

# Controlling the Interfacial Response of High Performance Polymer Fibre Composites using Functional Plasma Polymer Coatings

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## ABSTRACT

Functional coatings of acrylic acid and 1,7-octadiene was deposited onto high strength and high modulus poly(p-phenylene benzobisoxazole) (PBO) fibres using plasma polymerisation. The adhesion of the fibres to an anhydride cured epoxy resin was improved. X-ray photoelectron spectroscopy (XPS) after Trifluoroethanol derivatisation confirmed that the PBO fibre was covered completely with the plasma copolymer and that the deposit contained a quantitative concentration of carboxylic acid groups. The microdebond test was used to evaluate the interfacial shear strength (IFSS) which was a function of the surface functionality. The interlaminar shear strengths of high volume fraction composites showed a similar trend. The tensile strengths of single fibres with or without coating were comparable. These results show that the plasma polymerised coatings can control the interfacial bond between PBO fibres and the matrix resin without any damage to the mechanical properties of the fibres.

## 1. INTRODUCTION

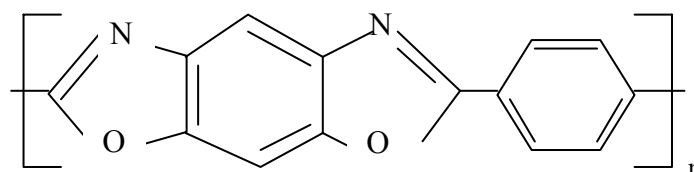
Reinforcing fibres for composite materials are usually coated with a sizing resin to provide protection during handling and manufacturing processes. It is also necessary to provide the surface of the fibre with a mechanism of adhesion to the resins. For example, carbon fibres are electrolytically oxidised prior to sizing whereas with glass fibres, silane coupling agents are added to the coating emulsion. In the latter, it is assumed that the silane is preferentially adsorbed at the glass surface to provide a mechanism for chemical reaction (coupling) to the resin matrix. For high performance polymer fibres, such as the aramids, reactive functional coatings are used to size the fibres for compatibility with the resin matrix. The choice of fibre surface treatment and/or sizing has a major influence on the ease of manufacture and the durability of the moulded artefact. All of these technologies have been developed to meet these requirements, on a case by case basis. There is a need for future functional sizing techniques which can be readily tuned for compatibility with the selected resin. This technology needs to be environmentally clean and able to provide a conformal coating whose chemistry can be adjusted to match that of the matrix.

Plasma polymerisation can be used to deposit conformal coatings with retained functionality. By choosing an appropriate monomer, the surface chemistry can be matched to that of the adhesive or matrix resin. The concentration of the functional groups can either be controlled by changing the plasma power or preferably by employing an 'inert' comonomer to dilute the number of functional groups. A comonomer helps to ensure that the deposit is mechanically stable while providing control over the coating process [1].

We have examined the above hypothesis in a series of papers. Firstly, we used single carbon fibres to demonstrate that the degree of adhesion could be controlled by changing the functionality [2, 3]. A systematic variation of the composition of an acrylic acid/1,7-octadiene demonstrated that the degree of adhesion could be optimised [4]. Furthermore, the analysis methodology for determining a stress transfer efficiency from fragmentation data could be validated. More recently, we have applied the techniques to aramid fibres [5] and E-glass fibres [6]. In the latter, a reactor for semi-continuous coating of the reinforcing fibres was constructed.

Poly(p-phenylene benzobisoxazole) (PBO) fibre (i) is a high performance organic fibre [7, 8], which has been developed by Toyobo Co., Ltd under the trade name of ZYLON<sup>®</sup>. PBO has a

rigid rod polymer structure so that fibres spun from a liquid crystal solution have a highly axially organized crystalline morphology. This means that the fibres can have a modulus of 370 GPa [9] and a high failure strain. Besides their superior mechanical properties, the fibres have a low density and excellent thermal and flame resistance. They can be used in a variety of applications, such as aerospace structures, fire resistant protective textiles and high performance ropes. Its application as a reinforcement in advanced composite materials is one of the most important.



(i)

The good mechanical properties of composite materials are in part dependent on the efficient stress transfer between the resin matrix and the fibre. This can be realised by optimising the interfacial adhesion between the components. In the case of PBO fibres, an improvement in interfacial adhesion between the fibre and the resin is key to the development of composite applications. Various kinds of surface treatment such as corona treatment, plasma treatment and chemical coupling have been used on PBO fibres to address this problem [10, 11].

In this paper, we report a study of the functionalisation of poly(p-phenylene benzobisoxazole) (PBO) fibres using conformed plasma polymer coatings. The adhesion of the fibres to an anhydride cured epoxy resin was quantified using the microdebond test and interlaminar shear strength measurements.

## 2. EXPERIMENTAL

### 2.1 Plasma Polymerisation

The plasma reactor, shown in Figure 1, was designed specifically to deposit a plasma polymer continuously onto the fibres within the tow. The plasma is generated in the glass barrel reactor by a 13.56 MHz radio frequency power supply and matching network supplied by Coaxial Power Systems Ltd (UK). The fibres were contained on spools, within the aluminium end-pieces, which were designed to prevent parasitic deposition of plasma polymer within the end-piece region by incorporation of a baffle between the end-piece and the barrel, so that deposition within the barrel of the reactor dictates the surface chemistry. Glass spools, which were present within the end-pieces, facilitated the movement of the fibre tow through the plasma reactor. Glass was chosen because it should not contaminate the fibre surface. Needle valves were used to allow the metered flow of monomer into the reactor.

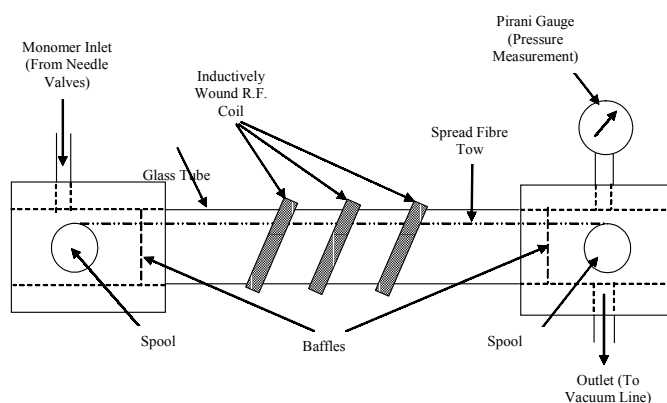


Fig. 1. Schematic of plasma reactor for continuous coating of plasma polymer tows [6]

The reactor was evacuated to a base pressure lower than  $2 \times 10^{-3}$  mbar. The total flow rate of the monomers was set at 2 sccm ( $\text{cm}^3$  (at STP) per minute). The pressure during plasma polymerisation is generally  $3\text{-}4 \times 10^{-2}$  mbar. All samples were placed in the middle of the plasma chamber. Single filaments for the microdebond test were extracted from the fibre tow and bonded to a wire frame support to avoid a shadowing effect. The deposition time was set to 15 minutes. Monomers were left flowing for 30 minutes after switching off the plasma and before exposure to atmosphere to reduce the possibility of post-reactions.

The monomers, acrylic acid (AA) and 1,7-octadiene (OD), for the plasma copolymerised coating were supplied by Aldrich Chemicals (UK). Acrylic acid (AA) provides the plasma polymer with the carboxylic acid functionality which has high reactivity to epoxy groups in the epoxy resin. 1,7-octadiene (OD) was used as the diluent comonomer for varying the concentration of acrylic acid in the monomer feed and hence the concentration of carboxylic acid groups in the coating. 1,7-octadiene has previously been shown to improve the mechanical stability of the plasma polymer films by introducing crosslinks [1,12]. The monomers were degassed using several freeze-thaw cycles.

## 2.2 Materials

PBO fibres were manufactured without a finish or size, in a small scale pilot plant. PBO films were also prepared from the same spinning dope for precise surface analysis by XPS.

However, for the interlaminar shear tests the fibres had a light textile finish, which was not removed prior to plasma polymer deposition. The composition of the coating will therefore vary slightly from that given for the analyses presented here.

An epoxy resin system, Epikote 828 (Shell Chemicals, London, UK) was used for the microdebond test. This was cured with 82 phr (parts per hundred of resin by weight) nadicmethylenetetrahydrophthalic anhydride (NMA) (Stag Polymers and Sealants, UK) and 31 phr Capcure 3-800 (Henkel-Nopco, Leeds, UK), a mercaptan terminated polymeric curing agent. The matrix system was thermally cured at  $80^\circ\text{C}$  for 4 h, followed by  $130^\circ\text{C}$  for 3 h followed by cooling overnight in the oven.

For the interlaminar shear strength (ILSS) measurements, a second higher modulus resin was chosen. In this case Epikote 828 was cured with 80 phr of NMA using 4 phr of Epikure K61b at  $120^\circ\text{C}$  for 2 hours. After preparation of the coupons, the resin was post cured at  $180^\circ\text{C}$  for 16 h followed by cooling in the oven.

## 2.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra were obtained with a VG Clam 2 spectrometer using Mg-K $\alpha$  X-rays. The X-rays source was operated at 100 W. The electron take-off angle was  $30^\circ$  relative to sample surface. A wide-scan (0-1100 eV) spectrum was recorded together with narrow scans. The pass energy was set to 100 eV for the wide scans and 20 eV for the narrow scans. The spectra were corrected for charging of the sample by referencing them to the binding energy of C1s peak for aliphatic hydrocarbon to 285.0 eV. Curve fitting of the C1s peaks was used to quantify the surface functionality of plasma polymer coatings. Curve fitting was performed using Scienta software. The C1s peaks from plasma polymer coated PBO films were fitted with component peaks of equal full width at half maximum (FWHM) of 1.5-1.7 eV and a linear background was applied to the peaks in all cases. The shape of the component peaks was also kept equal and varied between a Gaussian to Lorentzian (G/L) mix of 0.8-1.0. Curve fitting of trifluoroethanol (TFE) derivatised samples was carried out using the same procedure. TFE derivatisation was used to quantify the surface concentration of COOH groups. Full details of the analysis are given elsewhere [6, 13, 14]. High resolution XPS spectra were obtained with the SCIENTA 300 (Daresbury Laboratory, UK). XPS spectra were taken directly from PBO single fibres and tows using monochromated Al K $\alpha$  X-rays at 2.8 kW at a take-off angle of  $45^\circ$  relative to the sample surface.

#### 2.4 Microdebond test

The microdebond test was used to study the adhesion of PBO fibres to the resin matrix. The principle of this method is illustrated in Fig.2. Droplets of freshly prepared liquid epoxy were deposited onto each filament using a thick fibre “brush” for transferring the resin. After curing, the droplet length was measured by optical microscopy. The length was 100-200  $\mu\text{m}$ . The droplet was debonded using load points set at a spacing of 30  $\mu\text{m}$  as shown in Fig.2. The loading rate was set to 200  $\mu\text{m s}^{-1}$ . The force required to debond the droplet was measured with 10 N load cell. The interfacial shear strength (IFSS) was calculated from  $F/\pi dl$ , where  $F$  is the pull-out force,  $d$  is the fibre diameter  $l$  is the embedded length. At least 50 microdebond tests were carried out for each sample.

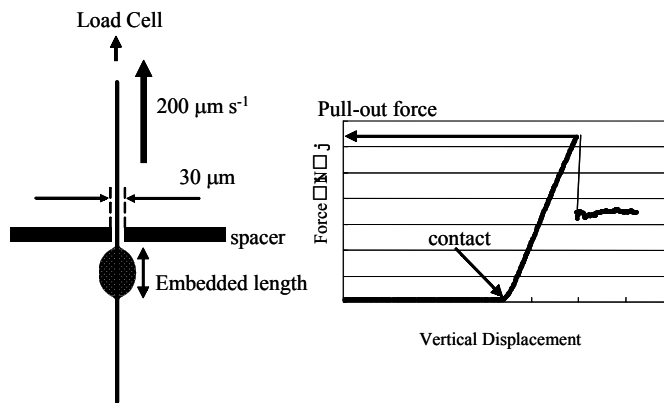


Fig. 2. Microbond test geometry with a typical force-displacement curve

#### 2.5 Interlaminar Shear Strength Tests

Filament wound frames were impregnated with degassed resin between release films using a press-clave. The curing schedule was as described above. Coupons 20x10x2  $\text{mm}^3$  were cut from the coupons using a laser. The span to depth ratio during the test was maintained at 5, to ensure shear failure.

#### 2.6 Single fibre strength measurement

Single fibre strength measurements were carried out to examine the influence of the plasma polymer coatings on the fibre mechanical properties. Single fibres were selected at random from the coated and uncoated (non-sized) fibre bundles. The details of the sample preparation are given elsewhere [2]. The gauge length was set at 6.25 mm. The single fibre samples were loaded at a displacement rate of 0.52  $\text{mm min}^{-1}$ . The failure load was measured with a 10 N load cell. The diameter of the fibre was measured in a scanning electron microscope, (Camscan Series 2). More than 60 filaments were tested for each sample. The Weibull modulus for the distribution in strength of the various coated fibres was determined using the standard graphical methodology, which has been described elsewhere [15].

### 3. RESULTS

#### 3.1 Single-filament tensile strength

The single-filament tensile strengths of the plasma polymer coated and untreated fibres are given in Table 1. The strengths of the plasma polymer coated fibres are similar to the untreated fibres, however there is a trend to higher values. The thickness of plasma polymer

coating has been shown to be less than 100 nm. Therefore, the small differences in diameter are mainly a result of variations in the manufacturing process rather than the presence of the plasma polymer coatings. The Weibull modulus of the coated fibres is clearly higher than that of the untreated fibres, showing that the variability in fibre strength is reduced.

**Table 1.** The average single filament tensile strength and Weibull modulus of Plasma polymer coated PBO fibres

Monomer feed (Mole%)	Plasma power (W)	Tensile strength (GPa)	Fibre diameter ( $\mu\text{m}$ )	Weibull modulus
90% Acrylic acid	10	$5.48 \pm 0.45$	$12.27 \pm 0.79$	13.25
90% Acrylic acid	1	$5.22 \pm 0.55$	$12.44 \pm 0.95$	10.96
100% Octadiene	1	$5.34 \pm 0.33$	$12.47 \pm 1.01$	11.99
Uncoated	-	$5.25 \pm 0.64$	$12.15 \pm 0.70$	9.10

### 3.2 XPS

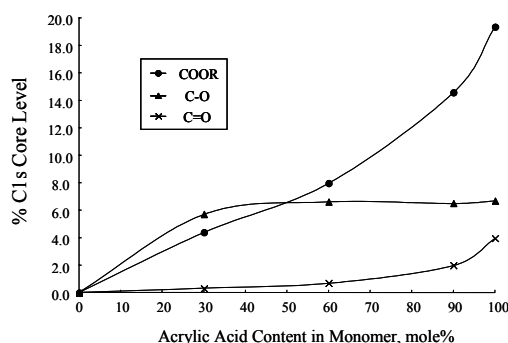
The chemical structure of the plasma polymer coating was studied using XPS. Plasma polymers were deposited onto especially prepared PBO films with a flat surface, to avoid complications associated with the uncertainty in the analysis angle with uneven fibrous samples. In this way higher resolution XPS spectra could be obtained which were more easily interpreted with certainty. XPS survey spectra obtained from PBO films coated with plasma polymer for 5 min did not exhibit a signal from the substrate. This means that the surface of the PBO film was completely covered with plasma polymer. The coating thickness cannot be calculated precisely because of the exponential nature of photoelectron emission process. However, the XPS sampling depth can be estimated from the mean free path of a core electron and was found to be less than 5 nm, for a take-off angle of  $30^\circ$  relative to sample surface. Therefore, the thickness of the 15 min-deposited sample can be estimated to be greater than 5 nm.

The effect of acrylic acid concentration in the monomer feed on surface functionality retention was studied at a plasma power of 1 W. The distribution of carbon functionality within the C1s peak as a function of monomer concentration is given in Fig.3. The concentration of COOR groups in the surface of the coated fibres is shown to increase with acrylic acid concentration in the comonomer composition. Elements other than carbon were not detected on the 0% acrylic acid (100% 1,7-octadiene) plasma polymer coated PBO film. For a definitive identification of COOH groups, quantitative TFE derivatisation was used. The C1s peak of the derivatised sample consists of CH (referenced to 285.0 eV),  $\underline{\text{C}}$ -COOR (285.7 eV), C-O (286.5 eV), O- $\underline{\text{C}}$ -CF<sub>3</sub> (287.5 eV), C=O (288 eV), COOR (289.3 eV) and CF<sub>3</sub> (293.0 eV). The peaks at 287.5 and 293.0 eV, can only arise from the fluorinated ester (labelled carboxylic acid groups). Therefore, a comparison of the intensity of the CF<sub>3</sub> peak with that of the COOR peak enables the fraction of the COOR groups which exist as COOH in the original deposit to be calculated. The results of TFE derivatisation of each plasma polymer are shown graphically in Fig.4. It can be seen that 67% of COOR groups in the plasma polymer film with a 100% AA monomer feed, were retained carboxylic acid groups.

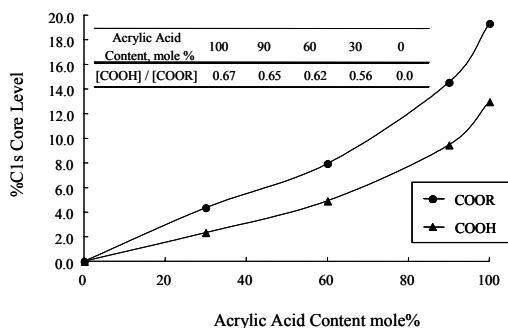
### 3.2 Microdebond test

Fig.5 shows the IFSS values of plasma polymer coated PBO fibres as a function of the surface concentration of COOH groups. These results show that the introduction of COOH groups onto the PBO fibre surface increases IFSS significantly. The 100% OD plasma polymer coated fibre exhibits a lower IFSS than the untreated uncoated fibres. Addition of AA to the monomer feed provided the fibres with significantly higher values of IFSS. Interestingly, the degree of adhesion, as shown by the value of IFSS, of 100% AA plasma polymer coated fibre

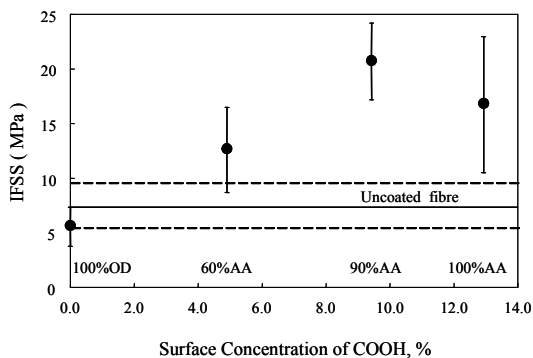
was lower than that of the 90% AA coated fibre, although the surface concentration of COOH groups was higher. However, the degree of scatter in the microdebond data for the 100% AA plasma polymer coated fibre was significantly larger, so that some other factor than the retained carboxylic acid group concentration may be responsible for the apparent reduction in adhesion. In previous studies, it was reported that the hydrocarbon comonomer provided the mechanical stability to these films prepared at low plasma power [1,12]. Therefore, the 100% AA plasma polymer deposit can be considered to have a relatively low crosslink density with a soluble component which can be partially solubilised by the liquid epoxy resin during the preparation of the composite sample. This can give rise to an interphase region of more variable adhesion to the fibre and hence a less perfect interfacial bond. This aspect has also been observed with glass fibres and discussed elsewhere [16].



**Fig. 3.** Relative concentrations of functional groups in the C1s peak (from curve fitting) from acrylic acid and 1,7-octadiene plasma copolymers on PBO films as a function of the monomer composition



**Fig. 4.** The COOR and COOH (from TFE derivatisation) contributions to the C1s peak of the XPS spectra of the plasma polymers on PBO films as a function of monomer composition



**Fig. 5.** Microbond IFSS between PBO fibres, with and without plasma copolymer, and an anhydride cured epoxy resin, as a function of surface concentration of COOH groups. The dotted lines represent the standard deviation in the microdebond test data for the uncoated fibres

## 4. DISCUSSION

### 4.1 Surface chemistry of plasma polymer coated PBO films

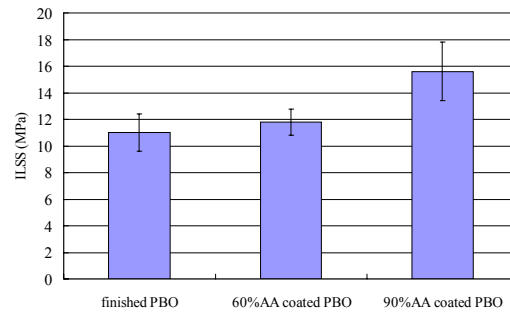
A low plasma power is favourable for depositing plasma polymer coatings with a high retention of COOH. [17,18]. Copolymers of acrylic acid and 1,7-octadiene have been deposited at a plasma power of 1 W. The relative concentrations of functional groups in the plasma polymer as a function of the composition of the monomer feed are shown in Fig.3. Fig.4 shows the surface concentrations of COOH and COOR. The fraction of the COOR groups which are retained as COOH in the deposit differs from that observed for deposits on glass and carbon fibres, reported elsewhere [2, 3, 6]. The COOH concentration in the plasma polymer coatings on the PBO fibre is lower than that on carbon fibres, but higher than that on glass fibres. Especially in the case of glass fibres, the difference is large, although the same plasma reactor was used for the deposition. Marks and Jones [6] attributed the reduced retention of COOH groups on glass fibres to the presence of adsorbed water on the glass fibre surface. The concentration of adsorbed water on the surface of PBO fibres is expected to be much lower. Therefore, these results support the previous conclusion that the concentration of retained COOH is strongly affected by the presence of adsorbed water on the fibre surface.

### 4.2 Promotion of adhesion of PBO fibres by functional plasma polymer coatings

The acrylic acid containing plasma polymer coating has been shown in Fig. 5 to be effective in the promotion of the adhesion of PBO fibres to epoxy resin. This is demonstrated by an increase in IFSS with the surface concentration of COOH groups. 90% AA plasma polymer coated fibres exhibited an IFSS which was  $\approx 180\%$  higher than that for uncoated PBO fibres. The IFSS of 100% AA plasma polymer coating, which had the highest concentration of COOH, had an apparently lower level of adhesion. However, the IFSS values were within the scatter band for the data. The variability in microdebond adhesion was also higher. It is reported that 90% AA plasma polymer is more stable than the 100% AA plasma polymer in water [1,12]. It was concluded that the latter deposit had a reduced degree of crosslinking and probably contained a soluble component. Partial dissolution of the 100% AA plasma polymer coating in the epoxy resin is expected to lead to a more variable interfacial shear strength because of interphase formation and less effective bonding between the two components. Therefore, the addition of 1,7-octadiene comonomer provides a mechanism of introducing crosslinking into the plasma polymer film at low power [1,12]. Thus the 90% AA plasma polymer can be considered to be more stable than the 100% AA plasma polymer film in contact with the liquid epoxy resin, producing a more defined interfacial region. With the 100% AA plasma polymer, partial dissolution and swelling in the presence of the adhesive resin may be responsible for a more complex interfacial region with variable microdebond adhesion. The true mechanism needs further research.

The low value of IFSS for the 100% OD plasma polymer coated fibres shows that the lack of functionality on the fibre surface is responsible for the poor adhesion to epoxy. Since the value is less than that for the uncoated fibre it can be concluded that the fibre surface is not activated by the plasma polymerization process. The uncoated PBO fibres have oxygen and nitrogen atoms in the surface which provide stronger intermolecular forces than the hydrocarbon plasma polymer. Overall the role of chemical coupling between the functionalised fibre coating and the epoxy resin has been demonstrated.

High volume fraction composites were also prepared for ILSS determination. Figure 6 shows a similar trend to that in Figure 5 confirming that the continuous coating of the fibres is effective. The correlation between single filament tests and laminate tests demonstrates the benefits of a functional plasma coating. For these experiments, the fibres were lightly sized. This illustrates that it is also possible to functionally size fibres with a dressing.



**Fig. 6.** Interlaminar Shear Strengths (ILSS) of high volume fraction composites from plasma polymer coated PBO fibres

## 5. CONCLUSIONS

Acrylic acid and 1,7-octadiene plasma copolymerised coatings were deposited onto PBO fibres. X-ray photoelectron spectroscopy (XPS) together with trifluoroethanol derivatisation was able to quantify the concentration of retained carboxylic acid groups. The adhesion of the PBO fibre to an anhydride cured epoxy resin was evaluated with the microdebond test. The adhesion was promoted in the presence of an acrylic acid containing plasma polymer coating. The degree of adhesion was a function of the surface concentration of carboxylic acid groups. The highest IFSS was observed with the 90% AA plasma polymer coating. With the highest concentration of carboxylic acid groups in the surface (100% AA plasma polymer coating) a slightly lower interfacial shear strength, but with higher scatter, was observed. This was attributed to a reduced stability of the plasma polymer coating in the presence of the epoxy resin leading to a more variable interfacial bond or weak interlayer. Chemical coupling involving carboxylic acid groups has proved to be the mechanism of adhesion. The plasma polymer coating is shown to protect the fibre from strength degradation during processing. The benefits of the continuous plasma polymer coating process was also demonstrated in interlaminar shear strength tests.

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