broken fibres and cracked matrix evident in the upper 0^{o} ply. This damage, which is part of the surface preparation for adhesive bonding in this study, does not penetrate the full depth of the upper lamina.

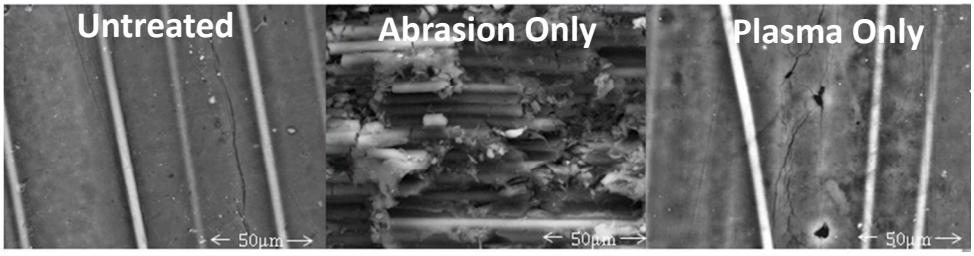

Figure 8: SEM of PEKK/carbon surface untreated, abraded only and plasma treated

5.4.2 Optical profilometry measurement of plasma treated surface

A microscale analysis using optical profilometry (Alicona InfinteFocus), to measure the arithmetic mean height (S_a) of the surface roughness peaks of each sample, yielded the results given in figure 9. The plasma surface treatment reduced the mean peak height by 49.5%. This reduction in surface roughness diminishes the well-established surface interlocking effect that can improve LSS.

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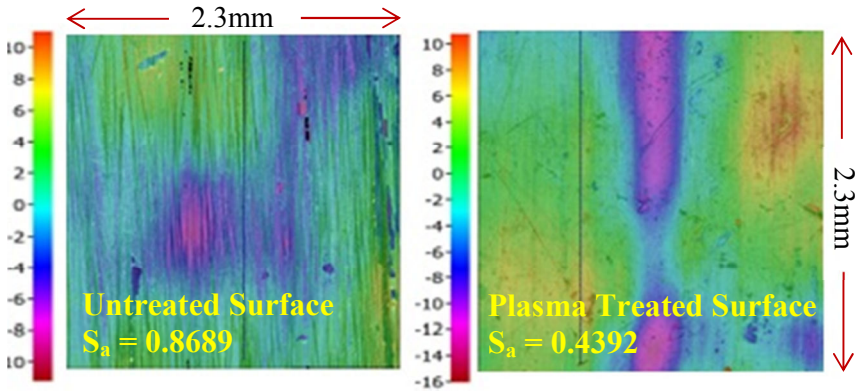

Figure 9: Surface roughness profiles of untreated and plasma treated PEKK/carbon surfaces

The kurtosis sharpness (S_{ku}) of the roughness profile denotes the distribution range of surface peak heights. For these samples, the distribution of peak heights yields a normal distribution (where, $S_{ku} \approx 3$) for the untreated surface, but is leptokurtic (where, $S_{ku} > 3$) (i.e. more concentrated about the mean peak height value) for the plasma treated surface. This measurement shows that the plasma treated surface has a more uniform distribution of surface peaks than the untreated surface. It implies that the plasma treatment method was performed evenly and indicates that plasma treatment could provide relatively low variation in process outcomes. Additionally, the uniformity of the surface roughness

distribution could be beneficial as a mechanically interlocking mechanism as it promotes a greater degree of contact between opposing surface peaks.

The peak height is considered to consist of an upper (V_{mp}) and lower (V_{vv}) peak region, occurring at 10 and 80% of material ratio, according to the standardised surface texture areal measurement methods [8], table 1. The core (V_{vc}) and valley (V_{vv}) void volume of the surface provide insight into the shape of the surface topography by quantifying volume between surface roughness peaks over a given area, table 1. These measurements differ greatly for untreated and plasma treated surfaces. Note, since the peak material volume (V_{mp}) is similar for both untreated and plasma treated surfaces, comparing the sum of V_{vc} and V_{vv} gives an accurate method to determine the surface volume of each sample. The overall core and valley void volume ($V_{vc} + V_{vv}$) shows a decrease in overall volume after plasma treatment. This reduction in overall volume may be detrimental to the adhesive properties of the surface, since it reduces the volume into which a low viscosity adhesive can ingress and reduces the surface area to which the adhesive can bond**.**

Roughness Parameter	Untreated Surface	Plasma Treated Surface
S_a	0.8689µm	0.4392µm
S_{ku}	3.7563	14.9014
S_k	2.8231µm	1.3743µm
V_{vc}	1.2112	0.6617
V_{vv}	0.6617	0.0660

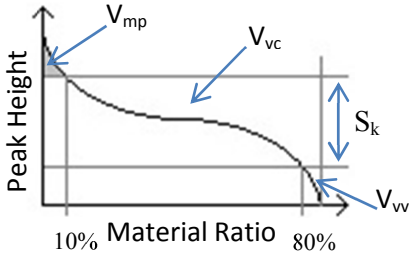

Table 1: Roughness parameters for untreated and plasma treated PEKK/carbon with figure

5.4.3 AFM analysis of plasma treated surface

Investigation of the nanoscale surface topography, using AFM, was performed on the PEKK resin regions that occur between the carbon fibres, figure 10. The PEKK resin region was analysed in isolation as the diameter of the carbon fibres (7µm) exceeds the maximum upper limit that can be measured using AFM peak height analysis, which is approximately 500nm.

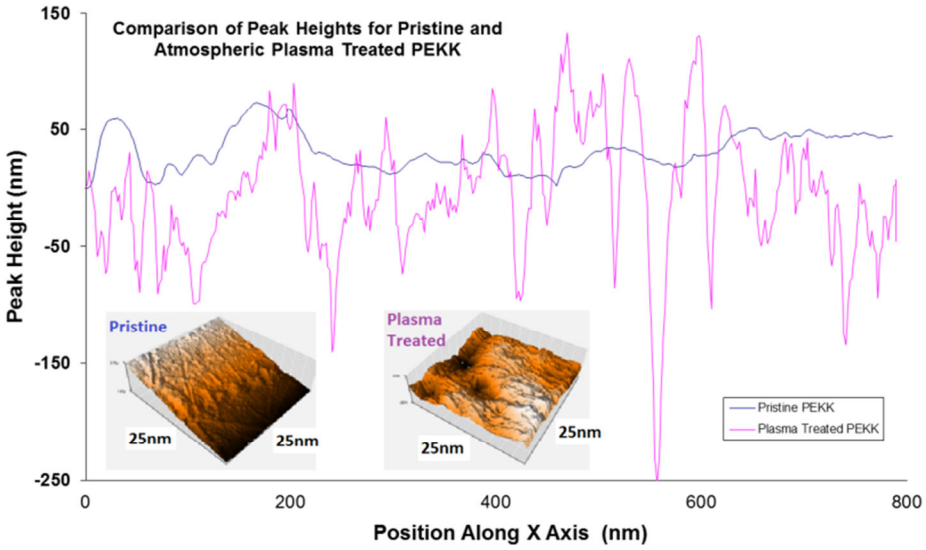

Figure 10: AFM surface analysis of untreated and plasma treated PEKK

This analysis reveals a surface roughening effect on the PEKK regions produced by plasma surface treatment.

Roughness Parameter	Untreated Surface	Plasma Treated Surface
S_a	40.524nm	59.524nm
S_{ku}	1.579	1.700

Table 2: Nanoscale roughness parameters for PEKK regions on composite surface

The roughness of these regions is seen to increase by 46% after plasma ablation, when compared to the untreated surface. The kurtosis of the peak height distribution is similar for both untreated and plasma treated material and denotes a broad, relatively even range of surface peak heights. Since the topography of the surface is known to consist of peaks up to 1μm (from optical profilometry analysis), the roughening effect shown by the AFM analysis is a secondary ablation on the microscale surface peaks previously discussed in figure 9.

6. The effect of substrate surface modification on epoxy adhesive

All the SLJs, that were subjected to surface modification treatments, exhibited the same tensile lap shear failure mechanism, cohesive failure in the adhesive layer. The behaviour (i.e. LSS) of this failure mechanism should be dominated by the material properties of the adhesive layer. It is contradictory that LSS varies for different surface modification methods since the epoxy adhesive (FM300k) and cure method is identical for all SLJs. In addition, the untreated SLJs also failed primarily through cohesive failure of the adhesive layer and should arguably have a LSS similar to the surface-modified SLJs than is evident here, where the disparity is between 18.2 and 22.2%, depending on surface modification method.

The degree of cure, i.e. extent of development of long chain molecule crosslinking, is a determining factor in both the stiffness and shear strength of an epoxy polymer. For a cured epoxy, the degree of cure can be determined by quantifying its endothermic behaviour during a thermally dynamic process. Differential scanning calorimetry (DSC) was performed on the epoxy adhesive removed from SLJs that were untreated, UV/O_3 surface treated and atmospheric plasma surface treated, figure 11. Three samples were analysed for each experimental condition to ensure a statistically reliable result [9]. A clear endothermic reaction occurs at the cure temperature (176.79^{o}C) for the epoxy adhesive removed from the untreated SLJs. There is no residual cure evident for the adhesive from the SLJs that had been subjected to surface modification. In addition, an increase in thermoset degree of cure correlates with an increase in glass transition temperature (T_g). The T_g of a thermosetting polymer can be quantified by identifying the occurrence of a change in heat capacity (C) of the polymer. Measurements of the T_g from similar transitions of C during heating show that the T_g increases from 100^o (untreated SLJ adhesive) to 105^{o}C after atmospheric plasma surface treatment. There is no statistically significant change in T_g after UV/O_3 treatment.

It is possible that the increase in polar surface energy observed after atmospheric plasma surface treatment, is improving the degree of crosslinking occurring during the epoxy cure cycle, and therefore its degree of overall cure. This improvement in degree of cure of the epoxy adhesive may be contributing to the overall improvements in LSS.

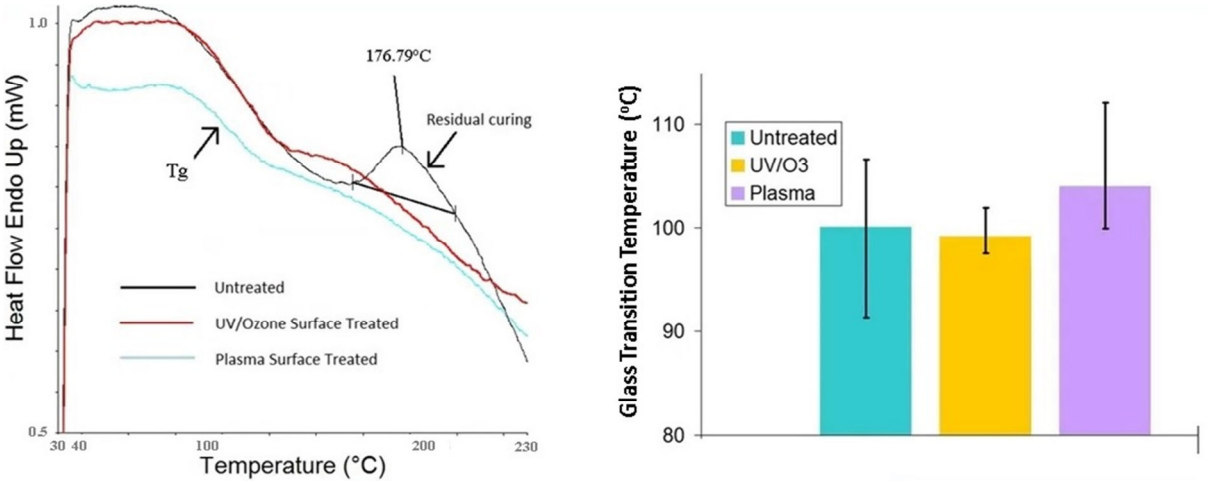

Figure 11: Residual epoxy cure identification using DSC and comparison of T_g for SLJ epoxy adhesive

7. Conclusions

- The surface modification methods discussed in this paper both demonstrate an improvement in single lap joint tensile shear strength. UV/O_3 treatment improves LSS by 18.2 ± 6 % and the atmospheric plasma discharge treatment improves LSS by 22.2 ± 1.9 %.
- The interfacial bond strength was improved using both UV/O_3 and atmospheric plasma surface treatment methods as the mode of failure changed from a partial bondline failure for untreated SLJs to cohesive failure of the adhesive layer.
- The relatively fast hydrophobic recovery of the UV/O_3 surface modified PEKK/carbon, which is a relative measurement of the surface adhesive properties, potentially limits practical application of this treatment method.
- The mechanical ablation effect of the atmospheric plasma on the surface topography of the PEKK/carbon contributes to an overall smoothing and reduction of surface volume. However, analysis shows that this plasma treatment method generates a low variation in surface topography peak distribution. This effect is also evident in the LSS results, where a relatively small variance can be seen for the plasma SLJ LSS compared to the untreated adhesive only and UV/O_3 treated SLJ LSS.
- Both UV/O_3 and atmospheric plasma surface treatment methods improve the degree of cure of the epoxy resin adhesive. The improvement in degree of cure of the epoxy adhesive potentially contributes to greater epoxy toughness and surface adhesion, both of which enhance LSS.

Acknowledgement

The corresponding author would like to acknowledge the financial support of Bombardier and the Royal Academy of Engineering.

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