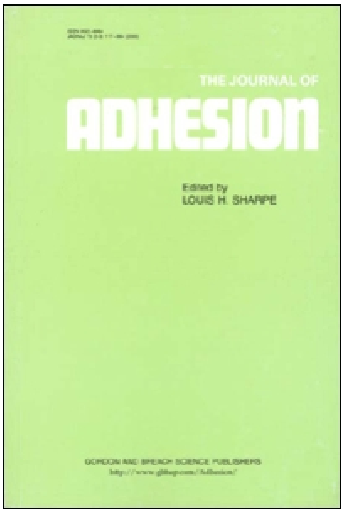

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Surface Treatment of Carbon Fibers Using Low Temperature Plasma

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Low temperature plasma treatment experiments were conducted on AS4 and AU4 type fibers in the presence of air, argon and nitrogen to study their effects on the resulting fiber-matrix adhesion in the composites fabricated with the fibers. Optimum conditions for the introduction of maximum surface oxygen and nitrogen functional groups on AS4 and AU4 fiber surfaces were derived. X-ray photelectron spectroscopy was performed on the fiber surfaces to determine the effect of plasma treatment on the amount and types of surface functional groups introduced. Scanning electron microscopy was performed on the fiber surfaces and the amount of surface etching and pitting was correlated to the plasma treatment conditions. Transverse tensile specimens were fabricated from treated fibers representing a few plasma treatment conditions, and their transverse tensile strengths were measured experimentally. An attempt was made to determine the effects of factors such as amount of chemical groups on the fiber surfaces, mechanical interlocking, molecular level entanglement and physical interactions to explain the data.

KEY WORDS Low temperature plasma; carbon fibers; composites; surface functional groups; fiber-matrix adhesion; transverse tensile strength.

INTRODUCTION

The technological demand for materials that exhibit improved specific strength and stiffness characteristics has led to considerable research and development in the field of fiber-reinforced resin-matrix composites. When fibers such as carbon, boron, and glass are combined with various epoxy, polyester, and polyamide resins, they produce a class of materials possessing specific tensile properties that can exceed those of the best metal alloys currently in production, depending on the fiber-matrix combination. By using specific combinations of fiber and matrix, it is possible to tailor structural materials that are superior for specific applications.[1]

Among the types of fibers, carbon is used for large-volume commercial applications based on three significant advantages. They are a) stiffer, b) lighter, and c) corrosion resistant in certain environments where glass fibers are vulnerable. However, the potential for carbon fiber reinforced composites is limited by their low transverse mechanical properties that are directly attributed to the poor adhesion between the fibers and the matrix. The adhesion between untreated carbon fibers and epoxy matrices has generally been poor. Therefore, it is important that the fiber surface have certain qualities that enhance its adhesion, which are: a) a large external surface area free from superficial defects, b) a high degree of roughness, and c) sufficient number of surface functional groups.[2]

The objective of this work was to study the effect of low temperature plasma treatment of carbon fibers on the enhancement of surface oxygen and nitrogen functional groups on AS4 and AU4 type carbon fibers. Initial studies were also conducted to examine the effect of plasma treatment on the transverse mechanical properties of plasma treated carbon fiber reinforced epoxy matrix composites. The transverse mechanical properties can be represented by either the transverse tensile strength (TTS) or the interlaminar shear strength (ILSS). These properties are strongly affected by the fiber-matrix adhesion at the interface, which is controlled by the surface properties of the carbon fibers, enhanced by creating a strong fiber-matrix interfacial bond. This could be created by i) chemical bonding ii) mechanical bonding and entanglement, iii) physical interaction or a combination of all of the above. In this study, plasma surface treatments were done on two types of carbon fibers under different conditions. Optimum plasma treatment conditions for introducing the maximum oxygen and nitrogen surface functional groups were derived. Initial transverse tensile strength results for the AS4 type carbon fiber/epoxy composite are presented as a function of plasma treatment conditions and types of plasma. Scanning electron microscopy results are also presented to correlate the plasma treatment conditions and the amount of surface etching and pitting. The transverse tensile strength results of the composite as a function of the treatment conditions and type of plasma are presented.

BACKGROUND

Surface Treatment Methods for Carbon Fibers

Carbon fibers in their natural, manufactured state do not bond well with resin matrices such as epoxies, leading to a low interlaminar shear strength. This has been described to be primarily due to a weak bond between the fibers and the matrix.[3-4] It has been reported that surface treatment of carbon fibers greatly increases their adhesion strength to polymeric materials. These surface treatments could be classified into either of oxidative or non-oxidative in nature.

A desirable surface treatment is a process that enhances the bonding with resin systems without detriment to other major fiber properties. The effect of surface treatments has mostly been determined by composite shear properties such as transverse tensile strength and interlaminar shear strength.

Gas Phase Oxidative Treatments The common gas phase oxidative treatments for carbon fibers have reportedly been carried out with air, oxygen, or oxygen-carrying gases such as CO_2. Molleyre and Bastick[5] carried out the oxidation of PAN-based carbon fibers in air at 550°C, and studied the internal and external characteristics of the fibers before and after the oxidative treatment. They found that the oxidative treatment increased the surface area, surface rugosity, and pore sizes on the fiber surface. The increase in surface rugosity increased the composite shear strength. Molleyre and Bastick[5] also compared the effect of oxidation of PAN-based carbon fibers in the presence of oxygen and CO_2. They found that the treatment with CO_2 smothed the initial pores on the fiber surface and produced new pores with small dimensions, while the treatment with oxygen only increased the original pore sizes. Treatment with CO_2 also served to smooth fiber surfaces.

Bansal and Chhabra[6] oxidized PAN-based carbon fibers by suspending them in water and bubbling ozonized oxygen containing about 3% ozone, for 6 hours. This treatment reportedly resulted in low weight loss (6%), chemisorption of appreciable amounts of oxygen, and an increase in the surface area of the carbon fiber. However, no comparable composite properties were reported in this study.

In a study quoted extensively, Drzal and coworkers[7] studied the plasma treatment of PAN-based carbon fibers in air. They suggested that the adhesion of carbon fibers to epoxy materials operated through a two-part mechanism. Firstly, a weak outer layer is removed by the plasma treatment and, secondly, surface chemical groups are added to the fiber surface, which could increase the interaction with the matrix chemically, leading to improved fiber matrix adhesion.

Otani *et al.*,[8] and Rand *et al.*,[9] have reported that the wettability between the fibers and resin was improved by the introduction of polar groups such as carboxyl (COOH), carbonyl (—C=O), and hydroxyl (—OH) groups on the fiber surface. Drzal *et al.*,[10] and Mujin *et al.*,[11] also report a similar correlation between the presence of surface groups and wettability between the fibers and matrix.

The effect of air plasma on carbon fiber surfaces was also studied by Jones *et al.*,[12–13] They concluded that air plasma resulted in increased surface oxygen groups, which could aid in improving fiber matrix adhesion. However, this study did not try to correlate the increase in surface groups with any composite properties. Similar correlations of surface oxygen groups with fiber matrix adhesion has been reported by Allred and Stoller[14] for Kevlar fibers, Mujin *et al.*,[11] for PAN-based carbon fibers, and Zang *et al.*,[15] for PAN based carbon fibers. Jones *et al.*, also found that the plasma treatment of PAN-based carbon fibers in the presence of argon increased the amount of surface oxygen on the fiber.[12–13] They argued that argon plasma treatment induced the formation of radicals that are highly reactive; the radicals then reacted with oxygen and moisture in atmospheric air on exposure after treatment to form the surface oxygen groups. A possible explanation for this phenomenon was suggested by Allred and Stoller.[14] They felt that a pretreatment of the fibers in argon for a short time could create reactive sites on the surface of the fibers, which then could react with any other gas, increasing the amount of surface groups introduced on the fiber surfaces.

Recent studies by Drzal[16] and Yip *et al.*,[17] have tried to correlate the amount of surface functional groups with the fiber matrix adhesion. Results showed that chemical bonding contributed to only a minor extent to fiber matrix adhesion in these studies.

Liquid Phase Oxidative Treatments Several liquid oxidizing agents have been used with varying degrees of success. These treatments are milder than gas phase treatments and, consequently, do not cause excessive etching and pitting, with very little degradation in the fiber properties. Nitric acid, acidic potassium permanganate, acidic potassium dichromate, sodium hypochlorite, hydrogen peroxide, and potassium persulfate have been used. Among these, the treatment of carbon fibers in the presence of nitric acid has been the most widely used and extensively studied.

Fitzer and co-workers[18] and Cziellok[19] oxidized type I and II PAN-based carbon fibers by refluxing the fibers with 65% nitric acid, followed by extraction in water and drying at 150°C for 48 hours. Both types of carbon fibers showed an increase in their surface oxygen content, which increased with increasing time of treatment. Similar results were reported by Manocha[20] who performed thermogravimetric analysis of PAN carbon fibers after oxidation with nitric acid. Hanmin *et al.*,[21] treated carbon fibers in refluxing 65% nitric acid aqueous solution at 120°C for five hours, followed by cleaning with water and drying at 150°C for 1 hour under vacuum. They found that the concentration of oxygen-containing groups on the fiber surface increased after this treatment, without seriously degrading the fiber properties. Bahl *et al.*,[22] found that the treatment of PAN-based carbon fibers with 50% nitric acid for 50 minutes was the optimum condition and resulted in the maximum improvement of the strength of fibers. This resulted in surface smoothening and the introduction of an appreciable amount of acid functional groups, which increased with increased concentration of nitric acid and the time of treatment. However, prolonged exposure to nitric acid was also found to reduce the strength of the fiber, possibly due to the etching of fibers.

Bansal and Chhabra[6] and Bansal *et al.*,[23] oxidized PAN-based carbon fibers with mild oxidizing agents such as aqueous solutions of hydrogen peroxide and potassium persulfate, by immersing the carbon fibers in closed bottles containing the solutions for up to 24 hours. Both treatments were found to introduce appreciable amounts of oxygen on the fiber surfaces, the amount being proportional to the etching or burnoff of the fiber by the treatment. These treatments were found to be milder than the treatment with nitric acid. Anodic oxidation of fibers using the fibers as anodes in aqueous acidic solutions was also found by Ehrburger *et al.*,[24] to increase surface oxygen. The wettability of the fibers showed an increase toward organic, inorganic, and polymeric liquids.

Donnet *et al.*,[25] used a novel surface treatment method to improve the fiber-matrix interfacial bond. This method consisted of electrochemical oxidation of the fibers as a continuous process that was studied by a technique of superficial nickel deposition. The deposit was then fixed by dipping in an epoxy resin and curing. The electrolytic oxidation technique improved the reliability of the composite, by increasing the Weibull modulus of the tested composite and the smoothness of the fibers.

Nonoxidative Surface Treatments Several nonoxidative fiber surface treatments have been used by researchers to improve the transverse mechanical properties of the resulting composite. These include whiskerization, grafting of different kinds of polymers, and certain kinds of coatings of organic and polymer materials.

Whiskerization involves a nucleation process and the growth of very thin and high strength single crystals of chemical compounds such as silicon carbide, titanium dioxide, and silicon nitride on the fiber surface perpendicular to the fiber axis. The whiskers grow from individual inhomogeneities or imperfections. A three to five fold increase in the interlaminar shear stress has been reported for PAN-based fibrous composites.[26] This process is not used widely because it is expensive and difficult to carry out precisely.

The fiber matrix interfacial bond can also be improved by coating the carbon fibers with organic polymeric materials such as poly(divinyl benzene) and several alternating and block polymers[27] in PAN-based carbon fibers. Cziollek and co-workers[19] modified type II PAN carbon fibers by coating the preoxidized fibers (preoxidized with 65% nitric acid) with a liquid epoxy resin and a liquid diamine. They reported an increase in composite shear strength by a margin of 30 to 50%.

The use of vapor phase deposition of pyrolytic carbon on PAN-based carbon fibers to enhance adhesion with the matrix and to improve the oxidation resistance has been reported by Fitzer *et al.*,[28] and Gebhardt *et al.*[29]

Effect of Oxidative Treatments on Composite Properties

The effect of surface area and surface functionality on the shear properties has been the subject of several studies.[6-7, 10, 16-18, 24, 30-35] Mimeault and Mckee[30] heated oxidized carbon fibers in vacuum at 950°C to remove surface functionalities, and found no difference in the shear properties of the composite made with treated carbon fibers. However, they observed that the surface area of the fibers increased considerably. Since the increase in surface area may have compensated the decrease in concentration of the surface functionalities, these researchers felt that it was difficult to assess the relative importance of surface functionalities and surface area of the treated fibers. Mimeault and Mckee[30] argue that the improved shear properties of the resulting composite may be due to the removal of the defects or flaws from the fiber surface.

Brooks *et al.*,[31] also have suggested that the relative importance of surface area and surface functionality in improving the composite shear properties is inconclusive, since the treatments to increase the surface functionalities may also increase the surface area simultaneously. In their opinion, it is more likely that the average number of bonds formed between the resin and the surface groups per unit length of the fiber significantly controls the fiber matrix adhesion than the concentration of the surface groups themselves. Clarke *et al.*,[32] also observed a relationship between the degree of oxidation and the properties of the composites, which was attributed to both the surface area and the surface functionalities.

However, Fitzer *et al.*,[18] and Ehrburger and Donnet[34] observed a direct correlation between the concentration of the surface functionalities and the composite properties. Fitzer *et al.*,[18] found that the wetting between the carbon fibers and epoxy or hardener or a mixture of both was improved after the oxidation treatment. They felt that the improvement in bonding was due to the chemisorption of the amine hardener on the carboxylic acid groups. Ehrburger and Donnet[34] have reported similar results for oxidized fibers and epoxy composites.

Fitzer *et al.*,[35] chemically analyzed the hardener-treated carbon fibers by removing the excess of unreacted hardener. The concentration of amine groups was found to be twice that of carboxylic acid groups, which indicated a stoichiometric chemical bonding between the hardener and the carboxylic groups. The removal of the hardener with formic acid revealed the presence of hydrogen bonds. Fitzer *et al.*,[35] believe that the reaction mechanism could be (a) by the formation of hydrogen bonds between the oxygen atoms of the carboxylic group or, (b) between the hydrogen atom of the carboxylic group and the nitrogen atom of the amine group and bonding of the prepolymer to the nitrogen atoms of both amine groups.

Ehrburger *et al.*,[24,34] examined the influence of various surface oxidations on the mechanical properties of acrylic carbon fiber reinforced polymer composites. The presence of two types of surface groups, (a) strongly acidic groups such as carboxylic and phenolic which could be neutralized by sodium hydroxide, and (b) weakly acidic groups (hydroxylic) which could be neutralized by sodium ethoxide were examined. The oxidized fibers were degassed by heat treatment at 1000°C in the presence of argon that removed the strong acidic groups almost completely. The weak acidic groups were restored by exposing the fibers to air for one night. The resulting ILSS showed a slight decrease compared with the oxidized fibers, but it was still higher than the ILSS of composites prepared with untreated fibers. This suggested the influence of the acid groups on the fiber surface on the resultant shear properties of the composite.

Recently, Dorey and Harvey[36] have investigated the effect of fiber surface treatment for adhesion to epoxy resins. Their studies suggested that the ILSS of the composite was not reduced by the removal of surface groups. Therefore, these investigators felt that it was important to distinguish the effects that are important to the fiber-matrix bond. Other studies by Drzal[16] and Yip *et al.*,[17] have reported that chemical bonding in carbon fiber reinforced composites may not be as important as was thought earlier.

Thus, despite a major effort by several researchers, the exact mechanism by which the fiber matrix adhesion is improved is still a matter of speculation. This paper is an attempt to clarify those mechanisms.

EXPERIMENTAL SETUP

Materials

Fibers The carbon fibers were supplied by Hercules, Inc., Wilmington, DE, USA. AU4 12K and AS4-6K types of fibers were used, which are graphitized at 1500°C. Table I gives the mechanical properties of the above fibers. The Hercules AU4 and AS4 fibers are manufactured from polyacrylonitrile (PAN) precursor and are about 7–8 μm in diameter. They consist of small crystallites of graphite, termed "turbostratic" in the literature,[37] an allotropic form of carbon. Hercules type A fiber contains approximately 13 graphitic layers over a width of about 40 Å.

Epoxy Resin Matrix The epoxy resin used in this study was Epon 828 (a Diglycidyl Ether of Bisphenol A (DGEBA)), supplied by Shell Chemical Company. It has an epoxy equivalent weight of 180–188 g/eq and a viscosity of 6500–9500 cP at 25°C. The chemical structure of the epoxy is shown in Figure 1.

Curing Agent The trade name of the curing agent used is Jeffamine T-403 (Texaco, Houston, Tx, USA) and its chemical name is polyoxypropylenetriamine.[38] This is a trifunctional primary amine, having an average molecular weight of approximately 440. Its amine groups are located on the secondary carbon atoms at the ends of

TABLE I
Properties of Hercules Graphite Fibers

Typical fiber properties	AU4	AS4
Filaments/tow	12K	6K
Tensile Strength, ksi	560	580
Tensile Modulus, msi	34	33
Tensile Strain	1.7	1.8
Approximate yield, ft/lb	1700	3400
Density, lbs/in^3	0.065	0.065

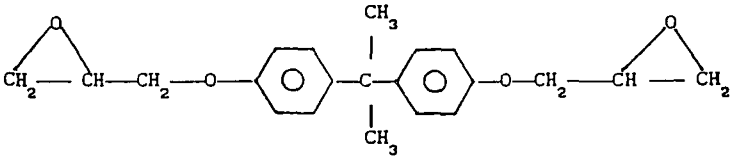

FIGURE 1 Chemical structure of epoxy resin.

aliphatic polyether chains. The stoichiometric ratio used is 10 gms of epoxy to 4.2 gms of T-403 triamine.

Setup for Plasma Treatment

A low temperature plasma of various gases, created by radio-frequency power (13.56 MHz) was used to treat the surface of carbon fibers. A schematic figure of the plasma reactor is shown in Figure 2. The plasma chamber used had an inner diameter of approximately 0.22 m (8.75″), and a length of about 0.48 m (19″). The chamber was surrounded by copper electrodes. The plasma reactor was a model 2100/3 with 2000T controller manufactured by Branson International Plasma Corporation. The plasma treatment conditions for the plasma treatment are given in Table II.

Plasma treatments were done in the presence of air, nitrogen and argon. To arrive at an optimum set of conditions for plasma surface treatment, several experiments were conducted on the two types of carbon fibers with varying experimental conditions. Parameters varied in the above experiments included, (a) wattage, (b) time of treatment, (c) argon pretreatment *versus* no argon pretreatment, (d) flow rate of the gas, and (e) gas type.

The fibers to be treated were cut into 0.2 m (8″) long bundles and taped on both ends for handling ease. The fibers were then spread on a flat aluminum tray and inserted into

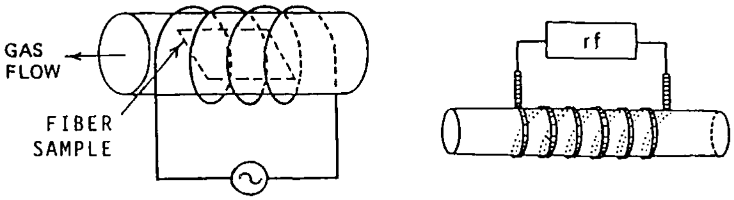

FIGURE 2 A schematic figure of the plasma reactor.

TABLE II
Low temperature Plasma treatment conditions

Electron temperature	1–10 eV
Electron density	10^{9}–$10^{12}\,cm^{-3}$
Power output	3–1500 Watts
Operating radio frequency	13.56 MHz
Pressure conditions	0.5–1.0 torr
Suitable gas flow	~ 100–300 cm^3/min

the reactor chamber of the plasma system. The chamber was then closed and evacuated at a rate that did not disturb the fiber bundles. The chamber pressure was brought down to a level of 5×10^{-2} torr with the help of a mechanical forepump. Once the background pressure was established, the gas flow rate was regulated with the help of a needle valve in the flow meter, to give an operating pressure of 0.5 to 1.0 torr. After stabilizing the operating pressure, the plasma was initiated by increasing the power from the high frequency RF generator to a desired level such that the chamber was illuminated with the plasma glow. After the required time of treatment, the RF power, gas flow, and the vacuum were turned off and the chamber was purged with a suitable gas to bring the chamber pressure back to the atmospheric pressure. The fiber bundles were then removed and stored for further analyses and testing.

Surface Characterization

An ISI SS-40 Model Scanning Electron Microscope (SEM) was used to examine the topography of the fiber surfaces. The elemental analysis of the carbon fiber surfaces before and after the plasma surfaces treatment was done using a Jeol JAMP 30 Model Auger Electron Spectroscope (AES) at the North Carolina State University, Raleigh, NC, USA. Analysis was done at an accelerating voltage of 5 KV, at a vacuum of 10^{-8} Pa and a beam size of approximately 1 μm, in the spot mode.

The chemical functional groups introduced on the carbon fiber surfaces due to the plasma treatment were determined by X-Ray Photo Electron Spectroscopy (XPS) on a Perkin Elmer Model 5400 XPS at the University of North Carolina at Chapel Hill, NC, USA. Measurements were carried out with a magnesium anode, an ESCA computer and curve analyzer. The C1s, O1s, and N1s photoelectron peaks were measured and analyzed.

Transverse Mechanical Properties

Unidirectional composite specimens were fabricated using the fibers from some of these experiments. Preliminary transverse tensile strength tests[39] were conducted on composite specimens fabricated using untreated, air-plasma-treated fibers under two different conditions, argon-plasma-treated and nitrogen-plasma-treated carbon fibers to study the fiber-matrix adhesion and correlate with the plasma treatment. Composite specimens were fabricated using epoxy resin (Epon 828) and a curing agent (Jeffamine T-403) in the ratio of 100:42 respectively. Standardized procedures were used for the fabrication and testing of the micro transverse tensile specimens.[39]

AS4 fibers plasma treated under four conditions were selected for preliminary measurements. For comparison purposes, composite specimens were also prepared from untreated fibers. The composite specimens were prepared from a random selection of four different treatment conditions (2 air plasma, 1 argon, and 1 nitrogen). A total of 10–15 specimens were prepared for each plasma treated fiber bundle. Six good samples were chosen by visual inspection from each lot and subjected to the transverse tensile tests.

EXPERIMENTAL RESULTS

The primary objective of this work was to study the effect of plasma treatment of carbon fibers on the adhesion between the fibers and the epoxy matrix. Many studies [10–12, 14, 15] have suggested that chemical bonding and oxygen functionalities on the carbon surface play an important role in the fiber-matrix adhesion. Consequently, a series of plasma treatment experiments were carried out to optimize the conditions for introduction of maximum amounts of oxygen and nitrogen functionalities on the fiber surface. The chemical analysis of the fiber surface was done using AES and XPS. Another significant effect that may influence the fiber-matrix adhesion is the alteration of the micro-structure of the fiber surface in response to the plasma treatment. To study this, the fiber surface after plasma treatment was analyzed using SEM. Finally, some preliminary data measurements were carried out for transverse tensile strengths of some unidirectional composite specimens fabricated from plasma treated fibers, thereby allowing some observations on the correlation between plasma treatment and transverse tensile strengths of these specimens.

Optimization of Surface Functionalities

The objective of these measurements was to determine optimum conditions to incorporate maximum amounts of oxygen and nitrogen functionalities on AU4 and AS4 fiber surfaces. Results were generated for air, argon and nitrogen plasmas. Preliminary Auger electron spectroscopy (AES) studies conducted on untreated and air-plasma-treated fibers suggested that factors such as plasma treatment time, power supplied and the flow rate of the gas play an important role in controlling the amount of oxygen on the fiber surfaces. A series of plasma treatment experiments were, therefore, conducted to obtain the optimum air plasma treatment conditions.

The AES results of experiments where the time of treatment was varied while the power and the flow rate of gas were kept constant are given in Table III (AS4 fibers). These are also presented in Figure 3. Similar results were obtained for AU4 fibers also. However, the relative concentrations of oxygen and nitrogen on the fiber surface was lower in AU4 fibers as compared with AS4 fibers. In the case of both AS4 and AU4 fibers, it was observed (Figure 3) that the oxygen and nitrogen contents increase initially as the treatment time is increased to approximately 10 minutes. However, it was seen that increasing the time of treatment to 15 minutes and above resulted in a decrease in the oxygen and nitrogen content on the fiber surfaces. In the case of AU4 fibers, the nitrogen content did not go through a maximum.

TABLE III
AES results and air plasma treatment conditions for AS4 fibers with variable time of treatment

Fiber : AS4		Gas : Air		Purge gas : Air
Variable : Time of treatment		Flow rate : 150 cc – /min		Power : 200 watts
Time of treatment (mins)	Oxygen %	Nitrogen %	Carbon %	Sulphur %
0.0	3.1	4.4	91.9	0.6
5.0	4.6	4.2	91.2	0.0
10.0	13.0	9.0	78.0	0.0
15.0	9.5	5.3	85.2	0.0
20.0	6.1	3.0	91.0	0.0
30.0	5.7	3.0	91.2	0.0

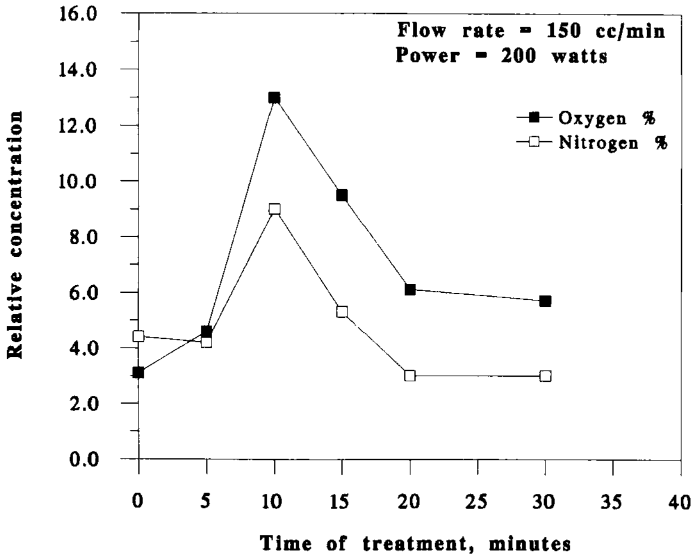

FIGURE 3 AES results after air plasma treatment of AS4 fibers; gas flow rate and power constant.

Two simultaneous reactions may be occurring on the carbon fiber surface during air plasma treatment.

$$C + O \rightleftarrows CO \tag{1}$$

$$CO + O \rightleftarrows CO_2 \tag{2}$$

No appreciable change in the surface oxygen content was seen by prolonging the treatment time. This could be due to:

a) Saturation of the active sites has already taken place.
b) A chemical equilibrium has been attained in the oxidation reaction between the available carbon atoms on the fiber surfaces and the oxygen atoms in the ionized gas, *i.e.*, the rate at which the C—O groups are incorporated is equivalent to the rate of removal of these groups by further oxidation to CO_2.

TABLE IV
AES results and air plasma treatment conditions for AS4 fibers with variable power

Fiber : AS4	Gas : Air		Purge gas : Air	
Variable : Power	Flow rate : 150 cc – /min		Time : 10 mins	
Power (Watts)	Oxygen %	Nitrogen %	Carbon %	Sulphur %
0.0	3.1	4.4	91.9	0.6
100	5.6	2.8	91.5	0.0
150	5.5	2.9	91.6	0.0
200	12.8	9.1	78.1	0.0
250	5.5	3.0	91.5	0.0
300	6.7	3.3	90.0	0.0
400	8.4	4.6	87.0	0.0

Therefore, it was concluded that the optimum treatment time needed to introduce the maximum amount of oxygen and nitrogen on AS4 and AU4 fiber surfaces in a plasma reactor of the size used in the current investigation was approximately 10 minutes. However, these conclusions are different from Jones *et al.*,[12] who reported the optimum treatment time to be < 20 secs. This could be due to the small volume of the plasma reactor used in their work.

Another set of experiments was carried out where power was varied while the flow rate and time of treatment were kept constant. The AES results are shown in (Table IV) (AS4 fibers). Here again, similar results were obtained for AU4 fibers. As determined by the previous set of experiments, the optimum time of treatment was chosen as 10 minutes. Figure 4 (AS4 fibers) indicated that the maximum amount of oxygen and nitrogen were introduced on the surface at a power of 200 watts. Increasing the power

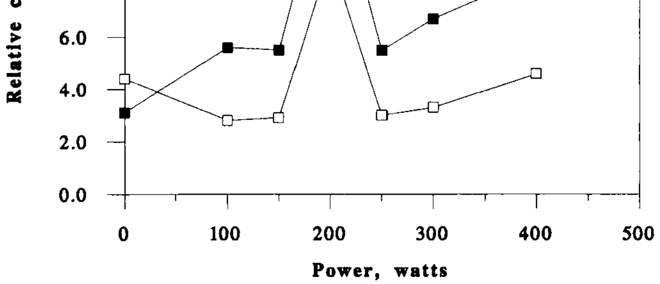

FIGURE 4 AES results after air plasma treatment of AS4 fibers; gas flow rate and time constant.

TABLE V
AES results and air plasma treatment conditions for AS4 fibers with variable flow rate

Fiber : AS4	Gas : Air		Purge gas : Air	
Variable : flow rate	Power : 200 watts		Time : 10 mins	
Flow rate (cc/min)	Oxygen %	Nitrogen %	Carbon %	Sulphur %
0.0	3.1	4.4	91.9	0.6
50	5.5	3.4	90.7	0.0
100	11.1	3.6	91.2	0.0
150	13.0	9.0	78.0	0.0
200	7.4	3.3	89.3	0.0
250	6.3	3.9	89.9	0.0
300	2.9	4.5	92.6	0.0
400	3.9	3.0	93.1	0.0

further did not increase the oxygen and nitrogen contents on the fiber surface. This behavior may again be due to the reasons given previously.

A series of experiments were now conducted to determine the optimum flow rate of gas required to incorporate the maximum amount of oxygen and nitrogen groups on the fiber surfaces (Table V). The time of treatment was kept at 10 minutes, while the power was held at 200 watts. Flow rate plays an important role not only in allowing the ionized gases to diffuse through the fiber bundles for uniform treatment but also in the removal of the byproducts formed to facilitate the primary forward reaction, *i.e.*, forming of C—O bonds on the fiber surface. It was seen that a gas flow rate of 150 cc/min and 200 cc/min incorporated the maximum amount of oxygen and nitrogen on the AS4 fiber surfaces (Figure 5).

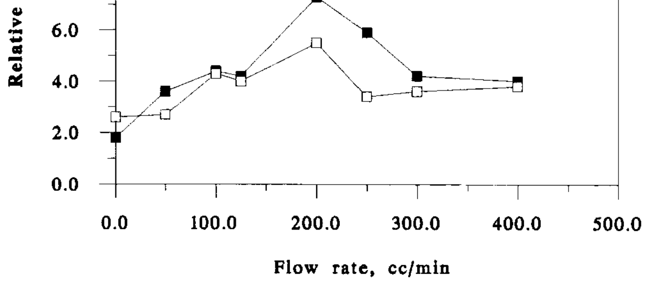

FIGURE 5 AES results after air plasma treatment of AS4 fibers;power and time constant.

TABLE VI
C1s spectra of AS4 Carbon fibers subjected to air plasma treatment

Power watts	Flow rate cc/min	Time of treatment	C 1s peak in %			
			Carboxyl 289.1	Carbonyl 287.6	Hydroxyl 285.7	Graphite C
0.0	0.0	0.0	4.86	8.42	22.91	63.81
200	150	10	5.29	9.32	17.12	68.28
300	150	10	7.01	9.29	16.84	66.86
400	150	10	10.76	7.64	22.36	59.24
150*	150	8	4.76	7.30	18.58	69.36

* After argon pretreatment at a flow rate of 150 cc/min, 100 watts, and 8 minutes treatment time.

XPS analyses were carried out to determine the chemical groups attached to the fiber surfaces. The C1s spectra in Table VI indicate that the oxygen content as shown by AES analysis is present as carboxyl (—COOH), carbonyl (—C=O), and hydroxyl (—OH) groups on the surfaces of both the plasma-treated and untreated fibers. The introduction of these polar groups also might serve to increase the wettability of the fiber surfaces.[8–11]

Plasma treatment experiments were performed using argon plasma for both AS4 and AU4 type fibers. AES analysis showed a higher amount of oxygen on the surfaces of the treated AS4 type carbon fibers, as shown in Table VII. Jones *et al.*,[12,13] have suggested that bombardment with argon plasma on the carbon fiber surfaces could induce the formation of radicals that are highly reactive. These reactive radicals on the surface could then react with oxygen and moisture in the atmospheric air on exposure after treatment to form the surface oxygen groups.

Nitrogen plasma treatment was found to introduce nitrogen groups on the surface of the carbon fibers. From Table VIII (AS4 fibers), it may be observed that there is an increase in the nitrogen content on the plasma-treated fiber surfaces as compared with the untreated fiber surfaces. This behavior could be explained by the fact that nitrogen is a less chemically reactive gas as compared with oxygen.

Stoller and Allred[14] have suggested that a pretreatment in argon for a short time creates highly reactive sites on the surface of the fibers which, on further treatment with any other gas, can increase the amount of chemical groups incorporated on to the fiber

TABLE VII
AES results and argon plasma treatment conditions for AS4 fibers

Conditions	Oxygen %	Nitrogen %	Carbon %	Sulphur %
Untreated fiber	3.1	4.4	91.9	0.6
Purge gas = Air Flow rate = 150 cc/min Power = 100 watts Time = 20 mins	8.9	4.8	84.6	1.7
Purge gas = Nitrogen Flow rate = 100 cc/min Power = 100 watts Time = 45 mins	10.2	4.7	84.1	1.0

TABLE VIII
AES results and nitrogen plasma treatment conditions for AS4 fibers

Conditions	Oxygen%	Nitrogen%	Carbon%	Sulphur%
Untreated fiber	3.1	4.4	91.9	0.6
Purge gas = Argon Flow rate = 150 cc/min Power = 400 watts Time = 20 mins	4.1	5.5	90.3	0.0
Purge gas = Nitrogen Flow rate = 150 cc/min Power = 200 watts Time = 10 mins	3.6	5.3	91.1	0.0

surfaces. The nitrogen and oxygen contents on the fiber surfaces after an argon pretreatment for air and nitrogen plasma treatments are presented in Table IX. The results were compared against AES results for air plasma (Table IV) and nitrogen plasma (Table VIII). It was observed that argon pretreatment before air plasma treatment was successful in increasing oxygen contents on the surfaces of the fibers in both the AS4 and AU4 type fibers. An improvement in the nitrogen contents on the fiber surfaces in argon pretreatment before nitrogen plasma treatment was observed only in the AS4 type fibers and not in the AU4 type fibers.

SEM Results for Micro-Structure of Fiber Surface

Air plasma treatment of carbon fibers resuls in much visible etching, as illustrated in Figures 6 and 7, as compared with the untreated AS4 and AU4 fibers, which have a very smooth surface (Figure 8). It may be clearly observed that the surface striations are parallel to the fiber axis, resulting in high surface roughness and increased surface area. It may also be observed that as the power input and time of treatment is increased, the amount of surface etching and pitting increases proportionately, as seen from Figures 6 and 7. Excessive treatment times may lead to degradation of the fiber strength and probably also lead to lowering of the total composite strength.

TABLE IX
AES results and argon pretreatment, and plasma treatment conditions for AS4 fibers

Argon pretreatment conditions	Plasma treatment conditions	Oxygen %	Nitrogen %	Carbon %	Sulphur %
Untreated AS4 fiber	Untreated AS4 fiber	3.1	4.4	91.9	0.6
Gas = Argon Purge gas = Nitrogen Power = 100 watts Flow rate = 150 cc/min Time = 8 mins AS4 fiber	Gas = Air Power = 150 watts Flow rate = 150 cc/min Time = 8 mins	7.1	5.3	87.6	0.0
Gas = Argon Purge gas = Argon Power = 100 watts Flow rate = 150 cc/min Time = 8 mins AS4 fiber	Gas = Nitrogen Power = 200 watts Flow rate = 150 cc/min Time = 8 mins	0.0	6.1	93.9	0.0

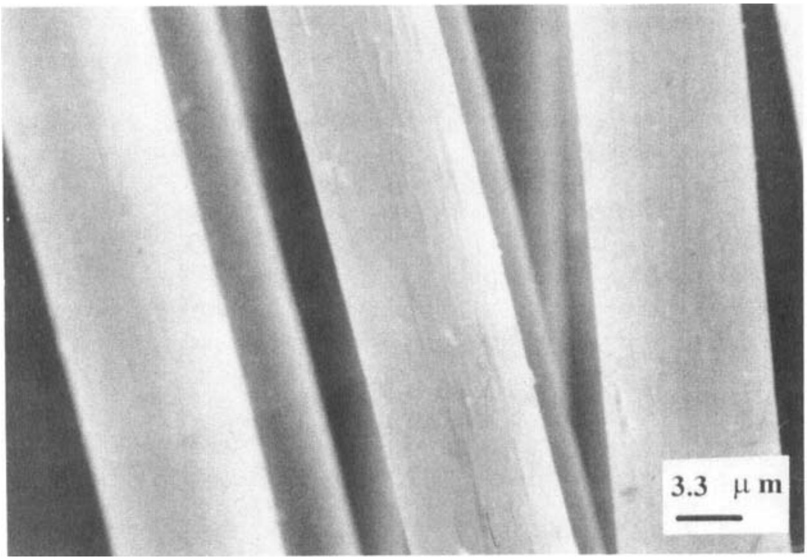

FIGURE 6 Air plasma treated AS4 fiber surfaces (100 watts, 20 min).

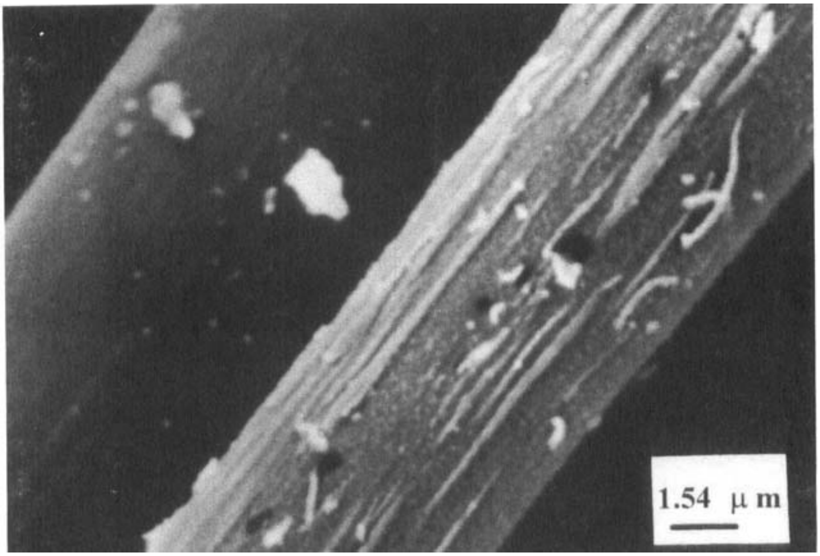

FIGURE 7 Another fiber surface showing excessive amount of etching and striations (250 watts, 30 min).

Nitrogen and argon plasma treated fibers do not show any visible etching, as seen in Figures 9 and 10. Any localized etching that might have occurred here must be in the range of a few graphite basal planes (less than 3) or too little to be detected in the SEM micrographs.

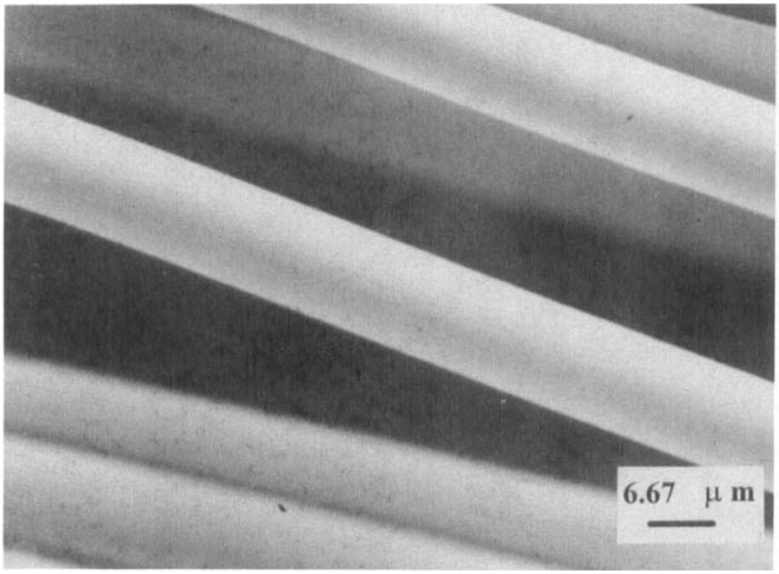

FIGURE 8 Untreated AS4 fiber surface.

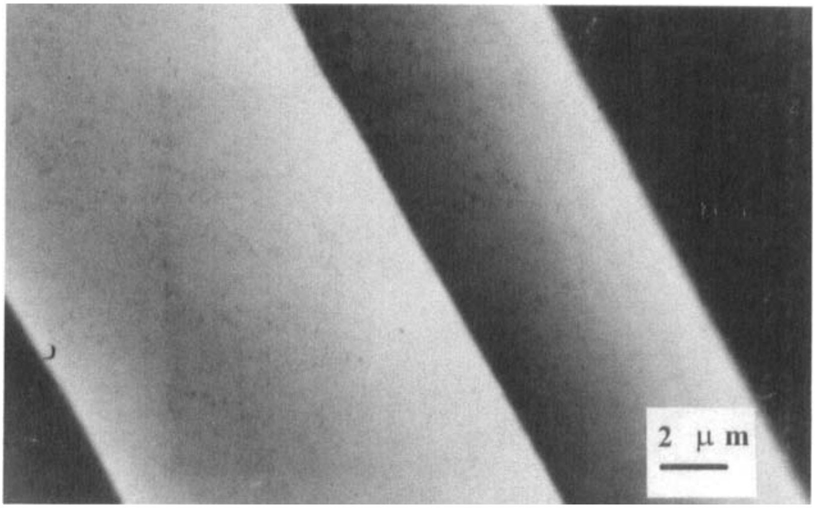

FIGURE 9 Nitrogen-plasma-treated AU4 fiber surface (150 cc/min, 200 watts, 10 min).

Transverse Tensile Strength Results

Preliminary transverse tensile strength measurements were conducted to determine the effect of plasma treatment on the fiber matrix adhesion in the final composite. The transverse tensile strengths of unidirectional composite specimens made from AS4 type fibers with different plasma treatments were determined. The complete results for the

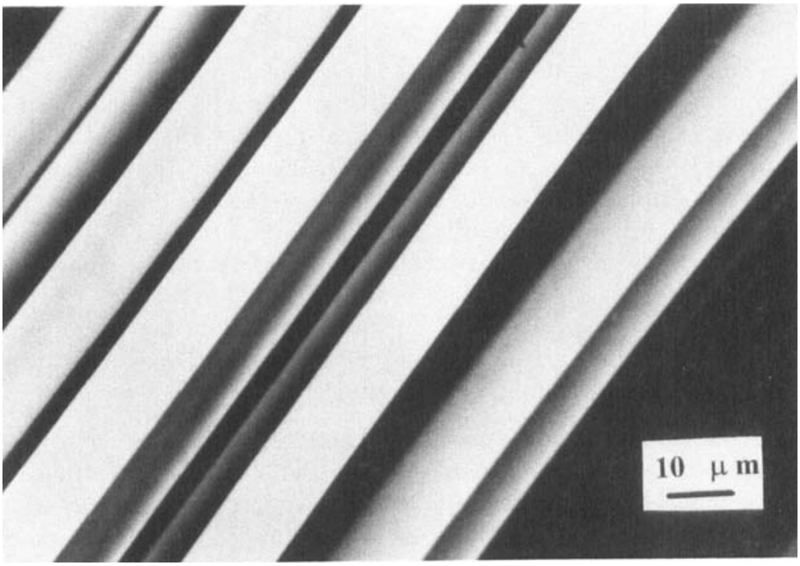

FIGURE 10 Argon-plasma-treated AU4 fiber surface (150 cc/min, 100 watts, 20 min).

five different cases of fiber/epoxy/plasma treatment condition combinations are shown in Figure 11. Each bar represents the average transverse tensile strength of six samples. The error bars represent the standard deviation of the population.

It can be observed that plasma treatment of the fibers before fabrication of the composite improved the average transverse tensile strength of the composite. It can also be seen that air plasma treatment gave the best average transverse tensile strength, followed by argon and then by nitrogen.

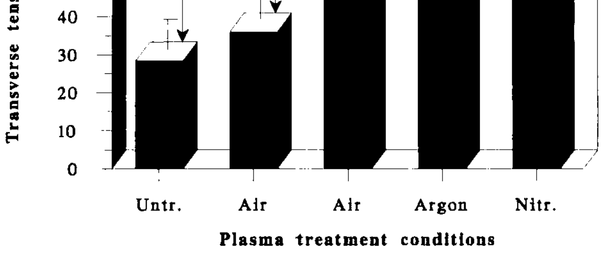

FIGURE 11 Transverse tensile test results, unidirectional composite, AS4 type fibers.

DISCUSSION

The experimental data presented in the last section provide valuable information about the conditions of plasma treatment for introduction of maximum amounts of oxygen and nitrogen functionalities on to the fiber surface. Also the SEM results show that the air plasma etches the fiber surface more than the argon and nitrogen plasmas. These are direct and very significant results of this work. In what follows, these results, in conjunction with the transverse tensile strength results, are used to investigate the phenomena governing the fiber-matrix adhesion in unidirectional composite specimens.

Adhesion between carbon fibers and epoxy matrices is an important controlling factor to achieve optimum composite properties. The extent of the fiber-matrix adhesion can be attributed to four major phenomena.[37]

i) Chemical bonding between the fiber surface and the epoxy molecules in the matrix.
ii) Mechanical interlocking of the fiber surface with the cured epoxy surface.
iii) Entanglement of the epoxy molecules with the chemical functionalities on the fiber surface.
iv) Physical interactions between the epoxy molecules and the fiber surface. These include van der Waals and Coulombic interactions.

The above four effects are listed in the order of decreasing strength, *i.e.*, adhesion by chemical bonding will be expected to form the strongest interface. In general, adhesion between the fiber and the matrix could be expected to occur due to all the above four effects. However, failure when subjected to transverse tensile stress will generally occur because of debonding corresponding to only one of these effects. The primary objective of this work has been to study the effect of plasma treatment of carbon fibers on the adhesion between the fibers and the epoxy matrix, as estimated from the transverse tensile strength measurements and interfacial characterization and analyses by SEM, AES, and XPS. Furthermore, we wish to relate the fiber-matrix adhesion to the four adhesion phenomena listed above.

For extensive surface bonding, the functional groups present on the carbon fiber surfaces after the plasma treatment must compete favorably for the epoxy and amine groups present in the resin matrix during the curing stage. Yosomiya *et al.*,[40] have described some possible reactions between the various surface functional groups and the resin. The difference in chemical kinetics of the competing reactions between the epoxy groups in the resin and the amine groups in the curing agent on the one hand and between the epoxy/amine groups and the fiber surface chemical groups on the other may also be playing a role in controlling the fiber-matrix interface. If the transverse failure is caused primarily by bond breakage, much higher values of transverse tensile strength (TTS) of about 10^6 to 10^7 psi could be expected. This can be shown from the dissociation energies and vibrational frequencies for the bonds concerned. This would make the fiber-matrix interface far too strong and the failure would occur in the matrix.

If mechanical interlocking were chiefly responsible for adhesion, transverse failure would be accompanied by either the rupture of the fiber or the resin material. Since carbon fibers have a higher tensile strength than the resin, fiber-matrix adhesion through mechanical interlocking will lead to cracking of the epoxy resin material.

Transverse tensile strength of an interface formed primarily by this type of adhesion will, therefore, be comparable with the tensile strength of the resin itself, which is approximately 12,000 psi. Thus, if the interface is formed by chemical bonding or mechanical interlocking, the TTS should show a maximum value of about 12,000 psi with the failure occurring in the matrix.

Flory[41] has suggested a molecular level mechanism to explain the tensile strength of an amorphous polymer. He has suggested that when an amorphous polymer is stretched, an arrangement is created in which the crystallites are aligned approximately parallel to each other and transformed into a crystalline polymer leading to a fracture typical of a crystal. In an analogous manner, one can also hypothesize that the interface between the fiber and the matrix is formed by molecular crosslinking and entanglement between the carbon fiber surface and the epoxy molecules.

Although an estimate of the transverse tensile strength (TTS) corresponding to adhesion by molecular entanglement is not attempted here, it is clear that this TTS should be directly proportional to the degree of molecular entanglement in the interface. Furthermore, it is fair to assume that the upper bound of this TTS should be the same as the tensile strength of the resin material or 12,000 psi. The overall picture, therefore, is that as the fiber surface is transformed from the smooth surface of the untreated fibers to rough and etched surfaces corresponding to various levels of plasma treatment, the degree of molecular entanglement at the interface increases. The functionalities on the surface of the plasma-treated fibers could also enhance the degree of molecular entanglement. This would explain the gradual increase in TTS from the value for untreated fibers (~ 30 MPa) to the best case of air-plasma-treated fibers (~ 80 MPa or 12,000 psi or close the tensile strength of the resin). Van der Waals forces are not expected to play any significant role in determining the TTS in these systems.

The two air-plasma-treated specimens exhibit very different TTS (40 MPa and 80 MPa). The SEM micrographs of the fibers corresponding to these two specimen are shown in Figures 6 and 7. The SEM micrograph of an untreated AS4 fiber is also shown in Figure 8. It is very clear that the air plasma alters the micro-structure of the fiber and etching of the surface is very visible. The results indicate that as the fiber surface gets rougher, the TTS increases consistent with our hypothesis of the molecular entanglement phenomenon.

Some more insight into the nature of the interface in these specimens is obtained by looking at the fracture surfaces in the TTS experiments. Figures 12 and 13 show the SEM micrographs of fractures corresponding to the untreated fiber specimen and the air plasma treated specimen, respectively. At low levels of adhesion, a frictional debonding and sliding of the matrix in relation to the fiber is observed as in Figure 12, which is from a fractured transverse tensile sample fabricated with untreated AS4 type fibers. As the fiber matrix adhesion is improved, as in transverse tensile samples fabricated from air-plasma-treated fibers, matrix cracking perpendicular to the fiber axis is observed in Figure 13. This indicates that the failure might be occurring in the matrix rather than at the interface.

Nitrogen and argon plasma treated fibers do not, in general, exhibit as much surface etching as in the case of air plasma (see Figures 9 and 10). However, these plasmas do introduce oxygen and nitrogen functionalities on the fiber surface and etching of the level of one or two graphite basal planes may very well be occurring. The interface in the

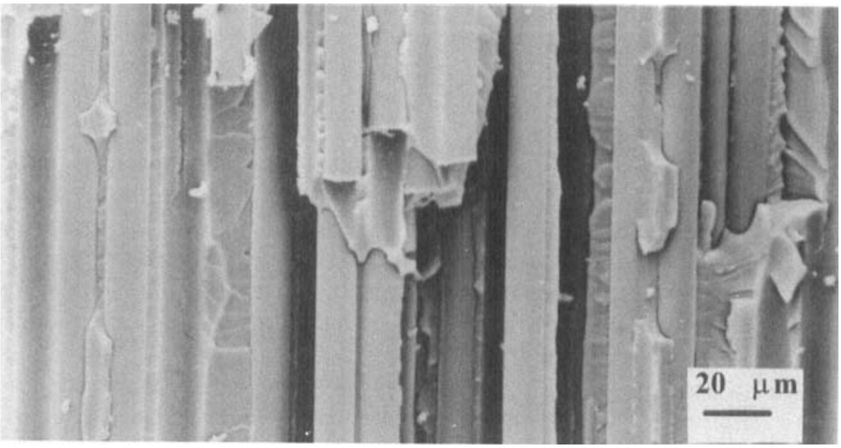

FIGURE 12 Fracture surface of untreated AS4 fiber reinforced composite transverse tensile specimen.

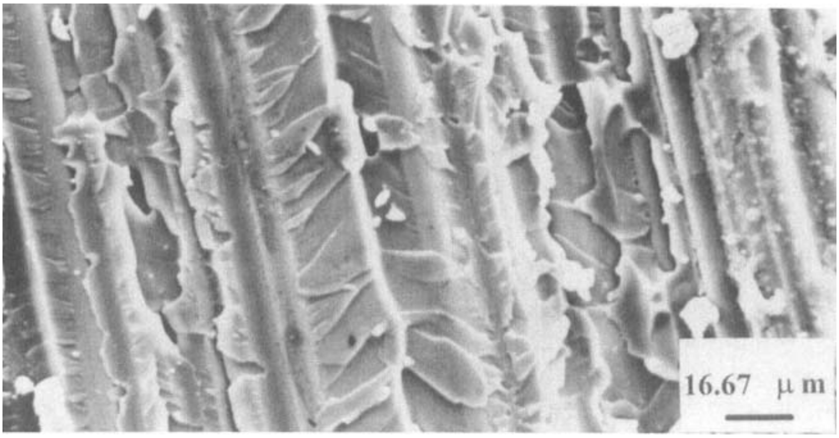

FIGURE 13 Fracture surface of air-plasma-treated AS4 fiber reinforced composite transverse tensile specimen.

specimen corresponding to these fibers would involve a larger degree of molecular entanglement than for an untreated fiber specimen. This would explain the intermediate TTS values of 55–65 MPa observed.

The conclusion that the forces resulting in the transverse tensile strength of these specimens may be of a physical rather than chemical nature is not a new one. Drzal[16] has recently studied the effect of surface oxygen groups on the interaction between the fiber and the matrix. He tried to correlate the Interlaminar Shear Strength (ILSS) of the composite with the amount of surface oxygen groups introduced on the fibers after plasma treatment. Drzal showed that as the amount of surface oxygen groups was increased, ILSS also increased. However, when the surface oxygen groups were removed completely by diazomethane reduction, the ILSS decreased by only 10%, and did not decrease to the level before the surface oxygen groups were introduced. This indicated that the surface oxygen groups were responsible for only 10% of the increase in adhesion, and that surface morphology and mechanical bonding could play a greater role than earlier thought. Drzal's results indicated that the addition of surface oxygen groups increased the interaction between the fiber and the matrix only to a minor extent and that the degree of chemical bonding that may exist at the fiber matrix interface is minimal.

Roughening of the fiber surface to promote interlocking and enhanced molecular entanglement seems to be an adequate mechanism to obtain an interface of strength equivalent to that of the matrix itself. Needless to say, any further strengthening of the interface is entirely unnecessary. It has been observed that argon pretreatment coupled with subsequent air plasma treatment can roughen the surface and incorporate higher amounts of oxygen functional groups for much less power input and time of treatment, as compared with fibers with no pretreatment. From a comparison of the fiber surfaces, evidently argon pretreatment can lead to the same degree of surface roughness but with a much higher surface oxygen content.

It might be useful to comment further on chemical bonding for strengthening the interface. This still remains the most potent means to obtain an interface of desired strength. Although for these composite systems with unidirectional fiber reinforcement, interfaces of high TTS as would be obtained by extensive bonding are unnecessary, this provides a good system to carry out studies on the conditions leading to interfaces of various strengths for application elsewhere. A detailed study of the fiber/epoxy composite systems prepared from both AS4 and AU4 type fibers subject to different plasma treatment conditions is necessary before concluding on the validity of the above findings, due to the preliminary nature of the findings. Much further work is, therefore, needed. Studies of competitive kinetics are also necessary and are being recommended for future consideration.

CONCLUSIONS

Low temperature plasma treatment experiments were conducted on AS4 and AU4 type carbon fibers in the presence of air, argon and nitrogen, to study their effects on the resulting fiber matrix adhesion in the unidirectional composite specimen fabricated with the fibers. Based on the experimental results, the following could be concluded.

1) The optimum conditions for the introduction of maximum surface oxygen and nitrogen functional groups on the fiber surfaces of the AS4 and AU4 type carbon fibers were derived. In the AS4 type fibers, these were: power = 200 watts; treatment time = 10 mins; and a gas flow rate = 150 cc/min. In the AU4 type fibers, these were determined to be: power = 200 watts; treatment time = 10 mins; and gas flow rate = 200 cc/min.
2) XPS analyses conducted on the fiber surfaces indicated the presence of carboxyl (—COOH), carbonyl (—C=O), and hydroxyl (—OH) groups on the surfaces of the air-plasma-treated AS4 and AU4 type fibers. These were found on the surfaces of the untreated fibers also, but in lesser amounts.

3) SEM micrography conducted on the surface of the air-plasma-treated AS4 and AU4 type fibers indicated that as the power input and the plasma treatment were increased, the amount of surface etching and pitting increased proportionately. Surface etching is present as surface striations parallel to the fiber axis that results in high surface roughness. Prolonged plasma treatment leads to degradation of fiber properties.
4) SEM micrography conducted on the surfaces of the AS4 and AU4 type carbon fibers that were plasma treated in the presence of argon and nitrogen indicated that these treatments did not remarkably alter the surface topography of the fibers.
5) Initial studies indicated that the transverse tensile strength of the unidirectional composite specimen fabricated from AS4 carbon fibers that were plasma treated was higher than that of the specimen fabricated from untreated AS4 type carbon fibers.
6) Among these, composites fabricated from air-plasma-treated AS4 type carbon fiber possessed the highest transverse tensile strength, followed by the argon-plasma-treated fiber specimen. The nitrogen-plasma-treated specimen also exhibited improved transverse tensile strength as compared with the untreated AS4 fiber reinforced composites.
7) Of all the possible effects influencing adhesion between fibers and epoxy resin, mechanical interlocking and molecular level entanglement seem to explain the TTS results best, hence these may be the most prevalent interfacial phenomena in these materials. This conclusion is also supported by the surface analysis of fibers and of fracture surfaces using SEM.

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