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THE EFFECT OF LOW POWER PLASMAS ON CARBON FIBRE SURFACES.[*] Part 2: A COMPARISON BETWEEN LOW AND HIGH MODULUS PAN BASED FIBRES WITH PITCH BASED CARBON FIBRES.

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THE EFFECT OF LOW POWER PLASMAS ON CARBON FIBRE SURFACE

Part 2:- A COMPARISON BETWEEN LOW AND HIGH MODULUS PAN BASED FIBRES WITH PITCH BASED CARBON FIBRES.

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ABSTRACT

A comparison of the effects of a variety of low power (<1W) plasmas (air, NH_3 and N_2) on highly ordered pyrolytic graphite (HOPG), polyacrylonitrile (PAN)-based and pitch based carbon fibres has been studied using X-ray photoelectron spectroscopy. Grazing angle techniques have been used to probe only the first 12-15 A of the fibre surface. Plasma treatments were carried out in an *in situ*plasma 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.

The reactivity towards a particular plasma is shown to be largely dependent on the structure of the fibre surface. Air plasmas proved much more reactive to the fibre surface than either nitrogen or ammonia plasma resulting in alcohol type groups being incorporated onto the basal planes and carboxyl groups onto the edge sites. Ammonia and nitrogen plasmas only attacked the edge sites with the formation of aliphatic and aromatic amines ($C-NH_2$) together with small number of immines(C=NH). The number of C/N groups produced on the higher modulus fibres was therefore undesirably low. Their concentration was increased by biasing the fibres to a negative potential (10-30V) during plasma exposure. Examination of these treated fibre surfaces showed that little, if any, etching of the fibre surface had taken place and hence damage to the fibre was minimal.

1.INTRODUCTION

Over the past couple of decades a great interest has developed in being able to improve and control the bonding between fibre and matrix in carbon fibre/synthetic resin composites. This would enable a greater degree of control over composite properties such as interlaminar shear and compressive strength. The more successful techniques to date involve treatment of the carbon fibre surfaces prior to their incorporation into resin. These treatments are mostly electrochemical oxidations in aqueous electrolytes[e.g.1] which remove weakly bound crystallites on the fibre surfaces providing a mechanically 'sound' surface to which the resin can adhere[2]. Chemical bonding between fibre and resin was thought not to play a dominant role in fibre/resin adhesion since the number of functional groups per unit area of the fibre surface was too low to have any effect.

In a comparison between electrochemical and plasma treatments of carbon fibres[3], the plasma treatments increased the surface concentration of these functional groups and hence may promote a greater number of chemical bonds to be formed between fibre and resin. The type of functionality introduced onto the fibre surface can be readily controlled by choosing a suitable gas plasma. A few research groups have studied the effect of plasma on reinforcing fibres [4-8] with a great emphasis on using ammonia plasmas to introduce amine groups onto their surfaces. These amine groups have the potential to react with many polymers especially epoxy resins. Most of these treatments however, remove a substantial amount of material causing pits to form in the fibre surface [5,6].

One of the main objectives of a successful fibre surface treatment is to alter the fibre surface chemistry while retaining the mechanical properties of the fibres themselves. This has led the authors to develop a low power plasma (<1W) treatment which only alters the chemistry of the immediate surface layers without causing severe etching of the fibre. In a previous publication [8] the effects of these low power plasmas on a type II PAN based fibre were discussed. In this paper we report a comparison between PAN and pitch based carbon fibres, together with highly orientated pyrolytic graphite (HOPG).

2. EXPERIMENTAL

The fibres used in this study included untreated and unsized T300 fibres (supplied by Amoco Performance Products) and HMU fibres (supplied by Hercules). Sized but untreated pitch based fibres from Amoco, thoroughly washed to remove any sizing, were also examined.

Fresh surfaces of single crystal graphite were achieved by cleaving the crystal (ie.removing the outer layer of the crystal with sticky tape) immediately prior to incorporation into the plasma chamber.

Plasma treatments were carried out in an *in situ* plasma chamber attached to a PHI 5400

X-ray photoelectron spectrometer (described elsewhere[8]). This enabled the immediate effect of the plasma on the fibre surfaces to be studied before being exposed to air. The fibre samples were electrically isolated from the supporting rod allowing a controlled bias to be applied to the fibres independent of the RF power exciting the plasma. Fibre surfaces were examined using X-ray photoelectron spectroscopy to determine the surface chemistry before and after treatment. The spectra were collected at grazing angles to enhance the signal from the immediate surface layers of the fibre[3]. All intensity ratios reported in this paper have incorporated the relative sensitivities calculated for a hemispherical analyser (C1s 0.296, N1s 0.477, and O1s 0.711) [9].

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

3. RESULTS AND DISCUSSION

3.1 *Air Plasmas*

Figure 1 shows the carbon 1s spectra of freshly cleaved single crystal graphite before and after exposure to an air plasma for 30 seconds. The spectrum of the untreated cleaved crystal consist of a single peak at a binding energy 284.3eV. This peak exhibits the characteristic tail towards higher binding energy arising from the conduction interaction in the photoemission process together with a plasmon feature approximately 6.9eV from the main peak[10]. The spectrum from the plasma treated sample consists of an additional chemically shifted species 1.8eV from the main graphitic peak. This arises from alcohol type functionality. However, it does not originate from isolated -OH groups attached to a graphitic ring as the expected chemical shift for these species lies between 1.4 and 1.6eV. Table 1 lists the chemical shifts obtained from alcohols in a variety of chemical environments. In a parallel study of this plasma oxidation[12] using scanning tunnelling microscopy, these -OH groups are found to initially be introduced in clusters on approximately 8 sites and sit directly above the carbon atoms. Patches of well oxidised area are also seen from which images could not be taken. This indicates that although the oxidation seems to remain within the surface layers it is not uniform. This hydroquinone-like structure is in keeping with electrochemical characterisation of plasmolysed graphitic surfaces [13]. Further oxidation of these alcohol groups does not occur since signals due to carboxyl functionality were not detected.

The corresponding carbon 1s spectra of several different fibres exposed to an air plasma for 30 seconds are shown in Fig.2. It can clearly be seen that each type of fibre has behaved differently to the plasma. The spectrum of plasmolyzed pitch based fibres is very similar to that of the HOPG. This is the first time that only one type of functional groups has been introduced onto a carbon fibre surface by any method. Both the high and low modulus PAN based fibre surfaces contain at least two types of chemical functionality. These plasma oxidised fibre surfaces are very similar to those which have been electrochemically oxidised in aqueous electrolytes [e.g. 14]. The chemical shift of the first species, however, is different in the two cases, 1.6eV for the lower and 2.1eV for the higher modulus fibres. A shift of 1.6eV almost certainly corresponds to alcohol functionality. However, a chemical shift of 2.1eV is far too large for a simple alcohol species or even those merely associated with other alcohol groups attached to the same ring. The only example of an alcoholic shift being as large as 2.1eV is when it is in the para position to a carboxyl group on a benzene ring[11]. It is therefore suggested that these groups possess ketoenol character in keeping with results obtained from fibres electrochemically oxidised in acidic solutions[14] and resembling the structure of graphitic oxide proposed by Boehm et al [15].

Carboxyl groups are present on both fibre surfaces giving rise to a peak at 4.1eV from the main peak. For lower modulus PAN based fibres, where the surface crystallites are small and not so well aligned, these carboxyl groups account for 30% of the overall carbon signal. Signals at higher binding energy arise from π-π^* shake up satellites. These satellites have been detected in the C1s spectra of a number of model compounds and polymers [11,16]

3.2 *Ammonia and Nitrogen Plasmas*

It has been shown previously [8] that both ammonia and nitrogen plasmas are successful in introducing C/N functionality onto fibre surfaces. It was also concluded that these were a combination of aromatic and aliphatic amines ($-NH_2$) and immines ($-C=NH$). Both Loh [4] and Evans [13] tried to compare the effects of ammonia plasma on structurally different carbon surfaces. Unfortunately, in both cases their samples were exposed to air before chemical analysis was carried out. The increase in the amount of oxygen they observed after treatment in ammonia plasmas has recently been shown[13] to be due to moisture adsorption from the environment and not a post treatment oxidation as suggested.

Fig.3 shows widescan spectra (taken at a take off angle of 15°-surface sensitive angle) from all three types of fibres after exposure to an ammonia plasma for 5 minutes. Once more each fibre has behaved differently to the plasma, the lower modulus PAN based fibre being the most reactive. The lack of reactivity shown by the pitch based fibres tends to indicate that chemical change has only occurred on the edge sites (and defects) and not on the basal planes. As the percentage of edge sites increases, so does the amount of "nitrogen" incorporated onto the fibre surface during treatment.

This lack of reactivity is undesirable since the aim of the treatment was to introduce amine groups in sufficient concentration to promote chemical bonding between the fibre and resin. The method suggested by Stoller and Allred [17] was to pretreat the fibres in an argon plasma for approximately 10 seconds prior to ammonia plasma exposure. This resulted in a 30% increase in the amount of amine functionality incorporated onto polyaramid fibres. In our case, the number of nitrogen containing groups did increase on the higher modulus fibres with Ar pretreatments but only by a very small amount. This is almost certainly due to the lack of sputtering taking place in these low power plasmas. In the higher power plasmas, argon pretreatments would tend to open up the rings of the graphitic lattice resulting in a very reactive surface. Pretreatments in an air plasma were also performed in a hope that the oxygen functionality on the surface would be substituted by nitrogen containing groups. In these cases, most of the C/O groups were removed and only a very small number of nitrogen containing species incorporated.

A more successful method of increasing the number of amine groups introduced was to accelerate ions from the plasma to increase their impact energy on the fibre surfaces. This was done by biasing the fibre samples to a negative potential with respect to a ground electrode within the plasma. Fig.4 shows the widescan spectra of HMU fibres that have been exposed to an ammonia plasma with and without sample biasing. The N:C ratio has increased from 0.07 to 0.18 on applying the sample bias and is approaching that of lower modulus fibre (0.22). A similar result was obtained for nitrogen plasma treatments. The nitrogen 1s spectra of these treated fibres is very similar to the lower modulus fibres in that three species are detected at 398.9eV, 400.3eV and 402.8eV. Their relative intensity ratios are very similar to the unbiased lower modulus fibres for both nitrogen and ammonia plasma exposures. An SEM micrograph (shown in Fig.5) reveals that little damage has been done to the fibre surface. It will be interesting to see if these treatments result in a similar interfacial shear strength in the corresponding composites. Although there was an increase in the amount of nitrogen functionality incorporated onto pitch fibres by biasing the fibres during treatment (N:C 0.01 to 0.05), the overall number of nitrogen containing species remained very small compared to the PAN based fibre and will be expected to have little effect on the interfacial shear strength of the composites. This increase in reactivity on biasing the fibres still seems to take places at edge sites and/or defects within the fibre surface. The basal planes remain unchanged.

Curve fitting the carbon 1s spectra in these cases would be an almost impossible task as one would have to take into account both the graphitic line shape (see Fig.1) and a more symmetric line shape for carbon species at edge sites. This contrasts with fibres treated with air plasmas where both the edge sites and basal planes have reacted to form an "oxidised layer". However, it is still beneficial to compare carbon 1s spectra from the unbiased with the biased sample (Fig.6). It can be seen that there is a substantial increase in the amount of chemically shifted species on the latter.

4. CONCLUSIONS

Amine groups are much more likely to be incorporated at the edge sites than on the basal planes. This is concluded by the lack of reactivity of the pitch based fibres which are very similar in structure to single crystal graphite. PAN based fibres, however, have a much more irregular surface with the graphite crystallites being tilted slightly off the fibre axis. This irregularity exposes many more edge sites and defects onto the surface which are reactive sites for the positively charged ions and other excited species within the ammonia (and nitrogen) plasma. These crystallites are smaller for the lower modulus fibres and hence the number of edge sites on their surfaces is greater. This accounts for their greater reactivity towards these low power plasmas. Biasing the sample to a negative voltage accelerates the positive ions near the sample surface and hence increases their impact energy, thus giving them enough energy to react on some sites which would normally not be affected.

Air plasmas have a much greater chemical reactivity towards graphite-like surfaces. It has clearly been shown that -OH groups are incorporated onto the basal planes of graphite and hence onto the basal planes in the carbon fibre surface. These groups, unexpectedly, are not oxidised to carboxylic acids. However, at the edge sites the expected oxidation stages take place and carboxylic acids are detected.

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REFERENCES

1. J.Harvey, C.Kozlowski and P.M.A.Sherwood, *J.Mat.Sci.*, 22, 1585 (1987).

2. L.T.Drzal, M.J.Rich and P.F.Lloyd, *J.Adhesion*, **16**, 1 (1982).

3. C.Jones, *Carbon*, **27**, No.3, 487 (1989)

4. I.H.Loh, R.E.Cohen, and R.F.Baddour, *J.Mat.Sci.*, **22**, No.8, 2937 (1987).

5. J.B.Donnet, M.Brendle, T.L.Dhami and O.P.Bahl, *Carbon*, **24**, No.6, 757 (1986)

6. Sun Mujin, Hu Baorong, Wu Yisheng, Tang Ying, Huang Weiqui and Da Youxian, *Composites Science and Technology*, **34**, 353 (1989)

7. J.C.Goan, US Patent 3,776,820 Dec.4 1973 assigned to the Great Lakes Corporation.

8. C.Jones and E.Sammann, submitted to Carbon.

9. Perkin Elmer 5400 XPS Software.

10. R.Schogl and H.P.Boehm, *Carbon*, **21**, 345 (1983).

11. C.Kozlowski, Ph.D Thesis (Newcastle Upon Tyne, England)

12. R.Brokenbrough et al., to be published.

13. J.F.Evans and T.Kuwana, *Analytical Chemistry*, **51**, No.3, 358 (1979).

14. C.Kozlowski and P.M.A.Sherwood, *J.C.S. Farad Trans.1*, **81**, 2745 (1985).

15. H.P.Boehm, U.Hofman and A.Clauss, *Proc. 3rd Conf. on Carbon*, Buffalo, Pergamon Press, 241, (1959).

16. D.T.Clark, B.J.Cromarty and A.Dilks, *J.Polym.Sci., Polym.Chem. Ed.* **16**, 3173 (1978)

17. H.M.Stoller and R.E.Allred, *Proc. of 18th Internat. SAMPE Tech.Conf.*, 993 (1986).

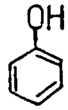
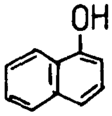
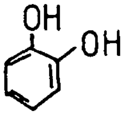
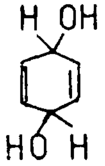
Compound	Molecular Structure	Binding Energy (eV)	Chemical Shift(eV)
Phenol		286.22	1.62
Napthol		285.94	1.34
Catechol		286.09	1.49
Hydroquinone		286.30	1.70

TABLE 1 Chemical Shifts obtained from alcohols in a variety of compounds[11].

FIGURE CAPTIONS

Figure 1 Carbon 1s spectra of freshly cleaved HOPG a) before and b) after plasma oxidation

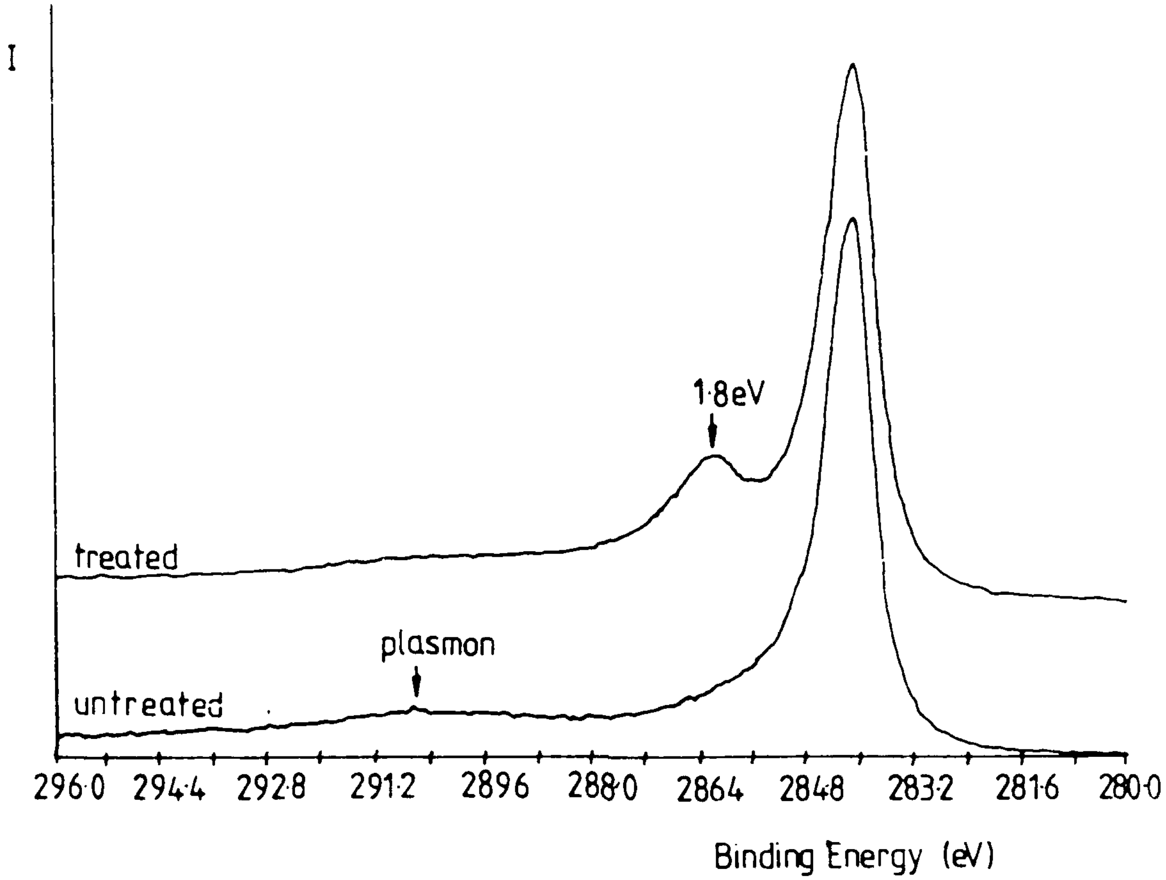
Figure 2 Carbon 1s spectra of carbon fibres exposed to an air plasma

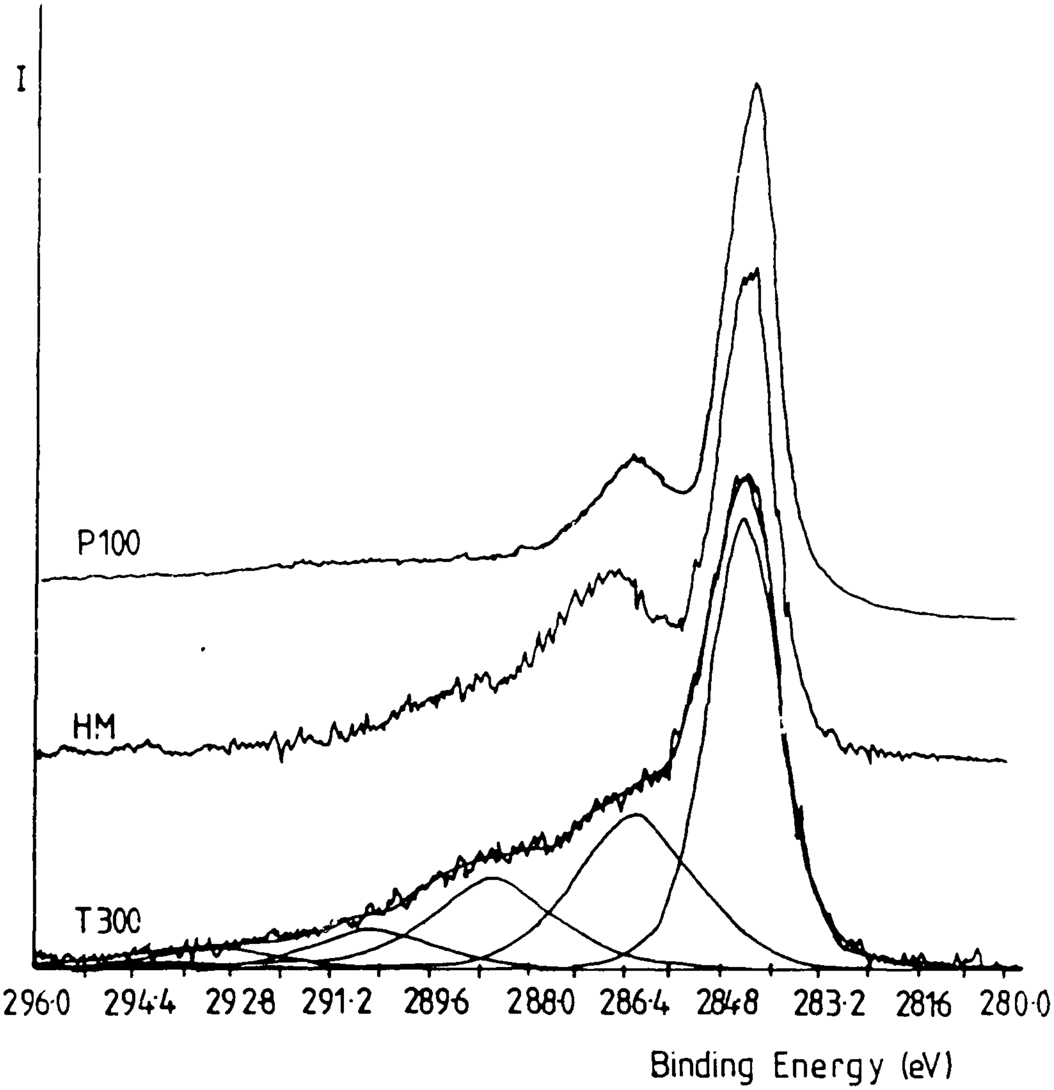
Figure 3 Widescan spectra of carbon fibres exposed to an ammonia plasma

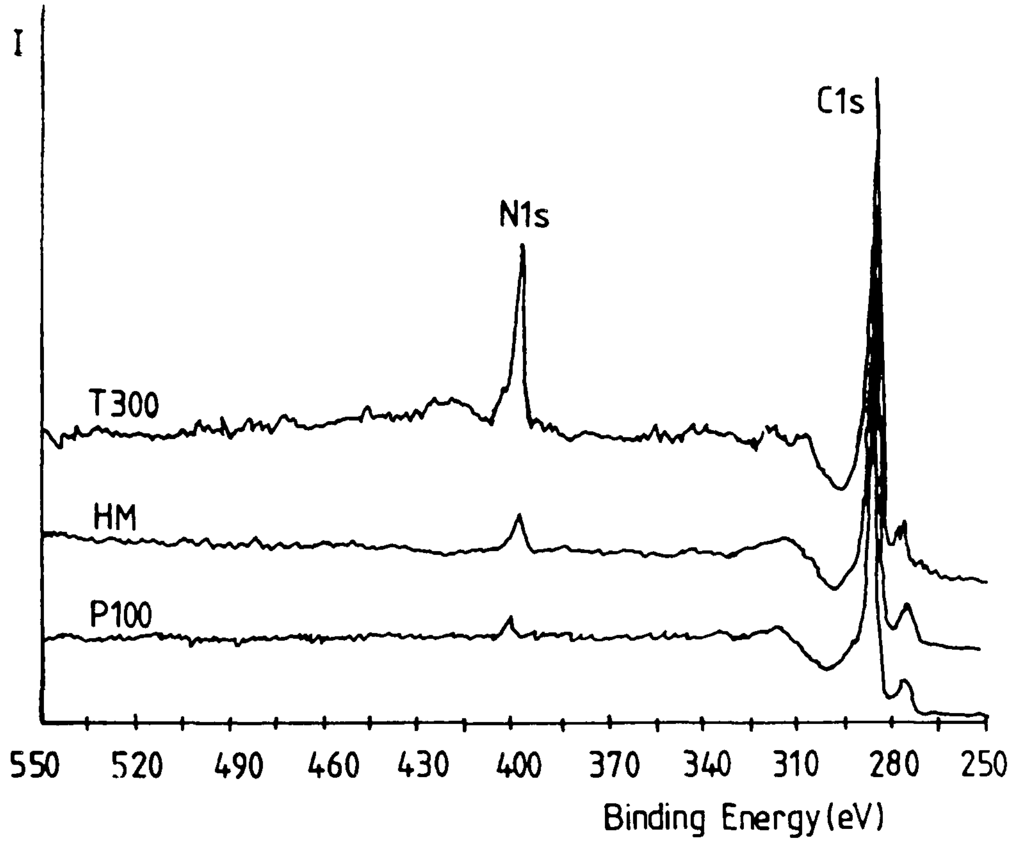
Figure 4 Widescan spectra of HMU fibres after exposure to an ammonia plasma a) with, and b) without sample bias.

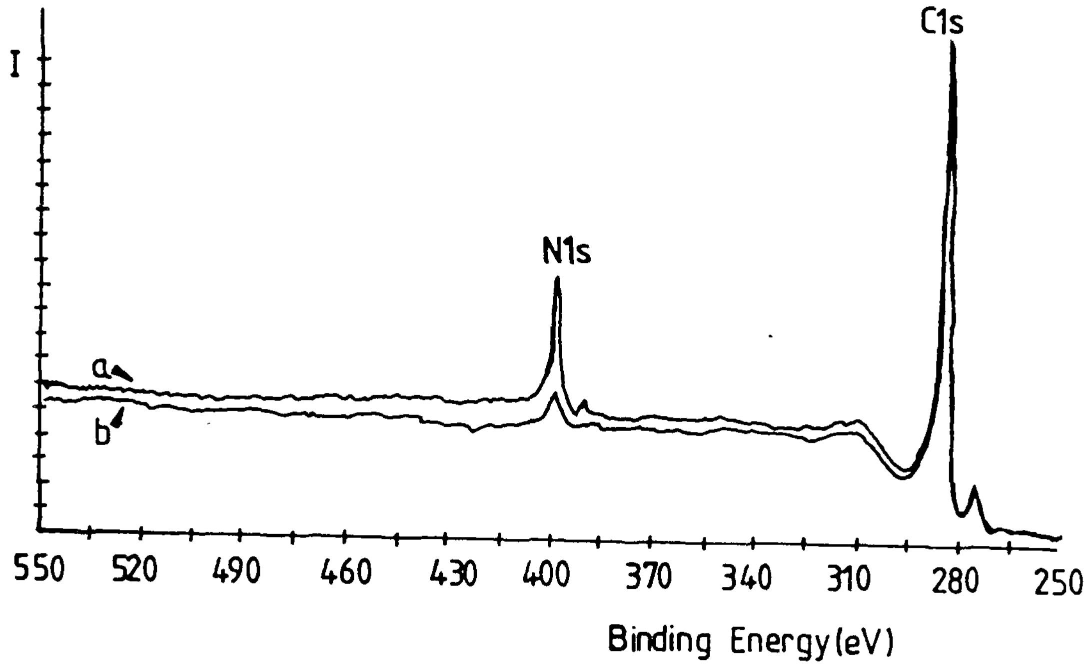
Figure 5 Scanning Electron Micrograph of HMU fibres exposed to an ammonia plasma with a sample bias of 30V.

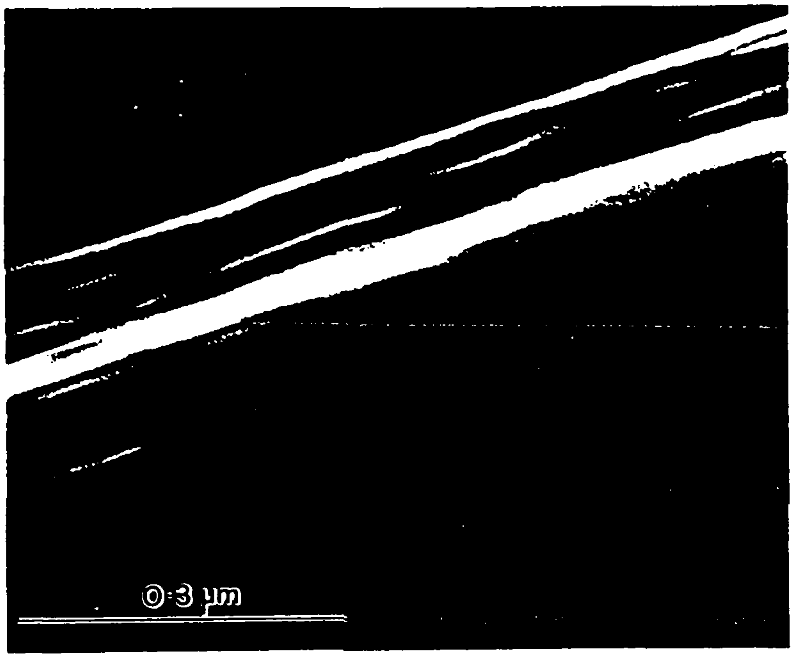
Figure 6 Carbon 1s spectra of fibres treated with an ammonia plasma a) with, and b) without sample bias.

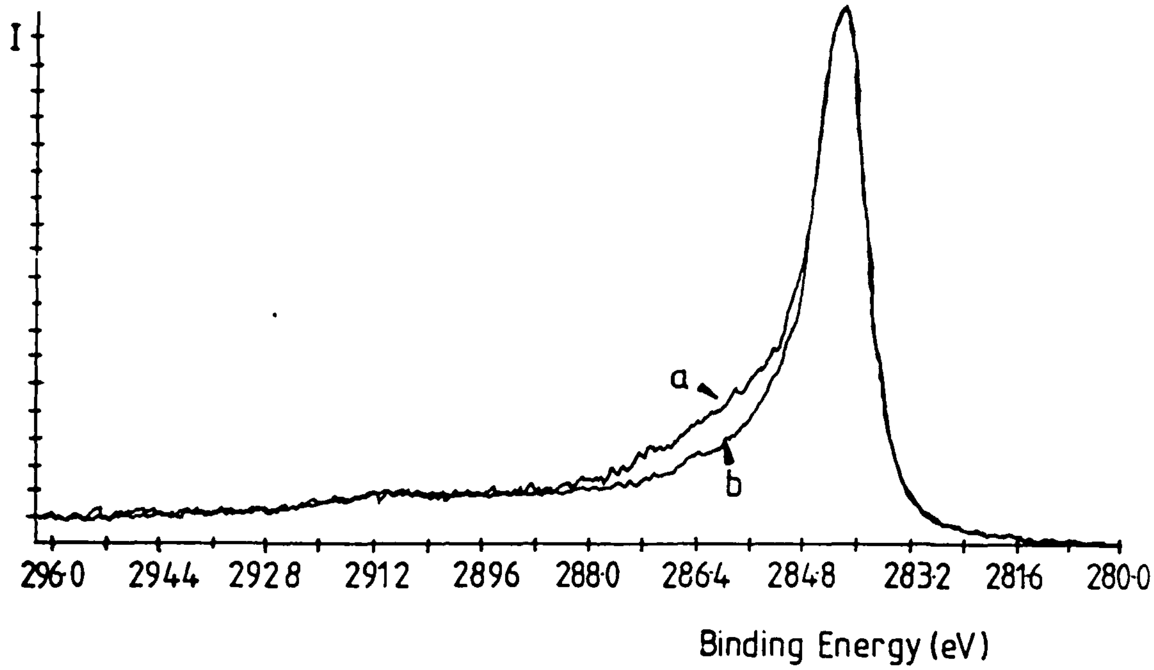

I
1·8eV
treated
plasmon
untreated
296·0
294·4
292·8
291·2
289·6
288·0
286·4
284·8
283·2
281·6
280·0
Binding Energy (eV)


I
P100
HM
T300
296·0
294·4
292·8
291·2
289·6
288·0
286·4
284·8
283·2
281·6
280·0
Binding Energy (eV)


I
C1s
N1s
T300
HM
P100
550
520
490
460
430
400
370
340
310
280
250
Binding Energy (eV)


C1s
N1s
I
a
b
550
520
490
460
430
400
370
340
310
280
250
Binding Energy (eV)


0.3 µm


I
a
b
296·0
2944
2928
2912
2896
288·0
286·4
284·8
283·2
281·6
280·0
Binding Energy (eV)