



Control of interfacial adhesion in continuous carbon and Kevlar fiber reinforced polymer composites

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Carbon fiber surfaces were treated by cold plasmas of oxygen, nitrogen, argon, ammonia, and propylene. A two-component bismaleimide, an epoxy, and a model thermoplastic resin polypropylene were used as the matrices for composites. The effectiveness of various plasmas in improving the interfacial adhesion between carbon fibers and matrix resins was demonstrated. Predominant adhesion promotion mechanisms as influenced by various plasma treatments were determined. Oxygen and argon plasmas were found to promote mechanical keying by increasing the level of fiber surface roughness and porosity. The wettability of carbon fiber surface by the matrix resin was also enhanced by oxygen plasmas and argon plasmas (to a lesser extent), as evidenced by the increased total surface energies and their polar components. These surface energy increases are mainly due to the various oxygen-containing functional groups observed on the oxygen plasma-treated surface. For the cases of ammonia and combined ammonia/argon plasma treatments, possible chemical bonding between bismaleimide and the plasma-deposited amine groups is one important promoter of interfacial bonding. In these cases increased wettability was also observed. Ammonia and ammonia/argon plasmas appear to be the more appropriate treatments for carbon-fiber/thermoset resin composites considering that they generally do not induce any appreciable reduction in fiber strength. In contrast, excessively prolonged exposure of carbon fibers to oxygen, nitrogen or argon plasma could lead to a significant reduction in fiber strength. The plasma-polymerized polypropylene deposited on the fiber surface was capable of improving the compatibility and adhesion between the fiber and the polypropylene matrix.

Keywords: interface, carbon fiber, Kevlar fiber, plasma treatment, polymer composite, epoxy, polypropylene

1 INTRODUCTION

Fiber/matrix interfacial adhesion plays an important role in determining the mechanical properties of a polymer composite. A better interfacial bond will impart to a composite better properties such as interlaminar shear strength, delamination resistance, fatigue and corrosion resistance.

The adhesion between untreated carbon fibers and common aerospace-grade resins is usually

poor. A variety of surface modification techniques have been developed to promote interfacial bonding in carbon fiber composites. In one approach, fibers were oxidized either with liquid oxidizing agents¹ such as concentrated nitric acid, or with gaseous media² such as air, oxygen, and ozone. Generally, oxidation etches the fiber surface and possibly implants carbonyl and hydroxyl groups onto the fiber surface, resulting in an increase in interfacial bond strength. In a second approach, polymers such as vinyl, phenolic, and epoxy resins have been coated onto fibers to the extent of some 1–2% by weight of fibers. These coatings resulted in a varying

degree of improvement, but thickness control of the coating has been a problem.

Solutions of reducing agents, such as FeCl_3 , have also been used to improve the carbon-fiber/epoxy interfacial bond strength.^{3,4} A substantial improvement in composite interlaminar shear strength has been observed without an appreciable loss in fiber strength. However, the iron compound residues could possibly catalyze oxidation reactions during the intended service period, leading to high temperature instability.

Vapor phase deposition, in which the fiber surface is 'whiskerized' by deposited whiskers (e.g. silicon carbide) to provide mechanical bonding sites, led to a significant improvement in the interlaminar shear strength.⁵ Nevertheless, the grown silicon carbide whiskers added additional weight to the composite. Fiber surfaces can also be coated with a thin layer of polymer through electrodeposition or electropolymerization. Moderate improvements in the interlaminar shear strength and the impact strength of composites have been reported^{6,7} for such treatments.

Gas plasma activated by microwave or radio frequency (RF) radiations has been extensively applied for processing semiconductor and other materials. In the cold plasma state, ionization, excitation, dissociation, recombination, and other reactions can occur as a result of the collision of electrons and other species in the plasma medium. Consequently, when the plasma contacts a solid material, a highly efficient energy exchange can occur. Plasma chemical vapor deposition (CVD), plasma etching, and plasma polymerization are all plasma processing methods that make full use of this energy exchange mechanism. If properly controlled, plasma can be used to modify the physical and chemical state of the material surface without significantly altering the bulk properties. Because of these attractive attributes, plasma treatments of fiber surfaces have been considered to be a prime candidate technique for the control of interfacial adhesion in composites.

Plasma treatments are known to enhance significantly the adhesion of polymer fibers to epoxy resins.⁸⁻¹¹ Amine plasma was claimed to promote formation of covalent bonds with epoxy resins, leading to a considerable enhancement of the epoxy composite strength.¹⁰ Carbon fibers and pyrolytic graphite blocks were treated with plasma polymer coatings from acrylonitrile and

styrene monomers.¹²⁻¹⁴ Additional work^{15,16} involving the use of plasma polymerization for modifying fibers also showed encouraging results. Treated fibers in some cases even exhibited higher tensile strengths than the untreated counterparts, suggesting the plasma coatings possibly healed some of the surface flaws of the fiber.¹²⁻¹⁶ However, more efforts are needed to verify this speculation. The plasma-coated fibers also exhibited increased functionality and lower contact angles. Single fiber interface testing results indicated a 100% increase in the interfacial shear strength. The interlaminar shear strength of epoxy composites improved by approx. 30% with minimal degradation in the flexural properties.^{15,16}

When treated with oxygen plasma, the surfaces of the polyethylene (PE) fiber exhibited a high concentration of hydroxyl and carboxylic acid groups, which could permit chemical bonding between the fiber and the resin. An increase in interlaminar shear strength was obtained with epoxy resin matrices.¹⁷⁻¹⁹ Similar functional groups were observed on the carbon fiber surfaces treated in an oxygen plasma.^{20,21} The presence of significant concentration of acid functionality on these fibers was confirmed by electron spectroscopy chemical analyses (ESCA) and titration techniques. The physical and chemical characteristics of carbon fiber surfaces were altered by the plasmas.²¹⁻³² The level of surface roughness in the form of pits and crevices was increased.^{21,22,27,29-32} Surface wetting properties of fibers were also improved; this would permit a more intimate fiber/resin contact.²⁹⁻³² Different functional groups were observed on different types of carbon fibers; both carboxyl and hydroxyl groups were observed on polyacrylonitrile (PAN)-based fibers while very few carboxyl groups were seen on pitch-based fibers.³³ Changes in the composite failure mode were observed in carbon/bismaleimide composites when the fibers were modified with a plasma.³⁴

Continuous plasma treatments of fibers have been proven feasible.^{16,19,21,22,35} However, mechanisms of interfacial adhesion as promoted by plasma treatments are not yet well understood. Plasma reaction parameters that might possibly govern the mechanical properties of the resultant composites remain to be identified. Also to be explored are the advantages and limitations of plasma techniques when applied to interface

control in imide-based high-temperature resin and advanced thermoplastic composites. In the present investigation, non-polymerizing gas plasmas, such as oxygen, nitrogen, argon, and ammonia, were utilized to treat the carbon fiber surfaces. In one case, plasma polymerization was applied to promote the compatibility of fiber surface with a thermoplastic matrix. This was done in an attempt to develop a generic approach to improving interfacial adhesion in thermoplastic composites. Efforts were also made to: (1) demonstrate the effectiveness of plasma treatments in tailoring interfaces for improved composite properties; (2) determine the mechanisms of adhesion promotion through plasma treatments; and (3) identify the plasma parameters that would dictate the resultant composite properties.

2 EXPERIMENTAL

2.1. Materials

PAN-based untreated and unsized HT-type carbon fiber yarns (Hercules, AU4-12K) were used throughout this investigation. A two-component bismaleimide (BMI) resin (Ciba-Geigy, Matrimid 5292) was used as one of the matrix resins in the present study. These two components are 4,4'-bismaleimido-diphenylmethane (component *A*) and 0,0'-diallylbisphenol A (component *B*). The ratio of *A* to *B* is 113/85 parts by weight (pbw). It was suggested³⁶ that initially the allyl function and the maleimide undergo an 'ene'-type linear chain extension reaction and the resulting 'substituted styrene' undergoes a Diels-Alder reaction with another maleimide residue.

For epoxy-based composites, graphite and Kevlar fibers were used as the substrate for nonpolymerizing plasma modification. The fabrics, with the commercial name Cofab, were obtained from Composite Reinforcement Inc. The samples for the qualitative wettability test were cut from a graphite rod which was obtained from the Union Carbide Corporation. Nomex paper was obtained from Du Pont to simulate Aramid fibers for a wettability study. A Ciba Geigy Araldite GY-507 epoxy resin with an HY-956 hardener was used as the matrix material. However, in some cases a mixture of epoxy resin (Epon 1001-A-80) and 'Z' curing

agent from Shell Chemical Company was used instead. Polypropylene films obtained from Plasticorp were used as the matrix material in Kevlar composites.

2.2 Plasma treatments

2.2.1 For the BMI resin matrix

Carbon fiber yarns, with the individual fibers slightly spread out by a minor air-blowing action, were carefully wrapped around a stainless steel frame. The frame along with the yarns was then placed inside the chamber of a plasma reactor. Two types of plasma reactors (13.5 MHz, 100 W) were used: a model PEII-A plasma reactor from Technic West Inc. and a Plasmod from Tegal Corporation. The treatment conditions for both plasma reactors are shown in Table 1.

Oxygen gas was introduced and excited by RF to alter the physical state of the carbon fiber surface and possibly to deposit desirable oxygen-containing functional groups onto the fiber surface. These functional groups may also vary the surface energies, and hence the wettability, of the fiber. Argon gas, being more inert, is expected predominantly to affect the physical characteristics of fiber surface by, for instance, removing the physically adsorbed surface species and creating surface porosity. Argon gas plasma will therefore facilitate a better fiber/resin contact and possibly promote the mechanical keying mechanism. Surface chemical functionality should not be significantly influenced by argon gas plasma treatments. By comparing the results from these two treatments we can obtain significant insight into the nature of fiber/matrix interfacial adhesion.

Ammonia plasma was utilized in the hope that amine groups could be attached to the carbon fiber surface for possible chemical reaction with the matrix resin. Amine groups are known to be highly reactive with respect to both epoxy and

Table 1. Plasma reaction conditions

	First reactor	Second reactor
Gases used	Oxygen and argon	Ammonia and ammonia/argon
Chamber pressure	53.3 Pa (0.374 torr)	25.7 Pa (0.18 torr) and 285 Pa (2 torr)
Flow rate of gas	40 sccm ^a	10 sccm and 35 sccm
Plasma power	50 W	70 W
Treatment time	1, 3, 5, 10, 20 min	1, 3, 5, 10, 20, 35 min

^a sccm = standard cubic centimeters per minute.

BMI resins. Different ratios of NH_3/Ar were also used in order to study the effect of inert gas in the mixture of plasma gases. This task was motivated by the fact that an enhanced dissociation of oxygen by collision with excited helium species in a gas mixture environment was observed.^{37,38}

2.2.2 Propylene plasma treatment of fibers for the thermoplastic matrix

The plasma-polymerized propylene (PPP) coating should have a similar chemical composition, and therefore natural compatibility, to the polypropylene (PP) synthesized by conventional techniques. Further, since plasma coatings are known to adhere well to any solid substrate, PPP should form a good bond with the carbon fiber. Therefore, PPP should serve as a 'coupling agent' between the carbon fiber and the PP matrix. Tasks were designed to validate this concept. The operating conditions of PLASMOD for propylene gas plasma were 1.2–1.5 mm Hg chamber pressure and 90% maximum output. The time duration for plasma treatment ranged from 30 s to 7 min.

2.2.3 For the epoxy matrix

The primary operating parameters of the plasma-etching experiment included input power, pressure, gas flow rate, and treatment time. Since only nonpolymerizing gas was used in this phase of the study, plasma was produced by keeping the input power in the range 40–50 W. The mercury manometer range at which plasma could be produced was limited to between 0.8 and 1.2 mm Hg. The flow rate and the treatment time were the two process parameters varied in the attempt to find the optimum conditions for nonpolymerizing gas plasma.

2.3 Sample preparation

Upon completion of the plasma treating process, the fiber-wrapped frame was removed from the reaction chamber. The yarns were impregnated with a resin to produce a small prepreg layer. For BMI composites, four prepreg layers for each treatment time were stacked into a mold, and compression molded under a contact pressure with the temperature being ramped from room temperature to 177°C at a rate of 3°C/min. The mold was subsequently held at 177°C for 10–15 min first under a light contact pressure,

then a pressure of 0.69 MPa for 1 h. The mold was then cooled to room temperature under this pressure. The demolded laminate was post-cured in an air circulating oven at 200°C for 2 h, then at 250°C for 6 h. The fiber volume fraction of this composite is about 0.67. EPON 1001 and GY-507 epoxy resins were cured at 135°C and 45°C, respectively, and were under similar pressurization conditions as in BMI.

2.4 Mechanical testing

2.4.1 Single filament tensile tests

At least 10 filaments each (up to 28 filaments in some cases) were taken from both the treated and untreated carbon yarns. The two ends of each filament were carefully glued between two small pieces of plastic plates with a 'super' glue. The distance between these two plates was approx. 5.08 cm. An Instron Model 1122 universal testing machine with a 50-g load cell was used to conduct tensile tests at a cross-head speed of 0.127 cm/min.

2.4.2 Transverse tensile tests

The transverse tensile test was chosen as the primary method for evaluating the relative interfacial strength of composites in the present study. This test was found³⁹ to be one of the more sensitive techniques for assessing the relative interfacial adhesion strength in composites. Each laminate fabricated was machined into three transverse tensile specimens with dimensions 10 cm × 2 cm × 0.1 cm. The same Instron testing machine (Model 1125) but with a load cell of 454 kg (1000 lb) was run at a cross-head speed of 0.051 cm/min. Two end tabs made of aluminum alloy were glued on both ends of each specimen to facilitate gripping.

2.4.3 Short-beam, flexural and impact tests

A short-beam shear test (ASTM D2344-84) was also conducted to assess the interlaminar shear strength of composites. The short-beam shear test involved loading of unidirectional laminates in such a way that failure occurs in a shear mode parallel to the fibers. This was normally achieved by choosing a small specimen span-to-depth ratio. In a few cases, the short-beam shear test was modified in such a way that each specimen contained a strand of fibers on the neutral axis of the beam. A special mold was designed to ensure that the fiber bundles lay exactly on the neutral

axis. Charpy impact tests and slower speed three-point bending tests (ASTM D 790) were conducted to determine the failure energy and flexural strength of a composite. The area under the load/displacement curve obtained from the flexural test can also be used as a relative index for composite toughness. An effort was made to tailor the interface via plasma etching to improve composite toughness without significantly lowering other mechanical properties.

2.5 Fiber surface characterization

2.5.1 Wettability measurement

The surface energy of a carbon fiber was determined by measuring the contact angles of a variety of liquids according to the method proposed by Kaelble *et al.*⁴⁰ Using the Wilhelmy plate technique,⁴¹ the contact force, M (μgm), between a single fiber of circumference C and a liquid of surface tension r_{L_v} is described by the following equation:

$$M = \frac{Cr_{L_v} \cos \bar{\theta}}{g} \quad (1)$$

where $\bar{\theta}$ is the advancing liquid/solid contact angle and $g = 980.6$ dyne/cm. Since M , r_{L_v} and C can be evaluated independently, $\cos \bar{\theta}$ can be calculated from eqn (1). In this study, M is measured by using a microbalance, and C is obtained from micrographs. In a typical Wilhelmy set-up, a carbon filament was attached to a small plastic plate with adhesive tape and then suspended from the loop of a Cahn model 2000 microbalance. A beaker containing a test fluid was raised by an elevator at a constant speed of 0.005 mm/s; this was sufficiently slow so that the dynamic contact angle was independent of velocity and identical to the static angle.⁴²

The surface energies of solids and liquids are considered to be the sum of separate dispersive (London— d) and polar (Keesom— p) contributions. From such a two-component model the following relationships can be derived for the polar and dispersive interaction between liquids and solids.

$$r_{L_v} = r_{L_v}^d + r_{L_v}^p = a_L^2 + b_L^2 \quad (2)$$

$$r_{sv} = r_{sv}^d + r_{sv}^p = a_s^2 + b_s^2 \quad (3)$$

where r_{L_v} = liquid/vapor surface tension, r_{sv} = solid/vapor surface tension, a_L , b_L = square roots of the respective dispersive $r_{L_v}^d$ and polar $r_{L_v}^p$ parts of r_{L_v} , respectively, and a_s , b_s = square roots of

respective dispersive r_{sv}^d and polar r_{sv}^p parts of r_{sv} , respectively.

The work of adhesion, W_a , is the decrease of Gibbs free energy per unit area when an interface is formed from two individual surfaces.⁴² The greater the work of adhesion, the greater the interfacial attraction. The work of adhesion W_a is defined by eqn (4):

$$W_a = r_{L_v}(1 + \cos \bar{\theta}) \quad (4)$$

From the relationship between W_a and the polar and dispersive components of the solid of interest, the work of adhesion can be expressed as

$$W_a = 2[a_L a_s + b_L b_s], \quad (5)$$

which can be rearranged to give the following expression:

$$W_a/2a_L = a_s + b_s(b_L/a_L), \quad (6)$$

The values of r_{L_v} , $r_{L_v}^d$, $r_{L_v}^p$ are known for the liquids used and the contact angle $\bar{\theta}$ can be measured. A plot of $(W_a/2a_L)$ versus (b_L/a_L) will yield a straight line; its slope and intercept will give the values of r_{sv}^d and r_{sv}^p , respectively, for the solid surface of interest.

2.5.2 Qualitative wettability test

Samples of 1.27 cm (0.5 in.) diameter were cut from a graphite rod. The two surfaces of each sample were polished to make them smooth and parallel to each other. In one sample, each specimen was plasma treated for 3 min with a fixed flow rate. Several specimens subjected to different flow rates were prepared. In the second sample, time was a variable with the flow rate being kept constant. A droplet of epoxy resin was then allowed to sit on each treated surface for a selected period of time (3 sec) and then the bubble diameter was read by a telescope-type Bausch & Lomb optical microscope. Each sample was subjected to an identical amount of epoxy resin in order to ensure the uniformity of the experimental conditions. This test was conducted before the Wilhelmy apparatus was installed.

2.5.3 Transmission IR absorption spectrum

The effect of propylene gas plasma on the fiber surface was examined by IR spectroscopy. Graphite fibers, both before and after plasma treatments, were ground into powders. The powders were mixed with KBr powder and

mounted in a mold at a pressure of 172.4 MPa and temperature of 120°C to form a disc-shaped specimen. Instead of being ground into powder, Kevlar-49 fibers were chopped into short segments before mixing with KBr powder. The mounting conditions were identical to those of graphite specimens. Transmission IR absorption spectrum analysis was conducted by using a Perkin Elmer 938 IR Spectrometer.

2.5.4 Dynamic mechanical analysis

Energy is expected to be dissipated at the fiber/matrix interface when the composite is subjected to continuous cyclic loading. The amount of internal energy dissipated at the interface depends upon the degree of adhesion. A weaker bond is expected to result in more energy loss which should be reflected by a higher damping coefficient. Thus it is possible to determine the amount of energy dissipation due to poor interfacial adhesion by any vibration-based technique. A dynamic mechanical thermal analyzer (DMTA) manufactured by Polymer Laboratories Inc. was used to obtain loss tangent values. The test involves forced vibration of composite bars over a range of temperatures at a selected frequency. A temperature range of 35–200°C at an increment rate of 3°C/min, with a single cantilever support and a vibration frequency of 1 Hz were used throughout this investigation.

2.5.5 Scanning electron microscopy

The surface texture of each filament before and after plasma treatment was examined with a JEOL JSM-840 scanning electron microscope (SEM). The diameter of each filament was measured from the SEM micrographs. SEM examination of composite fracture surfaces was conducted to help identify the failure modes and to provide a qualitative assessment of the interfacial adhesion strength.

2.5.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) can be used for qualitative and quantitative elemental analyses of the surface region and for characterization of the bonding state. The spectra were obtained from two XPS systems. A model XSAM 800 (Kratos) X-ray photoelectron spectrometer was operated in the fixed retarding ratio (FRR) scan mode with Mg K_{α} X-radiation (300 W) for the untreated carbon fibers and the

oxygen plasma-treated ones, and a Leybold-Heraeus PAH 10/11 XPS spectrometer with Al K_{α} X-ray (310 W) was used for the untreated, the argon plasma treated and ammonia plasma treated carbon fibers when the XSAM 800 was out of service. The base pressure of these two systems was typically 10^{-8} torr. In all cases fibers were glued at one end in a bundle arrangement with silver adhesive. A small piece of gold-coated copper foil was used to cover the silver glue so that no part of the silver glue and the sample probe could be detected during data scanning. The $4f_{7/2}$ peak (binding energy = 83.8 eV) of gold served as a reference for calibration. The surface compositions of various treated carbon fibers were identified and the elemental surface concentrations were calculated from the corrected XPS peak area. Curve fitting was carried out by means of an in-house software program based on nonlinear least-squares curve fitting with a Gaussian/Lorentzian production function.

3 RESULTS AND DISCUSSION

3.1 Carbon/BMI composites

3.1.1 Oxygen plasma treatments

Curve A of Fig. 1 indicates that, in response to oxygen plasma treatments, the transverse tensile strength of the composite increases gradually from 2.20 MPa (untreated) to 4.71 MPa (20-min

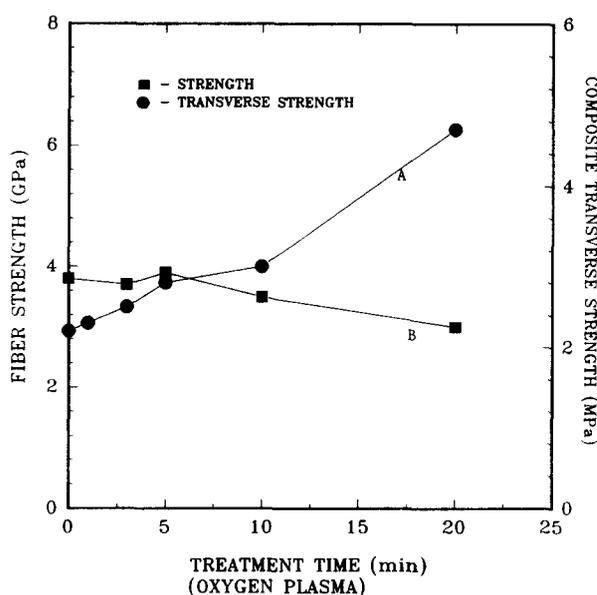


Fig. 1. The effect of oxygen plasma treatment of carbon fiber surface on the transverse strength of composites (curve A), and the tensile strength of fibers (curve B).

treated). The transverse tensile strength of a composite is a resin- and fiber-dominated property. This implies that, given the same matrix resin, the observed increasing trend in composite strength is induced by the improvement in interfacial adhesion. SEM fracture micrographs of the corresponding composites subjected to flexural testing (Fig. 2) clearly demonstrate the effect of these treatments in raising the interfacial adhesion in composites. For the composites containing untreated fibers, a pronounced fiber pull-out phenomenon is evident—Fig. 2(a). After the plasma treatment, fiber pull-out became less extensive—Fig. 2(b) and 2(c). After an oxygen plasma treatment for 20 min, the composite exhibited a brittle fracture mode with clean-cut fibers and very little fiber pull-out. The change in failure mode from interfacial failure to fiber breakage and matrix fracture in the treated fiber composites is ascribed to the improvement of interfacial adhesion.

Since a plasma consists of various highly energetic species, exposure of fibers to the plasmas for an extended period of time could produce a negative effect. As shown in Curve B of Fig. 1, the average tensile strength of fibers was slightly degraded from 3.80 GPa (untreated) to 3.01 GPa (20 min treated). At given plasma reaction conditions, however, there appears to exist an optimal treatment time where the interfacial adhesion can be significantly improved without reduction in filament strength.

Representative surface topographic features of carbon fibers, with or without oxygen plasma treatments, are shown in Fig. 3. When the treatment time was short (e.g. less than 1 min), the fiber surface seemed to become slightly smoother, possibly exhibiting the cleaning effect of a plasma. Contaminants such as CO, H₂O, CO₂ and other organic species are known to adsorb readily on the fiber surface.⁴⁰ Removal of such species may facilitate a better resin/fiber contact (improved wettability) and promote stronger van der Waals forces. The fiber surface became increasingly rough when the treatment time increased. This powerful solid surface etching capability is certainly more than adequate to remove those physically adsorbed contaminant species. Further, the increased fiber roughness, in the form of surface porosity, should promote the mechanical keying or interlocking mechanism between the fiber and the matrix.

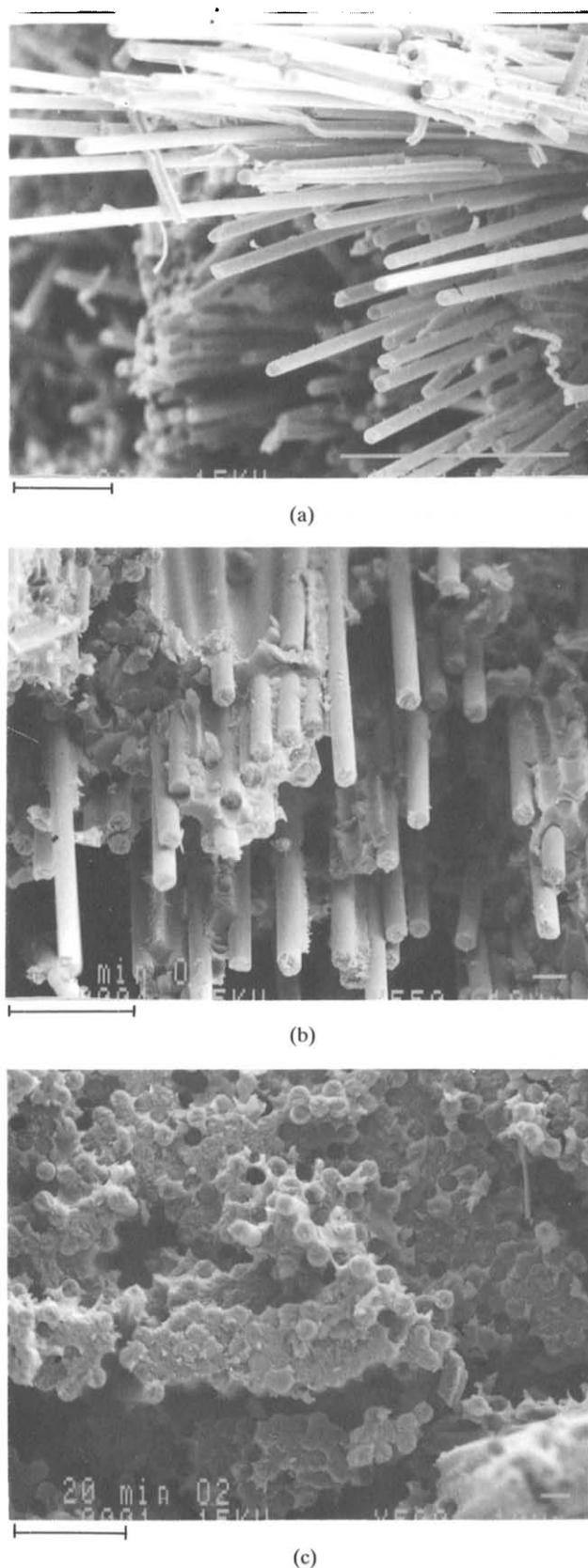


Fig. 2. The effect of oxygen plasmas on the transverse fracture surface of composites (after flexural testing) containing carbon fibers subjected to: (a) no treatment; (b) a 5-min treatment; (c) a 20-min treatment. (Scale bar = 40 μm .)

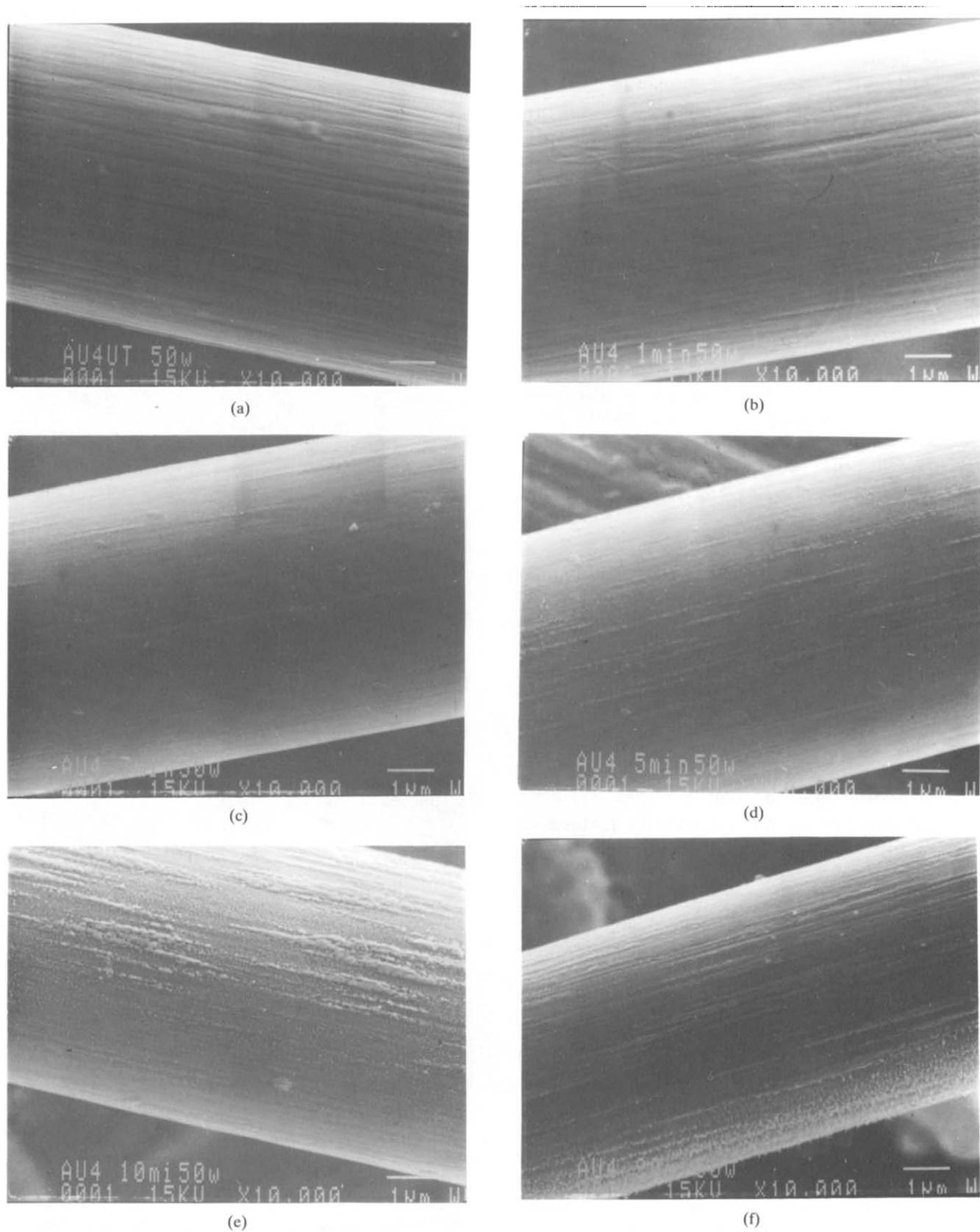


Fig. 3. SEM micrographs of carbon fiber surfaces after oxygen plasma treatment. (a) Control (no treatment), (b) 1 min, (c) 3 min, (d) 5 min, (e) 10 min, and (f) 20 min.

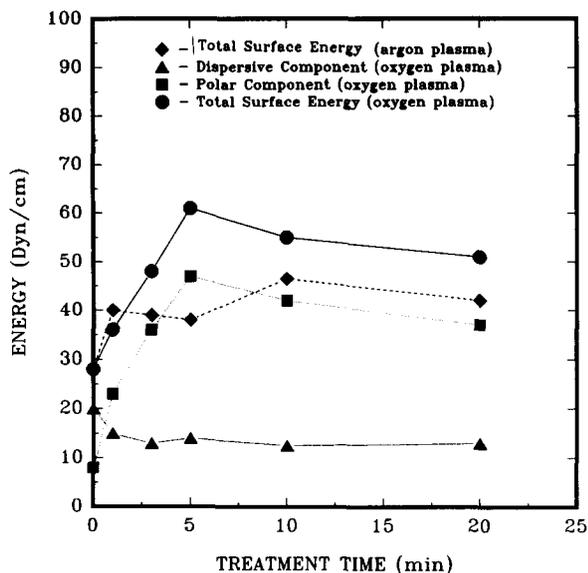


Fig. 4. Surface energy values of carbon fibers treated with oxygen and argon plasmas.

From eqn (6), a best-fit straight line can be obtained for each Wilhelmy data set by using a linear regression analysis. The slope and intercept of the straight line can be used to determine r_{sv}^p , r_{sv}^d , and r_{sv} for each treatment case. The surface energies of carbon fibers treated by oxygen plasma are summarized in Fig. 4. Scrutiny of the polar and dispersive components of the surface free energy indicates that the dispersive portion decreases to a small extent and then levels off, but the polar component increases with treatment time up to 5 min and then slowly decreases again. The total surface energy follows the same trend as does the polar component. The reason for the decreasing polar component of surface energy after 10 min treatment is unclear. A smooth substrate surface was usually assumed in the contact angle measurements.⁴⁰ This assumption may become unjustifiable for the samples treated for more than 5 min that contain a high level of surface porosity. As a consequence, the total surface energy is found to decrease, although the total surface energy is expected to reach a plateau value.

Relative atomic concentrations of oxygen and carbon on the fiber surface obtained by ESCA are shown in Fig. 5. Apparently, the oxygen concentration on the surface of fibers has been increased by oxygen plasma treatment from 10.47% of the untreated to 27.53% of the 20-min treated case. The results of curve fitting of possible peaks (peak synthesis) are listed in Tables 2 and 3, which indicate a significant

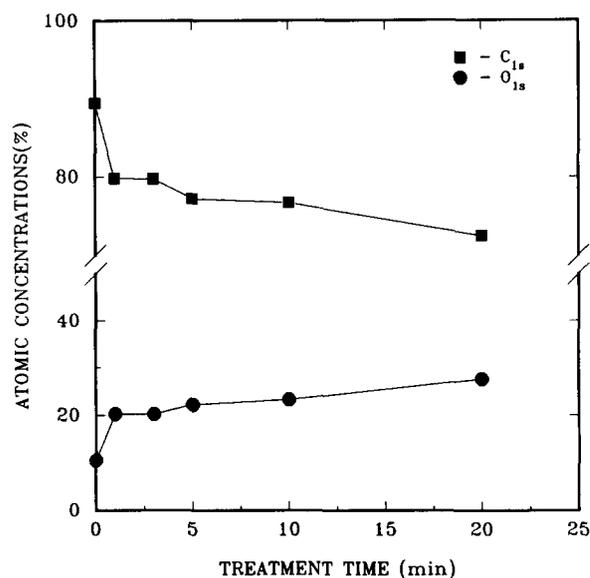


Fig. 5. Concentrations of oxygen and carbon atoms on the carbon fiber surface plotted versus oxygen gas plasma treatment time.

Table 2. Curve fitting results and relative areas for Cls spectrum of untreated carbon fibers

Peak position (eV)	Relative area ratio ^a	Chemical shift (eV)	Possible functional groups
284.53	1.00	0.00	Graphite
286.40	0.29	1.87	—C—OH and/or C=O and/or quinone
288.60	0.07	4.07	Carboxylic acid and/or ester
290.60	0.01	6.07	—CO ₃ type or plasmon

^a Relative area ratio = (area of peak_i)/(area of peak_{284.53}).

Table 3. Curve fitting results and relative areas for Cls spectrum of carbon fibers treated by oxygen plasma for 20 min

Peak position (eV)	Relative area ratio ^a	Chemical shift (eV)	Possible functional groups
284.50	1.00	0.00	Graphite
286.60	0.26	2.10	—C—OH and/or C=O and/or quinone
288.60	0.16	4.10	Carboxylic acid and/or ester
290.60	0.04	6.10	—CO ₃ type or plasmon

^a Relative area ratio = (area of peak_i)/(area of peak_{284.50}).

increase in carboxylic acid and/or ester groups by oxygen plasma treatment. Similar observations were made by several workers.^{13,19–21,27–29,43} In general, oxygen plasma treatment increases the oxygen content and the polarity of the fiber surface.

3.1.2 Argon plasma treatments

The results of composite transverse tensile tests again show an improvement in interfacial bonding as a result of argon plasma treatments.^{30,31} This strength is increased from 2.20 MPa (untreated) to 4.28 MPa (treated for 20 min), which is smaller than the value of 4.72 MPa for those treated for 20 min by oxygen plasma. Improved bonding could also be accompanied by a loss in tensile strength of the bulk fibers if subjected to a prolonged treatment; e.g. from 3.80 GPa for the untreated state to 3.22 GPa for the 20-min treated fibers.³¹ This degradation in fiber strength is probably due to the increased surface roughness, in the form of pits and crevices, which serve as stress concentration sites.

The surface morphology of argon treated fibers is similar to that of oxygen plasma treated ones (Fig. 6). The degree of surface roughness increases as the duration of argon plasma treatment increases. Argon plasma appears to have a similar level of etching power on the carbon fiber surface as oxygen plasma. It is of interest to note that this same degree of etching effect did not lead to the same extent of interfacial adhesion improvement. Obviously, the increased level of surface porosity, playing the role of promoting the key and lock mechanism, is not the only important reason for the observed interfacial adhesion improvement.

Figure 4 also shows the variations of fiber total surface energy by argon plasma treatments. The dispersive component does not change much, yet both the polar component (not shown) and the total surface energy exhibit an appreciable increase with increasing treatment time. However, the extent of enhancement in the polar and total surface energies is less than that caused by the oxygen plasma. Wettability of oxygen-treated fibers is superior to that of argon-treated ones. This is the second reason why the former is more effective in adhesion promotion.

XPS results show that the atomic concentration of surface oxygen increases to 17.90% for the 20-min treated fibers. This percent increase is much less than the value of 27.53% for the fibers treated for 20 min by oxygen plasma, and even less than that for fibers treated for 1 min by oxygen plasma which has a value of 20.22%. Oxygen was not deliberately charged into the plasma system with argon gas. The oxygen species which caused the increased oxygen

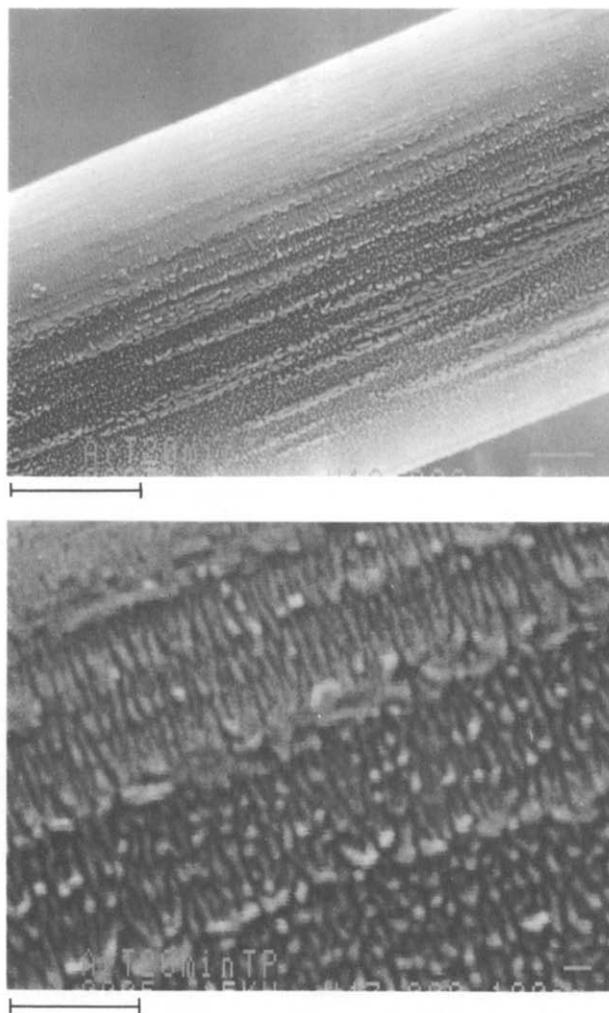


Fig. 6. SEM micrographs showing surface topographic features of carbon fibers after argon plasma treatment for 20 min.

content on the fiber surface possibly came from the residual impurities in the argon gas, vacuum leakage, and/or desorption from the reactor walls. Another possibility is the post-treatment oxidation which occurred when the treated samples were exposed to the open air. It is known that plasma-treated surfaces may contain a substantial amount of free radicals.⁴⁴ These highly reactive free radicals could conceivably react readily with the oxygen molecules present in the air. The curve-fitting results of Cls peak for the carbon fibers treated by argon plasma for 20 min are given in Table 4.

Fitzer & Weiss³⁹ proposed that reactions may occur between functional groups (e.g. carboxylic acid and hydroxyl groups) present on the fiber surface and the amine groups present in the hardener which then form a network with epoxy resins. However, chemical bonding may be

Table 4. Curve fitting results and relative areas for C1s spectrum of carbon fibers treated by argon plasma for 20 min

Peak position (eV)	Relative area ratio ^a	Chemical shift (eV)	Possible functional groups
284.50	1.00	0.00	Graphite
286.45	0.34	1.95	—C—OH and/or C=O and/or quinone
288.60	0.17	4.10	Carboxylic acid and/or ester
290.60	0.03	6.10	—CO ₃ type or plasmon

^a Relative area ratio = (area of peak_i)/(area of peak_{284.50}).

difficult to achieve in the BMI matrix composites because the fiber surface functionality may not readily react with the functional groups in either component of the BMI resin. The interlocking mechanism, as promoted by surface roughness, was found to play a major role in the carbon-fiber/epoxy adhesion.^{34,35} The drawback of improving carbon-fiber/BMI adhesion by oxygen and argon plasmas is a possible moderate loss in tensile properties of the carbon fibers, if the treatment time is too long.

3.1.3 Ammonia plasma treatments

The results of transverse tensile tests are summarized in Fig. 7 (Curve A), which again clearly demonstrates the effectiveness of plasma

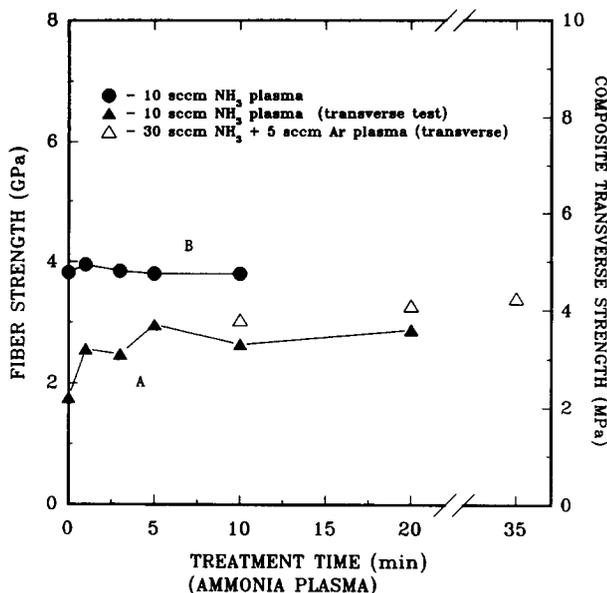


Fig. 7. The effect of ammonia plasma treatment on the transverse tensile strength (standard deviation $\leq 5\%$) of composites and the tensile strength (standard deviation is $\approx 15\%$) of carbon fibers.

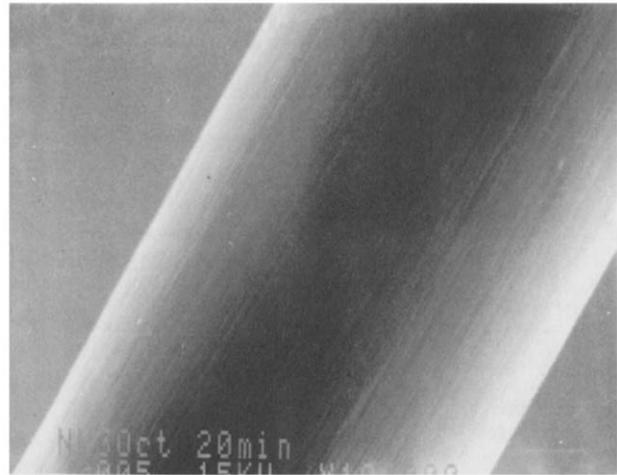


Fig. 8. SEM micrograph showing the surface of a carbon fiber after 20 min of ammonia plasma treatment.

techniques in enhancing adhesion. A 100% increase in the composite transverse tensile strength is observed for the samples containing fibers treated for 35 min. This improvement was achieved with a minimal penalty in filament strength reduction (Fig. 7, Curve B). The filament tensile strength is reduced from 3.80 GPa for the untreated to 3.65 GPa for the 35-min treated fibers by ammonia/argon plasma ($\text{NH}_3 = 30$ sccm and $\text{Ar} = 5$ sccm).

Unlike oxygen plasma and argon plasma, ammonia plasma has shown no obvious etching effect on the carbon fibers (Fig. 8). SEM micrographs show no appreciable sign of surface roughness change even up to 35 min of treatment. Ammonia plasma may have a less effective etching power. Ammonia plasma treatment of poly(ethylene terephthalate) filaments to improve adhesion to rubber⁴⁵ and ammonia plasma treatment of polyaramid filaments to enhance adhesion to epoxy resin¹³ also showed no noticeable effect on the bulk fiber properties.

The data on the variations in fiber surface energy as a result of ammonia and combined ammonia/argon treatments were reported earlier.³¹ The changes in the dispersive component are negligible while the increases in the polar component of surface energy are remarkable. As a consequence, the total surface energy is increased considerably, leading to an improved surface wettability of carbon fibers. This can partially explain the observed interface adhesion improvement.

As indicated in Table 5, the nitrogen content

Table 5. XPS atomic ratios of carbon fibers treated by ammonia and ammonia/argon plasmas

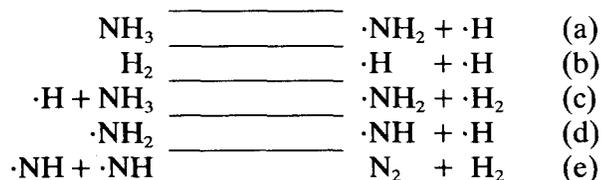
Plasma condition	Untreated	20 min 10 sccm NH ₃	20 min 35 sccm NH ₃	20 min 30 sccm NH ₃ + 5 sccm Ar	20 min 25 sccm NH ₃ + 10 sccm Ar
O/C	0.12	0.31	0.14	0.18	0.30
N/C	0.00	0.09	0.13	0.14	0.13
O/N	—	3.57	1.11	1.305	2.40

Table 6. XPS atomic ratios of carbon fibers treated by ammonia (30 sccm) and argon (5 sccm) plasma

Reaction times (min)	10	20	35
O/C	0.15	0.18	0.23
N/C	0.09	0.14	0.24
O/N	1.74	1.330	0.99

was increased when more ammonia was introduced into the reaction chamber; from an N/C ratio of 0.09 for 10 sccm ammonia to 0.13 for 35 sccm ammonia. An enhanced dissociation of oxygen by collision with excited helium species was observed in a similar plasma work involving the utilization of gas mixtures.⁴⁶ However, Table 5 indicates a minimal enhancement of nitrogen content by the introduction of argon gas. When the argon content is raised in the gas mixture the atomic ratio of oxygen also increases. A longer treatment time generally results in an increase in the relative nitrogen content with respect to either carbon or oxygen (Table 6).

A recent study of the plasma decomposition of ammonia has been reported by d'Agostino, *et al.*⁴⁷ The decomposition process was suggested to follow apparent zero-order kinetics through the following reaction sequence:



Reactions (a), (b) and (d) are nonequilibrium processes which occur through electron impact with ground state molecules, bimolecular dissociation of vibrationally excited molecules, or through a joint vibrational-impact mechanism as discussed by Capitelli & Molinari.⁴⁸ Reaction

(e) occurs at a very high rate and is the main channel for NH₂ disappearance.⁴⁷ These observations suggest that NH₂ is the most likely species available for recombination with surface radicals.⁴²

Since the aromatic diamine can convert bismaleimide building blocks into resins via a Michael Addition reaction,⁴⁹ incorporation of amine groups on the surface of carbon fibers is expected to improve the interfacial bonding between carbon fibers and bismaleimide resin possibly through chemical bonding. It is speculated that useful functional groups such as -NH₂ might have been deposited onto the carbon fiber surface to promote chemical bonding (primary or hydrogen) between fiber and matrix resin. The role of mechanical interlocking would be the less important mechanism to promote interfacial adhesion by ammonia plasma treatment.

3.2 Fiber treatments for improved thermoplastic composite properties

After propylene gas plasma treatment, the fiber surface tension values were measured by means of the Wilhelmy technique. The contact angles of fiber surface with distilled water are shown in Fig. 9. These data indicate that propylene gas plasma treatments tend to decrease the surface tension of the fiber, in direct contrast to the treatment results using other gas plasmas. A

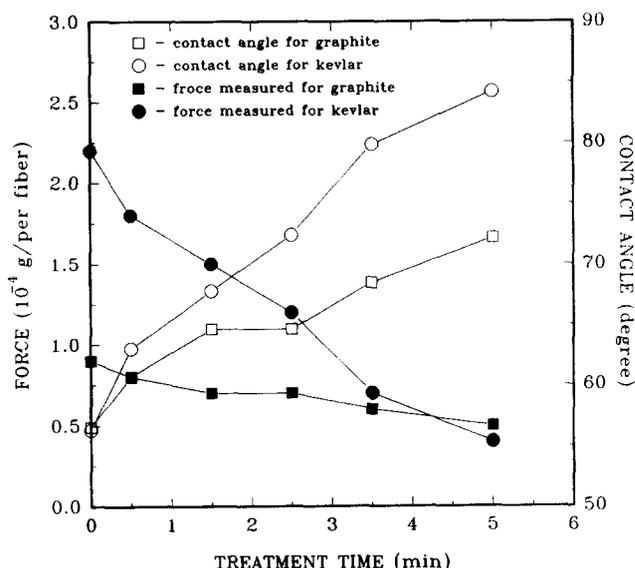


Fig. 9. The surface contact force and contact angle of carbon fiber by water (as measured by the Wilhelmy technique), plotted as a function of propylene gas treatment time.

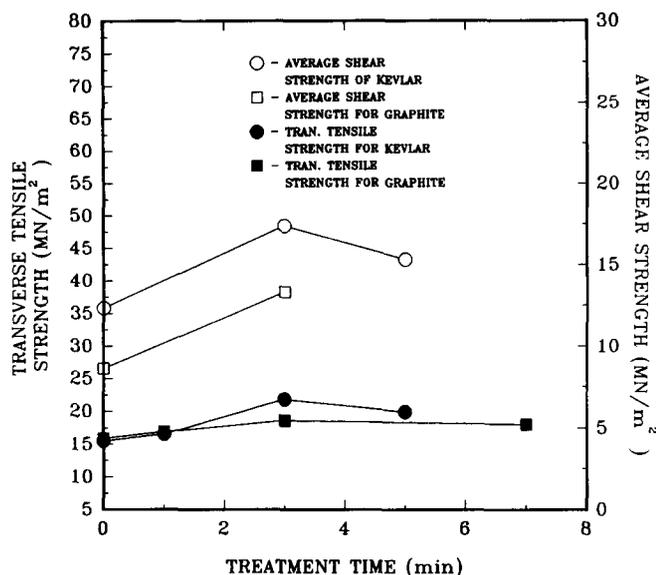


Fig. 10. Flexural shear strength and transverse tensile strength of polypropylene-based composites containing fibers treated with PP gas plasma.

possible reason for this decrease is that a layer of PPP has been deposited on the fiber surface. These molecules are relatively nonpolar, thereby reducing the wettability of fibers by highly polar water molecules. However, this PPP layer should have natural compatibility with the polypropylene matrix and therefore provide an intimate contact between carbon fibers and the matrix. The interfacial adhesion is therefore expected to be improved.

The change in interfacial adhesion was evaluated by transverse tensile tests and fiber bundle pull-out tests. The data, summarized in Fig. 10, show that the propylene-gas plasma treatments have improved the interfacial adhesion by up to 40% for PP/Kevlar composites and 20% for PP/graphite composites. An effort was made to detect the change of surface structure by means of transmission IR absorption spectroscopy. Unfortunately, no significant difference between plasma-treated fiber and as-received fiber was found. This observation may simply imply that the conventional transmission IR absorption technique is not adequate to detect the surface functionality of fiber. The penetrating depth of IR may have been too deep to resolve the signals from an ultra-thin PPP layer on the fiber surface. SEM examination shows that the surface profile of a Kevlar fiber has been slightly altered by plasma treatment. Several 'debris' particles were found on the plasma-treated Kevlar fiber surface. But the physical structure of

graphite fiber surface did not seem to exhibit any appreciable change at a magnification of $\times 5000$.³²

3.3 Fiber surface treatments for epoxy composites

Tensile strength and percent elongation values of plasma-treated fibers are summarized in Fig. 11. The tensile strength reaches a minimum at an intermediate flow rate range of 30–50 cc/min. Figure 12 shows the bubble diameter in a surface wettability test as a function of the gas flow rates. The diameter of each bubble was measured after 30 s from the moment the bubble was placed on the sample. Maximum diameter bubbles were observed for the flow rates of 30–50 cc/min. Since a larger bubble diameter means a better wettability, this simple qualitative experiment indicated that wetting was a maximum in the flow rate range of 35–50 cc/min. Thus the number of parameters required to define an optimum condition for plasma treatment with non-polymerizing gas can be reduced to only one, i.e. time. Therefore, throughout the remainder of this research program, plasma treatment time was taken as the working parameter in order to optimize the mechanical properties of composites.

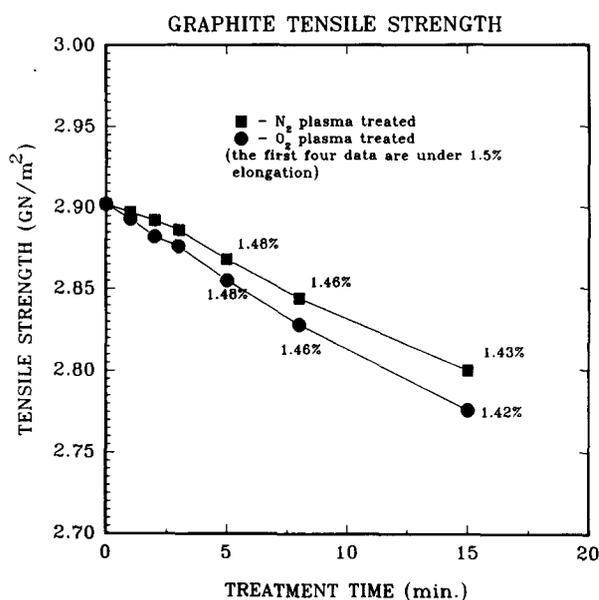


Fig. 11. Tensile properties of carbon fibers after various plasma treatments (flow rate = 30 cc/min). The percent value associated with each data point indicates the corresponding average failure strain. The standard deviation of the strength values varies between 15% and 20%.

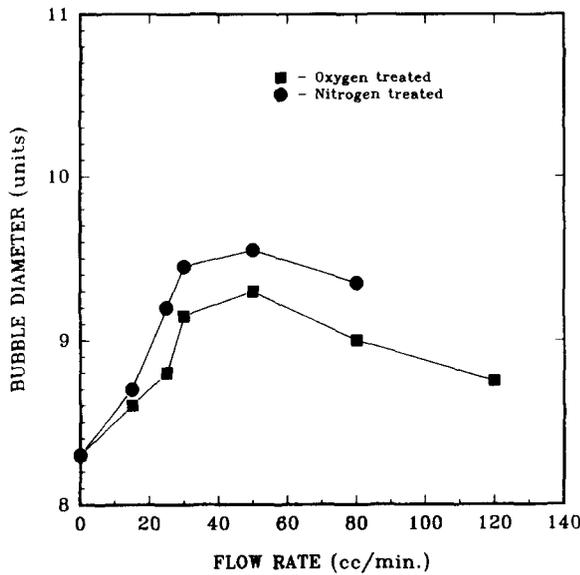


Fig. 12. The results of a qualitative wettability test. A higher bubble diameter implies a better prepared surface for wetting.

The data obtained from the fibers treated for use in epoxy composites³² also revealed that the tensile strength decreased with an increase in the plasma treatment time at a constant flow rate. Fiber strength degradation only occurred to a negligible extent for the first 2 min of nitrogen and first 3 min of oxygen treatments. Optimization of the treatment time is essentially to the achievement of balanced adhesion and other mechanical properties. Again, surface porosity was observed when the fibers were treated for an excessively long time. An upper limit of 5–10 min was chosen to be the proper length of time for these plasma treatments.

The values of loss tangent in composites, as measured by the DMTA method, as a function of fiber treatment times are summarized in Fig. 13. Since a poor fiber/matrix bond will promote interface friction, this will be reflected by a higher value of the loss tangent.⁵⁰ For nitrogen-treated fiber samples, the minimum loss tangent value (or a maximum bonding strength) occurs at a fiber treatment time of 1 min. For oxygen-treated samples, minimum loss tangent occurs at a treatment time of 8 min. The short-beam shear test results of epoxy composites containing the oxygen and nitrogen plasma-treated graphite fibers are shown in Fig. 14. Again, SEM micrographs revealed extensive fiber pull-out in the sample containing untreated fibers.³² These composite specimens containing untreated fibers exhibited rougher fracture surfaces than the treated specimens.

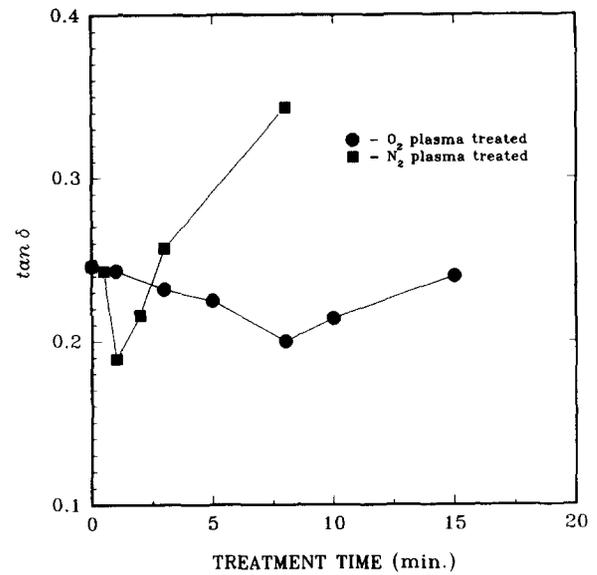


Fig. 13. The loss tangent values of composites as a function of fiber treatment time.

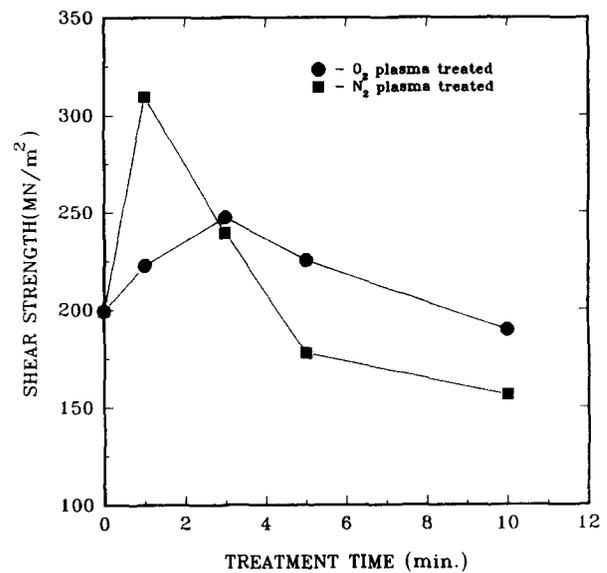


Fig. 14. Composite shear strength plotted as a function of fiber treatment time.

3.3.1 Adhesion mechanisms

The fiber/matrix interfacial adhesion in a polymer composite can be improved by the following means:

- (1) by increasing the wettability of fiber surface by the matrix resin;
- (2) by removing the weak boundary layer, e.g., contaminant species or gas molecules physically adsorbed on the fiber surface. This would provide a more intimate contact between the fiber and the matrix polymer to ensure a significant level of van der Waals force which,

being a short-range force, would otherwise be relatively weak;

(3) by allowing the matrix molecules physically to entangle with, or diffuse into, the molecular network of polymer coating applied on fibers;

(4) by promoting mechanical interlocking between the fiber and the matrix. This can be achieved by creating surface porosity, into which resin molecules can penetrate;

(5) by increasing the number of active sites on the fiber surface for subsequent chemical bonding with the unreacted species in the matrix resin;

(6) by applying a thin layer of 'coupling agent' that will chemically bond to both fiber and matrix.

In the present study, plasma etching and polymerization techniques were used to improve the interfacial adhesion of Kevlar and graphite fiber composites. The plasma techniques involve the use of a low-pressure gas activated by an RF excitation to produce metastable excited species which are allowed to impinge upon the substrate to be treated. The gas plasma consists of ionized species, free electrons, free radicals, and excited molecules or atoms. The activated gases may be controlled to operate one or more of the above functions. By varying the plasma reaction conditions one can conveniently tailor the surface structure and properties of fibers.

A fully polymerized polypropylene will not have any unsaturation in the backbone chain and, therefore, will not form a covalent bond with Kevlar and graphite fibers. Propylene plasma, however, is expected to remove a weak boundary layer so that a layer of PPP could adhere well to the substrate fiber. This PPP, with a similar chemical structure to the conventional PP, is likely to be compatible with the PP matrix. This would contribute to the improvement in fiber/matrix adhesion. A plasma cleaned fiber surface, even when not covered by PPP, would permit more intimate contact with polymer to ensure a significant level of van der Waals force.

For treatments with an inert gas such as argon, surface contaminants can be removed and the level of porosity can be increased. The latter will promote mechanical keying while the former will improve the fiber wet-out and raise the van der Waals force. A more active gas like oxygen can, in addition to the above two mechanisms, create active surface sites or functional groups, e.g. carbonyl and hydroxyl groups, that will react with the matrix resins. These polar functional groups

further increase the fiber surface energy, on top of the improvement obtained by the removal of surface contaminants. Evidence of this is provided by the greater surface energy observed on the oxygen-treated surface than on the argon-treated one. Compared to an inert gas, oxygen plasma is more effective in promoting fiber/resin adhesion. These plasmas, however, can produce some adverse effects on the fiber integrity.

Organic vapor such as ammonia or hydrocarbon molecules can be activated and deposited on the carbon fiber surface. This deposition process appears to compete with the 'etching' effect of the plasma. The latter serves to clean the surface and then possibly to destroy and remove some of the surface structure.²¹ In contrast, the former process can coat the surface and possibly heal the flaws. Organic species can be selected to create desirable functionality in accordance with the chemical compatibility with the intended matrix resin. Deposition in this case is very thin, in contrast to the generally thicker plasma polymer discussed earlier.

The methodology used in the present study could be applied for the optimization of plasma treatments of other fiber/resin systems. Essentially an unlimited number of gases could be used as a precursor to the plasma state.

4 CONCLUSIONS

The following concluding remarks can be drawn from the present investigation:

1. The effectiveness of plasma treatments in improving the interfacial adhesion in polymer composites has been demonstrated. For BMI composites, ammonia/argon plasma appears to be the best plasma system in enhancing the interfacial adhesion without producing undesirable reduction in the fiber strength. In contrast, oxygen and argon plasmas show a greater etching effect on the carbon fiber surface and could degrade fiber integrity.

2. Various adhesion mechanisms can be promoted by plasma treatments. These include: (a) possible removal of surface contaminants to provide better fiber/resin contact; (b) an enhanced degree of mechanical keying between the fiber and the matrix because of the increased fiber surface roughness; (c) an increased surface energy which would promote wetting of the fiber

by the matrix; and (d) deposited functional groups for possible chemical interactions between the fiber and the matrix resin. Mechanisms (a) and (d) could affect (c).

3. Each mechanism works to a different extent in a different plasma. For oxygen, nitrogen and argon plasmas, mechanisms (a), (b) and (c) all work to some extent; however, oxygen plasma is the most effective in improving the wettability. This vastly improved wettability could be a result of the plasma-deposited oxygen-containing groups on the carbon fiber surface—mechanism (d). For ammonia and ammonia/argon plasmas, the chemical bonding between amine groups and bismaleimide (Mechanism d) and the enhanced surface wettability—mechanism (c)—are the two important factors in increasing the interfacial adhesion in carbon fiber/BMI composites.

4. Plasma polymerization can be used to promote interfacial adhesion between carbon fibers and thermoplastic resins. Plasma polymer is capable of adhering well to any substrate. The plasma polymer coating on the fiber surface can be designed to provide necessary chemical characteristics (functional groups, compatibility, etc.) to facilitate fiber-matrix adhesion.

5. The operating parameters for oxygen and nitrogen plasma treatments of carbon fibers can be optimized for composite performance. Gas flow rate and treatment duration are two of the more important parameters to manipulate.

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