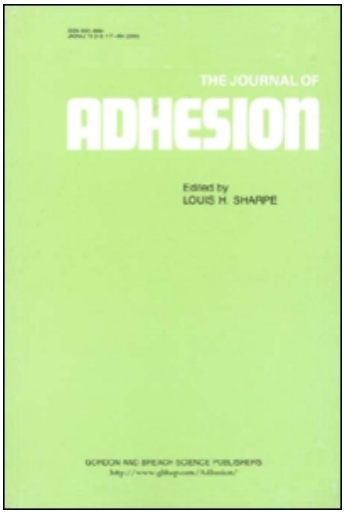

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Farrow, G. J. and Jones, C.(1994) 'The Effect of Low Power Nitrogen Plasma Treatment of Carbon Fibres on the Interfacial Shear Strength of Carbon Fibre/Epoxy Composites', The Journal of Adhesion, 45: 1, 29 — 42
To link to this Article: DOI: 10.1080/00218469408026627
URL: http://dx.doi.org/10.1080/00218469408026627

J. Adhesion, 1994, Vol. 45, pp. 29–42
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Printed in the United States of America

The Effect of Low Power Nitrogen Plasma Treatment of Carbon Fibres on the Interfacial Shear Strength of Carbon Fibre/Epoxy Composites*

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(Received February 23, 1993; in final form July 6, 1993)

Type II (high strength) carbon fibres have been given a low power nitrogen plasma treatment. It is shown that this plasma treatment has no effect on the fibre diameter, no detrimental effect on fibre strength and can significantly improve fibre/resin adhesion. It is proposed that this improvement is due to chemical interaction *via* amine/epoxy bonding at the edge sites together with the interaction of the epoxy with activated basal planes present on the fibre surface. This improvement is only achieved if the fibres are immersed in resin before being exposed to air. Exposing the treated fibres to air drastically reduces fibre/adhesion due to the adsorption of moisture from the environment. Heating these latter fibres in a vacuum at 130°C for one hour allows some recovery of the interfacial strength. It is also demonstrated that the interfacial shear strength falls dramatically when the nitrogen-containing functional groups are completely removed from the fibre surface.

KEY WORDS fibre diameter; fibre strength; fibre/matrix adhesion; interfacial chemical reaction; interphase; epoxy resin; surface treatment of fibres; XPS analysis; single fibre fragmentation tests.

INTRODUCTION

The level of adhesion at the carbon fibre/resin interface has a significant effect on the overall mechanical performance of a composite material. In order to improve adhesion between carbon fibres and epoxy resins, manufacturers have developed several types of fibre surface treatments. These usually involve chemical or electrochemical oxidation, the main aim being to promote chemical bonding by introducing functional groups such as carboxylic acid (—COOH) or hydroxyls (—OH) onto the fibre surfaces. These groups are then capable of reacting with the epoxy resin system during the curing process to form a stronger bond. However, it has been shown that chemical bonding as a result of electrochemical treatments *does not* play a major

*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

role in fibre/resin adhesion.[1] Drzal *et al.*[2] proposed that the number of functional groups introduced onto the fibre surface is *too small* to have a significant effect. The observed improvements in interfacial strength as a result of commercial treatments were attributed to the removal of weakly bound crystallites on the fibre surface, providing a superior surface to which the resin can adhere.

Using X-ray photoelectron spectroscopy, Jones[3] has shown that exposing the fibres to a low power air plasma can introduce a much higher concentration of functional groups on the immediate surface of the fibres compared with electrochemical anodisation in ammonium bicarbonate solutions. Because these functional groups have the capability of chemically reacting with the epoxy resin, it has been suggested that this type of treatment would increase the number of chemical bonds formed between the fibre and resin and hence improve adhesion.

One of the most common set of curing agents are amines, which can react with the resin at room temperature. It may, therefore, be beneficial to introduce amine groups onto the fibre surface which could also react with the epoxy during cure. Several research groups have studied the effects of radio frequency ammonia plasmas on carbon fibres and other carbon substrates [e.g., Refs. 4 and 5]. Jones and Sammann[6] have shown that by subjecting the fibres to a nitrogen plasma treatment, significant amination of the fibre surface can also be achieved. It was suggested that the small amounts of hydrogen present on the fibre surface and in the system were enough to be incorporated with the nitrogen to produce an aminated surface. Using nitrogen has obvious advantages over ammonia since it is less noxious and less expensive. This paper presents a study of the effects of low power nitrogen plasma treatments on carbon fibre/epoxy resin adhesion.

EXPERIMENTAL

Materials

The fibres used in this investigation were Courtaulds XAU (untreated and unsized) and XAS (commercially treated but unsized) type II PAN based carbon fibres. The resin used was EPON 828® epoxy (Shell) used in conjunction with *meta*phenylenediamine (MPDA) hardener.

Plasma System and Treatment

The plasma cell is a half-wavelength helical resonator,[6,7] formed from a 100-turn coil wound directly on the outside of a glass which is located centrally within a 3″ (7.6 cm) diameter brass tubing. A simple self-excited, two-transistor oscillator delivers radio frequency energy to the centre of the helix at a suitable resonant frequency. Low power (<1W) levels are sufficient to sustain a plasma within this tube. Continuous gas flow is maintained from a leak valve at one end of the tube to a butterfly valve at the other, which opens to a wide-range turbomolecular pump. The carbon fibre tow which was to be treated was mounted on a glass frame and introduced into the plasma cell. The chamber was then sealed, pumped out and

then flushed through with nitrogen gas. The fibres were then exposed to a nitrogen plasma for ten minutes. After plasma treatment, the fibres were removed from the cell and immediately immersed in the epoxy resin (EPON 828). Excess resin was subsequently washed off with toluene leaving a very thin residual layer of resin size on the fibre surface. In some cases, after a nitrogen plasma treatment, the fibres were immersed in resin before exposure to air. This was achieved with the use of a nitrogen-filled glove bag which surrounded the cell. The fibres were then sized as described above. In each case, the carbon fibres could subsequently be singled out for use in the single fibre fragmentation test.

Single Fibre Fragmentation Test

In order to test the effect of the plasma treatment on fibre/matrix adhesion, the interfacial shear strength, τ, was measured using the single fibre fragmentation test.[8] In this method, a single carbon fibre is embedded in a matrix material such that the strain to failure of the matrix is at least three times that of the fibre. When a tensile stress is applied to the sample, the fibre fails first at its weakest point. The stress at the broken fibre end is zero, but the stress is transmitted back into the fibre by shear forces at the fibre matrix interface over a length known as the "ineffective length" (l_i). If the fibre is long enough, the tensile stress eventually reaches a level greater than the local fracture strength of a fibre flaw, and the fibre fractures again at that point. A large fragment can break into any length greater than l_i, but the matrix cannot transfer a stress greater than the tensile strength of the fibre to pieces shorter than $2l_i$. In an ideal situation, therefore, a fibre will break into fragments of length ranging between l_i and $2l_i$, the latter being known as the critical length, l_c. While carrying out the test, it is assumed that the shear stress along the fibre is constant throughout the length of the specimen. The interfacial shear strength, τ, is given by:

$$\tau = \sigma_f d/2l_c \tag{1}$$

where d is the average fibre diameter and σ_f is the tensile strength of the fibre at the critical length, l_c. In practice, a distribution of fragment lengths is obtained due to variations in fibre properties such as defects and variations in fibre diameter. A statistical description of the fibre lengths reflecting the Weibull nature of this distribution must therefore be made, leading to a modified expression for τ:

$$\tau = (\sigma_f/2\beta)\,\Gamma(1 - 1/\alpha) \tag{2}$$

where α and β are the Weibull shape and scale factors of the two-parameter Weibull distribution and Γ is the gamma function.[9]

Fibre Diameter and Tensile Test Measurement

Since calculation of the interfacial shear strength, τ, requires a knowledge of the carbon fibre diameter and tensile strength, σ_f, of the fibres at the critical length, it was essential to determine whether or not the nitrogen plasma treatment was affecting these parameters. The diameter of both plasma-treated and as-received

fibres was measured from digital images of 25 separate filaments taken on a Cambridge S1000 scanning electron microscope (SEM).

It is well known that the strength of fibres varies with gauge length, short fibres being stronger than long ones. Since direct measurements of σ_f at lengths approaching l_c (<1mm) are impossible, it is necessary to use some form of extrapolation of fibre strengths at several gauge lengths. The estimation of the fibre strength at l_c has been made using a linear logarithmic dependence of tensile strength on gauge length. This method of extrapolation was proposed by Asloun *et al.*[10] who considered several types of extrapolation and found that this was the simplest and most accurate method. Tensile tests were carried out on single filaments at several gauge lengths by gluing the fibres to tapered card tabs. Fifteen filaments were tested at each gauge length. Load was applied by slowly adding water to a light plastic container attached to the bottom tab. At failure, the break load was measured by weighing the container, water and bottom tab. The details of this simple but very effective method have been described elsewhere.[11]

XPS

Analysis of the carbon fibre surface composition was performed using X-ray photoelectron spectroscopy (XPS) on a VG Microlab instrument which is equipped with an Al Kα X-ray source (1486.6eV). The fibre samples were mounted on a specially-designed sample holder in which the fibres were surrounded by a gold mask. Elimination of the XPS signals due to the gold ensured that only those from the fibres were detected. Fibre samples for XPS analysis were not coated in EPON 828 resin. In addition to carbon fibre samples, XPS analysis was also performed on highly-orientated pyrolytic graphite (HOPG). All spectra were taken at bulk-sensitive angles, *i.e.* the angle between the analyser axis and the fibre axis was 90°. Data collection at surface-sensitive angles from carbon fibre surfaces as described by Jones[3] has not yet been achieved with the above spectrometer.

Dogbone Sample Fabrication and Testing

Single fibre dogbone tensile specimens were prepared using a mould made from SILCOFORM S2 (Hobby Time) rubber moulding compound. The mould could be used to make 7 dogbone specimens simultaneously. The epoxy resin was prepared by heating 14.5g of MPDA hardener and 15g of EPON 828 resin at 60°C until the hardener melted. The two were then mixed together and kept at 60°C for 1 minute. The mixture was then added to 85g of EPON 828 resin, thoroughly mixed and placed in a vacuum oven to degas for one hour. Single carbon fibres were carefully removed from a tow without being touched by hand and mounted along the centre of the mould, holding it in position using adhesive tape. The resin mixture was then poured into the mould and any air bubbles in the gauge length were carefully removed. The samples were then cured for two hours at 80°C, post cured for two hours at 150°C and allowed to cool overnight.

The finished dogbone sample was placed in the jaws of a hand-driven tensile rig, designed so that the sample could be observed between the cross polarised filters

of a Metalloplan large field optical microscope (Leitz Wetlar). Figure 1 shows typical photographs of a sample being tested using transmitted polarised light. Fibre fracture can be observed *in situ* while the sample is gradually strained. An increasing load was applied to the sample until fibre fracture ceased. After the test, the individual fibre fragment lengths were measured using the vernier scale on the microscope.

To ensure that the single fibre fragmentation tests were being carried out successfully, a comparison of the interfacial shear strengths of untreated XAU and commercially-treated XAS fibres embedded in epoxy resin was made. The fibres used in these preliminary tests were **not** given the sizing procedure described above.

Dogbone samples containing single carbon fibres which had undergone the following treatments were prepared.

1) XAU fibres as received, coated with EPON 828 resin and rinsed in toluene (*i.e.* sized).
2) XAU fibres treated with a nitrogen plasma for 10 minutes and sized before exposure to air.
3) XAU fibres treated with a nitrogen plasma for 10 minutes and sized after exposure to air.
4) XAU fibres treated with a nitrogen plasma for 10 minutes, heated in a vacuum for 18 hours at 130°C and sized.
5) XAU fibres treated with a nitrogen plasma for 10 minutes, heated in a vacuum for 1 hour at 1000°C and sized.

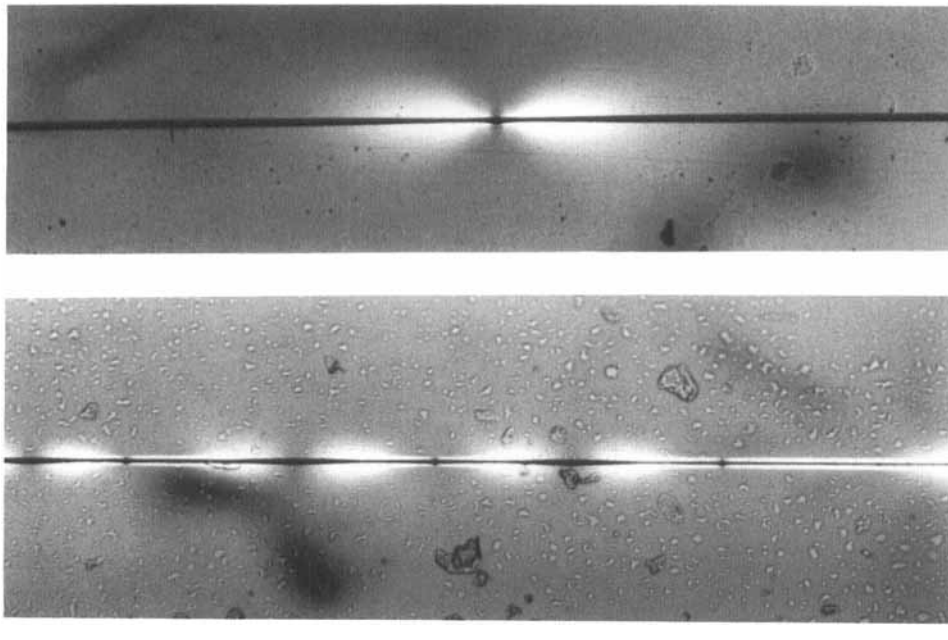

FIGURE 1 Typical micrographs of a single fibre fragmentation sample viewed under transmitted cross polarised light.

RESULTS AND DISCUSSION

Fibre Diameter and Tensile Strength Determination

Figure 2 shows an example of the carbon fibre strength/length extrapolation, the example shown being that for the nitrogen-treated fibres. The equation of the line of best fit was subsequently used to calculate the strength of the fibre at the mean fragment length obtained from the appropriate single fibre fragmentation test. Table I summarises the results of the strength of the fibres at a length of 0.6mm. The mean fibre diameters from SEM measurements are also listed. SEM investigations showed no surface roughening or pitting on the fibre surfaces before or after plasma treatment.

The results presented in Table I show that low power nitrogen plasma treatment has no effect on the XAU fibre diameter even after relatively long treatment times.

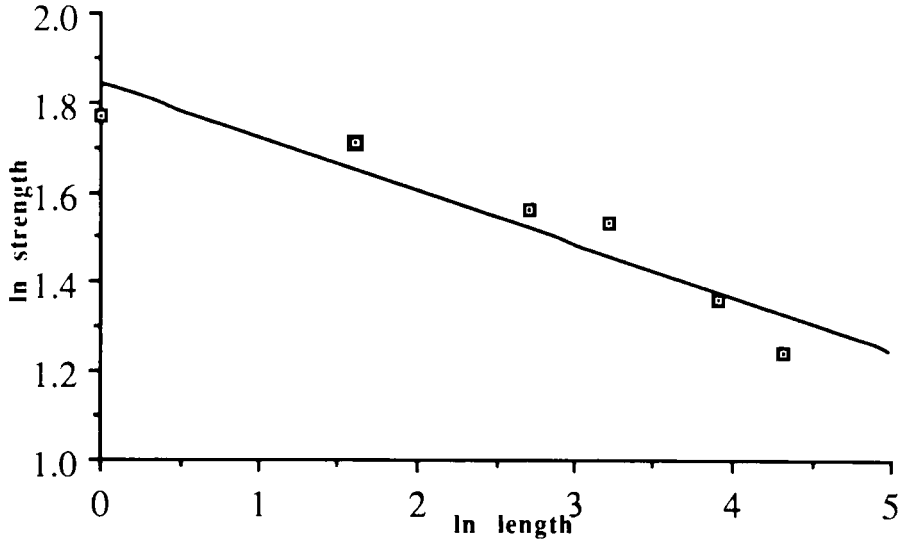

FIGURE 2 Strength/length extrapolation for carbon fibres treated with a nitrogen plasma for 10 minutes.

TABLE I
Tensile strengths and diameters of as-received XAU and XAS carbon fibres and XAU fibres subjected to low power nitrogen plasma treatment for 10 minutes. One standard deviation of the measurements are shown in brackets

Fibre type	Tensile strength at 0.6mm(GPa)	Mean diameter (μm)
XAU as-received	5.8(0.8)	6.8(0.3)
XAS as-received	6.0(0.4)	7.2(0.3)
XAU N_2 Plasma 10 mins	6.7(0.7)	6.8(0.3)

There is also an apparent increase in the tensile strength of the plasma-treated fibres. Such an increase has also been reported by Harris *et al.*[12] after plasma polymerisation treatments on type II carbon fibres. Care must be taken when assessing such results since the scatter in carbon fibre tensile strength measurements is notoriously large. It can be said with some confidence, however, that the plasma treatment is **not** causing a reduction in tensile strength.

XPS Analysis

In previous studies, it was shown that the immediate effect of nitrogen plasma treatment was to introduce at least two types of nitrogen-containing functional groups onto the fibre surface. The N1s spectrum shown in Figure 3 consisted of two main signals at 398.9eV and 400.4eV and a third much smaller peak at 402.8eV. The two main signals were assigned to aromatic amines (and possibly imines) and aliphatic amines, respectively.

On exposure to air a significant increase in the O1s intensity was observed as shown in Figure 4. It has been suggested that this is due to a strongly-adsorbed layer, most probably moisture from the environment.[6] This layer was stable enough to withstand the low pressures (10^{-9} Torr) inside the spectrometer analysis chamber for at least one hour. This adsorbed layer could inhibit chemical bonding at the fibre resin interface.

In a previous comparison between the reactivity of different types of carbon fibres with an ammonia plasma, it was concluded that amine functionality was only

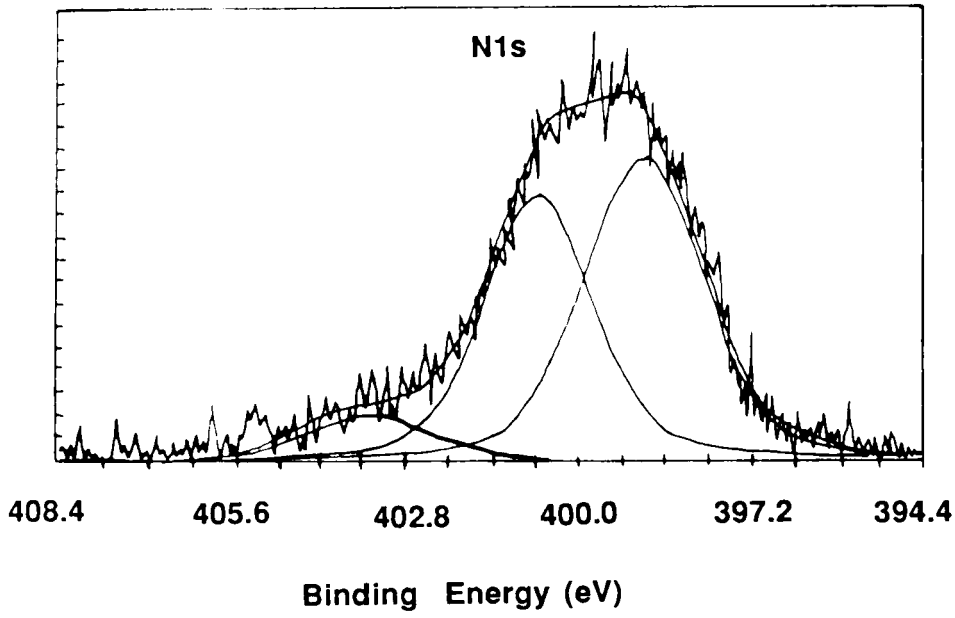

FIGURE 3 N1s (XPS) spectrum of nitrogen plasma treated type II carbon fibres.

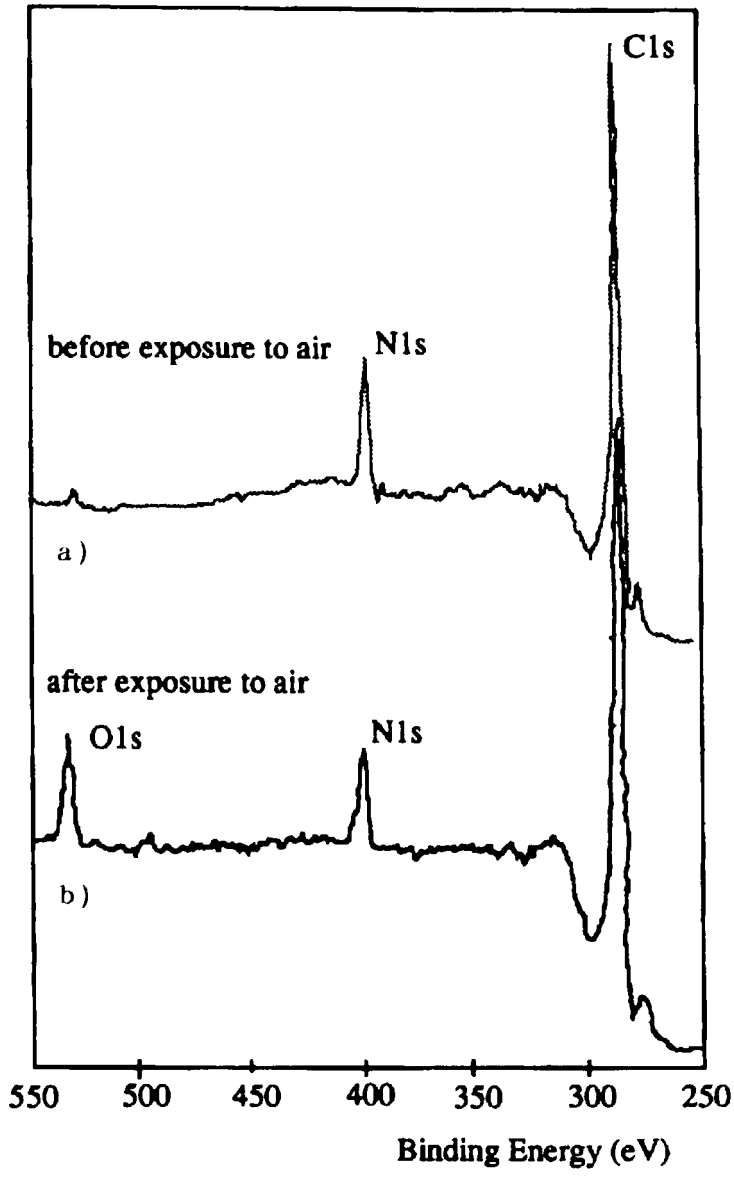

FIGURE 4 Widescan spectra of nitrogen plasma treated fibres: a) before and b) after exposure to air.

introduced onto the edge sites and not the basal planes of the fibre surface.[13] This is a direct contradiction of results reported by Loh *et al.*,[4] who proposed a model for an aminated carbon fibre surface in which the plasma aminated both the edge sites and basal planes. However, the power of the plasma (50W) used in the latter case was much higher than that (<1W) used for our experiments. To determine whether or not the nitrogen plasma was behaving in a similar manner, a sample of

highly-orientated pyrolytic graphite (HOPG) was also treated. The widescan spectra of HOPG before and after nitrogen plasma treatment for ten minutes are shown in Figure 5. The spectrum from the untreated surface was as expected, with only the C1s signal being detected. After plasma treatment, only a C1s and O1s signal were detected. The total absence of an N1s signal in the spectrum suggests

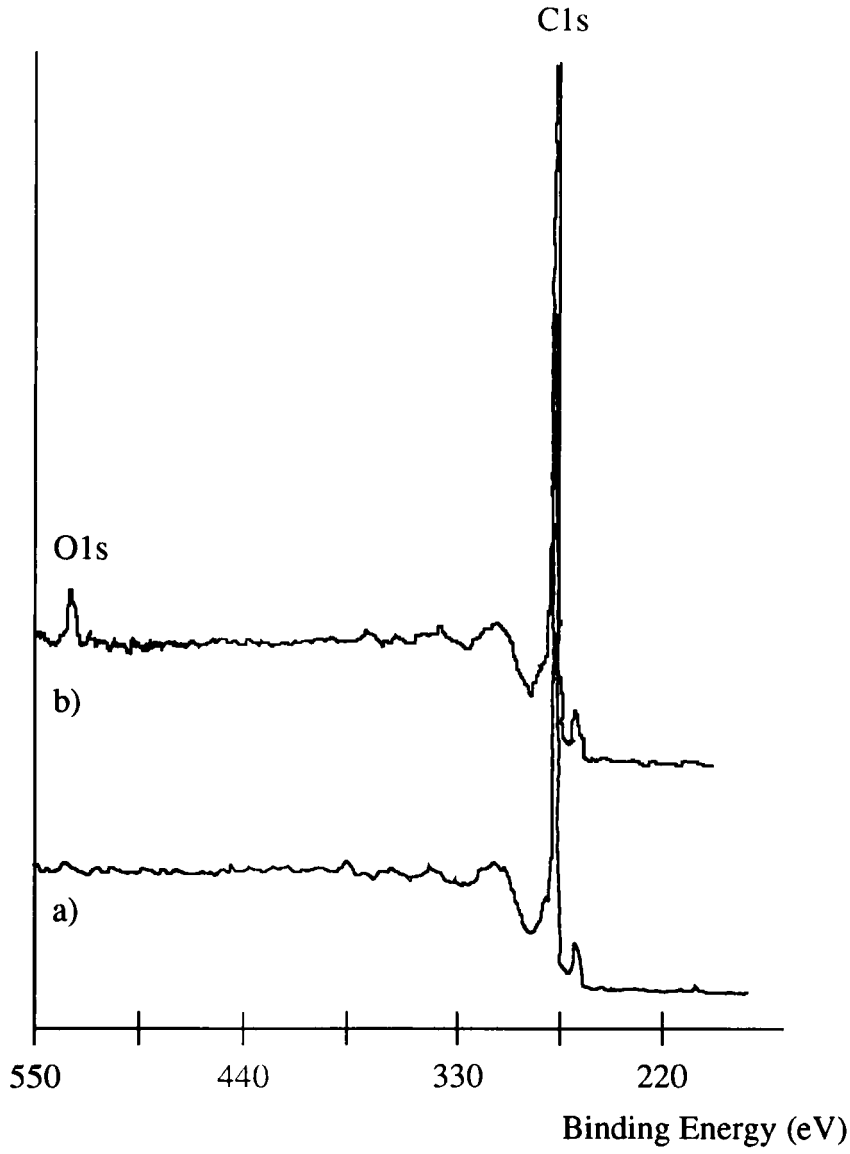

FIGURE 5 Widescan spectra of: a) untreated and b) nitrogen plasma treated, highly orientated pyrolytic graphite (after exposure to air).

that nitrogen had not reacted with basal plane graphite, confirming that chemical reaction with the nitrogen plasma is confined to the edge and defect sites. Nevertheless, the basal planes had been activated in some way by the plasma and, on exposure to air, adsorption of oxygen/moisture was observed to have taken place. The nature of this activation is currently being investigated.

In order to remove all the induced chemical functionality, the treated fibres were heated to 1000°C under high vacuum, a method which proved successful for electrochemically-treated fibres.[1] The XPS spectrum shown in Figure 6 confirms that most of the chemical groups had been desorbed.

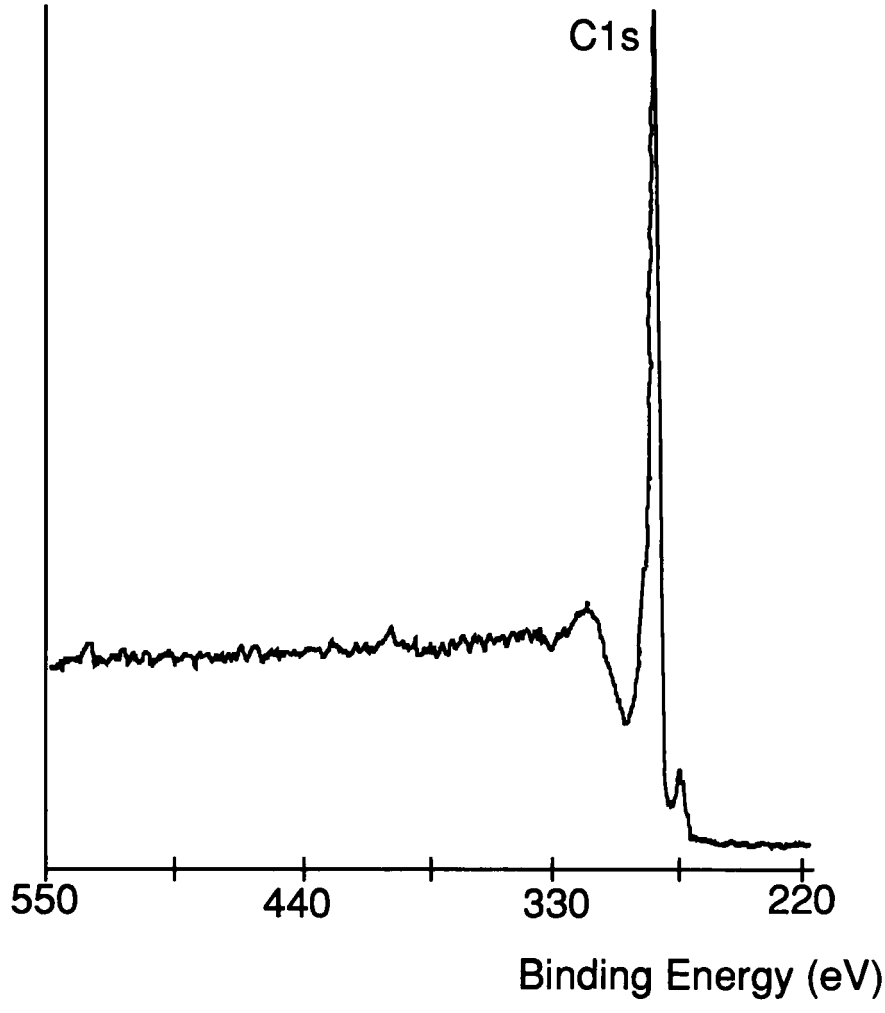

FIGURE 6 Widescan spectra of nitrogen plasma treated fibres heat treated at 1000°C in a vacuum for 1 hour.

Single Fibre Fragmentation Tests

The results of the fragmentation tests on the as-received XAU and XAS are shown in Table II. Values of τ calculated from both equations 1 and 2 are presented for comparative purposes. These values are very similar to those obtained by other research groups using similar fibres and resin system[12,14,15] yet much lower than those reported by Drzal [e.g., Ref. 16]. These results clearly show that the commercial treatment improves the interfacial shear strength as would be expected.

TABLE II
Results of the single fibre fragmentation test for as-received fibres

Fibre type	Mean fragmentation length (mm)	τ (MPa) (eq 1)	τ (MPa) (eq 2)*
XAU as-received	0.82	26.7	36.8
XAS as-received	0.61	35.4	46.2

*Values of τ calculated from equation 2 are those used in the discussion.

Results for the fragmentation tests on samples made from fibres which had been subjected to various treatments are shown in Table III. The low power nitrogen plasma treatment dramatically improves fibre to resin adhesion from a value of 23.7MPa in the untreated case, to 61.5MPa for our treated fibres. It must be emphasised that this value was obtained from samples in which the fibres after plasma treatment had been coated in a resin size **before** exposure to air. This improved value of τ is much higher than that achieved from commercially-treated fibres (XAS). The plasma alters the surface by introducing nitrogen-containing functional groups which have the potential to react chemically with the resin. These functional groups are only introduced onto edge sites, which means that any chemical interaction *via* an amine/epoxy bond can only take place at these sites. The low power nitrogen plasma, however, also seems to activate the basal planes. The exact nature of this activation is not known, at present, but it is clear that plasma-activated basal

TABLE III
Results of single fibre fragmentation tests for sized XAU and plasma-treated XAU fibres.

Fibre type/ treatment	Mean fragmentation length (mm)	τ (MPa) (eq 1)	τ (MPa) (eq 2)*
XAU as-received; sized with EPON 828 resin and rinsed in toluene	1.0	21.4	23.7
XAU/Nitrogen plasma sized before exposure to air	0.44	53.6	61.5
XAU/Nitrogen plasma sized after exposure to air	0.84	26.0	32.3
XAU/Nitrogen plasma heated in vacuum at 130°C for 1 hour	0.60	37.9	45.0
XAU/Nitrogen plasma heated in vacuum at 1000°C for 1 hour	0.81	27.1	36.4

*Values of τ calculated from equation 2 are those used in the discussion.

planes readily pick up moisture from the environment. Hence it is reasonable to postulate that these activated basal planes may also adsorb resin in a similar fashion.

On exposure to air after the nitrogen plasma treatment, the fibres pick up moisture from the environment. It has been suggested that this may inhibit chemical interaction between the epoxy and the nitrogen-containing groups introduced onto the fibre surface as a result of the plasma treatment. From Table III, it can be seen that this is indeed the case, since the value of τ drops from 61.5MPa down to 32.3MPa. The fragmentation length distributions from these two sets of samples are shown in Figure 7. The distribution is much wider in the latter case. This decrease in interfacial shear strength may also be attributed to the deactivation of the basal planes.

Heating the fibres in a vacuum to 130°C for 1 hour to remove this adsorbed layer results in some recovery of the interfacial bonding with $\tau = 45.0$MPa. This value is still substantially lower than that originally achieved from plasma treatment. However, the value of τ is very close to the value of 46.2MPa obtained when using commercially-treated XAS fibres.

To determine whether or not this improvement was due to chemical interaction or just due to "cleaning" up the fibre surface, the fibres were heated in a vacuum at 1000°C for one hour. The value of τ from the fragmentation test using these fibres was 36.4MPa, which is somewhat higher than the value of 23.7MPa obtained for untreated XAU fibres. It can, therefore, be concluded that the presence of nitrogen-containing functionality does play a significant role in fibre/resin adhesion. This is in direct contrast to results obtained by Harvey *et al.*[1] from electrochemically-oxidised

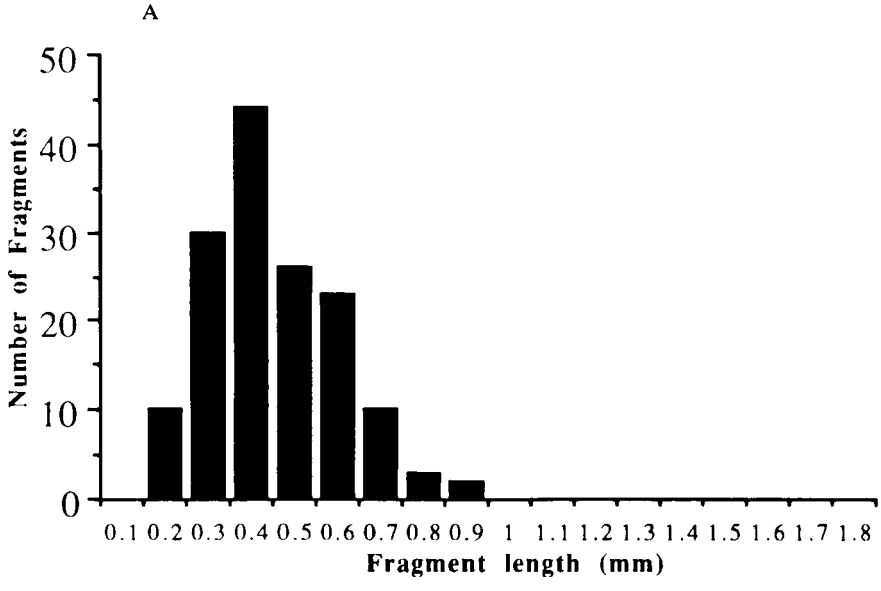

FIGURE 7 Fragment length distributions from single fibre fragmentation samples prepared with: A) nitrogen plasma treated fibres *before* exposure to air, and B) nitrogen plasma treated fibres *after* exposure to air.

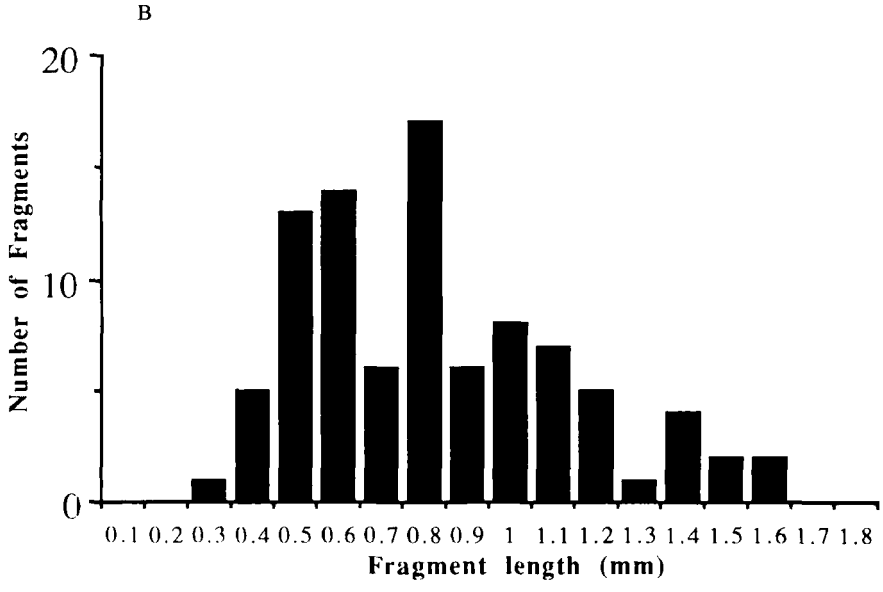

FIGURE 7 *(Continued)*

carbon fibres, where removal of chemical functionality did not result in a decrease in fibre resin adhesion. Drzal *et al.*[2] found that only a slight decrease in τ was obtained in similar experiments using commercially-treated fibres.

CONCLUSIONS

It has been shown that low power nitrogen plasma treatments of type II carbon fibres has no effect on the fibre diameter, no detrimental effect on fibre strength and can significantly improve fibre/resin adhesion. Furthermore, it has been demonstrated that any increase in interfacial bonding due to plasma treatment is apparently lost if the fibres are not sized before exposure to air. This leads us to conclude that during nitrogen plasma treatment, nitrogen surface functionality is introduced onto the fibre surface which is capable of reacting with the epoxy during the curing process. Activation of the basal planes also occurs which may lead to improved wetting by the epoxy resin.

Size protects the fibre from adsorbing moisture from the atmosphere which would inhibit the desired interfacial chemical reaction. Bonding can only be partially recovered for fibres that have been exposed to moisture when they are heated at 130°C; this results in an interfacial shear strength similar to that obtained with commercially-treated fibres. Heating the fibres after plasma treatment in a vacuum for 1 hour at 1000°C removes all surface functional groups. The resulting interfacial shear strength significantly decreases but still remains slightly higher than that measured from samples made from untreated fibres.

Acknowledgements

This work is currently being sponsored by the Science and Engineering Research Council, UK, (grant number GR/H/06705). The authors wish to thank Mr. E. Sammann for his initial help with designing the plasma cell, Miss Nicola Fluck for providing the data on plasma-treated carbon fibre strengths and diameters and Mr. S. O'Kell for providing the HOPG data.

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