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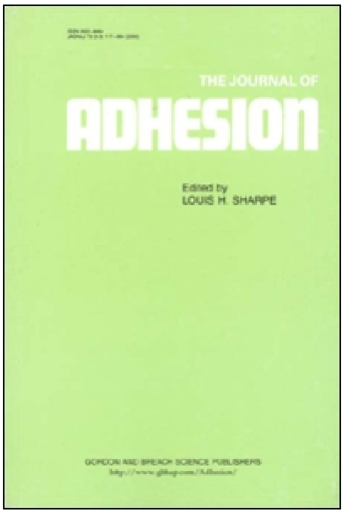

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Plasma Modifications to the Interface in Carbon Fiber Reinforced Thermoplastic Matrices*

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Radio frequency glow discharge oxygen plasma was used to modify the surfaces of PAN-based and mesophase pitch-based carbon fibers. Surface chemical changes to the fibers were monitored by X-ray photoelectron spectroscopy and by fiber wetting studies evaluated in terms of dispersive-polar components of surface energy and acid-base contribution to the work of adhesion. Physical changes to these fibers were monitored by scanning electron microscopy. Stress transferability of these fibers was evaluated by the embedded single fiber test in poly(methyl methacrylate), poly(ethyl methacrylate), poly(methacrylonitrile) and poly(vinyl chloride) as these matrices offered varying degrees of dispersive-polar and acid-base character. Experimentally determined critical aspect ratios were compared to the theoretical work of adhesion determined by dispersive-polar interactions and with the Lewis acid-base nature of the matrices.

KEY WORDS oxygen plasma treatment; surface free energy; acid-base interactions; single fiber test; polymers; composites; XPS; fiber wetting studies; interfacial interactions; fiber/matrix adhesion; fiber surface morphology.

INTRODUCTION

The interface between reinforcing fibers and polymeric matrices in composite materials is an important factor which influences stiffness, strength, and durability. It has been recognized that the function of the interface is to transmit stress from the matrix to the reinforcing fiber. In the case of carbon fibers, attention has been placed on improving the stress transfer capability of the interface by improving the "bond" between the fiber surface and polymer matrix. The key mechanisms which are generally thought to act at the interface are: 1) mechanical interlocking of the matrix with the fiber surface, 2) intermolecular interactions between the fiber

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surface and matrix and 3) the formation of chemical bonds between the fiber surface and matrix. In the case of thermoplastic matrices, the first two mechanisms are of importance since the formation of chemical bonds between the fiber surface and matrix are considered to be associated only with thermosetting polymer matrices. In the work presented here, we probed the nature of molecular interactions between the fiber surface and thermoplastic matrices, specifically both dispersive-polar interactions and acid-base interactions, with various amorphous thermoplastic matrices. It was the purpose of this study to determine whether monitoring of either type of interaction gave insight into the relative ordering of adhesive strength. The matrices used in this study are poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(methacrylonitrile) (PMAN) and poly(vinyl chloride) (PVC). These matrices were chosen because they possess various degrees of basic and acidic character as well as varying degrees of polar contribution to their surface energy. These matrices were characterized by contact angle goniometry. Radio frequency (RF) glow discharge oxygen plasma modification of PAN-based and pitch-based carbon fiber was chosen since plasma treatments are able to introduce various functional groups at the fibers' surface. The changes induced by the oxygen plasma treatment in the fibers' surface chemistry and morphology were characterized by X-ray photoelectron spectroscopy (XPS), fiber wetting analysis, and scanning electron microscopy (SEM). The technique used here to evaluate fiber-matrix adhesion is the embedded single-fiber technique, introduced by DiBenedetto and co-workers.[1,2]

EXPERIMENTAL PROCEDURES

Materials

The carbon fibers used in this study were PAN-based Hercules AS4 fibers and mesophase pitch-based Mitsubishi Kasei Dialead K-135 (MKD) fibers. The latter were purchased from the Mitsubishi Kasei Corporation (Japan). The properties of each fiber are given in Table I as supplied by the manufacturers' literature. All four matrices were purchased from Scientific Polymer Products (Ontario, New York).

Fiber Preparation and Modification

Pretreatment The fibers were cleaned prior to surface modification because thermal desorption GC-MS of the as-received fibers revealed the presence of processing aids and antioxidants from the packaging film in which the fibers were shipped and stored. Thirty-inch segments of fiber tow were heated in a quartz tube

TABLE I
Fiber properties

Fiber	Modulus (GPa)	Density (g/cm^3)
Hercules AS4	235	1.80
Mitsubishi Kasei Dialead K-135	550	2.10

TABLE II
Plasma processing conditions

Gas	High Purity Oxygen
Flow Rate	45 cc/minute
Reactor Pressure	250 μm
Plasma Power	40 W @ 13.56 MHz
Treatment Times	1, 3, 5, 10, 30 minutes
Reaction Termination	Dry Air Quench to Atmosphere

at 400°C in a flow of ultrahigh purity nitrogen for a period of three hours. The fibers were allowed to cool to room temperature under the flowing nitrogen before use. Subsequent tests by thermal desorption GC-MS and XPS confirmed that the "cleaned" fiber surfaces were devoid of the previous contaminants from the packaging film. The resulting "cleaned" fibers are considered "untreated" in the context of this work.

Plasma modification Foot-long segments of fiber tow were wound onto a glass spool. The spool was placed in a bell jar plasma reactor with external capacitive electrodes. The system was evacuated to a base pressure of 10^{-4} Torr for one hour. High purity oxygen gas was then allowed to flow in until the reactor pressure reached 400 Torr. At this point the oxygen flow was stopped and the system was evacuated to 10^{-4} Torr. This process was repeated twice to ensure complete removal of air and saturation of the system with the oxygen gas. Table II describes the processing conditions for the oxygen plasma modifications.

Surface Chemistry

X-ray photoelectron spectroscopy Surface chemistry changes induced by the oxygen plasma treatments were monitored by XPS. Spectra were collected with a Perkin-Elmer Phi model 5300 spectrometer. This instrument is equipped with a monochromatic Al Kα X-ray source, hemispherical energy analyzer, and a position-sensitive detector. All spectra were collected with the X-ray source operated at 15 kV and 600 W. All samples were run at a 62-degree take-off angle, as this setting gave the highest count rate. Sensitivity factors for carbon, oxygen and nitrogen were calibrated on the instrument using silver acetate, poly(ethylene terephthalate) (PET) film and PMDA-ODA polyimide film as reference materials. The spectrometer was typically run in the 10^{-9} to 10^{-10} Torr vacuum range. Wide energy range survey scans were run at the 89.5 eV pass energy. Core level spectra were collected at both 8.95 eV and 35.75 eV pass energies, the former for curve fitting and the latter for elemental composition analyses. Data acquisition and analyses were performed with an Apollo 3500 series computer. Segments of carbon fiber tow, two centimeters in length, were carefully cut and positioned parallel to form a mat on the XPS sample holder. They were held in place by a tightly-fitting stainless steel frame which exposes a 1 cm × 1.5 cm area for analysis.

Fiber wetting analysis Fiber wettability was measured by a modified Wilhelmy technique using formamide and glycerol. In some instances, ethylene glycol and water were also used. Fiber perimeters and diameters, d, (AS4—6 μm diameter; MKD—10 μm diameter) were obtained using hexadecane, which completely wet the fibers. Single carbon fibers were glued to Nichrome wire with a fast curing cyanoacrylate adhesive and were allowed to cure in a glove box purged with dry nitrogen. Fiber wetting tests were performed on a Cahn 322 Dynamic Contact Angle Analyzer. The Nichrome wire/fiber was suspended from the arm of the microbalance while a precision elevator raised or lowered the liquid along 3 mm of fiber at a rate of 20 μm per minute. A microcomputer recorded mass differences periodically during each fiber run. Apparent mass differences (ΔW) were converted into advancing contact angles (θ) by the Wilhelmy equation (1):

$$(\Delta W) = p\gamma_L(\cos\theta) \tag{1}$$

where p is the perimeter of the fiber ($p=\pi d$), and γ_L is the surface tension of the test liquid.

Contact angle goniometry Thin films of each polymer were cast onto clean microscope slides from a 5 weight percent polymer solution of 50/50 (weight percent) acetone and THF. After drying the films at room temperature for 24 hours in a dry nitrogen-purged glove box, a Ramé-Hart goniometer was used to measure the contact angles of water, formamide, glycerol and ethylene glycol on the polymer films. 100 μl of test liquid was used to form the test drop. Thirty-six separate measurements were performed for the contact angle of each liquid on the polymer films.

Fiber Surface Morphology

Scanning electron microscopy An Amray 1200B SEM was used for morphological examination of the fiber surface. Imaging was performed using secondary electrons and 15 kV and 30 kV accelerating voltages.

Adhesion Testing

Preparation of test specimens PMMA, PEMA, and PMAN were pressed into ~ 1 mm thick sheets between Teflon®-coated Kapton® sheets in a hot press at 165°C. The PVC, which was pure and devoid of processing aids and anti-oxidants, degraded at the higher hot-pressing temperatures and, as such, PVC sheets had to be prepared by casting from solution. The PVC sheets were prepared by casting from 10 weight percent THF solution onto clean virgin poly(ethylene terephthalate) (PET) sheets. The PET sheets provided a substrate from which the PVC could be easily removed. The PVC sheets were dried at room temperature in a dry nitrogen-purged glove box for a period of 24 hours and were then further dried in a vacuum oven at 90°C for 24 hours to remove any residual solvent. Type V (ASTM D 638-89) dogbones were stamped out of the resulting polymer sheets. The polymer dogbones were thoroughly washed with n-hexane so as to remove any contaminants introduced by

TABLE III
Matrix drying conditions

Matrix	Time/temperature
Poly(methyl methacrylate)	24 hrs @ 25°C 24 hrs @ 60°C 24 hrs @ 110°C
Poly(ethyl methacrylate)	24 hrs @ 25°C 24 hrs @ 60°C 24 hrs @ 70°C
Poly(methacrylonitrile)	24 hrs @ 25°C 24 hrs @ 60°C 24 hrs @ 120°C
Poly(vinyl chloride)	24 hrs @ 25°C 24 hrs @ 60°C 24 hrs @ 90°C

the stamping procedure. Subsequent analyses by XPS confirmed that the samples were free of contaminants.

The embedded single fiber specimens were prepared by positioning a single fiber down the center of a polymer dogbone and then coating the fiber with the same polymer cast from a 5 weight percent polymer solution of 50/50 (weight percent) acetone and THF. The solvents were removed by drying the specimens in a conventional convection oven at the conditions indicated in Table III. The coatings were generally 0.1 mm thick.

A given batch of untreated and oxygen plasma treated MKD and AS4 fibers were embedded in all four matrices at roughly the same time after preparation of the fibers. The assumption was made that a given batch of fibers possessed the same amount of surface roughness and fiber strength so that only the nature and extent of molecular interactions was changed by variation of the matrices.

Mechanical testing The single fiber composites were uniaxially loaded in tension at room temperature on a MTS tensile tester equipped with a 1000-pound load cell and a MTS 458.20 microconsole recorder. The samples were loaded at a crosshead speed of 0.005 inches (0.127 mm) per minute until 6% deformation, because this deformation assured complete fracture of the fibers in the composite. The fragment lengths were observed using an optical microscope fitted with an optical micrometer. In accordance with the embedded single fiber testing technique, the fragment lengths obtained from testing of the single fiber composite systems were used to construct a cumulative distribution of fragment lengths. The mean value of the critical fragment length (L_c) was assumed equal to (4/3) of the mean fragment length at the midpoint of the cumulative distribution of fragment lengths.[3] From this value of critical fragment length, the critical aspect ratio (L_c/d) was calculated. The critical aspect ratio is considered to be an inverse measure of the stress transfer capability of the interface[4] according to the shear lag analysis of the embedded single fiber specimen. For this reason, the value of the critical aspect ratio gives insight into the level of adhesion at the fiber-matrix interface.

RESULTS AND DISCUSSION

XPS Analysis

Elemental and functional group concentrations for the oxygen plasma modification time series of the MKD and AS4 fibers are presented in Tables IV and V, respec-

TABLE IV
Elemental and functional group composition of oxygen plasma treated MKD fibers

Treatment time	Carbon %	Oxygen %
Untreated	97.9	2.1
1 Minute	86.5	13.5
3 Minutes	86.8	13.2
5 Minutes	86.9	13.1
10 Minutes	87.5	12.5
30 Minutes	86.7	13.3

Carbon 1s functional group composition

Treatment time	C—gr %	C—C %	C—O %	C=O %	O—C=O %	Plasmon %
Untreated	92.4	4.5	3.1	—	—	4.4
1 Minute	75.0	5.8	12.1	4.3	2.8	—
3 Minutes	74.6	5.6	12.5	4.7	2.6	—
5 Minutes	76.3	5.7	10.5	4.8	2.7	—
10 Minutes	79.5	3.6	9.5	4.9	2.5	—
30 Minutes	77.5	5.4	10.8	4.0	2.3	—

TABLE V
Elemental and functional group composition of oxygen plasma treated AS4 fibers

Treatment time	Carbon %	Oxygen %	Nitrogen %
Untreated	93.6	3.0	3.4
1 Minute	77.3	20.0	2.7
3 Minutes	76.7	19.6	3.7
5 Minutes	74.6	22.9	2.5
10 Minutes	74.6	22.7	2.7
30 Minutes	—	—	—

Carbon 1s functional group composition

Treatment time	C—gr %	C—C %	C—N %	C—O %	C=O %	O—C=O %
Untreated	70.0	17.0	7.6	3.3	1.5	—
1 Minute	58.6	8.4	6.2	12.6	8.4	5.8
3 Minutes	59.8	11.3	6.6	8.3	8.4	5.6
5 Minutes	68.9	9.1	6.2	6.2	6.3	3.3
10 Minutes	62.2	9.4	6.7	8.8	7.9	5.0
30 Minutes	—	—	—	—	—	—

tively. Peak positions and various curve-fitting information for the carbon 1s region can be found in Reference 5. As can be seen from the elemental and functional groups tables, both fibers showed an increase in the number of oxygen species incorporated into the surface. The nitrogen content of the AS4 fiber was observed to remain constant. The oxygen plasma species reacted quickly with both the MKD and AS4 fiber surfaces and equilibrium in oxygen incorporation was reached after around 1 minute of reaction time (Figure 1) with our reactor configuration. The AS4 fiber was modified to a much greater extent (~22% oxygen) than was the MKD fiber (~13% oxygen) once equilibrium was reached. The graphitic structure of the surface of both fibers, within the depth detection limits of XPS, was also noted to be disrupted by the bombarding species of the oxygen plasma as shown by the decrease of the graphitic carbon peaks and disappearance of the plasmon loss peaks. More detailed discussion can be found in Reference 5. Figures 2 and 3 present the carbon 1s regions of the untreated and oxygen-plasma-treated MKD and AS4 fibers, respectively. The 3-minute treated MKD fiber and the 5-minute treated AS4 fiber are shown, as these fibers represent the treatment levels where a maximum in surface chemical modification was achieved and they will be referred to in the remainder of the discussion. As can be seen from the curve-fitting analysis of the carbon 1s regions, hydroxyl groups (at 285.9 eV), carbonyl groups (at 287.3 eV) and carboxylic acid groups (at 288.5eV) are generated on both the MKD and AS4 fibers by the oxygen plasma treatment. The presence of these groups was qualita-

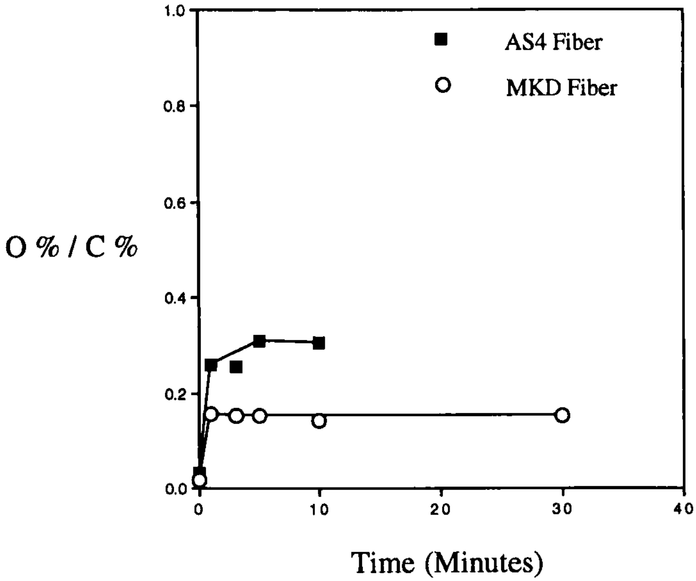

FIGURE 1 Oxygen %/Carbon % Ratio *vs.* Treatment Time for the 40 W Oxygen Plasma Treatment of the MKD and AS4 Fibers.

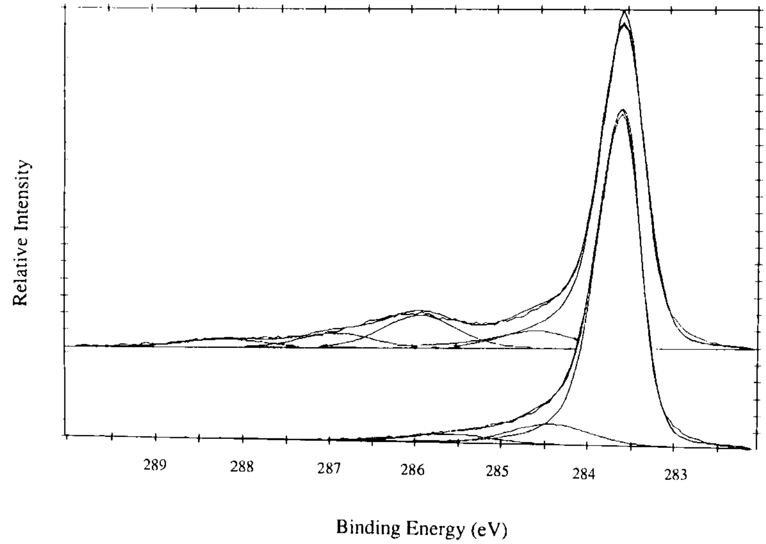

FIGURE 2 Carbon 1s Region for the Untreated (bottom) and 3-Minute Oxygen-Plasma-Treated (top) MKD Fibers.

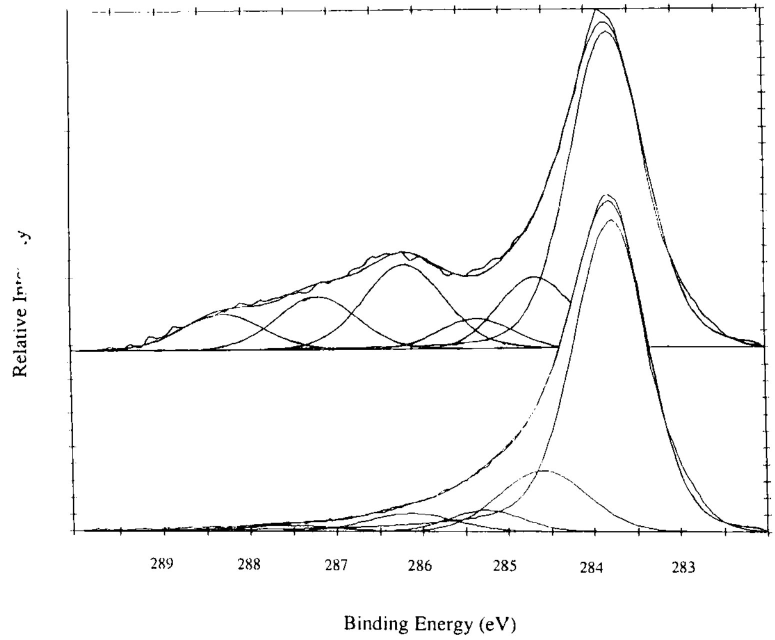

FIGURE 3 Carbon 1s Region for the Untreated (bottom) and 5-Minute Oxygen-Plasma-Treated (top) AS4 Fibers.

tively confirmed by derivatization reactions of the fibers with fluorine-containing tagging molecules in the method described by Takahagi and Ishitani.[6]

Surface Energetics

Table VI contains the dispersive (D) and polar (P) components of surface free energy calculated by the geometric mean equation (2) with data from the fiber (F) wetting experiments for both the untreated and oxygen-plasma-treated fibers.

$$\gamma_L(1+\cos\theta) = 2(\gamma_F^D\gamma_L^D)^{1/2} + 2(\gamma_F^P\gamma_L^P)^{1/2} \tag{2}$$

The untreated MKD and AS4 fibers have relatively small polar contribution to total surface free energy. There is a huge increase in the polar component of surface free energy of the oxygen-plasma-treated MKD and AS4 fibers due to the large amount of oxygen incorporated into their respective surfaces. The dispersive components of surface free energy of both fibers are also noted to decrease, most likely due to the disruption of the graphite lattices in the surface of the fibers as was noted by XPS. Table VII presents the acid-base component of the work of adhesion, W_a^{AB}, equation (3), as suggested by Fowkes,[7] using formamide and glycerol for the same fiber sets presented in Table VI.

$$\gamma_L(1+\cos\theta) = 2(\gamma_F^D\gamma_L^D)^{1/2} + W_a^{AB} \tag{3}$$

Formamide, a Lewis base, indexes surface acidity while glycerol, a Lewis acid, indexes surface basicity. The oxygen-plasma treatments raised the level of surface acidity and basicity significantly for the MKD and AS4 fibers due to the incorporation of the various oxygen functional groups into the surface of the fibers.

TABLE VI
Dispersive and polar components of surface energy for untreated and oxygen plasma treated MKD and AS4 fibers

Fiber	γ^D (dyne/cm)	γ^P (dyne/cm)	γ^{Total} (dyne/cm)
MKD-Untreated	29.5	2.5	32.0
MKD-3 Minute O_2 Plasma	25.4	31.2	56.6
AS4-Untreated	33.2	4.9	38.1
AS4-5 Minute O_2 Plasma	24.5	28.9	53.4

TABLE VII
Acid-base components of adhesion for untreated and oxygen plasma treated MKD and AS4 fibers

Fiber	$W_{a\text{-}b}$ formamide (dyne/cm)	$W_{a\text{-}b}$ glycerol (dyne/cm)
MKD-Untreated	13.8	17.1
MKD-3 Minute O_2 Plasma	48.3	58.5
AS4-Untreated	19.2	23.6
AS4-5 Minute O_2 Plasma	43.9	59.6

TABLE VIII
Dispersive and polar/Lewis acid and base components of surface energy for the polymer matrices

Matrix	γ^D (dyne/cm)	γ^P (dyne/cm)	γ^{Total} (dyne/cm)
Poly(methacrylonitrile)	32.5	8.7	41.2
Poly(methyl methacrylate)	36.9	6.5	43.4
Poly(ethyl methacrylate)	33.0	4.8	37.8
Poly(vinyl chloride)	34.2	6.8	41.0

	γ^- (dyne/cm)	γ^+ (dyne/cm)
Poly(methacrylonitrile)	17.9	0
Poly(methyl methacrylate)	13.4	0
Poly(ethyl methacrylate)	10.3	0
Poly(vinyl chloride)	3.1	0

The contact angle measurements performed on the polymer matrices were used to calculate the dispersive and polar components of their surface free energy with use of the geometric mean equation, equation (2), and these results are listed in Table VIII. The recent theory of acid-base interaction introduced by Good, Van Oss and Chaudhury[8] was utilized when considering the acid-base nature of the matrices, equation (4).

$$\gamma_L(1+\cos\theta)-2(\gamma_M^D\gamma_L^D)^{1/2}=2(\gamma_M^+\gamma_L^-)^{1/2}+2(\gamma_M^-\gamma_L^+)^{1/2} \tag{4}$$

Here, acid-base components of surface free energy are split into the terms, $\gamma+$ and $\gamma-$, where the former is a measure of the Lewis acid contribution to surface free energy and the latter is a measure of the Lewis base contribution to surface free energy. The subscripts M and L refer to the matrix and liquid, respectively. As can be seen from the magnitudes of these terms, also listed in Table VIII, there is a definite ordering of the polymer matrices. The order of the matrices according to the $\gamma-$ term is PMAN, PMMA, PEMA and PVC, where PMAN is the strongest base and PVC appears to be the weakest base. It was thought that the PVC would exhibit Lewis acid behavior and give a $\gamma+$ of some magnitude. This value of $\gamma-$ is, however, in agreement with the reports of Good, Van Oss and Chaudhury.[8] In either case, the PVC can be viewed as the least basic matrix used in this study.

Fiber Surface Morphology

SEM micrographs are presented in Figure 4. The untreated MKD fibers showed interesting striations[9] parallel to their length which may have originated in the precursor spinning process. The fiber's cross section indicated a highly-ordered internal structure which extends radially to the surface. Such a highly-ordered internal structure is consistent with mesophase pitch-based fibers.[10] The untreated AS4 fiber was essentially featureless and smooth at the 10,000 × magnification. There are no remarkable features on its cross-section except those produced by brittle fracture. The oxygen-plasma treatment of the MKD fiber created patches of pitting on that fiber. This treatment also caused extensive etching of the AS4 fiber

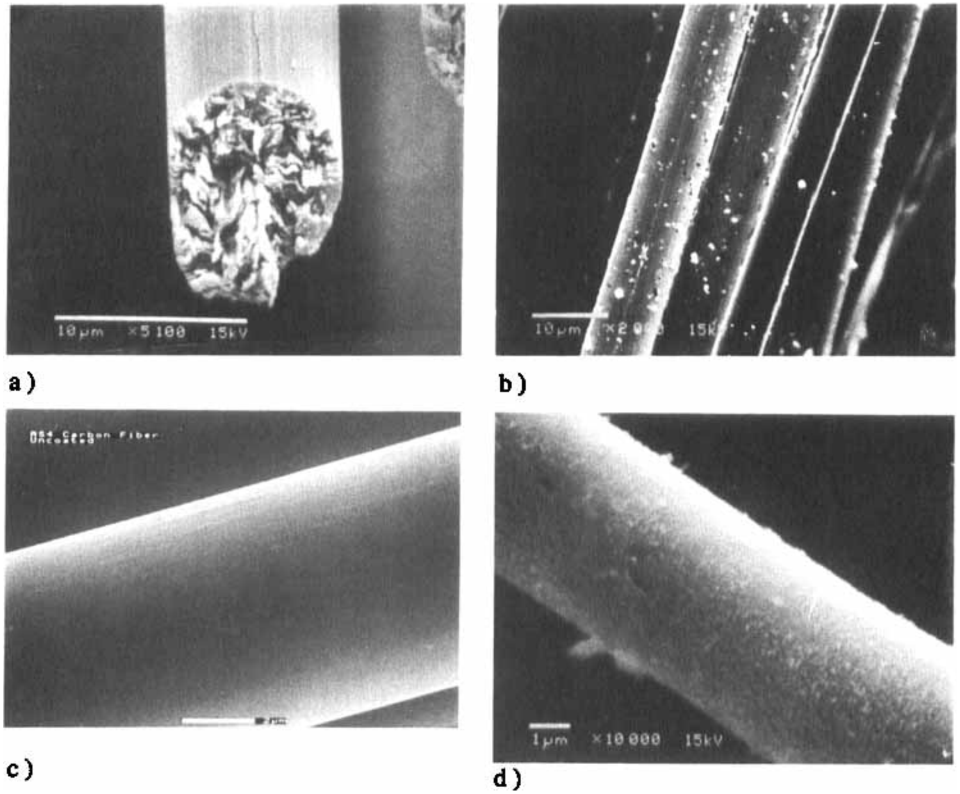

FIGURE 4 SEM Micrographs of a) Untreated MKD Fiber b) 3-Minute Oxygen-Plasma-Treated MKD Fiber c) Untreated AS4 Fiber d) 5-Minute Oxygen-Plasma-Treated AS4 Fiber.

as is indicated in the micrograph. Therefore, in both fibers, there was an increase in surface roughness and surface area caused by the oxygen-plasma treatment.

Fiber-Matrix Adhesion

Table IX contains measured critical aspect ratios for the untreated and oxygen-plasma-treated fiber in the four matrices. Very poor adhesion was observed with

TABLE IX
Critical aspect ratios for single fiber composites

Matrix	Fiber type		
	MKD-untreated L_c/D	MKD-O_2 plasma L_c/D	AS4-O_2 plasma L_c/D
Poly(methacrylonitrile)	143	41	49
Poly(methyl methacrylate)	147	50	59
Poly(ethyl methacrylate)	157	67	61
Poly(vinyl chloride)	145	76	80

the untreated MKD fiber in the four matrices as shown by the very high critical aspect ratios (143–157). It was observed that there was considerable fiber slip in the untreated single fiber specimens of all four matrices, which was also indicative of the poor adhesion between the fiber and matrix. The untreated MKD fibers, as previously mentioned, contain very low concentrations of oxygen-containing functional groups. It is unlikely, then, that specific molecular interactions would occur between the fiber surface and the matrices. For the untreated AS4 fibers, there was the occasional fiber fracture and a large amount of fiber slip in the four matrices. Untreated AS4 fiber adhesion was so poor with all four matrices that it was very difficult to collect a meaningful number of fiber fragments to calculate a critical aspect ratio for these samples. The untreated AS4 fibers also lacked any appreciable number of functional groups capable of interaction with the four matrices. Based on the low surface energies of both untreated MKD and AS4 fibers in comparison with the surface energies of the four matrices, the critical criterion for wetting of the fibers by the matrices is only barely met in a few instances. Therefore, due to the lack of specific interactions between the fibers and matrices, it is thought that only fiber-matrix friction developed by thermal compressive matrix stresses occurring during the cooling of the matrices to room temperature controls the stress transfer at the interfaces of these untreated fibers.

The oxygen-plasma-treated MKD and AS4 fibers exhibited much better adhesion with all four matrices as reflected by the large decrease in the critical aspect ratios. Observation of these fiber fragments of both fiber types revealed practically no fiber slip in the single fiber specimens for the PMAc, PMMA and PEMA. The plasma-treated MKD and AS4 fibers were observed to have a slight amount of slip in the PVC matrix, however it was much less than for the untreated fiber specimens. The increase in the adhesion of the plasma-treated fibers in comparison with the untreated fibers is thought to be due to: 1) the roughening of the surface of the fibers by the plasma which affords a larger surface area for mechanical interlocking of the matrix into the surface of the fibers and 2) the occurrence of specific molecular interactions between the surface of the fibers and the matrix by the introduction of the various high energy functional groups.

Correlation of Specific Interactions with Fiber-Matrix Adhesion

As noted in the Introduction, it was the purpose of this work to study the nature of the intermolecular interactions between the surface of the fibers and the polymer matrices. It is assumed that embedding a given batch of fibers in the four matrices normalizes the effects of fiber surface roughness and fiber strength and their contribution to adhesion in the four matrices. Based on this assumption, the effects of molecular interactions can be studied. Table X contains the theoretical work of adhesion, W_a, calculated by use of the extended geometric mean equation[11], equation (5), with the dispersive and polar components of surface free energy for the oxygen-plasma-treated MKD and AS4 fibers and with the dispersive and polar components of surface free energy of the four matrices.

$$W_a = 2(\gamma_F^D \gamma_M^D)^{1/2} + 2(\gamma_F^P \gamma_M^P)^{1/2} \tag{5}$$

TABLE X
Theoretical work of adhesion

Matrix	Fiber type MKD-O_2 plasma $W_{adhesion}$ (dyne/cm)	 AS4-O_2 plasma $W_{adhesion}$ (dyne/cm)
Poly(methacrylonitrile)	90.5	88.2
Poly(methyl methacrylate)	89.7	87.6
Poly(vinyl chloride)	88.1	85.9
Poly(ethyl methacrylate)	82.4	80.5

From these calculations the level of adhesion in the matrices should follow the order: PMAN>PMMA>PVC>PEMA. However, when the theoretical work of adhesion is plotted *versus* the critical aspect ratios of the plasma-treated MKD and AS4 fibers, as shown in Figures 5 and 6, respectively, the correlation factors of a straight line fit are 0.36 and 0.05, respectively. Although the polar component of surface energy of the MKD and AS4 fibers does increase greatly with oxygen-plasma

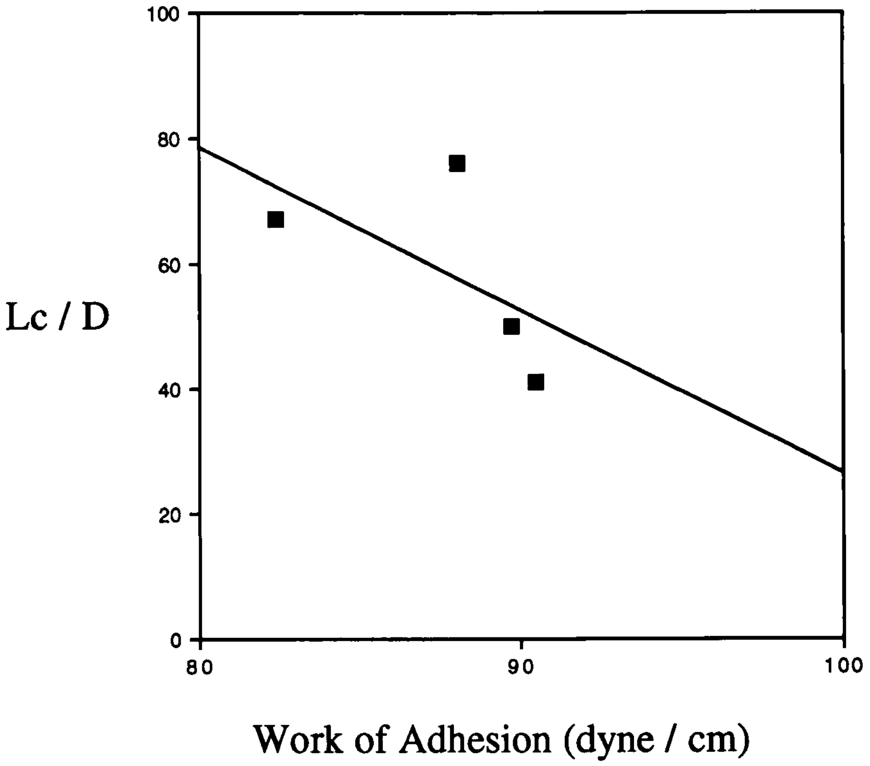

FIGURE 5 Critical Aspect Ratios of 3-Minute Oxygen-Plasma-Treated MKD Fiber *vs.* Theoretical Work of Adhesion for the four matrix polymers.

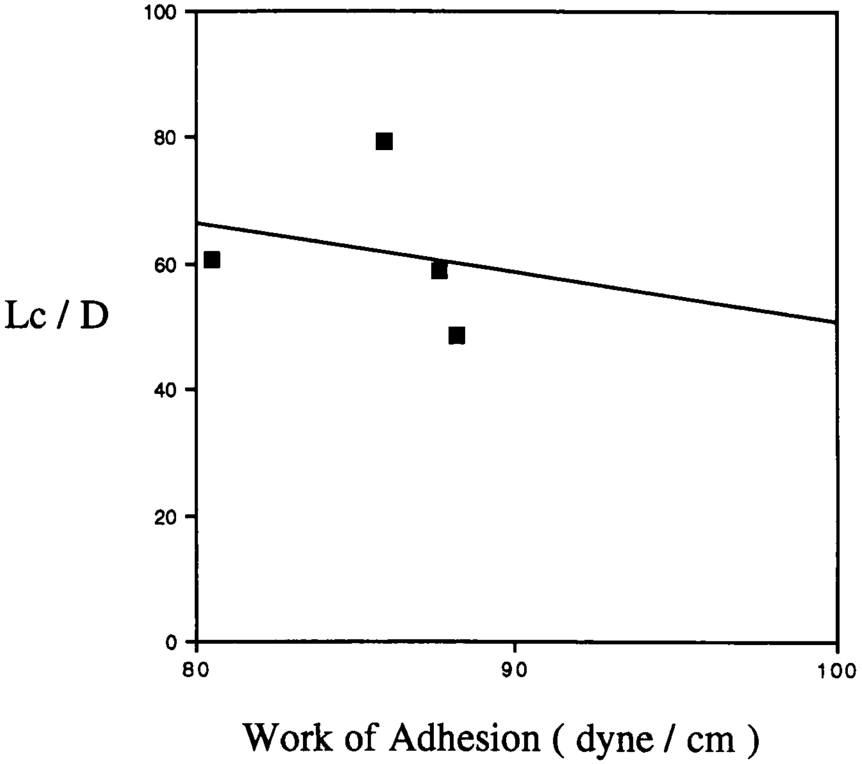

FIGURE 6 Critical Aspect Ratios of 5-Minute Oxygen-Plasma-Treated AS4 Fiber *vs.* Theoretical Work of Adhesion for the four matrix polymers.

treatment, the correlation between theoretical work of adhesion, based on the idea of polar interactions with the four matrices, and the experimentally-determined critical aspect ratios does not adequately describe the intermolecular interactions at work in the matrix/fiber interphases studied here.

From the XPS results, it is noted that there are a large number of hydroxyl and carboxylic acid groups introduced into the surfaces of the fibers by the oxygen-plasma treatments. These acidic-functional groups on the surface of the fibers are thought to be able to interact selectively with the basic groups in the PMAN, PMMA and PEMA through hydrogen bonding. The PVC is the least basic of the matrices used in this study and a much lower level of adhesion is expected with the plasma-treated fibers. Figures 7 and 8 are plots of the critical aspect ratios of the plasma treated MKD and AS4 fibers *versus* the $\gamma-$, the Lewis base contribution to surface free energy, of the four polymer matrices. The correlation factors of a straight line fit for these plots are 0.93 and 0.97 respectively. It is thus apparent that there is excellent correlation of the level of adhesion of the fibers with the four matrices in terms of acid-base interactions. Therefore, it is concluded that description of the relative ordering of adhesion in the systems studied here are well accounted for by acid-base interactions.

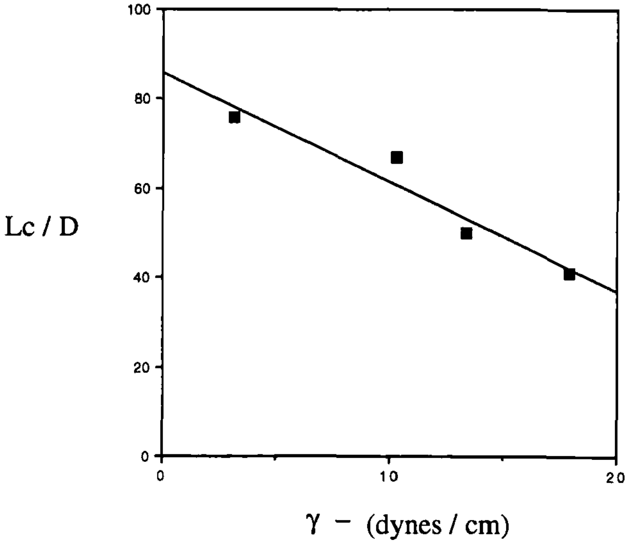

FIGURE 7 The Critical Aspect Ratios with the 3-Minute Plasma-Treated MKD Fiber *vs.* the Lewis base component of surface free energy (γ−) of the matrices.

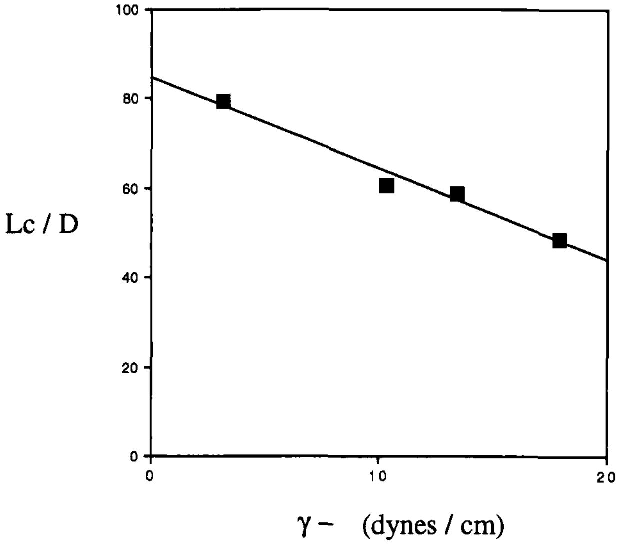

FIGURE 8 The Critical Aspect Ratios with the 5-Minute Plasma-Treated AS4 Fiber *vs.* the Lewis base component of surface free energy (γ−) of the matrices.

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