

The Influence of Plasma Gas Species on the Adhesion of Thermoplastic to Organic Fibers

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SYNOPSIS

Adhesion between organic fibers and thermoplastics in a composite material is usually weak because of the lack of chemical and mechanical bonding. This study investigated the influence of plasma gas species in a novel technique to improve interfacial adhesion of Kevlar 49 fibers to polycarbonate. Single Kevlar fibers were exposed to radio-frequency plasma discharge in atmospheres of argon, oxygen, and ammonia. Plasma treatment has been shown to generate reactive free radicals on polymer surfaces. The fibers that were coated immediately with a polycarbonate melt while still in the vacuum environment of a plasma reactor showed an increase in interfacial shear strength that was maximum at 4.1 s exposure and decreased at longer exposure times. At 4.1 s exposure, Ar and O₂ plasma treatment increased shear strength by 20 and 18%, respectively. NH₃ plasma treatment produced only a statistically insignificant increase at 4.1 s of exposure and a significant decrease in adhesion at 8.3 s of exposure. Fibers that were exposed to air for 1 h before coating showed no statistically significant increase or decrease in adhesion. The increase in adhesion of the directly coated fibers was attributed to free radical-initiated formation of covalent bonds between the Kevlar and the polycarbonate. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical performance of fiber composite materials, such as strength and modulus, is highly dependent on how well the load is transferred from the matrix to the fibers. To take full advantage of the mechanical properties of the fiber and matrix, the interfacial shear strength between the fiber and matrix must be greater than the failure shear strength of the matrix or of the fiber. Increased interfacial adhesion is commonly achieved by forming covalent interfacial bonds, by crystallizing the matrix on the fiber, by roughening the fiber, by modifying the surface energy, or a combination of these.^{1,2} These techniques have been successfully applied in some high-performance composite systems (i.e., carbon fiber/epoxy or carbon fiber/PEEK), thus

providing an interphase region in which failure is cohesive, not adhesive.

Interfacial failure between organic fibers and thermoplastic polymers has historically been epitomized by adhesive, not cohesive, failure. Organic fibers (Kevlar, polyethylene, etc.) usually have a smooth surface and have low surface energy, which decrease their ability to adhere to the matrix by way of mechanical interlock, enhanced wetting, or nucleation of crystalline growth. In addition, these high-performance fibers and thermoplastics are designed to be chemically and thermally stable; therefore, they usually contain no chemical functional groups at the surface through which covalent bonds can be formed. Chemically derivatizing the surface of organic fibers, like Kevlar, has shown only limited success.³⁻⁵

In this paper, we present further investigations of a new technique for increasing adhesion between organic fibers and thermoplastic matrix materials. In previous publications,^{6,7} we showed that argon and oxygen plasma treatment of Kevlar 49 polyaramid followed by immediate coating with a poly-

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carbonate melt increased interfacial adhesion by as much as 20%. In this paper, we will present and compare the results of ammonia plasma treatment on interfacial adhesion and we will speculate on some possible adhesion mechanisms.

The hypothesis underlying this technique is that free radicals that are generated on the surface of reinforcing filaments can form covalent bonds across the fiber-matrix interface if the radicals are immediately contacted with the thermoplastic matrix. Free radicals can be easily created by exposing the polymeric reinforcing filaments to a plasma discharge.⁸ They are chemically active radicals, as evidenced by their ability to initiate free radical polymerization.^{9,10} In a vacuum or under inert gas, these radicals can have lifetimes of hours¹¹ or days.¹² However, if they are exposed to air, the radicals will react quickly with oxygen to form peroxide or other oxygen species on the polymer surface.^{13,14}

In the plasma treatment and polymer coating process described in this paper, the thermoplastic coating is applied immediately to the fiber before the free radicals have been exposed to oxygen. This differs from conventional plasma treatment processes in which plasma-treated filaments are removed from the vacuum environment before the matrix is applied as a melt or from a solvent. This paper will show that immediate coating with thermoplastic is required to strengthen the interfacial strength. Theoretically, this technique could be applied to any organic fiber in any thermoplastic matrix or possibly even some thermosetting matrices.

Two previous observations have suggested that this technique might be successful. Wertheimer and Schreiber¹⁵ used microwave plasma in atmospheres of O₂, N₂, and Ar to oxidize the surface of Kevlar incorporated into a triazine (thermosetting) matrix material. They found that this treatment increased the strength of the resulting composite laminate. Of particular note to our hypothesis is their observation that increased laminate strength was maximized when the time interval between plasma exposure and resin contact was minimized. In another example, Nichols et al.¹⁶ used radio-frequency plasma discharge (RFPD) in a methane atmosphere to improve adhesion of poly-*p*-xylylene to glass. He noted that reduced adhesion occurred when the plasma-treated substrate was aged in air before the deposition of the polymer. Recently, Bascom and Chen¹⁷ studied the effect of RF plasma upon adhesion of carbon fibers to an epoxy matrix. They found that interfacial strength decreased as the time of air exposure increased. Although none of these examples involve thermoplastic matrices, they all show that

adhesion was maximized when exposure of the plasma-treated substrate to air was minimized.

EXPERIMENTAL

Single Kevlar 49 filaments from a 134 filament yarn (DuPont, 195 denier, 0° twist, type 968 yarn) were dried at 120°C for 24 h in a vacuum oven. They were stored in a vacuum desiccator with CaSO₄ until use.

Lexan 121 polycarbonate (General Electric, pellet form, lot #LQ2825) was dried at 80°C for approximately 24 h in a vacuum oven. It was stored in a vacuum desiccator with CaSO₄ until use.

The device used to process and coat the filaments is shown in Figure 1. The entire device was contained inside the vacuum chamber of a PS 0500 plasma reactor (Plasma Science, Foster City, CA) operating at 13.56 MHz. A single filament was pulled through the apparatus by a takeup spool driven by a stepper motor and microprocessor. The filament was pulled from the takeoff spool through a Teflon-coated eyelet that maintained proper alignment. The filament was pulled vertically downward from the eyelet between two parallel 8 × 8 cm plasma electrodes that had an 8 cm separation. The filament continued downward through the polycarbonate melt, which applied a thin coat of matrix material. After exiting the melt, the thermoplastic cooled as the coated filament traveled downward through another Teflon-coated eyelet and then to the takeup spool.

To process a fiber, the reactor chamber was first evacuated to less than 0.050 Torr, and then a 0.10 standard liter per minute flow of process gas was started. The gases used in this investigation were oxygen (99.6% pure), argon (99.999% pure), and ammonia (99.5% pure). The pressure was adjusted to 0.100 Torr. Several minutes (about 10 min) were required for the thermoplastic melt temperature to stabilize at 265°C. During this time, the reactor chamber was thoroughly purged with the process gas. When the temperature of the melt had stabilized, 1 m of a 6 m filament was pulled through the melt at 1.9 cm/s without striking plasma. At this point, plasma was struck at 24 ± 1 W. Subsequent 1 m length increments of the same filament were exposed to the plasma and coated sequentially at speeds of 1.0, 1.9, 2.9, and 3.9 cm/s. These speeds resulted in plasma exposure times of 8.3, 4.2, 2.8, and 2.1 s, based on the residence time between the electrodes. For a control set of experiments, the filament received the plasma exposure described above, but was not immediately coated with thermoplastic. Instead, it was removed from the vacuum

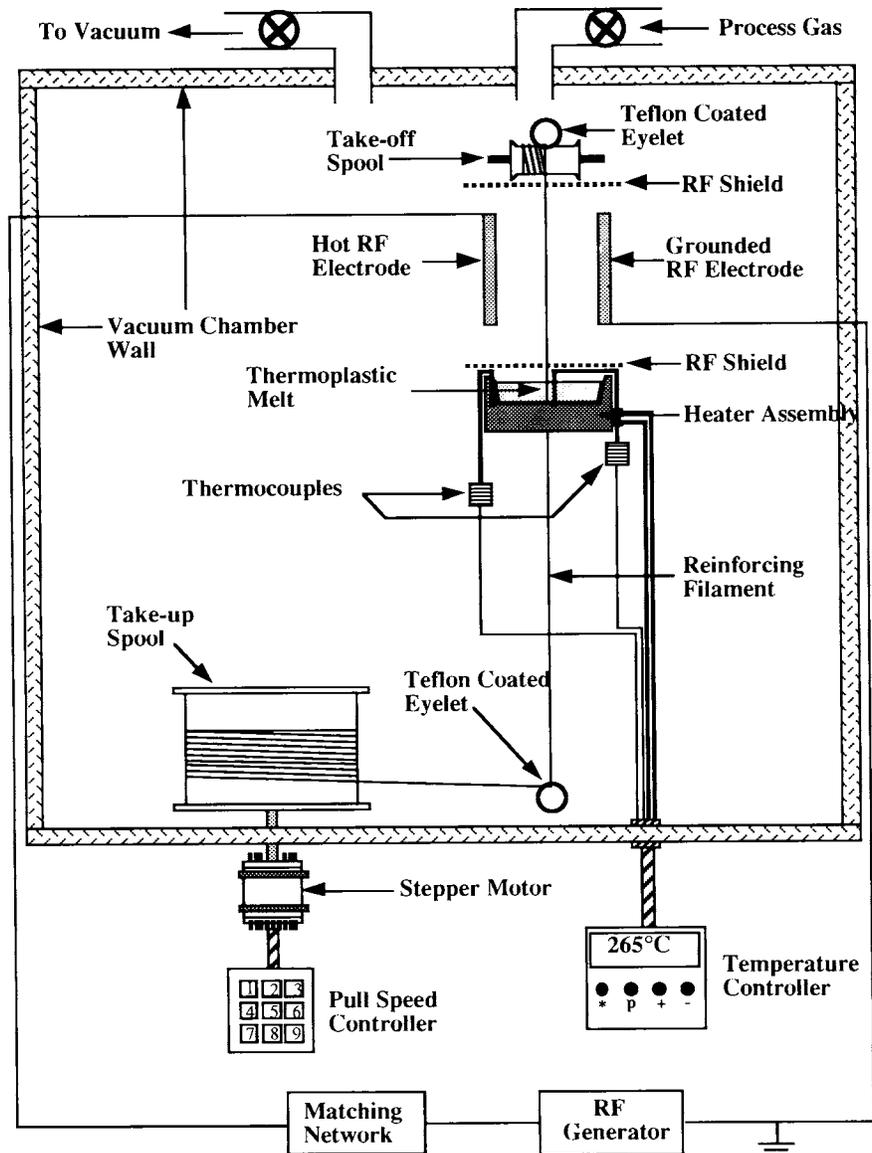


Figure 1 Schematic of the apparatus used to plasma treat and coat organic fibers with thermoplastic.

chamber and allowed to stand in the laboratory for 1 h (25°C, 30% relative humidity). The filament was then threaded back through the apparatus and, in the absence of plasma, was coated with thermoplastic as described above. These samples are referred to as "air-quenched." Each 1 m segment of the filament was coated at the same pull speed used for its plasma exposure. In both air-quenched and directly coated samples, the polycarbonate-coated Kevlar filaments had an average outside diameter of 30–40 μm .

The interfacial adhesion of the polycarbonate to the fiber was evaluated using the single embedded

filament composite test.¹⁸ The use of this test is subject to some controversy concerning whether absolute values of interfacial shear strength can be obtained. However, most researchers feel that the test can be used adequately for comparison between similar samples.¹⁹ This test is based upon a mechanical force balance between the stress required to fracture a fiber and the interfacial shear stress transferred to the fiber. As the strain on the embedded fiber increases, the fiber fractures successively along its length until no further fragmentation is possible. The maximum length that a fragment can have is called the critical length, l_c , given by

$$l_c = \frac{d\sigma_f}{2\tau} \quad (1)$$

where d is the fiber diameter; σ_f , the tensile strength; and τ , the interfacial shear strength. Because the resulting fragments have actual lengths varying between l_c and $l_c/2$, some have argued²⁰ that the mean fragment length, \bar{l} , may range from $0.75l_c$ to $0.889l_c$. Equation (1) can thus be written as

$$\bar{l} = \frac{d\sigma_f}{2\tau} (K) \quad (2)$$

where K may range from 0.75 to 0.889. For the purposes of this paper, it is more convenient to discuss the mean fragment length in terms of the tensile failure load of the fiber, L_f , instead of tensile strength. Equation (2) now becomes

$$\bar{l} = \frac{2L_f}{\pi\tau d} (K) \quad (3)$$

The samples were prepared by solvent welding (with methylene chloride) the coated filament to a dogbone cut from a 3 mm polycarbonate sheet (Lexan, General Electric). The methylene chloride was allowed to evaporate for 24 h at room conditions, with an additional 8 h in a vacuum oven at 0.8 atm vacuum and 75°C. Two dogbones from each segment were prepared and tested in the laboratory of Dr. Willard Bascom using procedures previously described.²¹ The distance between stress concentration sites around the filament (i.e., the critical length) was measured with a scale in the microscope eyepiece. To avoid experimenter bias, the samples were tested blindly.

There were variations in the number of data points obtained from each sample because some specimens had bubbles at the interface between the polycarbonate-coated filament and the dogbone that were formed during the solvent welding procedure. These flaws reduced the length of filament on which the birefringence patterns could be confidently measured.

Tensile tests on plasma-treated (but uncoated) fibers were performed with an Instron Model 1122 tensile testing machine equipped with a 500 g load cell. A full scale load of 100 g was used with a cross-head speed of 5 mm/min. Ten millimeter gauge length samples were tested.

The topographies of Kevlar filaments before and after plasma treatment were examined using a scanning electron microscope (Jeol JSM-840A) as described previously.⁶ The same publication also de-

scribes collection of photoacoustic infrared spectra before and after plasma processing, as well as techniques used to determine the average filament diameter by gravimetry, optical microscopy, and scanning electron microscopy.

RESULTS

Embedded Single-filament Testing

When the single-filament composite test specimens were subjected to tensile stress, birefringence nodes appeared adjacent to the fiber in patterns similar to those made by carbon fiber in polycarbonate.²¹ However, no transverse breaks in the Kevlar filament were observed near the birefringence nodes or anywhere else in the fiber.

The average distance between birefringence nodes is given in Table I. Figure 2 plots the mean and the 95% confidence intervals of the length between birefringence nodes as a function of plasma exposure time.

Tensile Properties of Single Filaments

Tensile tests were conducted on several individual Kevlar 49 filaments to examine filament-to-filament variations in tensile failure load. The mean failure load, standard deviation, and 95% confidence intervals are given in Table II. An examination of the 95% confidence intervals shows that the individual filaments do not have the same failure loads. For example, one can reject (at the .05 level) the null hypothesis that filament C has the same failure load as do filaments D, E, or F. Since the diameters on these particular filaments were not individually measured, we cannot unambiguously assign the difference in failure load to individual variations in diameter or strength. Wagner et al.²² found that for Kevlar 49 the filament diameter remains nearly constant over long lengths (up to 17 m), but the diameters vary significantly from filament to filament in a tow. They also found that the variability in strength along the length of a single filament was roughly the same as the variability in strength among different filaments. These data support the conjecture that the variability in filament diameter is largely responsible for the variations in failure load shown in Table II.

Considering all of these tensile data together, the average failure load and coefficient of variance (standard deviation/mean) on these 1 cm length filaments was 421 mN and .09, respectively. This

Table I Embedded Single Filament Test Data

Sample Treatment (Gas, Coating, Exposure Time)	n	Fragment Length (μm)		95% Confidence Intervals (μm)	
		Mean	SD	Upper	Lower
Argon, A.Q., ^a 0 s	25	434.0	153.1	497.0	371.0
Argon, A.Q., 2.1 s	20	451.5	146.1	519.8	383.3
Argon, A.Q., 2.8 s	28	432.3	108.5	474.3	389.4
Argon, A.Q., 4.1 s	35	428.8	140.9	475.1	381.5
Argon, A.Q., 8.3 s	11	483.0	114.6	560.0	406.0
Argon F1, D.C., ^b 0 s	35	307.1	107.6	343.0	272.1
Argon F1, D.C., 2.1 s	78	252.9	77.0	269.5	235.4
Argon F1, D.C., 4.1 s	49	256.4	82.3	280.0	233.6
Argon F1, D.C., 8.3 s	38	293.1	102.4	325.5	259.9
Argon, F2 D.C., 0 s	20	539.9	182.9	624.8	454.1
Argon, F2 D.C., 2.1 s	6	588.0	264.3	863.6	310.6
Argon, F2 D.C., 2.8 s	17	532.9	175.9	623.9	442.8
Argon, F2 D.C., 4.1 s	29	458.5	105.0	497.9	418.3
Argon, F2 D.C., 8.3 s	10	465.5	149.6	572.3	358.8
Oxygen, A.Q., 0 s	12	448.0	110.3	517.1	378.0
Oxygen, A.Q., 2.1 s	29	492.6	143.5	547.8	438.4
Oxygen, A.Q., 2.8 s	66	418.3	158.4	456.8	379.8
Oxygen, A.Q., 4.1 s	24	474.3	160.1	541.6	406.9
Oxygen, A.Q., 8.3 s	25	432.3	123.4	483.0	381.5
Oxygen, D.C., 0 s	41	300.1	83.1	325.5	274.8
Oxygen, D.C., 2.1 s	28	286.1	88.4	320.3	252.0
Oxygen, D.C., 2.8 s	61	257.3	79.6	277.4	238.0
Oxygen, D.C., 4.1 s	53	253.8	71.8	273.0	234.5
Oxygen, D.C., 8.3 s	40	347.4	70.9	369.3	325.5
Ammonia, A.Q., 0 s	37	439.3	105.0	473.4	406.0
Ammonia, A.Q., 2.1 s	43	413.0	126.0	450.6	375.4
Ammonia, A.Q., 2.8 s	34	401.6	87.5	430.5	371.9
Ammonia, A.Q., 4.1 s	33	441.9	123.4	483.9	399.9
Ammonia, A.Q., 8.3 s	27	403.4	84.9	436.6	369.3
Ammonia, D.C., 0 s	54	476.9	148.8	517.1	437.5
Ammonia, D.C., 2.1 s	60	467.3	128.6	499.6	434.9
Ammonia, D.C., 2.8 s	65	445.4	150.5	482.1	408.6
Ammonia, D.C., 4.1 s	56	438.4	163.6	487.4	401.6
Ammonia, D.C., 8.3 s	16	641.4	178.5	735.9	546.0

^a A.Q. signifies 1 h of air quench before thermoplastic coating.
^b D.C. signifies direct coating by thermoplastic following plasma treatment.

compares favorably to the data of Wagner et al.²² who found a mean and coefficient of variance of 376 mN and 0.13 for 5 cm gauge length samples of Kevlar 49.

Tensile measurements were also made on a single Kevlar 49 filaments that had been subjected to plasma exposure in order to determine if the plasma exposure had any effect on the filament failure load.

The results of the tensile measurements are shown in Table III and Figure 3. A paired *T*-test showed that none of the failure loads of the plasma-treated sections of the filament are significantly different (.05 level) than that of the untreated segment of the filament. An analysis of variance (ANOVA) showed that for a given filament, none of the failure loads are significantly (.05 level) influenced by the

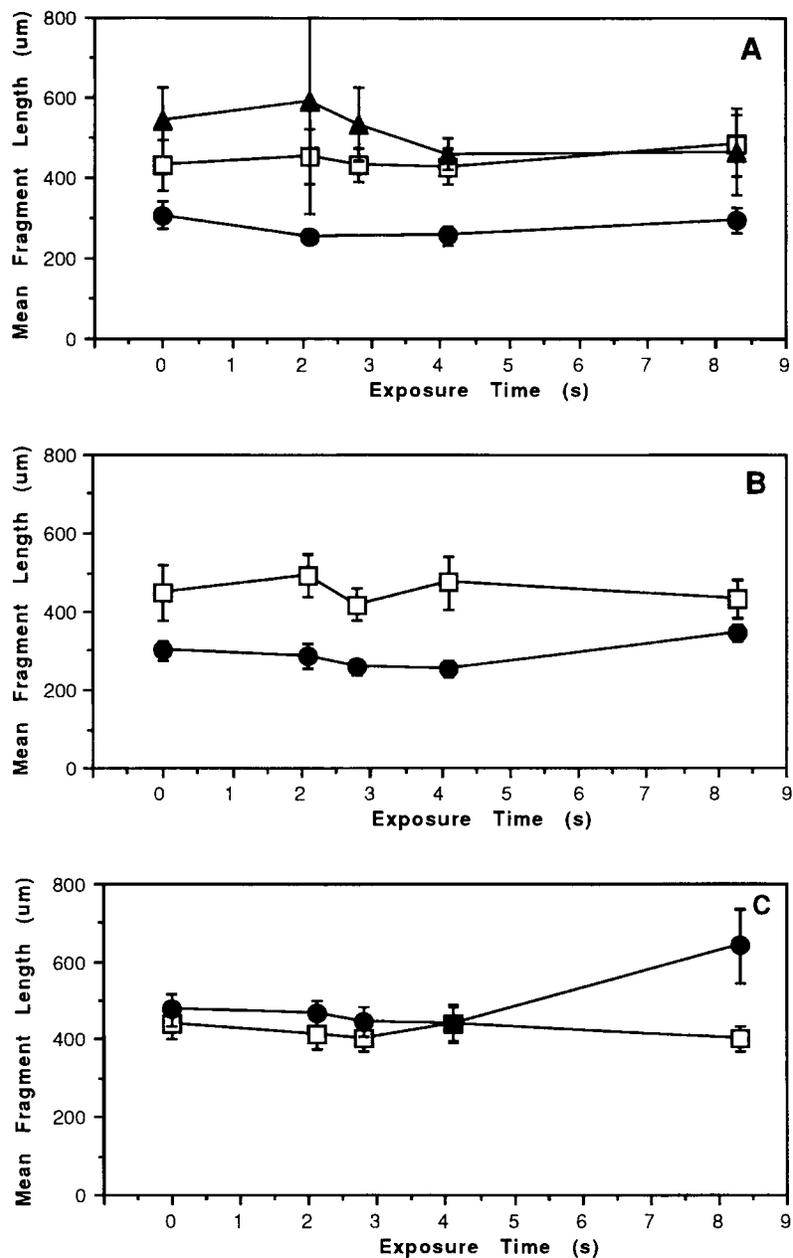


Figure 2 Mean and 95% confidence intervals of the mean fragment length from the embedded single-filament tests. The filaments were exposed to 24 W plasma in atmospheres of argon (Panel A), oxygen (Panel B), and ammonia (Panel C). Data from filaments coated directly with polycarbonate are represented by closed symbols, whereas the open symbols represent data from filaments exposed to air for 1 h before coating.

plasma treatment. This result indicates that the mild plasma exposure used in these experiments did not change the tensile properties of the filaments. This is consistent with our previous observations of the effects of plasma on the tensile failure load of organic fibers.²³

SEM Evaluation of Single Filaments

SEM micrographs revealed small flaws such as fibrils, gouges, and grooves that were randomly distributed along the otherwise smooth filaments. The micrographs were similar to those published previ-

Table II Tensile Failure Load of Several Individual Kevlar 49 Filaments from the Same Tow

Sample	n	Failure Load (mN)		95% Confidence Intervals (mN)	
		Mean	SD	Upper	Lower
Kevlar filament A	13	389	38	413	366
Kevlar filament B	13	432	57	466	397
Kevlar filament C	13	374	58	409	338
Kevlar filament D	13	470	58	505	434
Kevlar filament E	15	468	53	497	438
Kevlar filament F	15	454	47	481	428
Kevlar filament G	14	376	65	413	338
Kevlar filament H	15	393	51	422	365
Kevlar filament I	14	432	40	456	409

Table III Tensile Data on Single Kevlar 49 Filaments Subjected to Various Plasma Treatments

Plasma Exposure (Seconds)	n	Failure Load (mN)		95% Confidence Intervals (mN)	
		Mean	SD	Upper	Lower
Argon, 0	13	431	57	466	397
Argon, 2.1	12	449	86	504	394
Argon, 2.8	12	439	61	478	401
Argon, 4.1	13	447	49	477	418
Argon, 8.3	13	401	63	439	363
Oxygen, 0	13	374	58	409	338
Oxygen, 2.1	13	351	109	417	285
Oxygen, 2.8	13	411	45	438	383
Oxygen, 4.1	13	395	73	439	351
Oxygen, 8.3	12	418	76	467	369
Ammonia, 0	13	389	38	413	366
Ammonia, 2.8	12	379	48	409	340
Ammonia, 4.1	12	393	60	431	355
Ammonia, 8.3	13	376	43	402	349

ously.³ Some sections of filaments had extensive but random mechanical damage. It is important to note that these flaws were observed in both processed and unprocessed filaments. Qualitatively, no differences were noted in the average physical appearance of any of the plasma-processed filaments.

Filament Diameter

The results of the filament average diameter measurements have been presented previously⁶ and are only summarized here. The average diameter of unprocessed filaments in a tow is about 12.0 μm. The SEM measurements of diameter taken on filaments before and after plasma processing showed no significant difference in filament diameter. This is

consistent with the results of Allred et al.²⁴ who found no change in the surface area of Kevlar fabric that had been exposed to ammonia plasma for 3600 s.

FTIR Spectroscopy

A photoacoustic FTIR spectrum of an unprocessed tow and of a filament exposed to oxygen plasma for 8.3 s has been previously published.⁶ No changes in

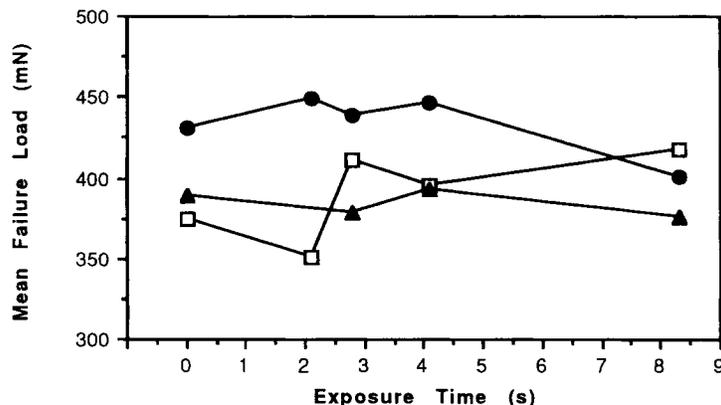


Figure 3 Mean tensile load (mN) of single Kevlar 49 filaments exposed to (●) argon, (□) oxygen, and (▲) ammonia plasmas.

chemical functionality are observed from the spectrum of the plasma-treated filament. Photoacoustic infrared analysis penetrates and samples the fiber to a depth of about $5\ \mu\text{m}$,²⁵ thus sampling most of the volume of the fiber. The lack of spectral changes suggests that any chemical changes caused by the plasma are small and are limited to the surface.

DISCUSSION

In previous reports in which the embedded single-filament test has been applied to more brittle fibers (such as carbon, SiC, and glass fibers), the stress birefringence nodes in the matrix were adjacent to points of complete transverse fracture of the fiber. Kevlar is known to break in a fibrillar manner over a length of 20–50 fiber diameters,²⁶ and thus the breaks may not be easily visualized. However, a fibrillar break will still transfer the load to the matrix adjacent to the region of failure, thus producing the birefringence nodes and revealing the points of failure in the Kevlar filaments. Recently, Jahankhani and Galiotis published a study of a single Kevlar fiber embedded in an epoxy matrix, and they showed such a fracture of Kevlar in epoxy.²⁷ Using Raman spectroscopy, they showed that the stress on the fiber region of failure dropped to almost zero. This observation is significant in that it supports the assumptions of the shear lag model from which eq. (1) was derived, further supporting the embedded filament model as a technique for studying interfacial shear strength.

The average distances between stress concentration sites, reported in Table I, give the value of \bar{l} defined in Eqs. (2) and (3). Equation (3) indicates that in addition to interfacial shear strength the filament diameter and tensile load at failure also contribute to the experimentally measured value of \bar{l} . To evaluate whether changes in \bar{l} are caused only by changes in interfacial shear strength produced by plasma treatment, one must properly account for any changes in filament diameter and failure load that may also have occurred during plasma processing. As discussed previously, the variation in diameter and strength along the length of a filament has been shown to be small, and our results have shown that the plasma exposures did not change the filament diameter or the failure load. Therefore, along the length of a single filament, L_f and d are constant, and a significant change in \bar{l} can be attributed directly to a significant change in τ .

We will now carefully examine the data of Table I and Figure 2 for significant changes in \bar{l} and τ .

Since the air-quenched samples and the direct-coated samples were taken from different filaments, the \bar{l} values cannot be directly compared. However, when the seven filaments were processed without plasma exposure (exposure time of 0 s), they experienced very similar plasma and coating processes and would be expected to have similar values of interfacial adhesion. Therefore, the difference in \bar{l} with no plasma exposure is presumed to represent the filament-to-filament variations in the diameter and failure load of the seven filaments. If this is the case, one would not expect the variance of the \bar{l} values to be less than the variance of the failure loads, and a statistical F test (comparison of variances) shows this to be true (0.05 level).

To examine the effects of plasma processing followed by direct coating or followed by air quench, the variability in d and L_f of each different filament was accounted for by subtracting the arithmetic mean of the \bar{l} values of the nonplasma-treated segment of each filament from all other \bar{l} values on the same filament. This normalization procedure effectively slides all the data to a common starting point with the nontreated \bar{l} of each filament at zero. Normalization by subtraction was considered to be superior to normalization by division because it maintained the relationship and magnitude of variations within the data. This normalization procedure was examined by comparing the normalized \bar{l} data for duplicate experiments on the two different filaments processed in argon and directly coated with thermoplastic. A 2-factor ANOVA on the normalized data showed that there was no significant difference that could be attributed to the use of two different filaments. Therefore, the normalized \bar{l} data for these two filaments was averaged for further analysis. Figure 4 shows the normalized \bar{l} data in bar graph form with error bars representing the 95% confidence interval around the sample mean.

Having accounted for inherent variation in d and L_f between filaments, we now turn our attention to any possible variations in these parameters caused by the plasma treatment. The effects of the independent variables of plasma gas, plasma exposure, and treatment were determined by a 3-factor ANOVA. The results of the ANOVA are summarized in Table IV, which shows that the main effect of plasma exposure time was statistically significant at the .05 level. In addition to the two-way interactions of gas \times treatment and treatment \times exposure, the three-way interaction of gas \times treatment \times exposure was also found to be statistically significant. This means that a significant change in adhesion is dependent upon appropriate levels all three of the fac-

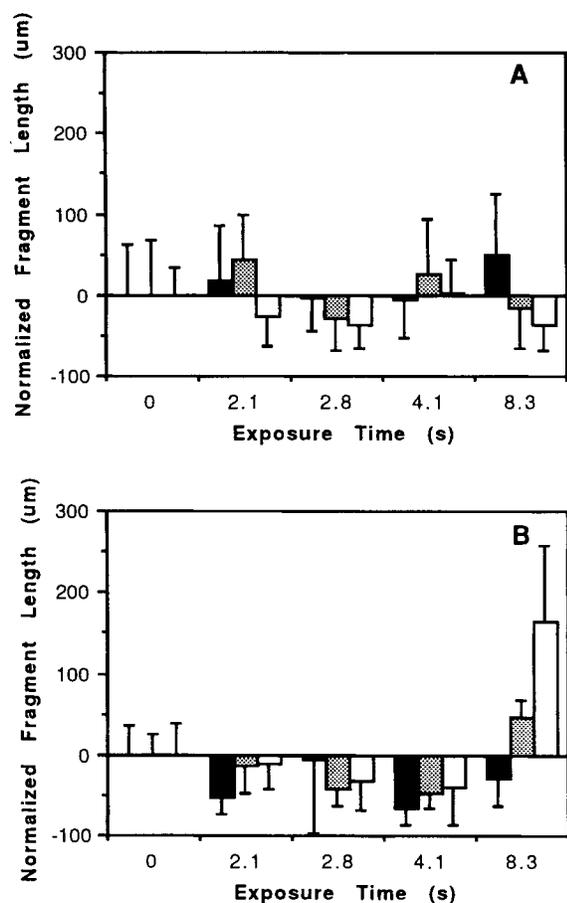


Figure 4 Normalized mean fragment lengths of Kevlar coated with polycarbonate (A) after 1 h of exposure to air and (B) coated immediately after plasma treatment. The shading of the bar represents exposure to (solid) argon, (gray) oxygen, and (white) ammonia plasmas.

tors acting in concert and that the effects of the factors (gas, treatment, or exposure time) are not linearly additive, but that the factors interact in some manner.²⁸

Because the three-way interaction was significant, it required that all the independent variables must be considered when attempting to find a minimum value of \bar{l} . Thus, it was necessary to break down the three-way interaction to determine which of the combinations of variables produced \bar{l} values significantly different from the others. A 1-factor ANOVA performed on each of the filament samples showed that none of the variables (gas species or processing time), when associated with the air-quench treatment, produced \bar{l} values that were significantly different from one another.

However, for the direct-coating treatment and a specific gas, the ANOVA revealed that some of the exposure times did produce \bar{l} values that were significantly different from the others. Therefore, three different post-hoc procedures (Duncan, Tukey-Kramer, and Games-Howell) were applied to determine which experimental parameters produced significant differences. The results of the post-hoc tests are summarized in Table V, which is read by selecting two plasma exposure times to be compared: one in a column and the other in a row. A numeral at the intersection of the row and column indicates the type of post-hoc procedure that found the \bar{l} values to be significantly different. A discussion of each of these post-hoc procedures can be found in Hochberg and Tamhane.²⁸ Because the Duncan post-hoc procedure was more liberal than the others in assigning significance, only the combinations that had significance indicated by two or three post-hoc procedures were considered truly significant.

The post-hoc analyses on the 1-factor ANOVA results showed that for any plasma gas with the direct-coating treatment the different plasma exposure times produced significant changes in the normalized values of \bar{l} . The set of parameters that displayed the largest decrease in the value of \bar{l} was argon plasma, direct coating, and 4.1 s of plasma exposure. These processing parameters resulted in a 16.4%

Table IV ANOVA Summary for Normalized \bar{l} Data

Independent Variable	df	SS	MS	F-Value	P-Value
Gas species	2	166.438	83.219	0.418	0.6584
Treatment (direct or air-quenched)	1	154.779	154.779	0.778	0.3781
Exposure time	4	3,840.697	960.174	4.823	0.0007
Gas × treatment	2	3,500.820	1750.410	8.793	0.0002
Gas × exposure time	8	2,309.323	288.665	1.450	0.1713
Treatment × exposure time	4	4,366.124	1091.531	5.483	0.0002
Gas × treatment × exposure time	8	4,001.782	500.223	2.513	0.0104
Residuals	1166	232,118.220	199.072		

Dependent variable: normalized \bar{l} data.

Table V The Effect of Processing Parameters on \bar{l} Values

	0 s	2.1 s	2.8 s	4.1 s	8.3 s
Fixed parameters: argon plasma, direct-coating treatment					
0 s		—	—	1,2,3	—
2.1 s	—		—	—	—
2.8 s	—	—		1	—
4.1 s	1,2,3	—	1		—
8.3 s	—	—	—	—	
Fixed parameters: oxygen plasma, direct-coating treatment					
0 s		—	1	1,2,3	1
2.1 s	—		—	—	1,2,3
2.8 s	1	—		—	1,2,3
4.1 s	1,2,3	—	—		1,2,3
8.3 s	1	1,2,3	1,2,3	1,2,3	
Fixed parameters: ammonia plasma, direct-coating treatment					
0 s		—	—	—	1,2,3
2.1 s	—		—	—	1,2,3
2.8 s	—	—		—	1,2,3
4.1 s	—	—	—		1,2,3
8.3 s	1,2,3	1,2,3	1,2,3	1,2,3	

—, Not a significant difference at the 0.05 level. 1, Significant difference at the .05 level, Duncan New Multiple Range post-hoc. 2, Significant difference at the .05 level, Tukey-Kramer post-hoc. 3, Significant difference at the .05 level, Games-Howell post-hoc.

decrease in the observed \bar{l} (compared to that of no plasma treatment on the same filament), which corresponds to an increase in τ of 19.6%. Oxygen plasma, direct coating, and 4.1 s of exposure showed a 15.5% decrease in the observed \bar{l} (compared to its respective nonexposure value), which corresponds to an increase in τ of 18.3%. The \bar{l} values for these two sets of parameters were not significantly different. Therefore, it was concluded that either argon or oxygen plasma with the direct coating treatment and 4.1 s of plasma exposure reduced the \bar{l} values by about 16%.

Surprisingly, a significant increase in \bar{l} was noted for some combinations of processing parameters. The combination of ammonia plasma, direct coating, and 8.3 s of exposure produced an \bar{l} value that was 34.3% higher than its nonexposed control value, indicative of decreased interfacial adhesion. A reduction in adhesion was also found for the combination of oxygen plasma, direct coating, and 8.3 s of exposure. This produced an increase in \bar{l} of 15.6% over

the nonexposed control value, but significance was only assigned by the more liberal Duncan procedure, and therefore this result may not be truly significant.

In addition to the objective statistical analysis presented above, there are some interesting trends in the \bar{l} data that merit discussion. First, there are several trends that the directly coated samples appeared to follow irrespective of the plasma gas species. (The air-quenched samples appeared to follow no trends.) For all of the plasma exposure times between 2.1 and 4.1 s, the values of \bar{l} decreased from the control values (see Fig. 4). Also, the minimum \bar{l} was at 4.1 s, and this minimum was significant for the samples subjected to Ar and O₂ plasma. The \bar{l} value at 8.3 s plasma exposure increased from that at 4.1 s exposure, and this increase was significant for O₂ and NH₃ plasma treatment. These data indicate that irrespective of plasma gas species the increase in interfacial adhesion apparently passes through a maximum somewhere near 4 s of plasma exposure. Prolonged plasma exposure beyond this point may not necessarily increase adhesion and, in fact, may decrease adhesion.

Second, the 1 h air quench is effective in precluding both the increase and the decrease (at 8.3 s) in adhesion of Kevlar to the thermoplastic. This suggests that the changes in adhesion are caused by some physicochemical interactions that are eliminated by exposure to air. This observation is consistent with our initial hypothesis that free radicals may be involved in the adhesive interaction. Although the exact nature of the interaction remains unknown, we can eliminate mechanical roughening of the fiber as a possible cause by the simple argument that if the roughness of the fiber was increased the effect on adhesion would not be eliminated by exposure to air.

Third, ammonia plasma does not appear to be nearly as effective as argon or oxygen plasma in increasing adhesion between Kevlar and polycarbonate. This suggests that the chemical nature of the plasma plays a role in promoting the adhesive interaction. Argon plasma consists of electrons, Ar ions, neutral atoms, and UV photons. The photons can penetrate into the bulk of the polymer substrate and cause cross-linking or other interactions.⁸ The electrons and ions, accelerated by the RF field, strike the polymer surface with enough energy to break covalent bonds,^{13,29} thus forming free radicals on the surface. In an oxygen plasma, free radicals in the form of atomic oxygen are present as well as the electrons, ions, and photons. Upon collision with the polymer substrate, these radicals can extract hydrogen atoms, leaving radicals behind on the surface. An ammonia plasma also contains radicals and

molecular fragments in many forms, but experimental observations suggest that ammonia plasmas are less reactive toward polymer substrates than are oxygen or argon plasmas.^{17,30} Ammonia plasmas are known to place amine groups on Kevlar,²⁴ whereas Ar and O₂ plasmas incorporate oxygen functionality into polymer surfaces.⁸ However, these chemical modifications are assumed to be present on both the air-quenched and the directly-coated Kevlar. The fact that the air-quenched fibers showed no increased adhesion suggests that any such chemical modifications resulting from this treatment are not sufficient alone to increase adhesion to polycarbonate.

A final point to address is whether the observation of a maximum in interfacial adhesion at about 4 s of plasma processing is consistent with the hypothesis that free radicals are involved in the adhesion mechanism. Suzuki et al.¹⁴ showed that when polyethylene (PE) was exposed to an RF plasma and then exposed to air the concentration of peroxide on the PE surface went through a maximum when plotted against plasma exposure time. In fact, in a 24 W argon plasma, the maximum in peroxide concentration was observed at 5 s of plasma processing. Oxygen and hydrogen (but not N₂) plasmas also produced maximums in peroxide concentrations at about 10 s exposure to an 11.5 W plasma. Suzuki et al. hypothesized that the maximum in peroxide concentration corresponded to a maximum in free radicals created on the PE surface. They further postulated that the maximum in free-radical concentration resulted from two competitive reactions: one reaction that generated free radicals from exposure to plasma and the other reaction in which two radicals combined to form cross-links. Shi et al.³¹ made a similar observation that the radical concentration on polyolefins reached a maximum after 15 s of Ar or O₂ plasma treatment.

Eggert et al. also concluded that in the oxygen plasma etching of poly(vinyl alcohol) two competitive reactions occur³²: one leading to cross-linking of the macromolecules and the other leading to degradation. The presence of two such competing reactions in our experiments with Kevlar and polycarbonate may be responsible for the observed increase and then decrease in adhesion. A possible scenario, e.g., might be that free radicals generated on the Kevlar are transferred to polycarbonate (e.g., by hydrogen abstraction) when the Kevlar is coated. These radicals on the thermoplastic could combine with other radicals on Kevlar, forming interfacial covalent bonds. In a competing set of reactions, the radicals on the fiber or the thermoplastic may cause chain scission of the macromolecules, thus reducing

the mechanical strength in the interphase region. At long processing times, the degradation reactions may weaken the interphase region sufficiently to counteract any increases in adhesion from interfacial covalent bonding. Other more speculative scenarios involve arguments that coating the fiber with molten polycarbonate and maintaining the elevated temperature for a couple of minutes (while the coating radiatively cooled) might provide energy and time for accelerated free-radical degradation of the interphase region that the air-quenched fiber does not experience. These scenarios are speculative and await further experimental study.

So far we have only discussed relative changes in interfacial shear strength because calculating the absolute values of τ require the knowledge of the failure load and diameter of each filament. We can, however, use average values of L_f (421 mN) and d (12 μm) and a K of 0.889 [see eq. (3)] to estimate a mean and standard error of the interfacial shear strengths. These values are 49 ± 9 MPa for all the nonplasma-treated samples and 45 ± 3 MPa for all the air-quenched samples. The sample that was directly coated following 4.1 s of Ar plasma had a τ of 60 MPa. This is comparable to interfacial shear stress values for Kevlar in various epoxy resins that range from 17 to 62 MPa as measured by filament pullout, critical fragment length, and Raman spectroscopy.²⁷

We can also estimate the surface density of bonds formed across the interface if we assume that an increase in τ of 10 MPa is due to formation of carbon-carbon bonds that have a strength of 5.8×10^{-19} J/bond. If we assume that the bond must be stretched by about 0.5 nm to break, the bond density is calculated to be about 0.009 bonds/nm². This density is fairly low compared to what others have achieved using organic reactions,³³ and our goal in future research is to increase this bond density and, thus, increase the interfacial strength.

CONCLUSIONS

The novel processing technique presented in this report is effective in increasing interfacial shear strength between Kevlar 49 and polycarbonate as measured by the embedded single-filament tensile test. The processing technique involves exposing the Kevlar fiber to a radio-frequency plasma discharge (RFPD) and then immediately coating the fiber with the thermoplastic while still in the low-pressure environment of the plasma reactor. In argon and oxygen plasmas at 24 W, the interfacial strength was maximized at 4.1 s of plasma exposure, producing an increase of 20 and 18%, respectively. Ammonia

plasma was ineffective in increasing adhesion and actually decreased adhesion at 8.3 s of exposure. When the fibers were exposed to air for 1 h, no significant change in interfacial shear strength was noted for any plasma gas species or exposure time.

These results are consistent with the hypothesis that the plasma generates free radicals on the fiber surface, which can then initiate formation of covalent bonds with the applied thermoplastic coating. If the radicals are exposed to atmospheric oxygen or other reactive gases before the thermoplastic coating operation, the radicals are extinguished or are otherwise rendered ineffective toward increasing interfacial strength.

The maximum in adhesion at about 4 s of plasma processing is speculated to result from two competing reactions: In one reaction, the radicals on the fiber, or those transferred to the thermoplastic, create interfacial covalent bonds. In the competing reaction, these radicals cause degradation of the polymer and a weakening of the interphase region. The mild plasma conditions used in this study do not appear to reduce the strength or the diameter of the fibers, nor do they change the surface roughness.

Although this new processing technology has been demonstrated only on the Kevlar/polycarbonate system, we believe that it may be applicable to organic fibers and thermoplastic matrix materials in general. Theoretically, the technique only requires a fiber upon which free radicals can be generated and a matrix to which free-radical-initiated bonding can occur.

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DEDICATION

This paper is dedicated to the memory of our friend and colleague, Dr. Bill Bascom, who pioneered many studies of interfacial behavior in polymeric composite systems.

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