ONR-URI Composites Program
Technical Report No. 16

UIUC-NCCMR-89-16

2

AD-A234 184

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

---

* submitted for publication in Carbon.

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

*** Research Engineer,
Materials Research Laboratory

91 3 27 108

THE EFFECT OF LOW POWER PLASMAS ON CARBON FIBRE SURFACES.

C.Jones (National Centre for Composite Materials Research, University of Illinois, Urbana, Il. 61801)

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

DIST A PER TELECON MR Y BARSOUM
ONR/CODE 1132 SM
4/1/91 CG

A-1

ABSTRACT

The effect of a variety of low power plasma treatments (e.g. NH_3, N_2, air and Ar) on low modulus carbon fibre surfaces have been examined using X-ray photoelectron spectroscopy. Grazing angle techniques have been used to probe only the first 12-15Å of the fibre surface. Plasma treatments were carried out in an *insitu* 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.

Air plasmas introduced both alcohol and carboxyl groups onto the fibre surfaces . Nitrogen plasmas gave very similar results to ammonia plasmas with the formation of three nitrogen containing species on the fibre surface. The signal at 398.9eV was assigned to a combination of aromatic amines ($-NH_2$), and -C=NH groups. Its relative intensity, as expected was greater for fibres treated in ammonia plasmas. Air exposure of these activated surfaces results in a strongly bound -O-H layer.

Significant etching or pitting was not observed in the scanning electron micrographs of these treated fibres. Comparing XPS spectra of the immediate surface with those taken at bulk sensitive angles, it can be concluded that chemical change only occurred in the first few atomic layers.

1.INTRODUCTION

There have been many methods used to alter the surface chemistry of carbon fibre surfaces in an attempt to promote chemical bonding between the fibre and resin in composite materials. The level of adhesion at the fibre/resin interface has a significant influence on properties such as interlaminar shear strength and compressive strength. Strong bonding allows good stress transfer between the two components. Most effective commercial treatments have been of an electrochemical nature. The reasons why these electrochemical oxidations improved fibre/resin bonding have 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 bonding 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, however, does not rule out the possibility of forming a strong 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 Goan in 1973 [5], described the use of ammonia plasmas to aminate fibre surfaces. 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 [e.g. 6,7,8)], however, in all cases significant etching and pitting of the fibres was observed. 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 plasma treatment. Air exposure deactivated the surface inhibiting fibre/resin bonding.

The above led the authors to develop a low power (<1W) plasma cell. This was expected to decrease the amount of etching occurring on the surface and only alter the chemistry of the first few atomic layers. Hence, the fibre mechanical properties would remain intact. For this work, the cell was attached to a PHI 5400 XPS allowing the immediate effects of the plasma to be observed without the fibre coming into contact with air.

2.EXPERIMENTAL

The fibres studied in these experiments were originally untreated T300 fibres supplied by Amoco Performance Products.

Fibre surface treatments were carried out in an *insitu* plasma cell attached to a PHI 5400 X-ray photoelectron spectrometer (schematically shown in Fig.1). A half wavelength helical resonator [10] was formed from a 100-turn coil wound directly on the outside of the tube and centred within a shield made from 3" diameter brass tubing. A simple self-excited two transistor oscillator delivered radio energy to the centre of the helix at resonant frequency (approx. 15MHz). Low power levels (<1W) were sufficient to sustain a plasma within the tube. Continuous gas flow was maintained from a 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 between the main chamber and the 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 conditions (10^{-10}T) 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 (hν =1253.6eV). The pass energy used in narrow scan spectra was 17.9eV in all cases. For wider scan spectra 89.9eV was chosen. All intensity ratios reported in this paper have incorporated the relative sensitivities given for a hemispherical analyser (C1s 0.296, N1s 0.477, and O1s 0.711)[11].

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 *SEM Observations.*

Fig.2 shows the SEM micrographs of fibres exposed to an ammonia plasma. No severe etching or pitting was observed, unlike the surfaces examined by Donnet et al. [7]. At very high magnifications the structure of the treated surfaces appeared to very similar to that of the untreated fibres with small undulations being present in the order of 100Å or less. This was true for all the plasma treatments described. One may assume that the mechanical properties of the fibre will not be severely degraded by using this method of surface treatment, unlike the higher power plasmas more commonly used [e.g.7].

3.2 *XPS Results*

One of the main difficulties encountered when studying the effect of carbon surface treatments is that the changes in XPS narrow scan spectra (i.e. carbon 1s spectra) are very small. This is because chemical changes only occur within the first few layers of the fibre surface. The

XPS experiment has a sampling depth of approximately 60 A so the carbon 1s spectra collected for these treated fibres are dominated by the signal from the backbone of the fibre itself. Most experimenters have overcome this by overtreating these surface to increasing the amount of chemical functionality and hence increase signal intensity from these functional groups. While this may be useful in preliminary studies, the results are limited by the assumption that the processes involved in overtreatment are the same as in the initial stages of treatment. This may not be the case. Further, on attempting to correlate the concentration of a particular functional group with the interfacial strength in the resulting composite, standard XPS techniques may include functional groups that are inaccessible to the resin, giving misleading results. For this reason, grazing angle techniques have been exploited to study these fibre surface. The technique is explained fully elsewhere [4]. This enables not only the surface signals to be enhanced but also gives non-destructive depth information. To emphasise the importance of this technique, the carbon 1s spectra of fibres which have been exposed to an ammonia plasma taken at two different angles (15° and 75°) are compared to the spectrum from the untreated carbon fibres (see Fig.3a). At the more conventional angle (75°) the spectral differences between treated and untreated are very small, but in the surface sensitive spectrum these differences become quite clear. Fig.3b shows the angle effect on the widescan spectrum of these fibres. The N/C ratio increases dramatically on changing the angle a from 0.10 at 75° to 0.23 at 15°, and hence the C/N functionality is more concentrated at the surface of the fibres. A more realistic view of the chemical changes induced by commercially viable fibre surface treatments can thus be obtained. For this reason most of the spectra collected in this study have been taken at surface sensitive angles. However, 'bulk' sensitive data have been collected to obtain a qualitative idea of the depth to which the treatment has effected the fibre.

3.2.1 *Air Plasmas*

The carbon 1s spectrum of fibres exposed to an air plasma is shown in Fig.4. This spectrum is very similar to that of fibre electrochemically treated in aqueous solutions [12,13]. The spectrum contains two chemically shifted species at 1.6 and 4.0eV from the main peak (284.6eV) corresponding to alcohol and carboxyl type functionality respectively.

There is a large difference between the amount of oxygen functionality at the surface (the first 12-15A), the O:C ratio being 0.24, compared to the first 60A where the O:C ratio is 0.12. This can be clearly seen by comparing the widescan spectra taken at the two angles (see Figure 5).

Even after prolonged exposures to the air plasma this difference remains the same. The concentration of the oxygen 1s species at the surface did not change with time (from 30 seconds to 30 minutes). Several different phenomena could lead to such a result.

a) Saturation of the active sites has taken place,

b) a steady state condition has been established in which the rate of incorporation of C/O groups has become equivalent to the rate of removal of these groups by further oxidation to CO_2.

Removal of loosely bound species could also occur by electron assisted desorption.

This method may be exploited to introduce acid and alcohol groups if so desired without damaging the fibre and could be a useful alternative to electrochemical oxidation in aqueous solutions. The treatment times needed to introduce the desired changes in the fibre surface chemistry are low (< 20secs), unlike those suggested by other workers (> 5mins). [5,7].

3.2.2 *Argon Plasmas*

Fibres subjected to an argon plasma always contained significant amounts of oxygen functionality on their surface. This could only be explained by oxygen pickup in the treatment cell. The argon plasma creates a very reactive surface which will react with any background oxygen present in the system. Pretreatments in an Ar plasma [9] which causes an increase in 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 been found 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 to the comparatively low RF power used, i.e. the impact energy of the ions are well below the sputtering threshold.

3.2.3 *Ammonia, and Nitrogen Plasmas*

Both nitrogen and ammonia plasmas are successful in introducing C/N functionality on low modulus carbon fibre surface. The surface sensitive widescan spectra are shown in Fig.6. It can be seen that the ammonia plasma introduced the greater amount of surface nitrogen. Ammonia plasma treatments also remove any of the original oxygen species present. The nitrogen plasma is not so successful. Both of these plasma introduce three types of nitrogen containing species with binding energies 398.9eV, 400.4eV and 402.8eV. The two main signals are very similar to those produced on electrochemical oxidation in ammonium salt electrolytes [13]. However, in this case, peak assignment to amide functionality is invalid as an oxygen 1s signal was not detected. The binding energy of $PhNH_2$ has previously been reported as 399.1eV [14]. The relaxation energy associated with the ejection of a photoelectron is far greater for a graphitic like lattice than for a benzene ring [15,16], and hence a shift of -0.2eV from that observed with $PhNH_2$ is not unlikely for amine groups on carbon fibre surfaces. -C=NH groups could also give rise to a signal around 398.9eV. The relative intensity of this peak is greater as a result of ammonia plasma treatment than for nitrogen plasma exposure. It also is greater in the surface sensitive spectrum of the ammonia treated fibres compared to the bulk sensitive data (see Fig.7a), indicating that these groups are present in greater quantities at the surface of the fibre. However, for fibres exposed to a nitrogen plasma the relative ratios remained constant at varying take-off angles.

The signal at 400.4eV arises from aliphatic amine functionality being present on the fibre surface. The peak at highest binding energy is most probably a positively charged ammonium species similar to that observed by Chang and Navalov [17]. Cyano groups (-C≡N) are not detected. These groups are unlikely to remain on the fibre surface as they would be prone to electron assisted desorption.

All of the chemically shifted signal intensity seen in surface sensitive carbon 1s spectrum (Fig.3a) is due to C/N functionality. The chemical shift expected for $-C-NH_2$ would be around 1.3-1.5eV from the main peak. -C=NH would be expected to give rise to a peak between 2 and 3 eV from the main graphitic peak. There is a difference between the untreated and the plasma treated fibre spectrum in this part of the spectrum. The signal intensity difference at around 6eV from the main peak is due to a $\pi - \pi^*$ shake-up satellite.

These aminated surfaces certainly have the potential to react with epoxy coatings. However, many other coatings materials containing suitable chemical functionality to react with these 'amines' could be chosen. The properties of the interface could then be controlled and varied depending on the material chosen. A carbon fibre/epoxy resin 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.

3.2.4 *Exposure to Air*

Both Allred et al.[9] and Wertheimer et al [18] have shown that plasma treated Kevlar fibre surface are deactivated when exposed to air. The latter suggested that this may be due to a recombination of free radicals on the fibre surface and/or oxidation of these activated sites. Fig.8 shows widescan spectra of fibres treated with an ammonia plasma before and after exposure to air. There is significant 'oxygen' pickup upon air exposure. However, no changes in the carbon 1s and nitrogen 1s spectra, e.g. increase in -COH signal intensity nor the formation of a N-O species, were observed. It was concluded that this oxygen pickup was due to a strongly bound physisorbed layer. The binding energy of the oxygen species is 532.4eV which is characteristic of a 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.

4. CONCLUSIONS

The chemistry of carbon fibre surfaces can be modified by using low power plasmas. In all cases, the plasma only effected the first few layers of the fibre surface. The treatment time needed to achieve the desired changes in fibre surface chemistry were in the order of 15-30 seconds which is very similar to that needed for electrochemical treatment [3], lending itself ideally to a commercial process. Nitrogen and ammonia gas plasmas can both be used to introduce amines onto fibre surfaces, the ammonia treatments removing all surface oxygen from the fibre. These groups have the potential to bond with epoxy resins and hopefully will improve fibre resin adhesion. Nitrogen is less noxious than ammonia and may prove more suitable for a commercial process.

Exposure of these activated 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 the induced surface chemistry on fibre/resin bonding, it is essential to handle the fibres in an inert environment and to immerse the fibres into resin (or coating material) immediately after plasma treatment before exposure to air. Failure to do this will result in similar conclusions to those drawn for electrochemically treated fibres.

Although the above method of treatment introduces the desired chemistry, it still has yet to be determined whether or not the weakly bound misorientated crystallites which lead to poor interfacial bonding, have been removed from the fibre surface. Hence the above treatment has been

FIGURE CAPTIONS

Figure 1. A schematic diagram of the *insitu* plasma treatment cell.

Figure 2. Scanning electron Micrographs of fibre exposed to an ammonia plasma.

Figure 3. a) Carbon 1s spectra and b) widescan spectra of fibres treated with an ammonia plasma collected at both surface and bulk sensitive angles.

Figure 4. Curve fitted carbon 1s spectrum of fibres exposed to an air plasma for 30 seconds.

Figure 5. Widescan spectra, collected at both surface and bulk sensitive angles, of fibres exposed to an air plasma.

Figure 6. Widescan spectra of fibres treated with a) an ammonia and b) a nitrogen plasma.

Figure 7. Nitrogen 1s spectra, collected at both surface and bulk sensitive angles, of fibres treated with a) an ammonia, and b) a nitrogen plasma.

Figure 8. Widescan spectra of fibres exposed to an ammonia plasma a) before and b) after exposure to air.

composite bars, the mechanical properties of which can then be tested.The results will be reported in a future publication.

Acknowledgments- The authors are grateful to Irena Dumler for her helpful advice with the scanning electron microcopy. Thanks also go to the guys in the workshop here in the Theoretical and Applied Mechanics Department.

This work was sponsored by the Office of Naval Research under contract No. N00014-86-K-0799, and was carried out in the Materials Research Laboratory at the University of Illinois supported by the U.S.Department of Energy under contract DE-AC 02-76ER)1198.

REFERENCES

1. J.V.Sharp and S.G.Burnay, *Radiation Eff.*, **22**, No.1, 45 (1974).

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

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

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

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

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

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

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

9. Allred and Stoller, *Proc. of 18th Internat.SAMPE Tech.Conf.*, 993 (1986).

10. W.W.Macalpine and R.O.Schildknecht, *Proc.IRE*, 47, 2099 (1959).

11. Perkin Elmer 5400 XPS Software.

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

13. C.Kozlowski and P.M.A.Sherwood, *Carbon*, **24**, No3. 357, (1986)

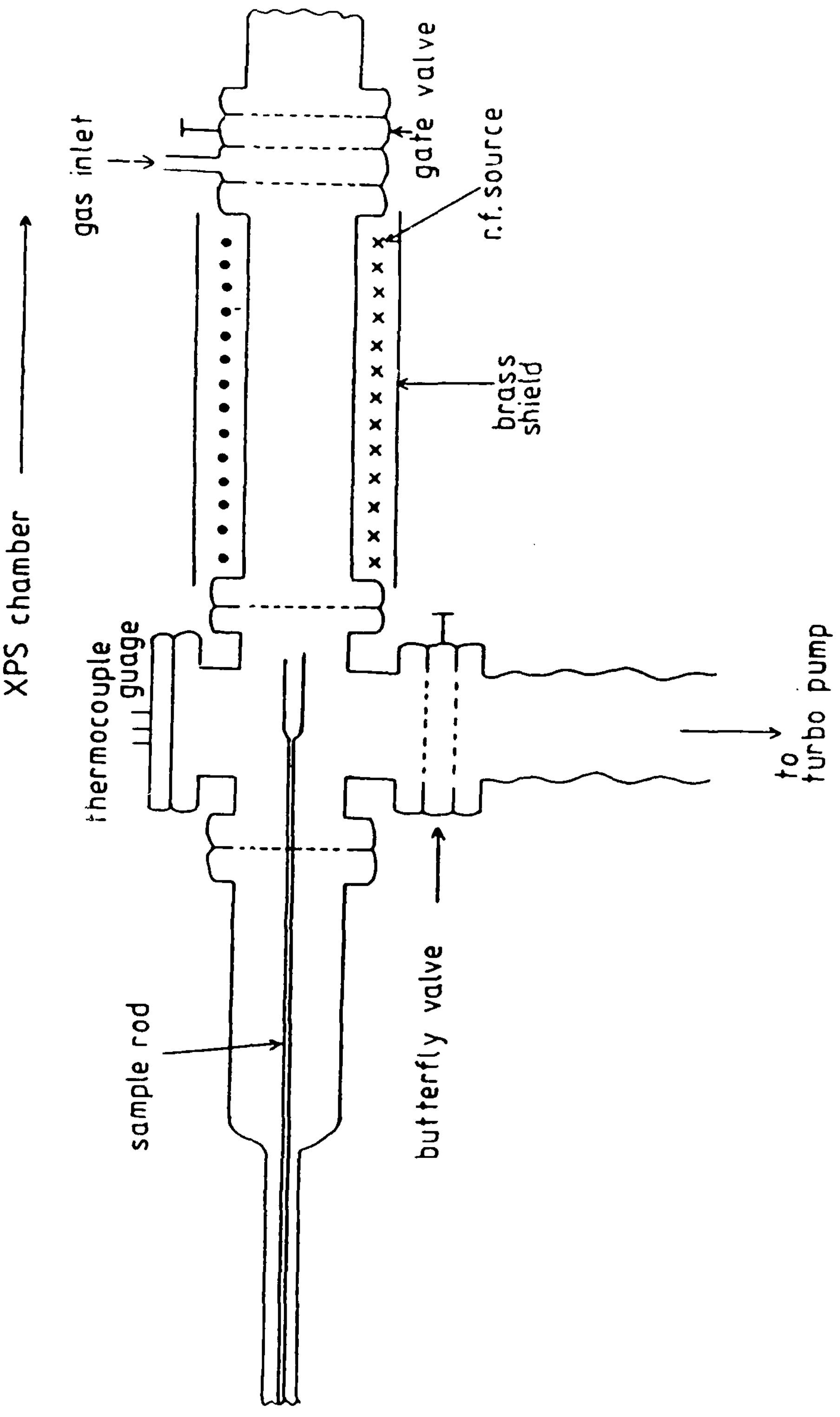
14. R. Nordberg, H.Brecht, R.G.Aldridge, A.Fahlmann, and J.R. Van Wazer, *Inorg. Chem.*, **9**, 2469 (1970).

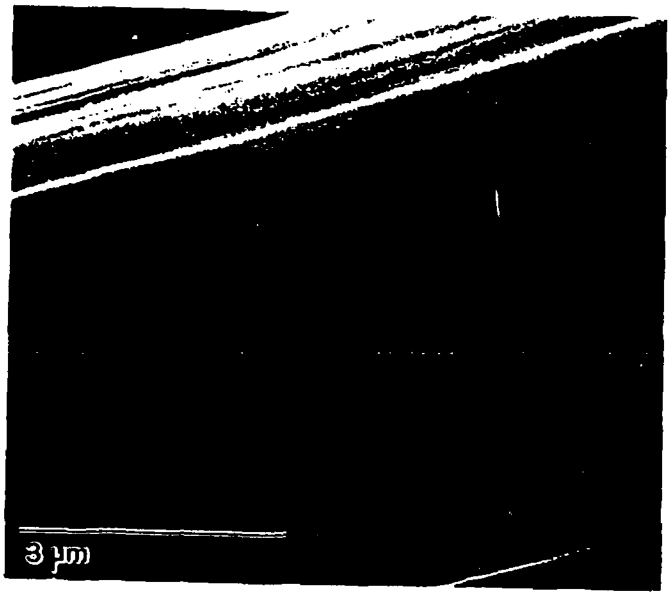
15. D.W.Davis and D.A.Shirley, *J.Elec. Spec. and Rel.Phenom*, **3**, 137 (1974).

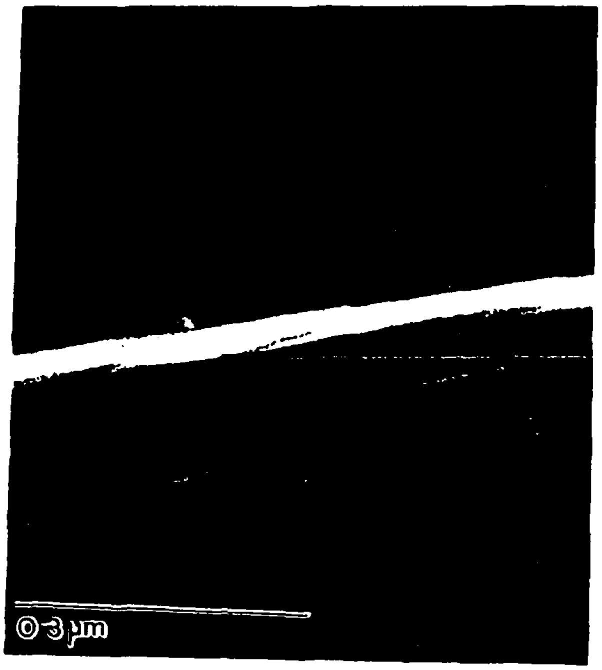
16. C.Kozlowski and P.M.A.Sherwood, unpublished results.

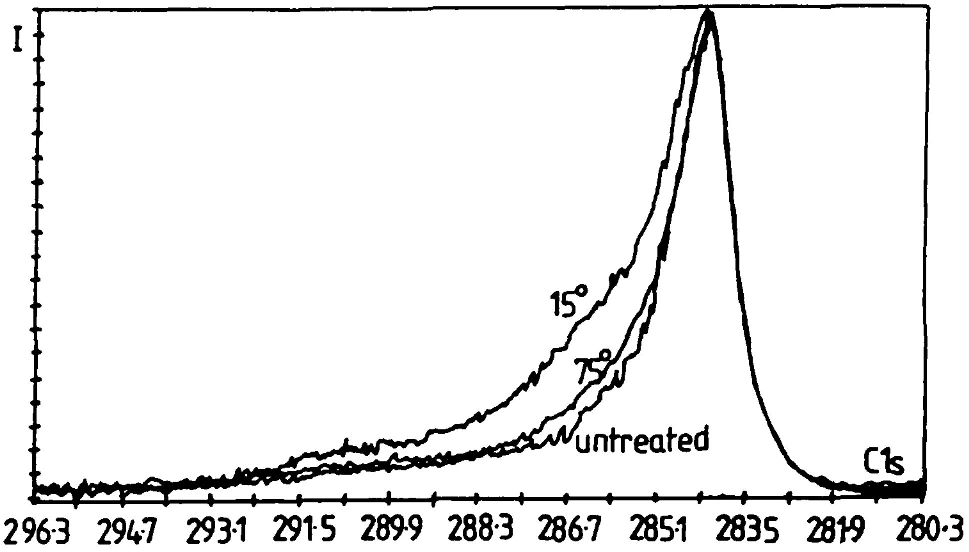
17. S.G.Chang and T.Novakov, *Amorphous Environment*, **9**, 495 (1975).

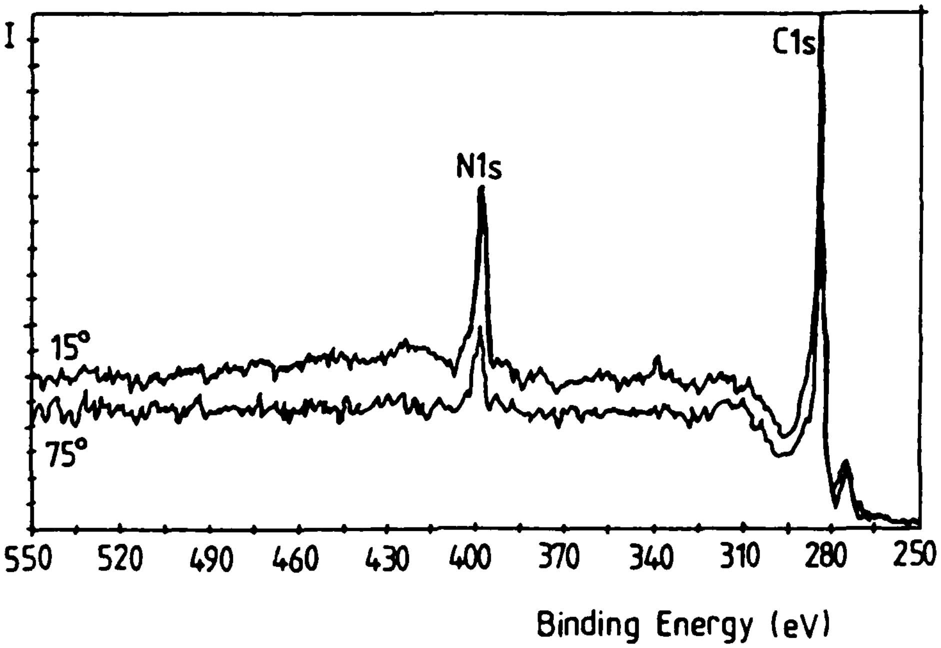
18. M.R.Wertheimer and H.P.Schreiber, *J. Appl. Polym. Sci.*, **26**, 2087, (1981).

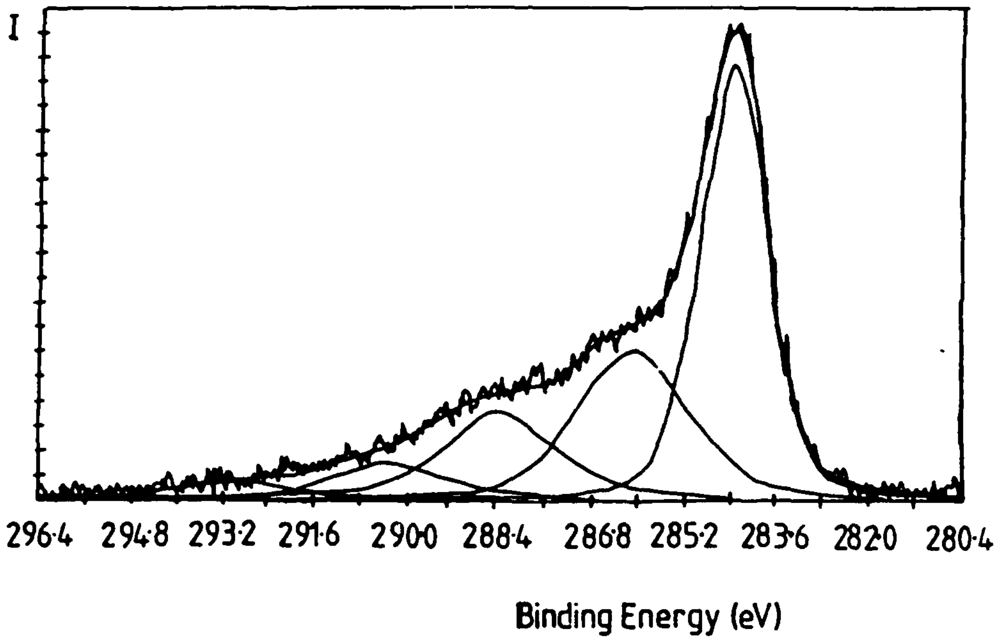

XPS chamber
gas inlet
gate valve
r.f. source
brass shield
thermocouple guage
to turbo pump
butterfly valve
sample rod

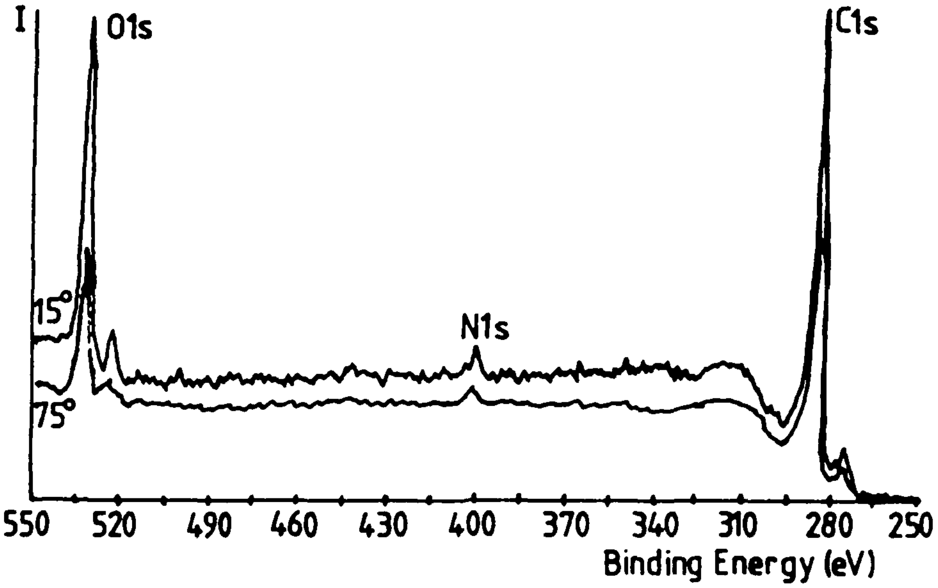

3 μm

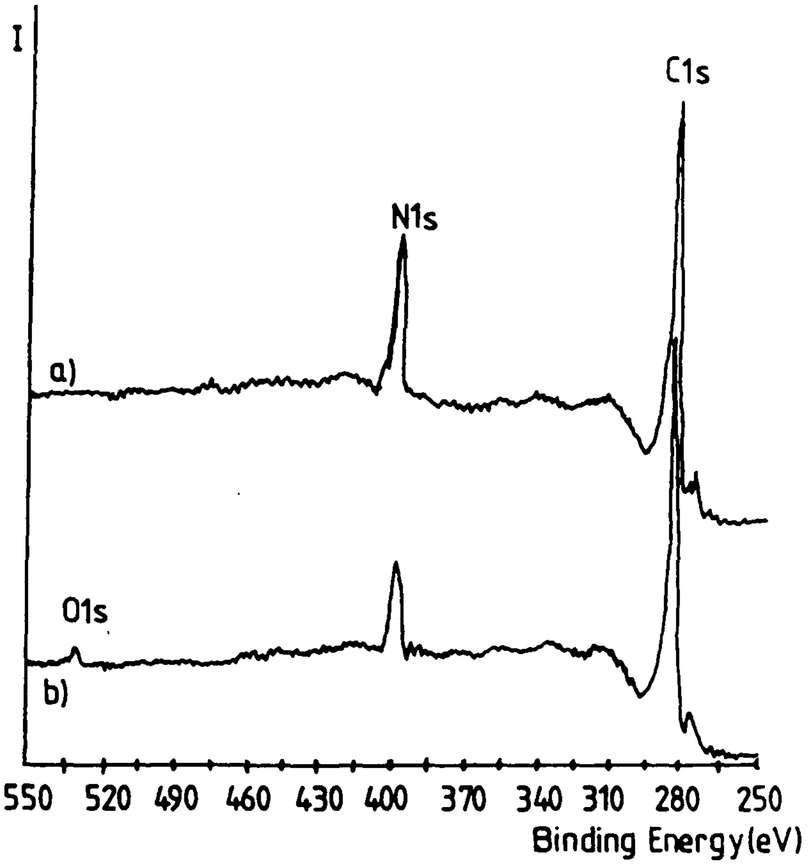

0·3 μm

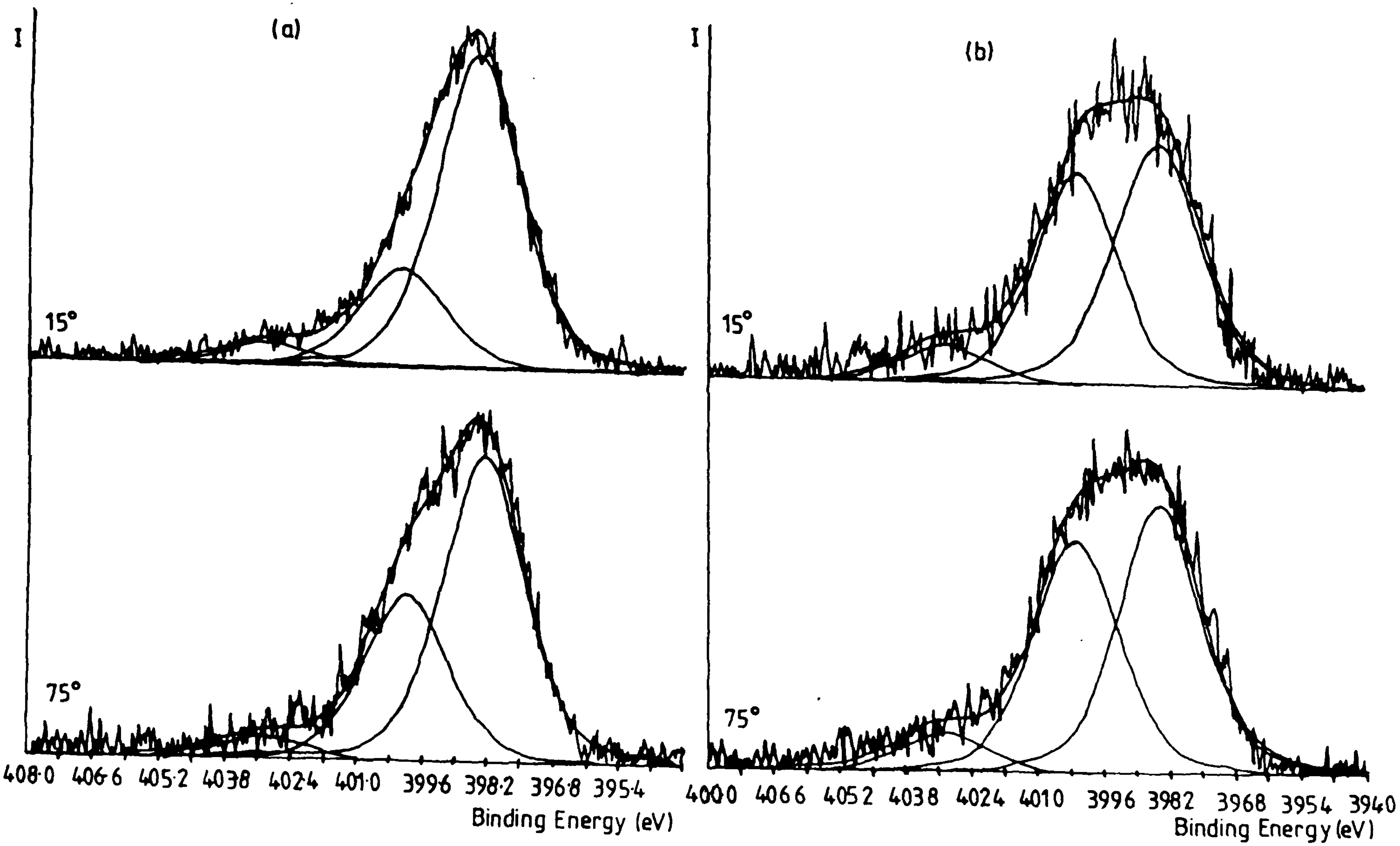

I
15°
75°
untreated
C1s
296·3
294·7
293·1
291·5
289·9
288·3
286·7
285·1
283·5
281·9
280·3

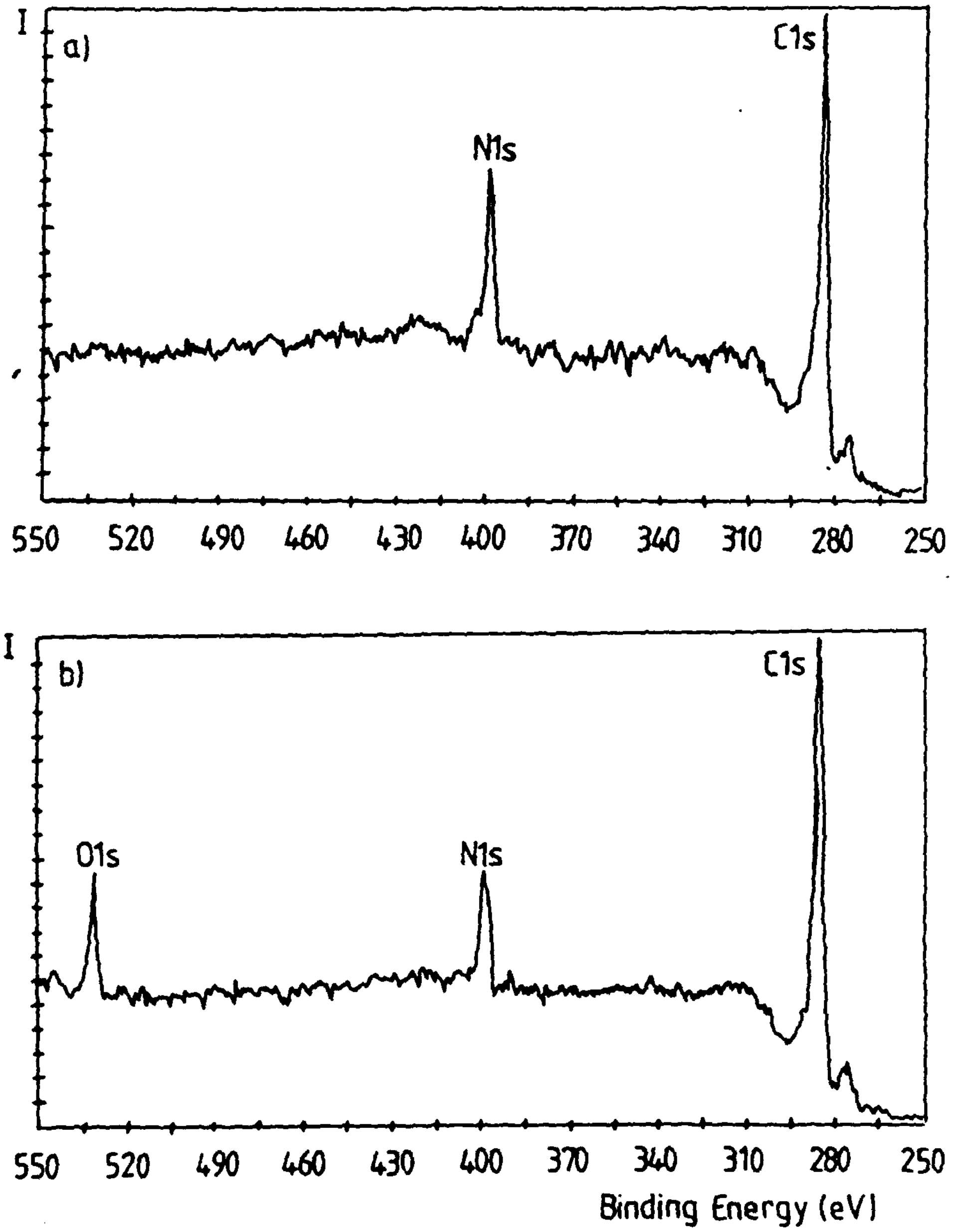

I
C1s
N1s
15°
75°
550
520
490
460
430
400
370
340
310
280
250
Binding Energy (eV)


I
296·4
294·8
293·2
291·6
290·0
288·4
286·8
285·2
283·6
282·0
280·4
Binding Energy (eV)


I
O1s
C1s
N1s
15°
75°
550
520
490
460
430
400
370
340
310
280
250
Binding Energy (eV)


I
C1s
N1s
a)
O1s
b)
550
520
490
460
430
400
370
340
310
280
250
Binding Energy(eV)


I
(a)
15°
75°
408·0
406·6
405·2
4038
4024
401·0
3996
398·2
396·8
395·4
Binding Energy (eV)
I
(b)
15°
75°
4000
4066
4052
4038
4024
4010
3996
3982
3968
3954
3940
Binding Energy (eV)


I
a)
N1s
C1s
550
520
490
460
430
400
370
340
310
280
250
I
b)
O1s
N1s
C1s
550
520
490
460
430
400
370
340
310
280
250
Binding Energy (eV)