AD-A234 183

THE EFFECT OF LOW POWER PLASMAS ON CARBON FIBRE SURFACES[*]

Carol Jones[**] and Ernest Sammann[***]

October, 1989

National Center for Composite Material Research
at University of Illinois, Urbana - Champaign
A DoD University Research Initiatives Center funded by the
Office of Naval Research, Arlington, VA

---

[*]   Invited presentation, 4th American Composite Society Meeting,
      October, 1989 .

[**]   Senior Research Scientist,
      National Center for Composite Materials Research

[***] Research Engineer,
      Materials Research Laboratory

91 3 28 048

THE EFFECT OF LOW POWER PLASMAS ON CARBON FIBRE SURFACES

Carol Jones (formerly Kozlowski), NCCMR, Talbot Laboratory,
University of Illinois, Urbana, Il.61801.
[currently at Dept. of Physics, IRC., Liverpool University
Liverpool, England]

E.Sammann, Materials Research Laboratory, University of Illinois,
Urbana, Il.61801.

A-1

ABSTRACT

The effect of a variety of low power plasmas (eg. NH3, N2, air and Ar) on carbon fibre surfaces has been studied using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). A comparison is made been two PAN based fibres (T300-from Amoco, and HMU-from Hercules), a pitch based fibre (P100-Amoco), and single crystai graphite. Grazing angle techniques have been used to probe only the first 12-15 A of the fibre surface and to obtain non-destructive depth information. Plasma treatments were carried out in an insitu plasma treatment cell which was attached to a PHI 5400 X-ray photoelectron spectrometer. This enabled the immediate effects of the plasma to be studied before the treated surface was exposed to air.

Air plasma treatments of single crystal graphite and pitch based fibres resulted in the incorporation of alcohol type functionality onto their surfaces, whereas the PAN based fibre surfaces contained both alcohol and carboxyl type groups. The effect of the air plasma on PAN based fibres is very similar to that of electrochemical oxidations in aqueous electrolytes.

Nitrogen plasma treatments gave very similar results to ammonia plasmas introducing amine functionality, however, the concentration of these groups, as expected, is greater for ammonia plasma treatment. The latter also removed all oxygen containing groups from the surface of the fibre. The high modulus PAN based fibre was less prone to attack by these plasmas. By biasing the sample to a negative potential the number of amine groups increased dramatically and the chemistry of the surface became similar to that of the treated lower modulus fibres. Pitched based fibres were less reluctant to react. The number of amine groups introduced was increased only slightly by increasing the sample bias. The lack of reaction is explained by the structure of the fibre surface itself.

Air exposure of these activated plasma treated surfaces resulted in a strongly bound -O-H layer due to the adsorption of moisture onto the surface. The amount was found directly proportional to the number of functional groups introduced by plasma treatment.

Significant etching or pitting was not observed in the SEM micrographs. Comparing XPS spectra representative of the immediate surface with those taken at bulk sensitive angles, it was concluded that chemical change only occurred in the first few atomic layers of the fibre. This suggests that the degradation of the mechanical properties would be minimal.

INTRODUCTION

There have been many methods used to alter the surface chemistry of carbon fibre surface in an attempt to promote chemical bonding between the fibre and resin in composite materials. Strong bonding allows good stress transfer between the two components. Most effective commercial treatments have been of an electrochemical nature. The reasons why electrochemical oxidations improved fibre/resin bonding has been a subject of much debate since the late 1960's.

Sharp et al [1] observed the presence of large misorientated crystallites weakly bound to the fibre surface and suggested that these were responsible for the poor interfacial bond between fibre and resin in the resulting composite. Drzal and his coworkers [2] showed that fracture in composites made from untreated fibres did occur between these weakly bound crystallites and the fibre itself, however, in composites made from commercially treated fibres fracture took place at the fibre/epoxy interface. They also postulated that the number of chemical groups on the fibre surface was too few to play a dominant role in fibre/matrix adhesion. Kozlowski et al.[3] came to a similar conclusion, observing that there was no relationship between the amount of chemical functionality on the fibre surface and the interfacial bond strength of the composite.

The above does not rule out the possibility of forming a chemical bond between fibre and resin, it just implies that electrochemical methods do not result in sufficient functional groups per unit area to play a significant role in fibre/resin adhesion. There is some evidence that plasma treatments may fit this requirement [4]. A patent submitted by J.C.Goan et al. in 1973 [5], described the use of ammonia plasmas to aminate the fibre surface. Amine groups are well known for their reaction with epoxy functionality. A few research groups have studied the effect of ammonia plasmas on carbon fibre surfaces [eg. 6,7,8], however in most cases significant etching and pitting of the fibres takes place. Allred and Stoller[9], in a study of Kevlar fibres, observed that the activated surfaces produced by a plasma reacted more effectively if the fibres were protected in an inert environment and immersed into the resin as soon as possible after treatment. Air exposure deactivated the surface inhibiting fibre/resin bonding.

The above has lead the authors to develop a low power (1W) plasma treatment cell. This would significantly decrease the amount of etching occurring on the fibre surface since the energy of the impacting ions within the plasma are well below the sputtering threshold. It will be shown that only the chemistry of the first few layers of the fibre is altered and the fibre properties would remain intact.

EXPERIMENTAL

The fibres studied in these experiments (void of commercial treatment and sizing) were T300 and P100 supplied by Amoco Performance Products, and HMU supplied by Hercules.

Surface treatments were carried out in an insitu plasma cell attached to a PHI 5400 X-ray photoelectron spectrometer (schematically shown in Fig.1). The cell itself consisted of a 1.5" diameter glass tube connected to the spectrometer by a gate valve
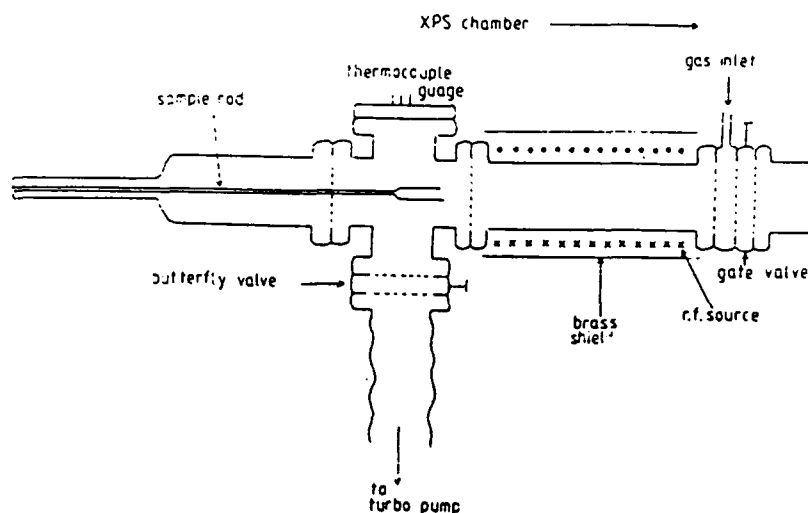
XPS chamber ⟶

Figure 1 Schematic Diagram of the *Insitu* Plasma Cell

which allowed the cell to be isolated from the main XPS chamber during treatments. A radio frequency of approximately 15MHz was coupled from an external coil by an unusual scheme that permitted low power operation (<1W). Continuous gas flow was maintained from the leak valve (as shown) at one end of the tube to a butterfly valve at the other, which opened to a turbomolecular pump. Samples were transferred to the main chamber to a plasma cell using a transport rod (Perkin Elmer Model 04-745) which had been extended with an aluminium bar.

After treatment, the plasma chamber was evacuated to 10-8 Torr allowing sample transfer back into the spectrometer in which UHV (10-10T) conditions were easily regained with the gate valve closed. XPS spectra were collected in both bulk and surface sensitive modes [4], using a Mg anode X-ray source (hv=1253.6eV).

SEM micrographs were obtained with a Hitachi S800 microscope. With its field emission gun magnifications of 100-300 thousand could be achieved.

RESULTS AND DISCUSSION

Air Plasmas

Figure 2 shows the carbon 1s spectra of freshly cleaved graphite before and after exposure to an air plasma for 30 seconds. The carbon 1s spectrum of the untreated cleaved crystal consists of a single peak at binding energy 283.4eV. This peak has a tail towards higher binding energy arising from the conduction band interaction in the photoemission process and the small feature at 6.9eV from this peak is due to a plasmon [10]. It can clearly be seen that exposure to an air plasma oxidises the crystal surface due to the presence of a chemically shifted peak at 1.8eV in the spectrum of the treated surface. This peak corresponds to alcohol type functionality. A comparison of spectra
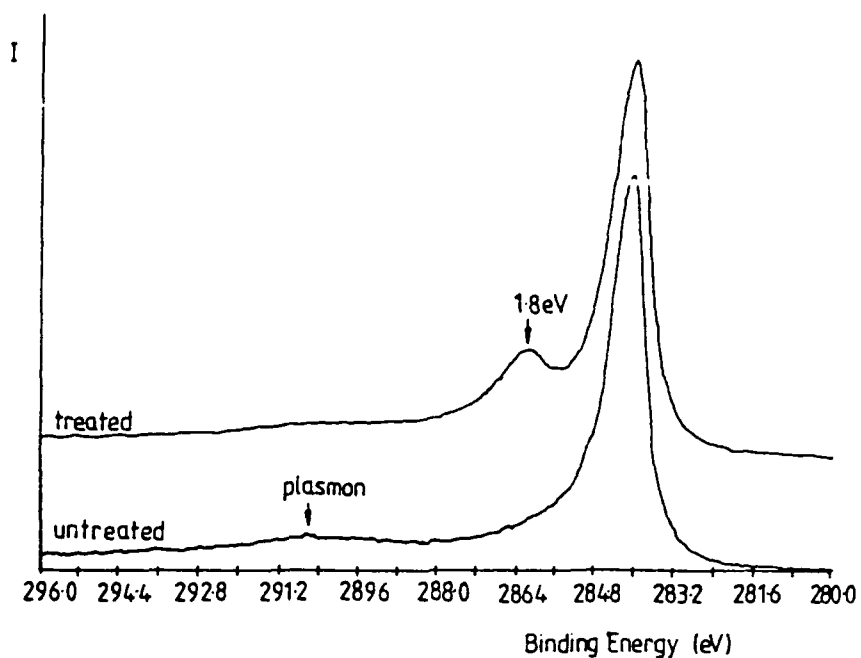
Figure 2 Carbon 1s Spectra of Freshly Cleaved Single Crystal Graphite Before and After Exposure to an Air Plasma.
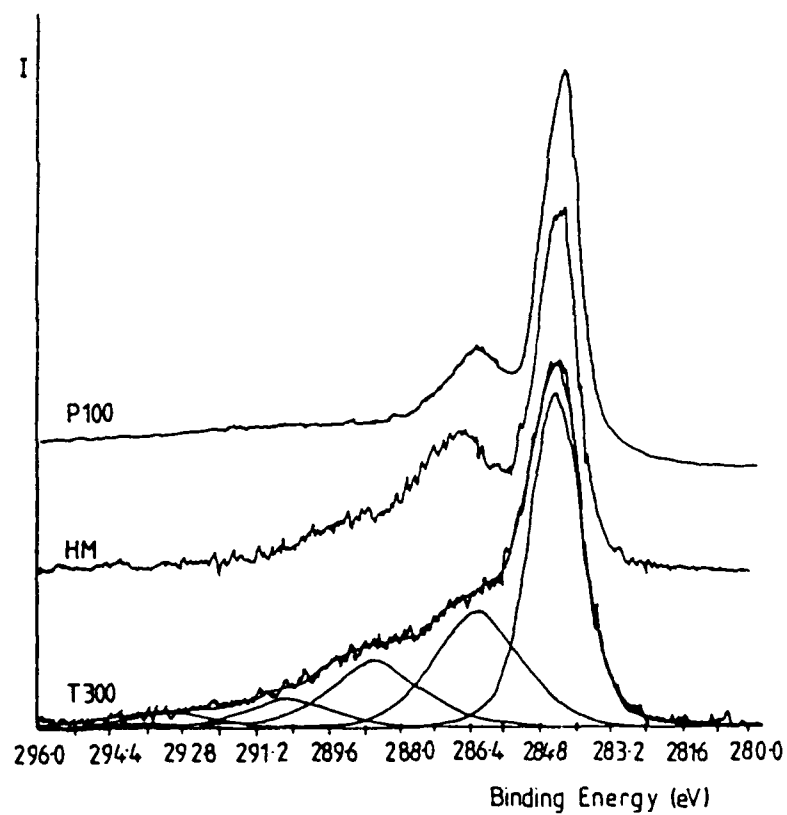

Figure 3 Carbon 1s Spectra of Carbon Fibres After Air Plasma Treatment

taken at surface and bulk sensitive angle reveals that oxidation has only taken place in the outermost layers of the crystal surface. Surprisingly, no carboxyl functionality is detected on these surfaces.

The corresponding carbon 1s spectra of several different fibres exposed to an air plasma for 30 seconds are shown in Fig.3. The spectrum of the pitch based fibres is very similar to that of single crystal graphite. This is expected since the structure of their surfaces are essentially the same. However, this is the first time that only one type of functional group has been introduced onto a carbon fibre surface by any method. Its effect on the interfacial shear strength in the corresponding epoxy resin composite can now be tested. The PAN based fibres possess two type of chemical functionality. Their carbon 1s spectra are very similar to those of carbon fibres electrochemically oxidised in aqueous electrolytes. The chemical shift of the first species is different in the two cases, 1.6eV for the lower and 2.1eV for the higher modulus fibres, the latter possessing keto-enol character seen for fibres electrochemically treated in acidic solutions. As noted previously from electrochemical oxidations[11], the relative intensity for the carboxyl groups increases on the fibres with the greater number of edge sites on their surfaces.

As seen for graphite, there are large differences in the amount of oxygen containing species detected at surface and bulk sensitive angles. Even after prolonged exposures the difference between surface and bulk oxygen concentration remains the same (from 30 seconds to 30 minutes). Two processes could be occurring,

a) saturation of the reactive sites has taken place, or

b) equilibrium has been reached between fibre surface oxidation and oxidation of the already existing groups to CO_2. Removal of loosely bound C/O species could occur by electron assisted desorption. The latter reason seems more likely, however this would lead to etching of the fibre surface and no such etching is observed in the SEM micrographs.

This is a perfect method to introduce acid and alcohol groups onto the fibre surface without damaging the fibre itself and could be a useful alternative to electrochemical oxidation in aqueous solutions. The treatment times needed to introduce the desired changes in fibre surface chemistry are low, unlike those suggested by other workers [5,6,7].

Argon Plasmas

Fibres subjected to an argon plasma always contained significant amounts of oxygen functionality on their surface. This could only arise by oxygen pickup in the treatment cell. The argon plasma creates a very reactive fibre surface which will react with any background oxygen present in the system. It must be remembered, however, that the pressures involved are .1Torr of argon and that transfer has taken place in 10^{-9} Torr. This implies that using Ar as a 'control' may be a little misleading. Pretreatments in an Ar plasma [9] which increases the amount of amine functionality introduced onto the fibre surface by an ammonia plasma is almost certainly a result of preactivation of the surface which reacts immediately with the ammonia gas present in the system. It has also been found [9] that exposure to argon plasma degrades the fibre properties and only short exposures are

recommended. With the system used in this study, the plasma may not have such a damaging effect due the comparatively low power used causing the impact energy on the ions in the plasma to be well below the sputtering threshold.

Ammonia, and Nitrogen Plasmas

Both nitrogen and ammonia plasmas are successful in introducing C/N functionality on carbon fibre surfaces, however, the amount depends on the structure of the fibres used (see Fig.4). Ammonia plasmas are also more successful at producing C/N groups onto the fibre. This would be expected since ammonia gas is more chemically reactive than nitrogen.

For the lower modulus PAN based fibres, exposure to an ammonia plasma removes all the oxygen species present, the nitrogen plasma is not so successful. Both of these plasmas introduce three type of nitrogen containing species, seen in the nitrogen 1s spectra (see Fig.5) of the treated fibre surface, with binding energies 398.9eV, 400.4eV and 402.8eV. The two main signals are very similar to those produced as a result of electrochemical oxidation in ammonium salt electrolytes [12], however, in this case peak assignment to amide is invalid since an O1s signal was not detected. The binding energy of a standard PhNH2 has previously been reported as 399.1eV [13]. The relaxation energy associated with the ejection of a photoelectron is far greater for a graphitic-like lattice than for a benzene ring [14,15] and hence a shift of -0.2eV from the observed PhNH2 is not unlikely for aromatic amine
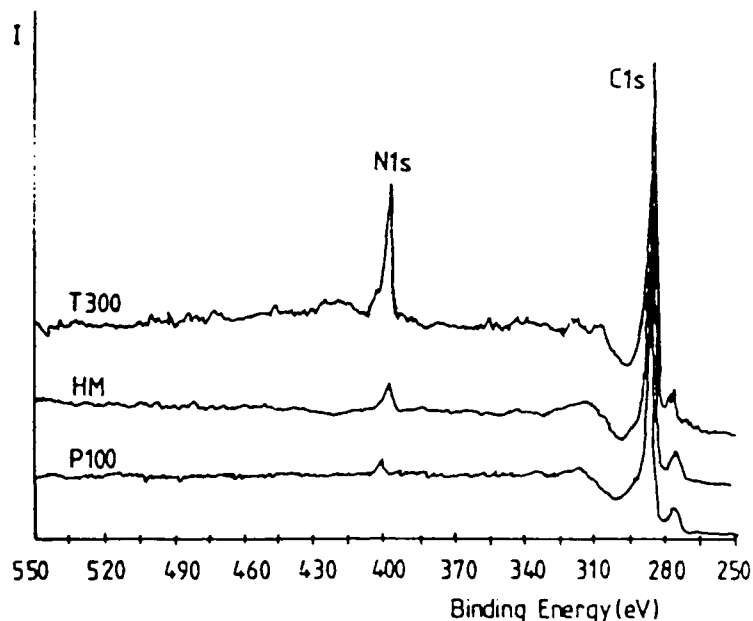

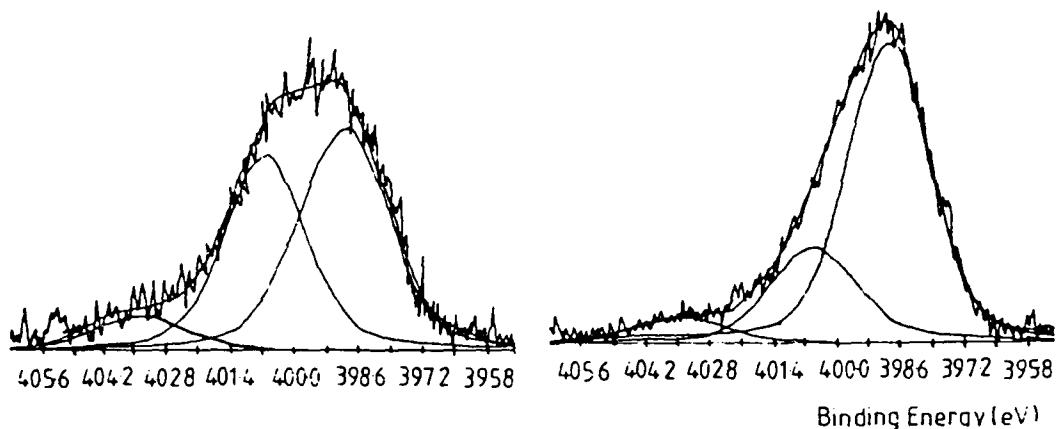Figure 4 Widescan Spectra of Carbon Fibres After Ammonia Plasma Treatment

Figure 5 Nitrogen 1s Spectra of T300 Treated With a)a Nitrogen Plasma,

and b) an Ammonia Plasma

groups on carbon fibre surfaces. The relative intensity of this peak is greater as a result of ammonia plasma treatment than for nitrogen plasma exposure. A closer look at bulk and surface sensitive nitrogen 1s spectra reveals that these amine groups are present in greater quantities at the surface. The peak at highest binding energy is most probably a positively charged ammonium species similar to that reported by Chang and Navalov [16]. The other peak at 400.4eV could be associated with aliphatic amines. Cyano groups (-C≡N) are unlikely to remain on the fibre surface as these would be prone to electron assisted desorption.

These aminated surfaces certainly have the potential to react with epoxy coatings, however, many other coating materials containing the chemical functionality reactive to amine groups could be chosen. A carbon fibre/epoxy interface void of any carboxyl or alcohol functionality is probably less likely to absorb water. Currently all electrochemically treated fibre surfaces do contain carboxyl groups.

As shown in Figure 4, the amount of surface nitrogen containing groups incorporated onto the higher modulus PAN based fibres was much lower than for the T300 fibres. This is undesirable since the aim of the treatment was to introduce a substantial amount of amine functionality to promote chemical bonding between the fibre surface and the epoxy resin. To improve the situation, these high modulus fibres were treated with an air plasma followed by an ammonia plasma to see if a substitution reaction could take place between the C/O species introduced by air plasma exposure and the ions in the ammonia plasma.
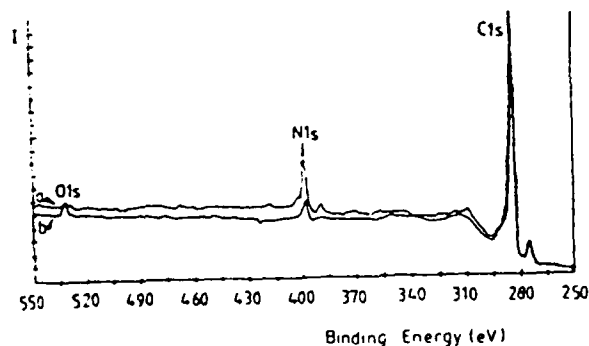

Figure 6 Widescan Spectra of HMU Fibres Treated in an Ammonia Plasma

a) With, and b) Without Biasing.

This did not occur. Instead, all of the C/O groups were removed and only a small number of C/N groups were incorporated onto the fibre in similar quantities to surfaces exposed solely to an ammonia plasma.

A more successful method of increasing the number of amine groups was to accelerate the ions inside the plasma itself ie. increase their impact energy. This was done by biasing the samples to a negative potential (10-30V) with respect to a ground electrode within the plasma. Fig. 6 shows the widescan spectra of HMU fibres that have been exposed to an ammonia plasma with and without biasing. By comparing the relative intensity N1s:C1s ratios, it can easily be concluded that biasing the fibres increases the number of C/N groups on the surface. SEM micrographs reveal no etching or pitting has taken place even with biasing the fibres during treatment(see figure 7). These surfaces appear very similar to the untreated fibres. A similar result was obtained for nitrogen plasma treatments. Closer examination of the nitrogen 1s spectra shows that a similar surface chemistry to the lower modulus fibres is obtained. It, therefore, seems reasonable to expect the bonding between these fibres and the resin will be similar to that of the lower modulus fibre and a comparable interfacial shear strength measured.

Pitch fibres did not behave in the same manner. Increasing the sample bias to several hundred volts (compared to a bias of -10V needed for the PAN based fibres) did not significantly increase the number of amines incorporated. This implies that amines are incorporated mostly onto edge sites or defects on the fibre surface.A
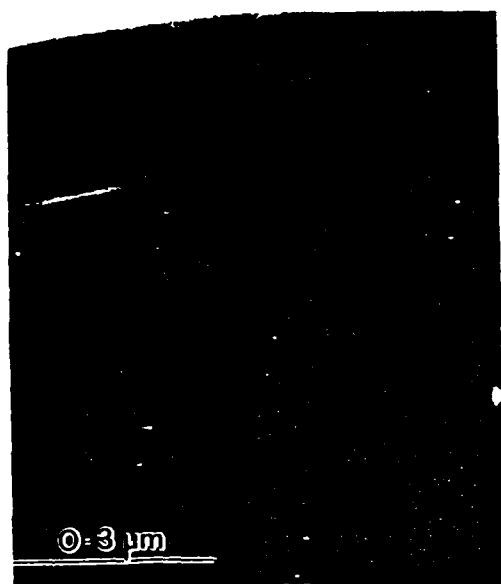

Figure 7 Scanning Electron Micrograph of
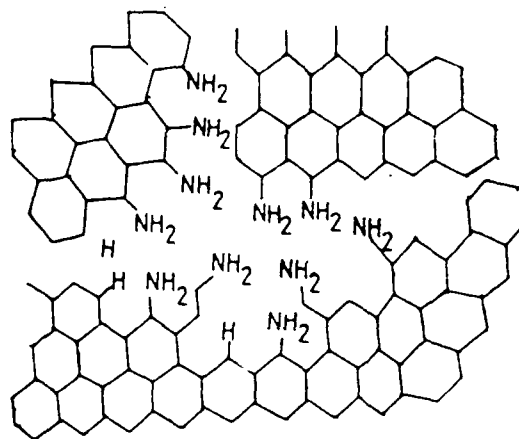HMU Fibres After Ammonia
Plasma Treatment with 30V Bias.

Figure 8 Model of PAN Based Carbon Fibres
Treated With an Ammonia Plasma

schematic model can be drawn for PAN based fibres exposed to ammonia plasmas and is shown in Fig. 8. This is unlike the surface produced by an air plasma where both the basal planes and the edge sites are oxidised to form a very thin 'graphitic-oxide' layer.

Exposure to Air

Both Alred et al [9] and Wertheimer et al [17] have shown that plasma treated Kevlar surfaces are deactivated when exposed to air. The latter suggested that this might be due to a recombination of free radicals on the fibre surface and/or oxidation of these activated sites. Fig.9 shows a widescan spectra of T300 fibres treated with an ammonia plasma before and after exposure to air. There is significant 'oxygen' pickup upon air exposure. However, no change in the carbon 1s and nitrogen 1s spectra was observed indicating that oxygen pickup was due to a strongly bound physisorbed layer. The binding energy of the oxygen species is 532.4eV which is characteristic of strongly bound -OH species and in this case most probably arises from moisture in the air. This physisorbed layer would certainly inhibit the desired fibre/epoxy bonding in composites. The amount of 'oxygen' pickup is directly related to the number of functional groups introduced onto the fibre surface during plasma treatment.

CONCLUSIONS

The chemistry of carbon fibre surfaces can be modified by using low power plasmas. Air plasmas give very similar results to electrochemical oxidations in aqueous solutions, however the depth to which the fibre is effected is less likely to cause damage to the fibre itself. Nitrogen and ammonia plasmas can both be used to introduce amine groups onto the surface, the ammonia treatments removing all the oxygen containing species in the lower modulus fibres. Exposure of activated plasma treated surfaces to air results in a strongly bound physisorbed layer of water which will inhibit the desired reaction with the epoxy resin. Hence to study the effect of induced surface chemistry on fibre/resin bond strengths, it is essential to handle the fibres in an inert environment and to immerse the fibres into resin immediately after plasma treatment before exposure to air. Failure to do this will result in similar conclusions to those drawn for electrochemically
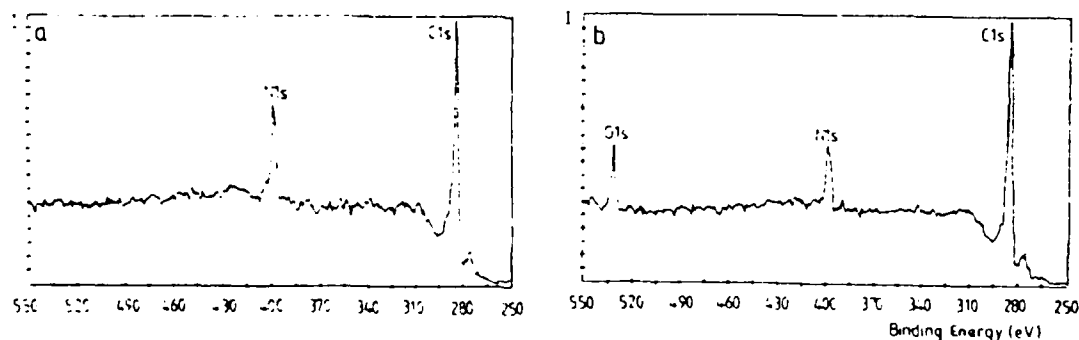

Figure 9 Widescan Spectra of T300 Fibres Treated with an Ammonia Plasma

a) Before, and b) After Exposure to Air.

treated fibres [3]

ACKNOWLEDGEMENTS

REFERENCES

1. Sharp, J.V., and Burnay, S.G., Radiation Eff., Vol.22, No.1, 1974, pp.45
2. Drzal, L.T., Rich, M.J., and Lloyd, P.F., J.Adhesion, Vol.16, 1982, pp.1.
3. Harvey, J., Kozlowski, C , and Sherwood, P.M.A., J.Mat.Sci., Vol.22, 1987, pp.1585.
4. Jones, C. Carbon, Vol.27, No.3, 1989.
5. Goan, J.C., US Patent 3,776,820 Dec.4 1973 assigned to the Great Lakes Corporation.
6. Donnet, J.B., Brendle, M., Dhami, T.L., Bahl, O.P., Carbon, Vol.24, No.6, 1986, pp.757-770.
7. Loh, I.H., Cohen, R.E., and Baddour, R.F., J.Mater.Sci., Vol.22, No.8, 1987, pp.2937-2947.
8. Sun, M., Hu, B., Wu, Y., Tang, Y., Huang, W., Da, Y., Composites Science and Technology, Vol.34, 1989, pp.353-364.
9. Allred, R.E., and Stoller, H.M., Proceedings of SAMPE Conf., 1988.
10. Boehm, H.P., and Schogl, R., Carbon, Vol.21, 1983, pp.345-358.
11. Kozlowski, C., and Sherwood, P.M.A., Carbon, Vol.25, No.6, 1987, pp.751-760.
12. Kozlowski, C., and Sherwood, P.M.A., Carbon, Vol.24, No.3, 1986, pp.357-363.
13. Nordberg, R., Brecht, H., Aldridge, R.G., Fahlmann, A., and Van Wazer, J.R., Inorg.Chem., Vol.9, 1970, pp.2469.
14. Davis, D.W., and Shirley, D.A., J.Elec. Spec. and Rel.Phenom, Vol.3, 1974, pp.137-163.
15. Kozlowski, C., and Sherwood, P.M.A., unpublished results.
16. Chang, S.G., and Novakov, T., Amorphous Environment, Vol.9, 1975, pp. 495.
17. Wertheimer, et al. Proceedings of SAMPE Conf., 1988.