JOURNAL OF MATERIALS SCIENCE 22 (1987) 2937–2947

Modification of carbon surfaces in cold plasmas

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Various forms of carbon, including carbon black, carbon fibre and pyrolytic graphite, have been surface-modified in a cold-plasma reactor. Plasma fluorination of the carbon surfaces was performed using variable flow rates, treatment times, and types of gas. The plasma-modified carbon surfaces were characterized using electron spectroscopy (ESCA), contact angle measurements, and scanning electron microscopy (SEM). The surface chemical structure of the plasma-fluorinated carbon blacks appeared to be similar to that of commercial Fluorographite. Nitrogen-containing groups were introduced into the surfaces of carbon blacks and carbon fibres by exposure to glow discharges in mixtures of ammonia and N_2–H_2. The surface concentration of functional groups containing nitrogen decreased with time. Several mechanisms for this degradation have been proposed. Plasma-modified carbon blacks and carbon fibres have potential for improving the properties of composites by achieving appropriate levels of adhesion between filler and matrix through physical compatibility and/or chemical bonding.

1. Introduction

The surface character of carbon materials dominates the performance of the final product in many applications. For example, the mechanical properties of composites are strongly influenced by the nature of the resin–carbon interface [1, 2]; lubricant properties are determined by surface tribological effects [3]; heart valves require surface biocompatibility [4]. Therefore, it is useful to be able to alter carbon material surface properties without changing the bulk properties.

The use of a radio-frequency generated plasma to alter the properties of polymer surfaces has been known for several years [5–12]. The purpose of this work was to adapt this technique to reactions between carbon surfaces and various types of plasma, and to characterize the surfaces produced by these reactions.

Experiments were conducted on various forms of carbon, including carbon black, carbon fibre and pyrolytic graphite. Methods which have been successful in the past for implanting fluorine-containing groups on to polymer surfaces through the use of fluorine-containing plasmas [13–15] were used in this study for the fluorination of carbon surfaces. A method for introducing amine surface functionality on to a variety of aliphatic polymers [16–18] using ammonia plasmas was adapted here to aminate carbon surfaces. ESCA, contact angle measurements and scanning electron microscopy were used to characterize the plasma-modified carbon surfaces.

2. Modifications of carbon surfaces

Carbon blacks, in the form of fine powders with characteristic dimensions less than 0.1 μm, are widely used as pigments and reinforcing fillers. A large number of carbon blacks, varying in specific surface area and structure, are available. In this study, we used Statex MT P43748 (Cities Service Co.) and Sterling R (Cabot Corp.).

Carbon fibres are also available in a variety of forms. We used a PAN-based continuous fibre (Thornel 300, Union Carbide Co.) and chopped carbon fibre papers (Panex CFP 30-05, Stackpole Fiber Co.). The as-received continuous fibres were treated with a sizing suitable for use in epoxy composites. This sizing was removed by alcohol prior to the plasma surface modification. The as-received chopped carbon fibre paper contained about 15 wt % polyvinyl alcohol binder. The pyrolytic graphite (Union Carbide) was used as a control for comparison purposes.

2.1. Plasma-enhanced surface fluorination of carbon

Previous work in this laboratory has demonstrated the effective use of fluorine-containing glow discharge plasmas to produce Teflon-like surfaces on various polymer substrates [13–15, 19, 20]. Here, the same techniques were adapted to alter carbon surface properties.

2.1.1. Plasma-enhanced surface fluorination of carbon blacks

Recently there has been considerable interest in the preparation and chemistry of fluorinated graphite or carbon black for application to novel products in the fields of lubrication [3] and high-energy-density batteries [21–23]. Commercial products of fluorinated carbon (Fluorographite, Ozark-Mohoning Co.) are produced by reactions of carbon black and graphite

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TABLE I Treatment conditions employed for and data obtained from ESCA spectra [31] of plasma-fluorinated carbon black (Statex MT)

Gas	Treatment conditions			F/C	O/C
	Flow rate (s.c.c.m.)	Power (W)	Time (min)		
Rotating reactor					
10% CF_4–He	24	100	60	0.066	0.120
10% CF_4–He	24	100	90	0.383	0.050
10% CF_4–He	24	100	120	0.330	0.060
10% CF_4–He	47	100	30	0.110	0.045
40% CF_4–He	25	150	80	0.236	0
5% F_2–He	30	100	30	0.098	0.110
Stationary reactor					
5% F_2–He	30	50	60	0.734	0.074
10% CF_4–He	42	50	65	0.880	0.052

with fluorine gas in the temperature range from 350 to 600° C [23] and for times in excess of 20 h. Fluorographites vary in composition, ranging from $CF_{0.4}$ to $CF_{1.26}$.

In addition to industrial thermal processes, a novel plasma processing technique was developed by Lagow *et al.* [24] to synthesize poly(carbon monofluoride). In that work, fluorination of flaked graphite was accomplished using a fluorine plasma in a fluidized bed reactor. A few years later, Cadman *et al.* [25] fluorinated graphite using a microwave discharge of SF_6 or C_2F_6. Recently, Taylor [26] patented a process for fluorinating diamond grit in an SF_6–He or SF_6–Ar microwave glow discharge.

In this study, the Statex MT was treated in two reactors, one stationary [19] and one rotating [20], using different reaction conditions as summarized in Table I. Total pressure was in the range of 3 to 5 torr; r.f. power, volumetric flow rate, reaction time, and gas phase composition were all variables. ESCA survey spectra of the carbon black before and after the treatment are shown in Fig. 1. The results show clearly that fluorine-containing groups exist on the surface of the plasma-treated carbon blacks.

The plasma-fluorinated carbon blacks and Fluorographite were compared. The colour of the Fluorographite is grey-white, while the plasma-fluorinated carbon black remains black in colour. The C(1s) spectrum of the plasma-treated carbon black is compared to the spectrum of the commercial Fluorographite (CF_x, $x = 1$) in Fig. 2. The chemical shifts in the C(1s) spectra are quite similar for both materials, which indicates that, on the surface, the two materials have the same chemical groups, such as CF, CF_2 and CF_3. However, the overall chemical compositions in the ESCA sampling depth (ca. 5 nm) are different for these two materials, as shown by the different intensities of the CF, CF_2 or CF_3 groups in the C(1s) spectra. The surfaces of plasma-fluorinated carbon black showed an atomic ratio of F/C as high as 0.880 in the stationary reactor. Some residual $-CH_2$ (or –C–) moieties were found. It is possible that the thickness of the plasma-fluorinated layer might be less than the 5 nm sampling depth of the ESCA experiment and, therefore, the observed F/C ratio is lower than that of the bulk-modified Fluorographite.

Surface fluorination of carbon black powder in a rotating reactor for 90 min yielded an F/C atomic ratio of only 0.383. This low level of fluorination is probably due to the agglomerating nature of the carbon blacks which shields much of the material surface from the UV photons thought to be crucial to the fluorination mechanism [27].

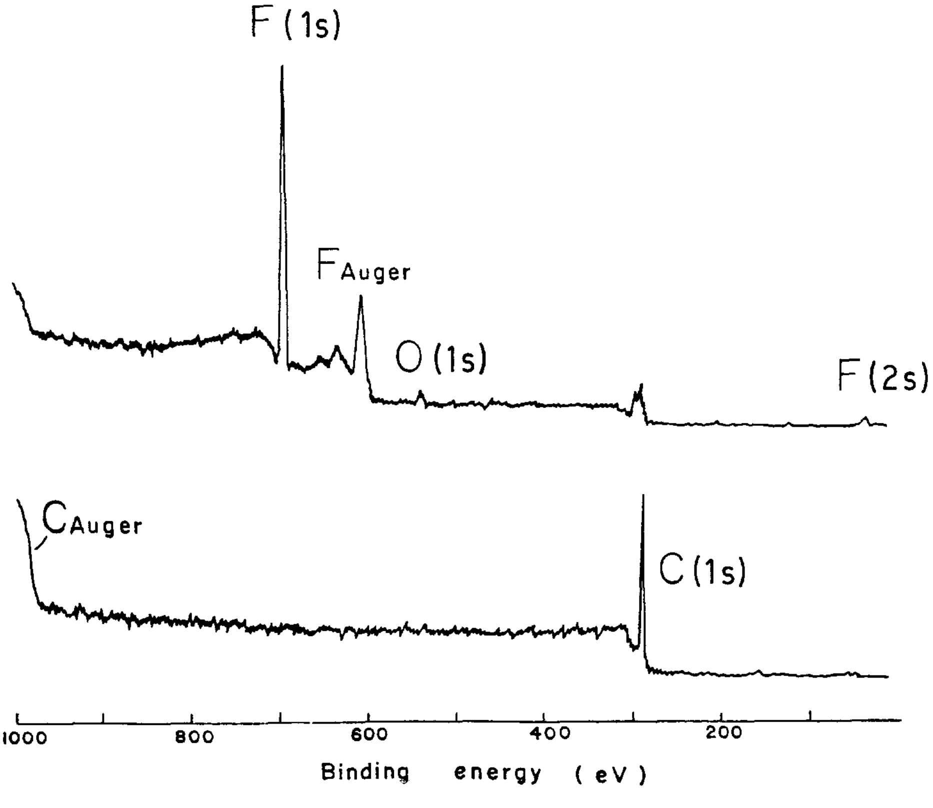

Figure 1 ESCA survey spectra of carbon black and fluorinated carbon black.

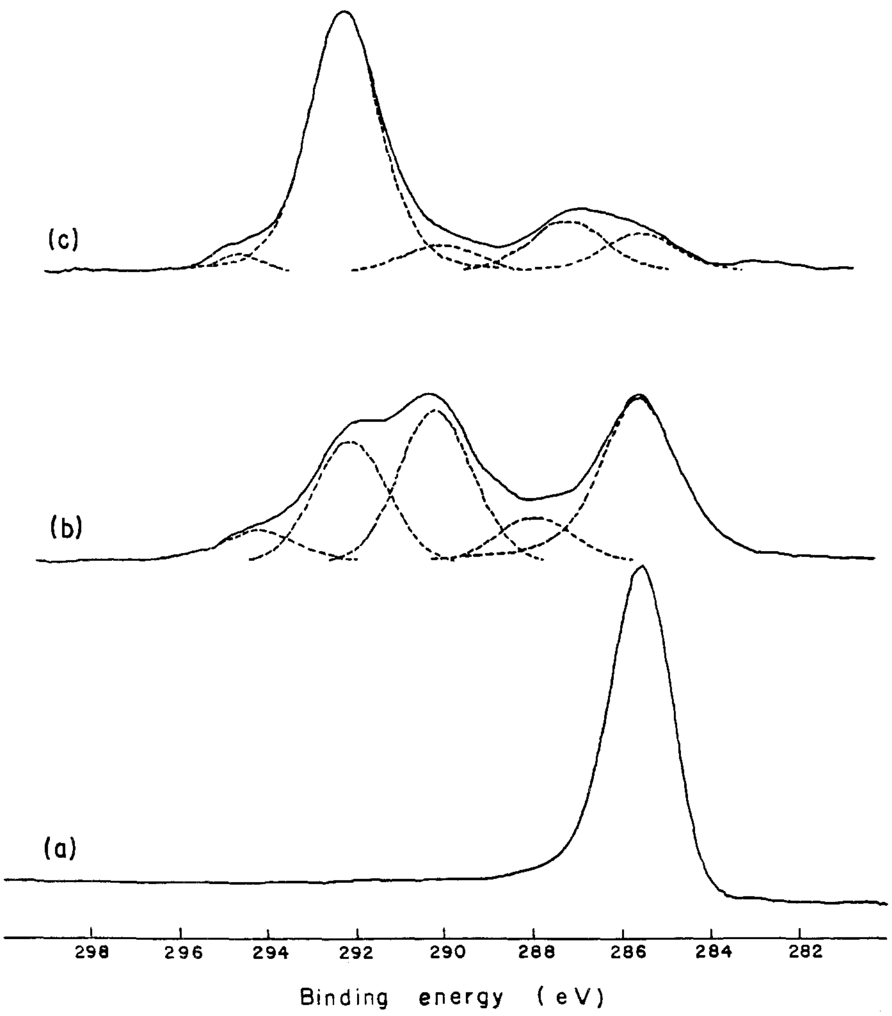

Figure 2 ESCA C(ls) spectra of (a) carbon black, (b) treated carbon black and (c) fluorographite®.

2.1.2. *Plasma-enhanced fluorination of carbon fibre surfaces*

Fluorination of carbon fibres was first studied by Fisher *et al.* [28], who carried out reactions in a mixed nitrogen–fluorine gas stream at 406° C and atmospheric pressure. Plasma surface fluorination of carbon fibres was carried out in this study using various flow rates, treatment times, and types of gas (Table II). The effects of these variables are reported here in terms of high- and low-resolution ESCA spectra.

ESCA survey spectra are shown in Fig. 3 for the PAN-based carbon fibre before and after exposure to a F_2–He plasma. The large F(ls) peak appearing near 700 eV indicates that extensive fluorination has occurred. In the high-resolution mode, the ESCA spectra reveal shifts of the C(ls) peaks resulting from different fluorine groups. This ESCA result is similar to that for the plasma-fluorinated carbon black shown in Fig. 2. A comparison between CF_4–He plasma and F_2–He plasma reactions is shown in Fig. 4. The reaction parameters were a flow rate of 30 s.c.c.m. and a reaction time of 60 min. It is evident from these data that F_2–He and CF_4–He are both effective for the surface fluorination of carbon fibres in a glow discharge environment. Surface atomic compositions are compared in Table II. The CF_4–He reaction is more successful in removing oxygen groups from the carbon fibre surface. Previous work [19] has established that the CF_4 gas plasma supplies carbon-containing species which tie up oxygen atoms in the gas phase (oxygen gettering) to form relatively stable volatile products (e.g. CO, CO_2) before the oxygen has a chance to migrate back to the polymer surface and react [29]. Therefore, the CF_4–He plasma is superior to the F_2–He plasma in creating a fluorinated surface on oxygen-containing materials.

A set of experiments on the Panex carbon fibre paper was conducted with the reaction time as the variable using a CF_4–He gas mixture at a CF_4 con-

TABLE II Treatment conditions employed for and data obtained from ESCA spectra [31] data of plasma-fluorinated carbon fibres

Gas	Treatment conditions			Atomic ratio	
	Flow rate (s.c.c.m.)	Power (W)	Time (min)	F/C	O/C
Panex carbon fibre paper					
(Control)	–	–	–	0	0.400
10% CF_4–He	40	100	30	1.00	0.135
10% CF_4–He	40	100	60	1.18	0.124
10% CF_4–He	40	100	120	1.29	0.207
10% CF_6–He	40	100	60	0.74	0.054
17% CF_4–He	30	100	60	0.83	0.088
29% CF_4–He	34	100	60	1.03	0.080
50% CF_4–He	35	100	60	1.00	0.064
PAN-based continuous fibres, Thornel 300					
(Control)	–	–	–	0	0.13
26% CF_4–He	30	50	60	0.91	0.06
5% F_2–He	30	50	60	0.77	0.14

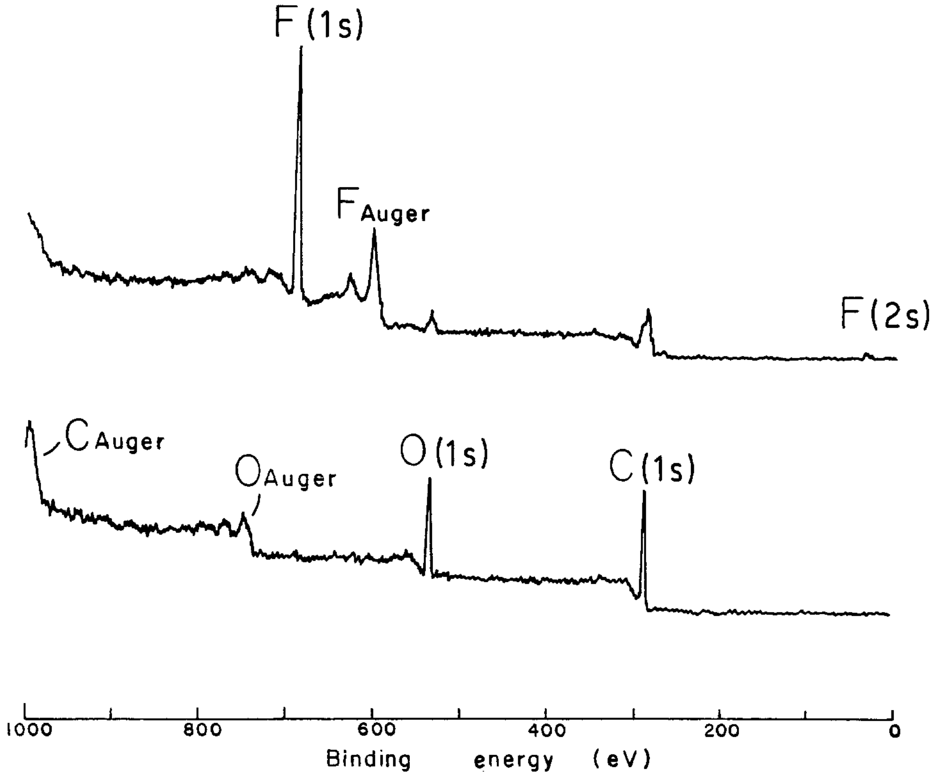

Figure 3 ESCA survey spectra of F_2–He plasma-treated and untreated carbon fibre.

centration of 10%. The flow rate was 40 s.c.c.m., and the input power was 100 W. ESCA spectra are shown in Fig. 5 and the calculated surface atomic concentrations appear in Table II. The peaks which appear in Fig. 5 on the left shoulder of the control C(ls) spectrum are due to oxygen groups attached to carbon. By increasing the reaction times, the portion of the peaks at higher binding energy, assigned to CF, CF_2, or CF_3, increases. Since Panex carbon fibre paper consists of two components, carbon fibre and poly(vinyl alcohol) binder, the extent of Panex fibre fluorination depends on the details of reactivity of the individual components. The fluorination reaction is essentially unaffected by the concentration of CF_4 in the gas mixture in glow reactions (Table II). This result is consistent with Corbin's findings [30]. The reaction can also be carried out successfully using SF_6 as the reacting gas, as shown in Table II.

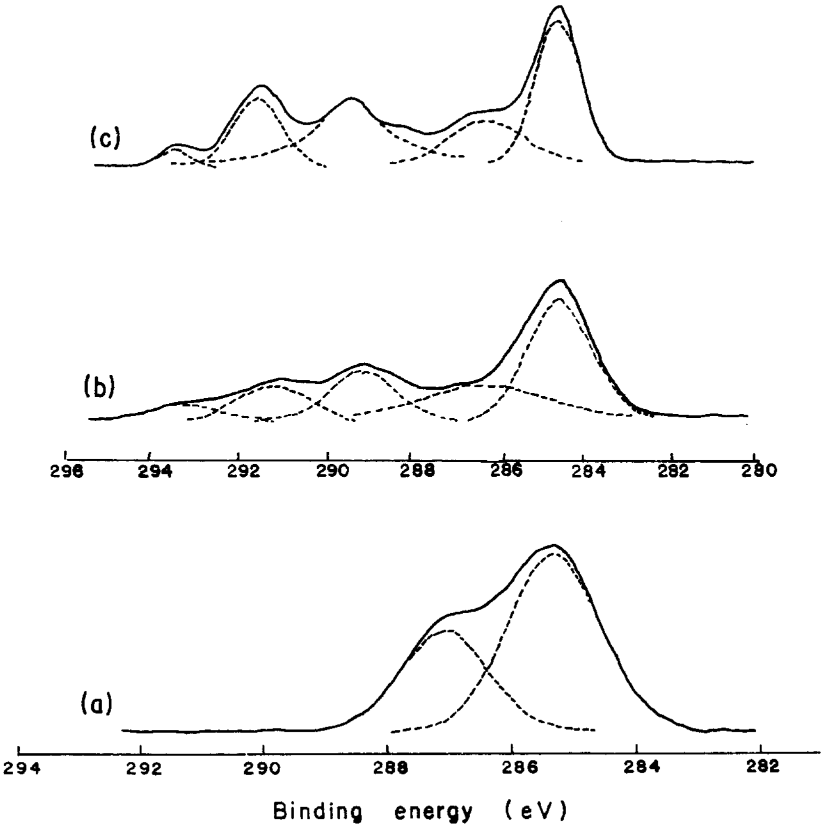

Figure 4 ESCA C(ls) spectra of (a) control, (b) F_2–He and (c) CF_4–He plasma-treated carbon fibre.

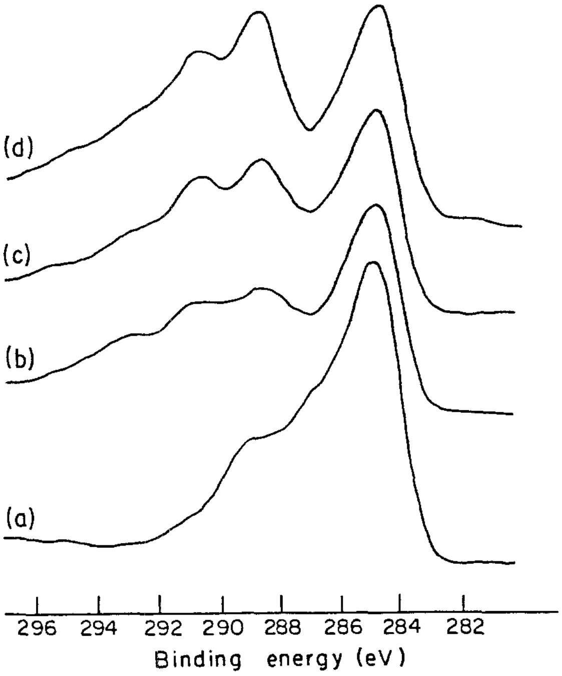

Figure 5 Variation of the C(ls) spectrum of fluorinated Panex fibre with reaction time. (a) Control: O/C = 0.40, F/C = 0. (b) 30 min reaction: O/C = 0.13, F/C = 1.00. (c) 60 min reaction: O/C = 0.12, F/C = 1.18. (d) 120 min reaction: O/C = 0.21, F/C = 1.29.

The plasma-fluorinated Panex carbon fibres were tested for thermal stability. This experiment was carried out by placing the plasma-treated carbon fibres in a vacuum oven at 293 or 343° C for various periods of time. The stability of the samples was based on ESCA results [31] to determine the amount of fluorine on the surface as a function of time. Fig. 6 summarizes the results of these experiments. A 70% loss of fluorine occurred when the samples were heated to 293° C for 10 min. Increasing the duration of the heating period from 10 to 40 min did not decrease the fluorine content further. At 343° C a 90% loss of fluorine was found after 10 min. The O/C ratio remained essentially unchanged in the thermal treatments.

2.2. Plasma-enhanced surface amination of carbon

The concept of plasma-enhanced surface amination was first presented by Hollahan *et al.* [16]. They demonstrated that amine surface functionality could be introduced on to a wide variety of aliphatic polymers by exposure to an ammonia glow discharge. Following this, other researchers [17, 18] have used ammonia plasmas to surface-treat various polymers in film or fibre geometries. However, only two carbon surface aminations have been reported: Goan [32] modified carbon fibre surfaces with an ammonia plasma; Evans and Kuwana [33] introduced nitrogen-containing functionalities on to the graphite basal plane using ammonia as the discharge gas.

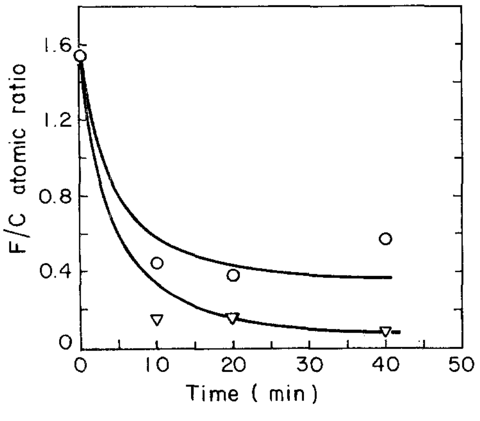

Figure 6 Thermal stability of plasma-induced surface fluorine groups: treatment at (○) 293 (▽) 343° C.

TABLE III ESCA data of plasma-aminated carbon blacks

Plasma gas*	Position (see text)	Binding energy			Elemental ratio		
		C	N	O	O/C	N/C	N/O
NH_3	A	285.11	399.2	531.6	0.11	0.18	1.65
N_2–H_2	A	285.67	399.2	531.2	0.10	0.06	0.53
NH_3	B	285.68	399.0	533.0	0.12	0.10	0.88
N_2–H_2	B	285.79	399.0	531.3	0.122	0.06	0.46
NH_3	C	285.59	399.0	531.0	0.108	0.13	1.22
N_2–H_2	C	286.14	399.2	532.0	0.135	0.05	0.36

2.2.1. Plasma-enhanced surface amination of carbon black

Plasma surface treatment of powders is influenced by operating parameters such as gas flow rate, power input, time of treatment, and the location of the substrate with respect to the glow region. The amination experiment was conducted in a stationary reactor. A tenth of a gram of carbon black was laid down evenly on a Teflon dish and placed inside the reactor. Samples were placed in the inlet (A) middle (B) and exit (C) portions of the reactor. The selected treatment condition was: power = 100 W, pressure = approximately 1 torr, flow rate = 35 s.c.c.m., and duration of treatment = 30 min. A one-minute helium plasma pretreatment was also employed in these runs. ESCA surface analyses for the modified carbon black are listed in Table III. Fig. 7 shows the ESCA survey spectra for the carbon black powder before and after plasma amination in the stationary reactor. The N(ls) peak appearing near 400 eV indicates that amination has occurred. However, the surface N/C atomic ratio of 0.10 to 0.18 indicates that only a small fraction of the carbon surface was aminated.

Hollahan *et al.* [16] indicated that both NH_3 and 1 : 2 nitrogen–hydrogen plasmas can add amino groups to the polymer surfaces. They also concluded that these two plasmas should have the same characteristics. Plasma treatments of carbon black were carried out here using a 1 : 2 mixture of N_2 and H_2 and reaction conditions of 21 s.c.c.m., 1 torr, 100 W power and 30 min reaction time. As reported elsewhere [31] the emission spectrum from the N_2–H_2 plasma was noticeably different from the NH_3 plasma spectrum. ESCA analyses (Table III) reveal significantly lower N/C ratios on the surfaces treated in the N_2–H_2 plasmas. Both of these observations suggest that NH_3 and N_2–H_2 plasmas are not entirely equivalent.

Large amounts of oxygen were discovered on the aminated surfaces, probably from the residual impurities in the NH_3 gas, such as O_2 and water. Another

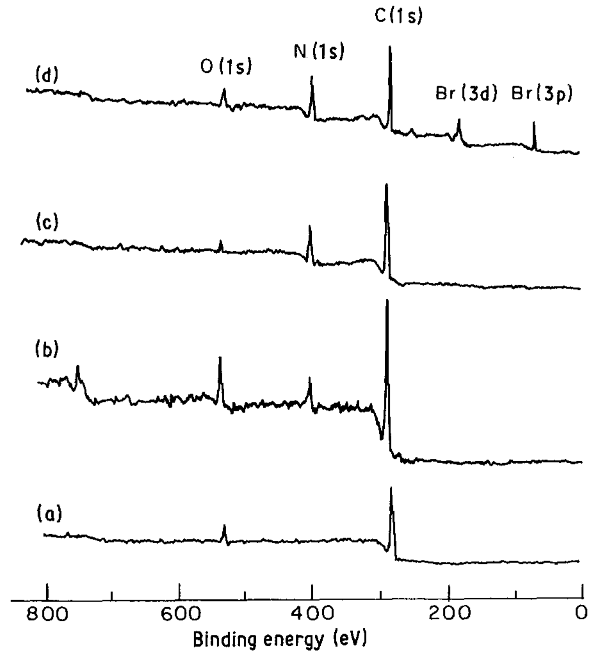

Figure 7 ESCA survey spectra of carbon black (sterling NS V-5855) and various plasma-aminated carbon blacks: (a) control, (b) N_2–H_2 plasma, (c) NH_3 plasma, (d) NH_3 plasma and HBr gas.

possibility is post-oxidation reactions when the treated samples are exposed to air. It is known that plasma-treated surfaces may contain a substantial number of free radicals with long half-lives [34, 35]. These active species can subsequently react with components of their environment. In view of this, two post-treatments were applied to the aminated carbon black surfaces immediately after the plasma treatment. The effects of these on the surface chemical structure were investigated using ESCA. Comparing the samples with and without hydrogen post-treatment shows that post-treatment in H_2 gas or H_2 plasma substantially reduces the extent of reaction with oxygen in air. It was also found that H_2 plasma post-treatment is more effective than H_2 gas post-treatment in preventing surface oxidation [31].

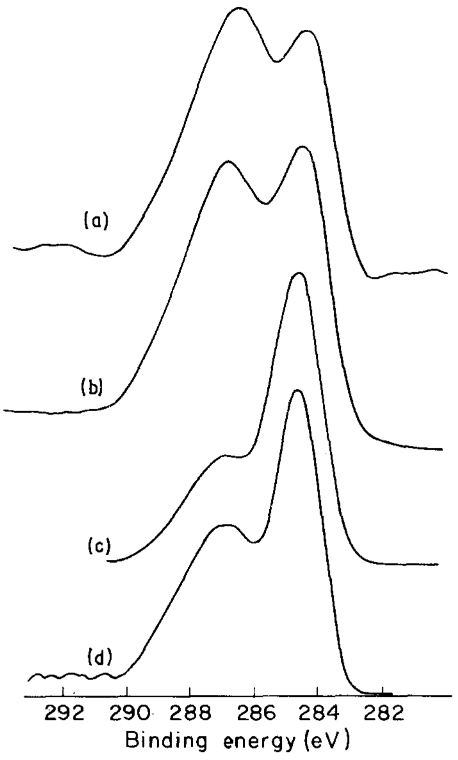

Figure 8 Variation of the C(ls) spectrum of aminated carbon black (sterling R) with time (in laboratory air). NH_3 plasma, flow rate 20 s.c.c.m., power 50 W, reaction time 50 min (stationary reactor). (a) After 2 h: atomic ratio O/C = 0.12, N/C = 0.99. (b) After 16 h: O/C = 0.12, N/C = 0.91. (c) After 30 h: O/C = 0.065, N/C = 0.67. (d) After 54 h: O/C = 0.085, N/C = 0.72.

Information was obtained on the relative concentrations of basic and non-basic nitrogen groups on the plasma-treated surfaces. As described in detail elsewhere [31, 33], the NH_3 plasma-treated samples were equilibrated with gaseous HBr and then were evaluated for surface chemical composition using ESCA. One of the ESCA survey spectra shown in Fig. 7 shows not only the N(ls), O(ls) and C(ls) signals but also the Br(3d) signal at 77 eV and Br (3p) at 189 eV. A quantitative study of surface elemental ratios is summarized in Table IV. The average Br/N ratio of 0.3 suggests that 30% of the surface nitrogen has formed an HBr salt, indicating that 30% of the nitrogen-containing functional groups introduced by the ammonia plasma are basic (amines, imines and amides).

It is important to measure the stability of the nitrogen groups on the aminated carbon black surface. To do this, a plasma-aminated carbon black sample was placed in a vacuum and another similarly treated carbon black was exposed to laboratory air. ESCA spectra were then obtained for these samples as a function of ageing time.

Surface nitrogen atoms were lost, as shown by the decrease of the N/C ratio and C(ls) peak intensity with increasing ageing times in Figs 8 and 9. One possible explanation for this behaviour is that the nitrogen groups on the treated carbon black surface may be the result of adsorbed ammonia. The experimental result shown in Fig. 10 indicates that carbon black exposed to ammonia gas in the absence of a plasma shows no evidence of adsorbed nitrogen groups. On the other hand, the plasma-treated carbon black shows a strong nitrogen signal on the surface. This weakens the argument for ammonia gas adsorption.

TABLE IV Surface atomic ratios

O/C	N/C	Br/C	Br/N
Carbon fibre			
0.239	0.190	0.075	0.39
0.122	0.206	0.044	0.21
0.282	0.219	0.042	0.19
0.198	0.151	0.047	0.31
0.198	0.104	0.019	0.18
0.116	0.128	0.040	0.31
0.182	0.117	0.041	0.35
0.128	0.124	0.017	0.14
0.168	0.105	0.021	0.20
0.165	0.137	0.029	0.21
Carbon black			
0.066	0.231	0.059	0.265
0.042	0.340	0.128	0.381
0.039	0.520	0.073	0.14
0.10	0.350	0.036	0.101
0.056	0.140	0.043	0.31
	0.134	0.052	0.39

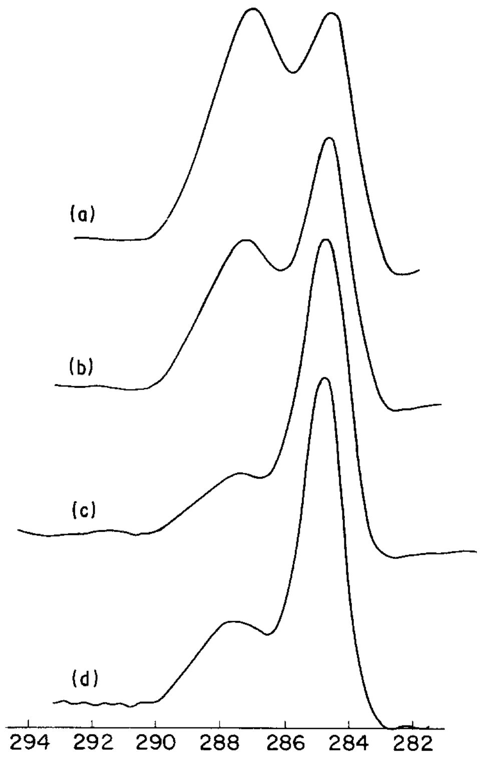

Figure 9 Variation of the C(ls) spectrum of aminated carbon black (sterling R) with time (in vacuum). NH_3 plasma, flow rate 20 s.c.c.m., power 50 W, reaction time 50 min (stationary reactor). (a) After 2 h: atomic ratio $O/C = 0.12$, $N/C = 0.83$. (b) After 16 h: $O/C = 0.11$, $N/C = 0.70$. (c) After 30 h: $O/C = 0.11$, $N/C = 0.40$. (d) After 54 h: $O/C = 0.082$, $N/C = 0.44$.

If the loss of nitrogen groups is not due to the desorption of NH_3 gas, it might arise from an oxidative process. If so, the sample exposed to air would be expected to oxidize faster and contain more oxygen groups than the one placed in the vacuum environment. However, the data (Figs 8 and 9) show no difference in the N/O atomic ratio for the two samples. Therefore, an oxidation reaction does not appear to be responsible for the observed loss of nitrogen groups. Some speculations on the mechanism of nitrogen-group loss have appeared elsewhere [31] and are outlined briefly here in the discussion section.

2.2.2. Plasma-enhanced surface amination of carbon fibres and pyrolytic graphite

Initial experiments with an ammonia discharge on carbon fibres showed that nitrogen-containing groups could be attached to the fibre surface. Fig. 11 shows the ESCA survey spectrum of the PAN-based carbon fibre before and after ammonia plasma treatments. A new peak at 400 eV, due to nitrogen atoms, was found on the ammonia plasma-treated fibre surface. ESCA data on plasma-treated carbon fibres are listed in Tables IV and V.

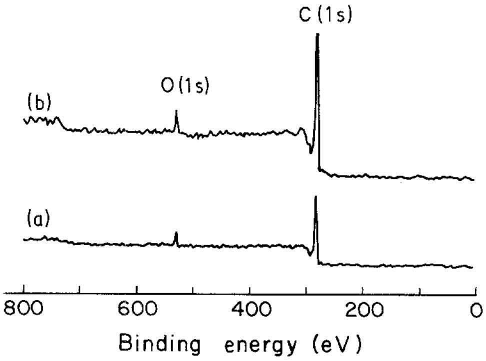

Figure 10 ESCA survey spectra of (a) carbon black and (b) NH_3 and HBr gas-treated carbon black (sterling NS V-5855).

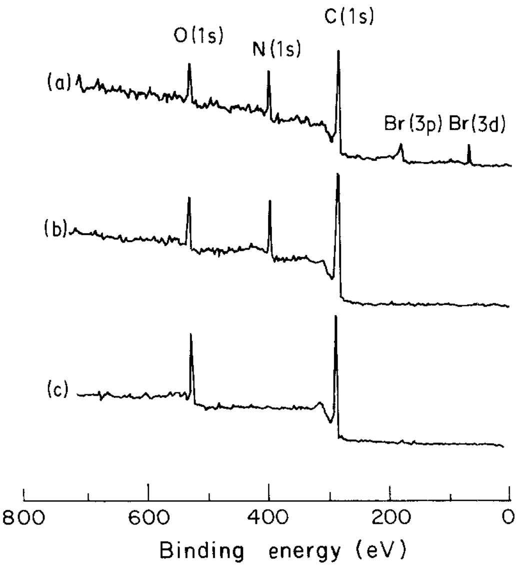

Figure 11 ESCA survey spectra of aminated carbon fibre (Thornel 300): (a) with and (b) without HBr equilibration; (c) control.

As described above, the treated carbon fibres were equilibrated with gaseous HBr and then evaluated for surface nitrogen composition using ESCA. N(ls), O(ls), C(ls), Br(3d) and Br(3p) signals are seen in the ESCA survey spectrum, as shown in Fig. 11. Quantitative data are summarized in Table IV. Twenty to thirty per cent of the nitrogen-containing functional groups were basic as a result of ammonia plasma treatments. As was the case with aminated carbon blacks, the aminated carbon fibres show nitrogen group instability as indicated in Fig. 12. In order to compare the effects of structure on the stability of amine groups, pyrolytic graphite (Union Carbide) was also plasma-aminated and aged. The loss of nitrogen groups on aminated graphite, as shown in Fig. 13, occurs at a slower rate than for the aminated carbon fibre.

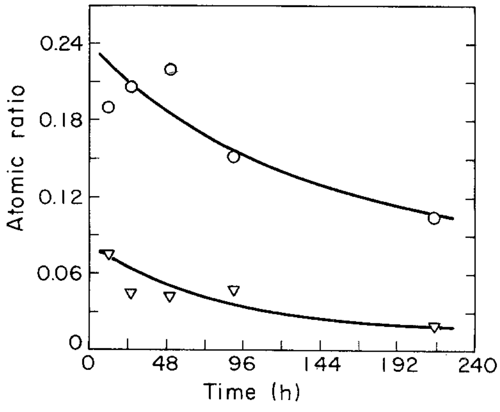

Figure 12 Stability of surface functional groups of aminated Panex fibre: (○) N/C, (▽) Br/C.

TABLE V ESCA data of plasma-aminated carbon fibres

Sample	NH_3 plasma treatment conditions			Atomic ratio	
	Flow rate (s.c.c.m.)	Power (W)	Time (min)	N/C	O/C
(Control)	–	–	–	0	0.24
CF066	50	90	30	0.17	0.133
CF085	35	100	45	0.112	0.133
CF087	35	75	60	0.162	0.126
CF089*	35	100	10	0.19	0.369
CF102*	35	100	10	0.11	0.27
CF104	35	100	60	0.135	0.115
Panex (control)	–	–	–	0	0.40
Panex	50	50	90	0.28	0.33
Pyrolytic graphite block	35	100	10	0.162	0.157
	35	100	30	0.26	0.102

*Helium plasma pre-treated for 3 to 10 min.

2.3. Discussion

The carbon fibres obtained from the various manufacturers have a surface composition consisting of appreciable amounts of oxygen and traces of hydrogen and nitrogen. Several studies have been carried out to characterize these surfaces [36–38]. Oxygen groups, including carboxyl, phenol, lactone, carbonyl and quinone, are the most important groups on carbon surfaces [37, 38]. A representation of the oxygen-related functionalities was suggested by Prest and Mosher [39] in which oxygen atoms comprise up to 15% of the surface atomic species. The data of Table II support this type of model for our carbon fibre surfaces.

The surface hydrogen content of carbon black varies from 1 to 10 atoms of hydrogen per 100 atoms of carbon, depending on the feedstock and on the process used [40]. This surface hydrogen is chemically reactive. Substitution by bromine [41] as well as by chlorine [42] has been accomplished at room temperature. In order to determine whether substitution of hydrogen by fluorine groups was possible in plasma surface reactions, information from emission spectra was employed. The experiment consisted of monitoring the hydrogen emission line before and after the insertion of carbon fibres into the plasma glow. After the insertion of the carbon fibre, the hydrogen line increased dramatically (Fig. 14), supporting the idea that surface substitution occurs during the plasma surface treatments of carbon.

Elemental bulk fluorination of graphite [3, 21–25] and carbon fibres [28] has been extensively studied. The fluorination reaction starts at the boundary of a carbon layer. From this primary reaction centre the C–F structure grows in two dimensions converting the original sp^2 carbon structure into a regular sp^3 C–F structure. Plasma-enhanced bulk fluorination of carbon black [24] demonstrated a similar fluorinated graphite structure with an sp^3 structure. Therefore, it is probable that the plasma-enhanced surface fluorination of carbon materials follows the same mechanism as elemental fluorination.

The structure of aminated carbon materials has not been proposed before. Some model structures, shown in Fig. 15, are suggested here based on the evidence of previous researchers [32, 33]. In the idealized structure of Model A, amine functional groups are attached to non-resonant carbon rings. Since the resonance structure can add stability by an amount of energy equal to about 35 kcal mol^{-1} (146 kJ mol^{-1}) [43], it is favourable for the Model A structure to release an ammonia

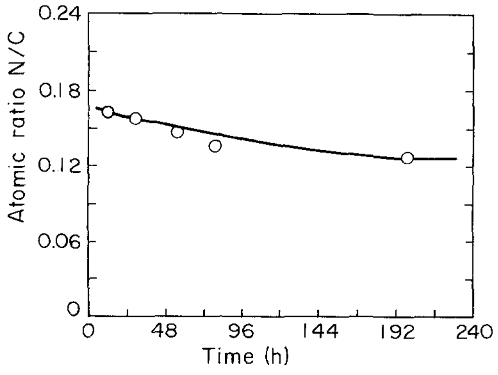

Figure 13 Stability of surface functional groups aminated pyrolytic graphite: (○) N/C.

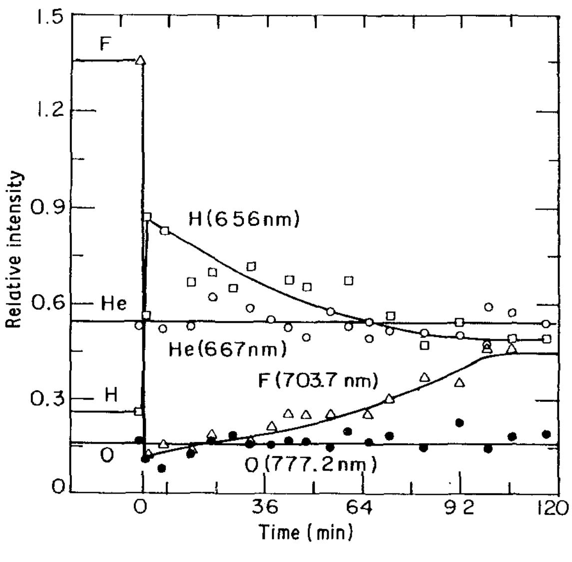

Figure 14 Emission spectral analysis of a CF_4–He plasma during the plasma reaction.

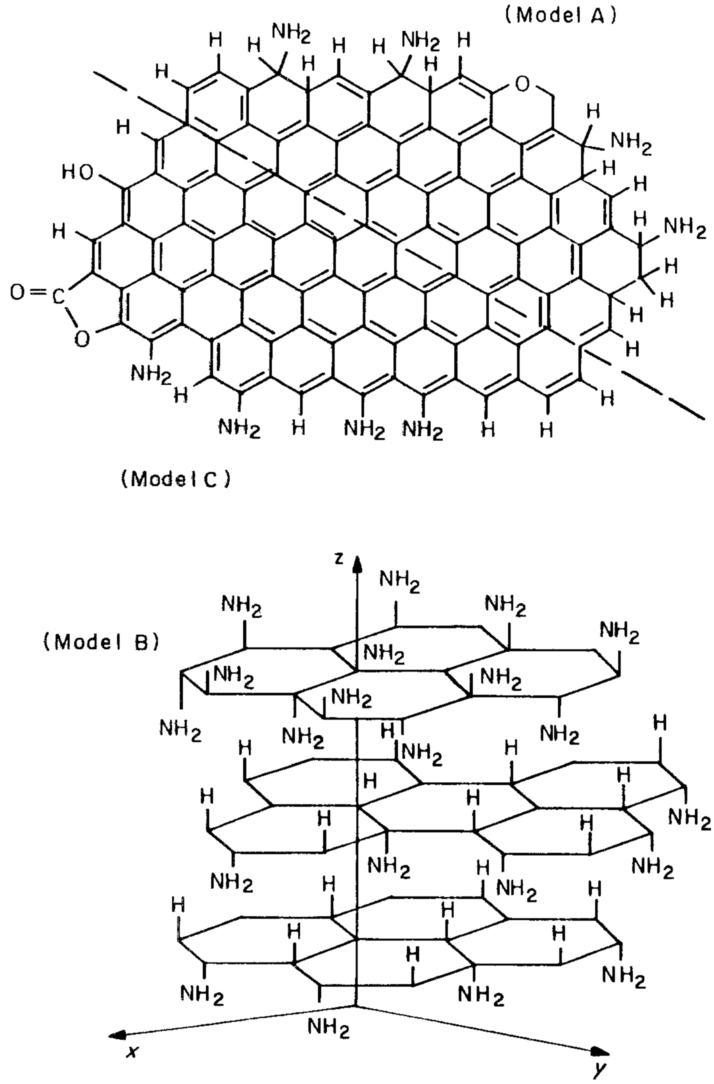

Figure 15 Schematic diagram of proposed aminated carbon structures.

molecule and form the more stable resonance structure. The structure of Model A is more suitable for amorphous carbon.

In the structure of Model B in Fig. 15, not only is the aromatic character of the carbon lost, but the hexagonal structure of the carbon atoms has been distorted by intercalating a bulky NH_2 functional group. There is a high probability that electron-rich NH_2 will react with hydrogen atoms on the adjacent layer and thus form an ammonia gas molecule. The structure of Model B could be used to describe graphite-like carbon structures. Although the structure of Model B is not as unfavourable as Model A in terms of structure stability, in either case the absence of long-term chemical stability is expected. In Model C, the NH_2 groups are attached to the stable aromatic rings by direct substitution reaction between NH_2 radicals and hydrogen atoms on the carbon surfaces. Model C has the most stable structure and is the likely source of the amine groups which remain on the surface after considerable ageing time.

Carbon black and carbon fibre consist largely of amorphous carbon and, therefore, most of their aminated carbon structure will be that of Model A. Pyrolytic graphite, with a high percentage of ordered crystalline carbon layers, is assumed to be aminated according to a Model B structure. The rate of forming ammonia gas can be expected to be slower for the aminated pyrolytic graphite, in keeping with the results presented earlier.

3. Potential applications

High-performance composites, for example carbon/graphite-filled polymeric materials, are finding increased use in applications requiring high strength, high stiffness, and low weight [1, 2]. In reinforced composites such as these, many important mechanical properties are largely determined by the nature of the resin–filler interface [2]. For this reason, it is always desirable to optimize the adhesion at the resin–fibre interface. In this way, fillers are made to distribute and carry as much of the stress load as possible. The simplest example is the use of coupling agents, which serve as intermediaries that bond to both the filler and the matrix materials. Thus, silane coupling agents are used for glass-fibre reinforced plastics. However, there has been less success in tailoring the interfacial bond strength between carbon fibres and fillers and polymeric matrices.

One purpose of plasma-treating fillers and fibres is to modify the surface of the reinforcing phase so that an appropriate level of adhesion through physical compatibility and/or chemical bonding can be achieved. Fluoropolymers pose a major problem in this regard because of the low-energy surface they present to the filler phase. Little or weak adhesion between fillers

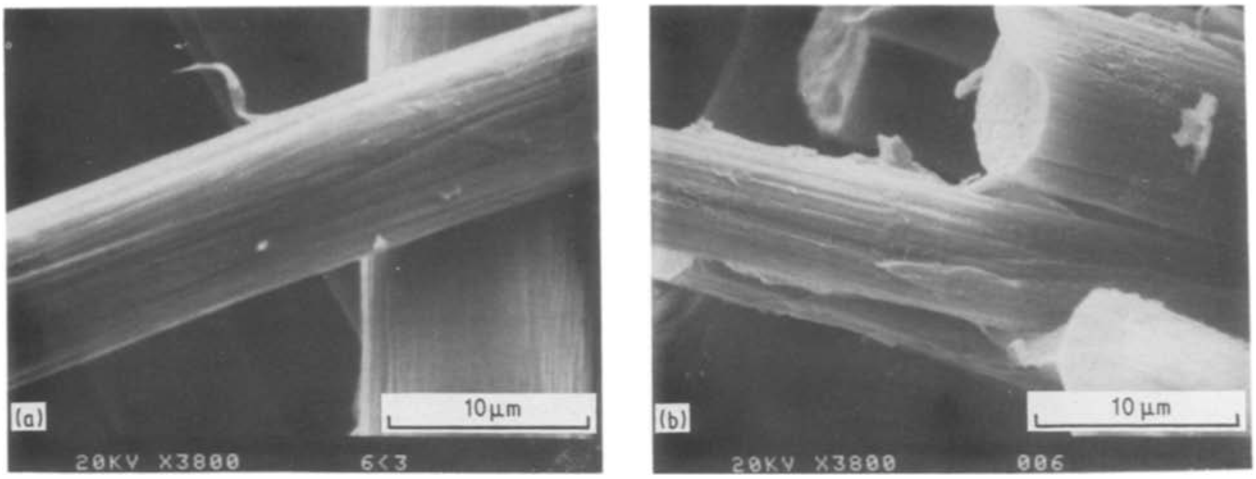

Figure 16 (a) Fracture surfaces of (a) carbon fibre-filled FEP composite, (b) fluorinated carbon fibre-filled FEP composite.

and fluoropolymers results, for example, in a sharp loss of strength at elevated temperatures [44]. It is also known that conventional carbon fibre–epoxy composites suffer a loss in mechanical properties when exposed to high humidity and temperature [45]. All of these problems are related to weak interfacial forces. Previous studies [16–18] have also indicated that amine groups introduced on to surfaces by exposure to ammonia plasmas can react with epoxides to form covalent bonds, thereby potentially improving composite performance.

In this work, three different composite systems, carbon black–fluororubber, carbon fibre–fluoroplastic, and carbon fibre–epoxy, were subject to preliminary testing. The results on all three systems are discussed elsewhere [31]. For the carbon fibre–fluoroplastic system the fracture surfaces of the composites were observed using SEM to see the nature of the failure. As would be expected, the pulled-out fibre surface is very clean for untreated fibre composites (Fig. 16a). However, fluorinated-fibre–fluoroplastic composites exhibit a residue of resin sticking to the pulled-out fibres (Fig. 16b). The longitudinal tensile behaviour of fluoroplastic composites with fluorinated carbon fibres (Table VI) shows enhanced strength and stiffness compared to the unmodified fibre counterparts. Young's modulus increased 10 to 45% after fibre fluorination. Ultimate strength increased up to 30%.

TABLE VI Tensile properties of fluorinated fibre-filled fluoroplastic composites

Degree of surface treatment (F/C)	Tensile strength (p.s.i.)*	Composite properties	
		Modulus $\times 10^5$ (p.s.i.)	Break elongation (%)
FEP composite			
0	6785	6.6	1.20
1.0	6406	7.3	1.38
1.18	7292	8.7	1.29
1.29	9112	9.7	1.18
1.3	9015	8.8	1.13
PFA composite			
0	6400 ± 17%	10.2 ± 13%	
1.54	8633 ± 10%	11.2 ± 13%	

*1 p.s.i. = 6895 Pa.

4. Summary

Plasma-assisted surface modifications of various forms of carbon, including carbon black, carbon fibre and pyrolytic graphite, have been described. ESCA, contact angle measurements, and scanning electron microscopy were used to characterize the plasma-modified carbon surfaces.

Plasma fluorinations of carbon surfaces were carried out in this study using various flow rates, treatment times and types of gas. Plasma-fluorinated carbon blacks exhibited a surface chemical structure similar to that of Fluorographite.

Nitrogen-containing groups were introduced on to the surfaces of carbon blacks and carbon fibres by exposure to ammonia and N_2–H_2 glow discharges. The stability of the nitrogen-containing groups was measured and discussed, and several mechanisms of degradation were suggested.

Plasma-modified carbon blacks and carbon fibres have potential for improving the properties of composites by achieving appropriate levels of adhesion between filler and matrix through physical compatibility and/or chemical bonding.

References

1. D. M. RIGGS, R. J. SHUFORD and R. W. LEWIS, in "Handbook of Composites", edited by G. Lubin (Van Nostrand Reinhold, New York, 1982) p. 196.
2. J. DELMONTE, "Technology of Carbon and Graphite Fiber Composites", (Van Nostrand Reinhold, New York, 1981) ch. 6.
3. N. WATANABE, *Solid State Ionics* **1** (1980) 87.
4. Private communication with Dr K. Johnson from Medronic Blood System Inc., Minneapolis, (1985).
5. B. CHAPMAN, (ed.), "Glow Discharge Processes" (Wiley, New York, 1980).
6. J. R. HOLLAHAN and A. T. BELL (eds), "Techniques and Applications of Plasma Chemistry" (Wiley, New York, 1974).
7. H. V. BOENIG (ed.), "Advances in Low-Temperature Plasma Chemistry, Technology, Applications" (Technomic, Pennsylvania, 1984).
8. M. SHEN (ed.), "Plasma Chemistry of Polymers", (Dekker, New York, 1976).
9. R. P. OUELLETTE, M. M. BARBIER and P. N. CHEREMISINOFF (eds), "Low-Temperature Plasma Technology Applications", Vol. 5, (Ann Arbour Science, Michigan, 1980).
10. H. K. YASUDA (ed.), "Plasma Polymerization and

Plasma Treatment", *J. Appl. Polym. Sci., Appl. Polym. Symp.* **38** (1984).
11. M. R. HAVENS, M. E. BIOLSI and K. G. MAYHAN, *J. Vac. Sci. Technol.* **13**(2) (1976) 575.
12. H. YASUDA, *J. Polym. Sci. : Macromol. Rev.* **16** (1981) 199.
13. M. ANAND, R. F. BADDOUR and R. E. COHEN, US Patent 4 264 750 (1981).
14. *Idem,* US Patent 4 404 256 (1983).
15. M. ANAND, R. E. COHEN and R. F. BADDOUR, *Polymer* **22** (1981) 361.
16. J. R. HOLLAHAN, B. B. STAFFORD, R. D. FALB and S. T. PAYNE, *J. Appl. Polym. Sci.* **13** (1969) 807.
17. G. C. COLLINS, A. C. LOWE and D. NICHOLAS, *Eur. Polym. J.* **9** (1973) 1173.
18. R. E. ALLRED, E. W. MERRILL and D. K. ROYLANCE, in "Molecular Characterization of Composite Interfaces", edited by H. Ishida and G. Kumar (Plenum, New York, 1985).
19. G. CORBIN, R. E. COHEN and R. F. BADDOUR, *Polymer* **23** (1982) 1546.
20. I. H. LOH, R. E. COHEN and R. F. BADDOUR, *J. Appl. Polym. Sci.* **31** (1986) 901.
21. P. KAMARCHIK and J. L. MARGRAVE, *Acc. Chem. Res.* **11** (1978) 296.
22. D. T. MESHRI, *Polym. News* **6** (1980) 200.
23. M. ARAMAKI and Y. KITA, *New Mater. New Proc.* **2** (1983) 498.
24. R. T. LAGOW, L. A. SHIMP, D. K. LAM and R. F. BADDOUR, *Inorg. Chem.* **11** (1972) 2568.
25. P. CADMAN, J. D. SCOTT and J. M. THOMAS, *Carbon* **15** (1977) 75.
26. G. W. TAYLOR, US Patent 4 343 628 (1982).
27. G. CORBIN, R. E. COHEN and R. F. BADDOUR, *Macromolecules* **18** (1985) 98.
28. L. FISCHER, U. SIEMANN and W. RULAND, *Colloid Polym. Sci.* **261** (1983) 744.
29. G. SMALINSKY and D. L. FLAMM, *J. Appl. Phys.* **50** (1979) 4982.
30. G. CORBIN, ScD thesis, Massachusetts Institute of Technology (1983).
31. I. H. LOH, ScD thesis, Massachusetts Institute of Technology (1985).
32. J. C. GOAN, US Patent 3 776 829 (1973).
33. J. E. EVANS and T. KUWANA, *Anal. Chem.* **51** (1979) 358.
34. H. YASUDA, "Plasma Chemistry of Polymers" edited by M. Shen (Dekker, New York, 1976).
35. N. H. SUNG, G. DAGLI and L. YING, in Proceedings of 37th SPI Annual Conference (Society of the Plastics Industry, 1982) p. 23-B.
36. A. ISHITANI, *ACS Polym. Prepri.* **24** (March 1983).
37. J. B. DONNET and R. C. BANSAL, (eds.) "Carbon Fibers" (Dekker, New York, 1984).
38. J. B. DONNET and A. VOET (eds), "Carbon Black Physics, Chemistry and Elastomer Reinforcement", (Dekker, New York, 1976).
39. W. M. PREST JR and R. A. MOSHER, in "Colloids and Surfaces in Reprographic Technology", edited by M. Hair and M. D. Croucher, ACS Symposia Vol. 200 (1982) p. 225.
40. J. B. DONNET and A. VOET (eds), "Carbon Black" (Dekker, New York, 1976).
41. H. P. GOEHM, U. HOFFMAN and A. CLAUS, in Proceedings of 3rd Conference on Carbon (1959) p. 24.
42. B. R. PURI and R. C. BANSAL, *Indian J. Chem.* **5** (1967) 381.
43. R. T. MORRISON and R. N. BOYD (ed.) "Organic Chemistry", 3rd Edn, (Allyn and Bacon, Boston, 1978).
44. J. W. MARTIN, T. V. BRASWELL and H. E. GREEN, *Rubb. Chem. Technol.* **51** (1978) 897.
45. G. S. SPRINGER (ed.), "Environmental Effects on Composites Materials" (Technomic, Westport, Connecticut, 1981).
46. D. C. CARBAUGH, F. J. MUNNO and J. M. MARCHELLO, *J. Chem. Phys.* **47** (1967) 5211.
47. R. H. VAREY, J. SMALLEY, P. H. RICHARDS, C. F. GOZNA and D. T. SWIFT-HOOK, *J. Phys. D:Appl. Phys.* **4** (1971) 520.
48. V. L. SYADUK and E. N. EREMIN, *Russ. J. Phys. Chem.* **49**(4) (1975) 536.
49. R. W. B. PEARSE and A. G. GAYDON, "The Identification of Molecular Spectra", 4th Edn, (Wiley, New York, 1976).
50. G. Y. BOTCHWAY and M. VENGOPALAN, *Z. Phys. Chem. N. F.* **120** (1980) 103.
51. R. D'AGOSTINO, F. CRAMAROSSA, S. De BENEDICTIS and G. FERRARO, *Plasma Chem. Plasma Processg.* **1**(1) (1981) 19.

Received 1 October 1986
and accepted 16 January 1987