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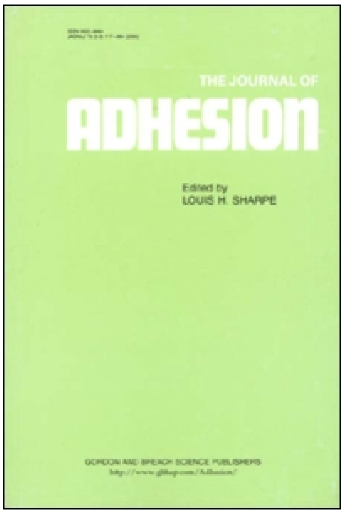

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Effect of Plasma Treatment on the Adhesion of Carbon Fibers to Thermoplastic Polymers

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Effect of Plasma Treatment on the Adhesion of Carbon Fibers to Thermoplastic Polymers

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A study has been made of the effect of RF plasmas on the adhesion of carbon fibers to polycarbonate and polysulfone. Treatment in oxygen plasma significantly increased the adhesion to both polymers. The effect is lost if the treated fiber is stored in air for a week. Surface analysis using XPS indicated an increase in atom percent oxygen but the spectra were unchanged for the stored fibers even though there had been a significant loss in adhesion. It is suggested that oxygen surface functionality is responsible for the improved adhesion but that this surface activation is lost on storage. Due to a sampling depth of 5–10 nm, XPS would not be expected to detect this small change in surface functionality.

KEY WORDS Adhesion; carbon fiber; plasma treatment; single embedded filament test; microcomposite; thermoplastic polymers; XPS analysis.

INTRODUCTION

Many commercial carbon fibers used as reinforcement in polymer matrix composites exhibit low adhesion to thermoplastic polymers. This low adhesion is evident from scanning electron microscopy examination of the fracture surfaces of these composites.[1,2] Recently, the adhesion of AS1 and AS4 fibers to a series of thermoplastic polymers was found to be significantly lower when compared with thermosetting epoxy polymers using a single filament adhesion test.[3]

Exposure to radio frequency plasmas of various gases has been shown to be effective in improving the adhesion of various fibers to matrix polymers[4] including carbon fiber.[5,6,7] In addition, a number of studies have been made of the effect of these plasma treatments on the surface energetics of carbon fiber surfaces.[8,9,10]

In the work reported here, AS1 and AS4 fibers were subjected to radio frequency plasmas in various gases and then tested for adhesion to two

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thermoplastic polymers, polycarbonate and polysulfone, using the single embedded filament test. The untreated fibers have been shown to exhibit low adhesion to these polymers.[3] The effects of these treatments on the fiber surface chemistry were monitored using X-ray photoelectron spectroscopy (XPS) and the effect on surface topography was followed using scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The carbon fibers, Magnamite AS1 and AS4, were obtained from Hercules Aerospace (Magna, UT, U.S.A.) with the manufacturers standard surface treatment but no sizing. The pertinent fiber properties are listed in Table I. The fibers used in this study were taken from the same spools used in the work described in Reference 3.

The polymers, polycarbonate (PC) and polysulfone (PS), were used as received from the manufacturers and were also from the same batches used in Reference 3. The pertinent properties of the polymers are listed in Table II.

The gases used in the plasma experiments were anhydrous ammonia (99.99%), argon (99.99%), nitrogen (99.995%) and oxygen (99.6%).

Plasma treatment

A radio frequency discharge plasma which creates a "cold" or "nonequilibrium" plasma was generated using the apparatus illustrated schematically in Figure 1. It

TABLE I
Carbon fiber properties

Fiber designation	Diameter d, μm	0° Laminate tensile properties Strength MPa (ksi)	Modulus GPa (Msi)	Elongation %
AS1	8.0	3103 (450)	228 (33)	1.32
AS4	6.84	3587 (520)	235 (34)	1.53

TABLE II
Polymer properties

Polymer	Tensile properties Strength MPa (ksi)	Modulus MPa (ksi)
Polycarbonate[a]	65 (95)	2400 (345)
Polysulfone[b]	70 (101)	2540 (365)

[a] General Electric Co., Lexan 101.
[b] Union Carbide Co., Udel.

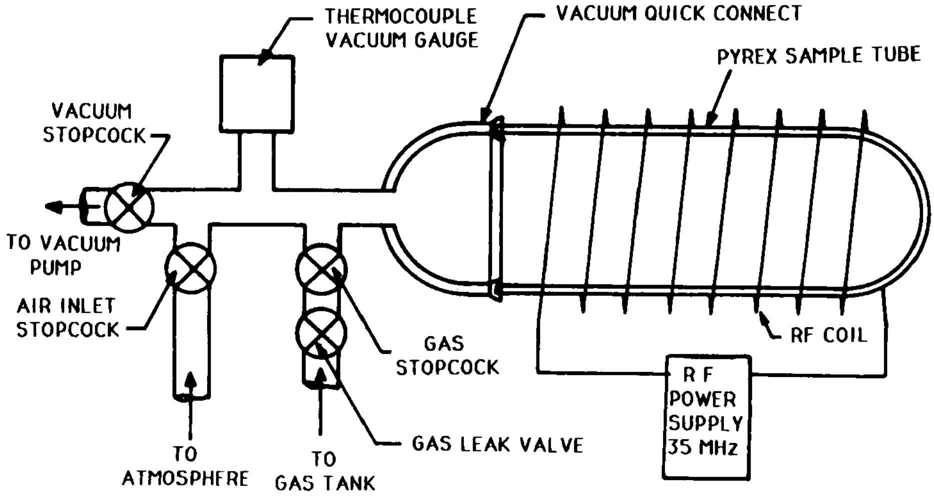

FIGURE 1 Schematic of RF plasma generator.

was built by Lyman and Smith[11] from a design similar to that of Gott and Baier.[12] The radio frequency energy was supplied by a 35 MHz generator. The diameter of the glass (Pyrex) discharge tube was 38 mm.

In order to obtain a uniform treatment, bundles of filaments were pulled from the 12,000 filament tows of carbon fibers and spread as thinly as possible on a glass support as shown in Figure 2. The carbon fibers were placed in the middle of the discharge chamber. The chamber was evacuated to 10 μm of mercury. The pressure was measured using a thermocouple vacuum gauge. The vacuum control stopcock was then closed and the gas control stopcock and the gas leak valve were both opened to introduce the desired treatment gas (argon, oxygen, nitrogen or ammonia). The chamber was evacuated again to 10 μm of mercury

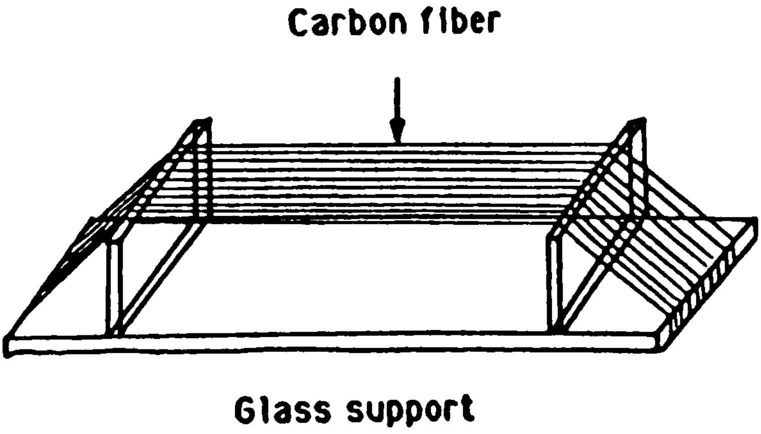

FIGURE 2 Arrangement for supporting carbon fibers on a glass frame for plasma treatment.

and the process repeated three to four times to make sure that only the desired gas was left in the chamber. Finally, with the vacuum still applied, the gas control stopcock was opened, and the gas leak valve was adjusted to attain a pressure of 200 μm of mercury. The radio frequency generator was then turned on to excite the gas. This low pressure was maintained during the treatment by a combination of continuous evacuation and gas inlet through the gas leak valve. After the plasma exposure was completed, the gas stopcock was closed and the system was evacuated to 10 μm of mercury. The air control stopcock was opened slowly to allow the chamber to return to atmospheric pressure.

Adhesion test method

The adhesion between fiber and polymer was measured using the embedded single filament test[13–18] which involves embedding a single filament in the polymer and pulling the specimen in tension using a micro-tensile test fixture that fits on the stage of an optical microscope. The specimen is stressed until the fiber is fully fragmented at which point the fragment length is equal to the critical length, l_c. The critical length is related to the fiber strength, σ_f, the fiber diameter, d, and the boundary shear strength, τ_c. If the interfacial shear strength exceeds the shear yield strength of the polymer then $\tau_c = \tau_y$, the shear yield strength of the polymer. If the interfacial shear strength is less than the shear yield strength of the polymer then $\tau_c = \tau_i$, the interfacial shear strength. Based on classical shear lag theory[19] the critical aspect ratio is given by,

$$\frac{l_c}{d} = \frac{1}{2\tau_c} \Sigma \sigma_f \qquad (1)$$

where $\Sigma\sigma_f$ denotes the fact that the carbon fiber tensile strength has a broad statistical distribution. In principle, the boundary shear strength, τ_y or τ_i, could be computed from the critical length measurements. However, an exact analytical form for the statistical strength distribution *within a polymer matrix* is not available. Although simplifying assumptions can be made, the significance of the calculated shear strengths is uncertain. Consequently, the approach taken here and in References 3 and 18 is to consider the experimental data, l_c/d, as an inverse measure of the boundary shear strength. Obviously, comparisons of critical aspect ratios provide only a measure of relative bond strength. Moreover, care must be taken not to make comparisons when the fiber strength and strength distributions are likely to be significantly different, *e.g.*, comparing Type I *vs.* Type II fibers.

If the polymer is transparent and exhibits stress birefringence, then the experiment provides additional information from the birefringence pattern that forms at fiber breaks. In Figure 3, the birefringence characteristic of "strong" adhesion (3A) is compared with the birefringence observed for "weak" adhesion (3B). This birefringence is the result of shear stresses at the fiber-polymer

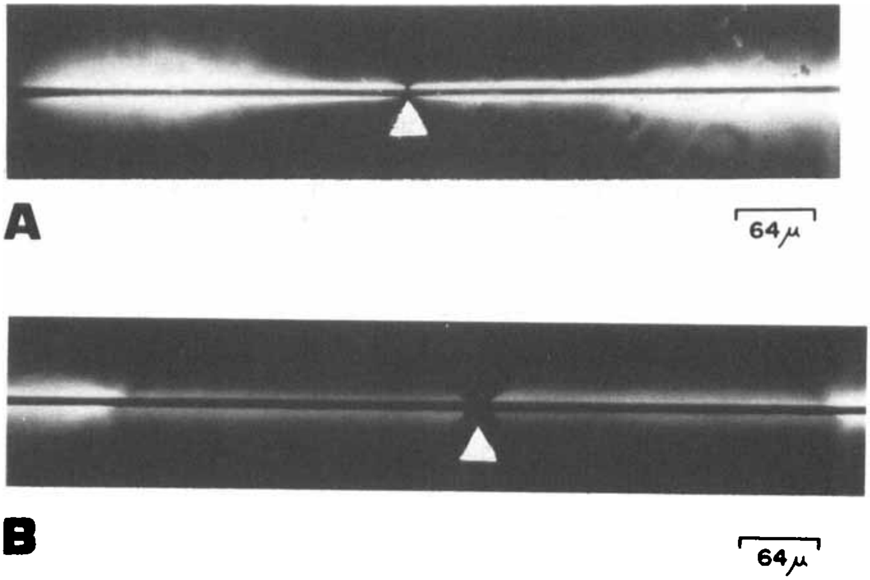

FIGURE 3 Stress birefringence characteristic of strong adhesion (A) and weak adhesion (B). White arrows indicate fiber breaks.

boundary close to the ends of a fiber break. In the case of strong adhesion, shear yielding of the polymer results in a "lip" of birefringence between the fiber ends and the principal birefringence node (Figure 3A). On the other hand, if the interface is weak in shear the birefringence nodes recede some distance from the fiber break as shown in Figure 3B. Further details concerning the stress distribution at fiber breaks can be found in References 16–18. For present purposes, this distinction between strong and weak adhesion is useful information when interpreting differences in the critical aspect ratios.

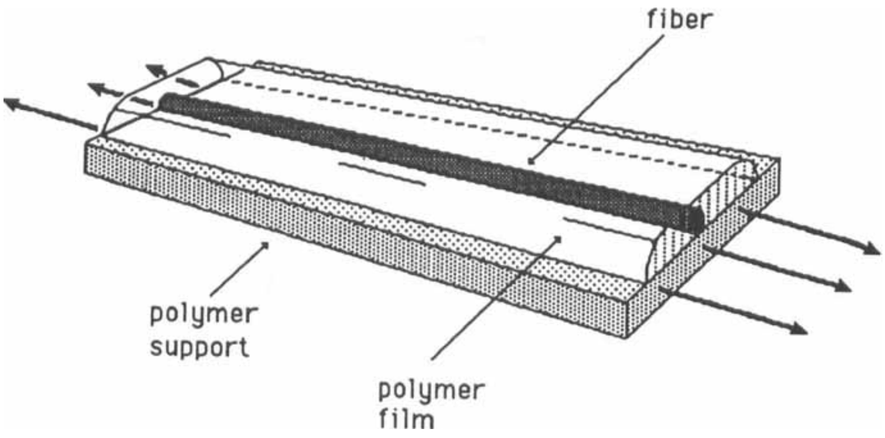

FIGURE 4 Schematic of specimen configuration for testing fibers in thermoplastic polymers.

The test specimens were prepared by placing a single filament on a small plate of the polymer and then coating the filament with the same polymer dissolved in methylene chloride (Figure 4). The coating was gently applied using a thin (3 mm) wood applicator until attaining a thickness of at least two fiber diameters. Trials at different coating thicknesses revealed no differences in the critical lengths even when the fiber was less than a fiber diameter below the coating surface. The solvent was removed by drying at 24°C for 24 hrs and then at 75°C for 16 hrs.

The specimens were placed in a tensile test fixture that fits on the stage of a light microscope and the load increased until there was no further fragmentation of the fiber and the fragment lengths correspond to the critical length. As would be expected from Eq. (1), the critical length exhibits a wide distribution due to the statistical variation of the fiber strength.[18] The data do not follow the two-parameter Weibull statistics so for the results reported here the statistical parameters were determined assuming a normal distribution of fiber fragment lengths. For each fiber/polymer combination, 10–12 specimens were tested and the fragment lengths combined and averaged. The statistical variance is reported as the standard error on the mean.

TABLE III
Effect of plasma treatments on critical aspect ratios

AS4 in Polycarbonate

Time	O_2		NH_3		N_2		Ar	
min.	l_c/d	sem*	l_c/d	sem	l_c/d	sem	l_c/d	sem
0	109	1.68	109	1.68	109	1.68	109	1.68
1	97	1.73	97	1.72	104	2.5	100	1.89
2	93	1.73	91	1.42	104	2.5	99	2.2
3	91	1.77	91	1.46	101	3.1	96	1.73
5	88	1.51	100	1.76	104	2.3	94	1.51
7	79	1.73	99	1.57	101	2.0	88	1.47
10	66	1.89						
AS4 in Polysulfone								
0	124	3.7	124	3.7			124	3.7
1	113	3.3	116	2.8			115	3.8
3	104	2.6	110	3.3			107	3.0
5	96	2.5	109	2.8			107	3.0
7	91	2.3	104	2.8			113	2.8
AS1 in Polycarbonate								
0	123	1.71	123	1.71	123	1.71	123	1.71
1	120	3.3	123	3.0	123	2.8	121	3.0
2	115	2.2	114	3.3	124	3.3	119	3.4
3	104	2.63	111	3.0	121	3.1	116	3.1
5	98	2.8	115	3.6	121	4.1	115	3.0
7	90	2.6	120	2.9	124	3.2	110	2.9
10	56	3.0						

* Standard error on the mean (of 10–12 specimens).

Surface analysis

The fiber surfaces were characterized using XPS. The spectrometer was a Hewlett–Packard 5950 B using Al Kα X-radiation. Data were analyzed on an HP 9845B computer. Scanning electron microscopy of the fiber surfaces was done using a Cambridge S-90 instrument.

RESULTS

The fibers were exposed to the various plasmas for times ranging from 1–10 min. Specimens were prepared within less than 3 min after exposure, the solvent allowed to evaporate and then tested for critical lengths. The results, expressed as critical aspect ratios, are presented in Table III. The average critical aspect ratios are plotted as a function of plasma treatment times in Figures 5–7.

Treatment in O_2 significantly decreased the critical aspect ratios in all three cases. The treatment in argon had a lesser effect on l_c/d. The other gases either had no effect or, in the case of NH_3 on AS4/PC (Figure 5), l_c/d went through a minimum at low (<4 min) exposure times.

The corresponding photoelastic stress birefringence patterns are shown in Figures 8–10 for AS4 and AS1 in polycarbonate after exposure to the O_2 plasma

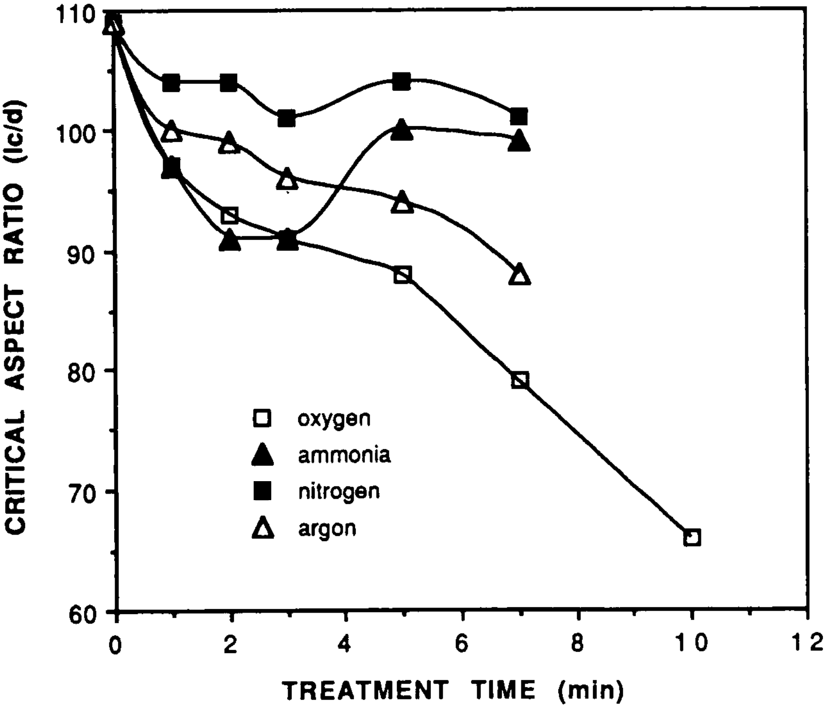

FIGURE 5 Stress birefringence at fiber breaks for AS1/polycarbonate after fibers treated (5 min) in ammonia (A), argon (B) and nitrogen (C) plasma. White arrows indicate fiber breaks.

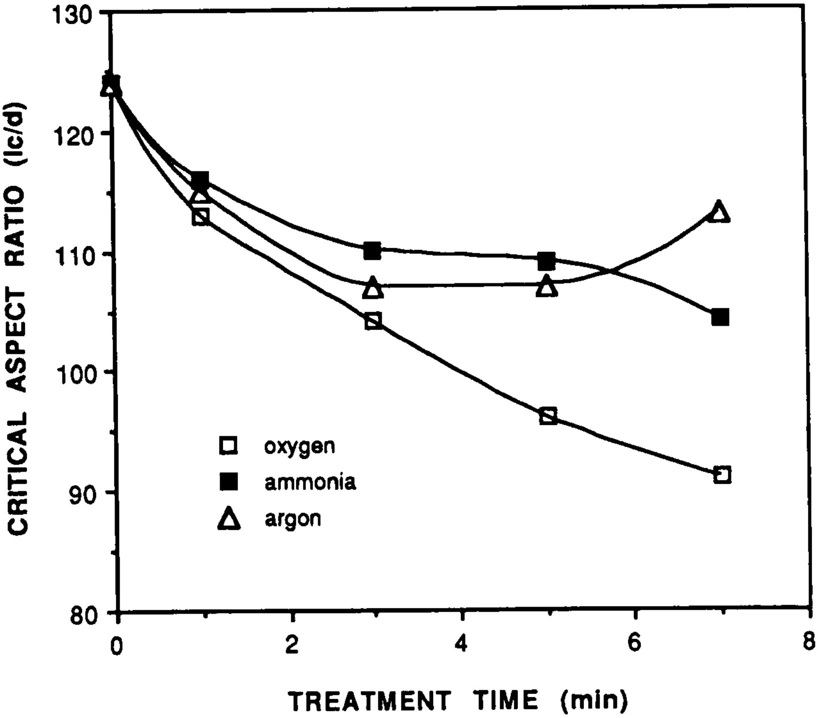

FIGURE 6 Effect of plasma treatment on the critical aspect ratio of AS4 in polysulfone.

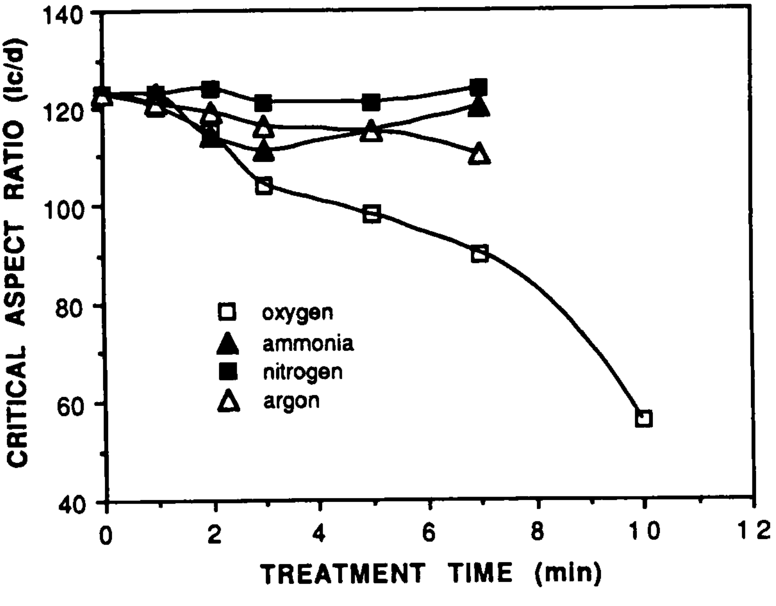

FIGURE 7 Effect of plasma treatment on the critical aspect ratio of AS1 in polycarbonate.

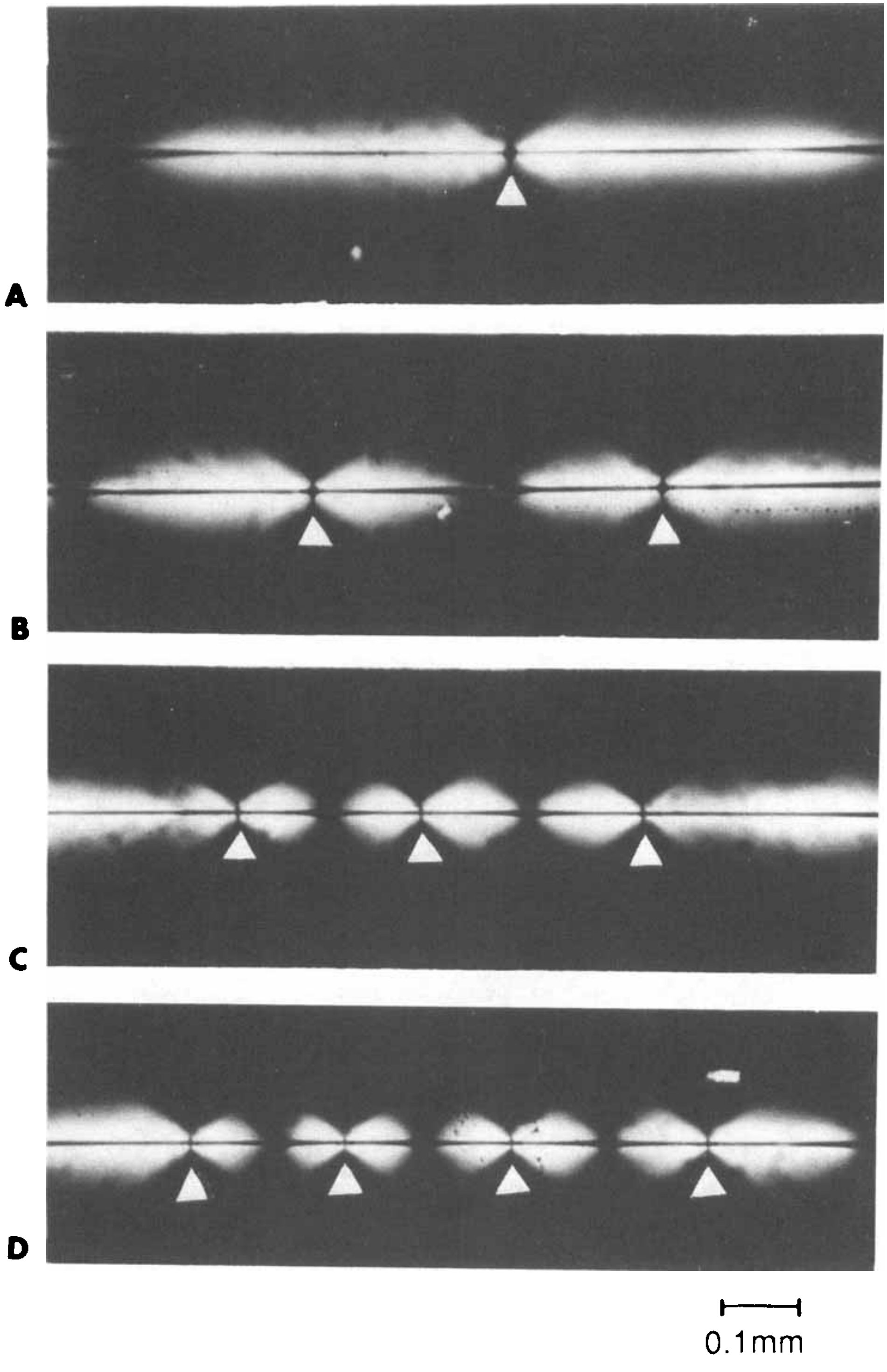

FIGURE 8 Stress birefringence at fiber breaks for AS4/polycarbonate after fiber plasma treatment in O_2 for 0 min (A), 1 min (B), 5 min (C) and 10 min (D). White arrows indicate fiber breaks.

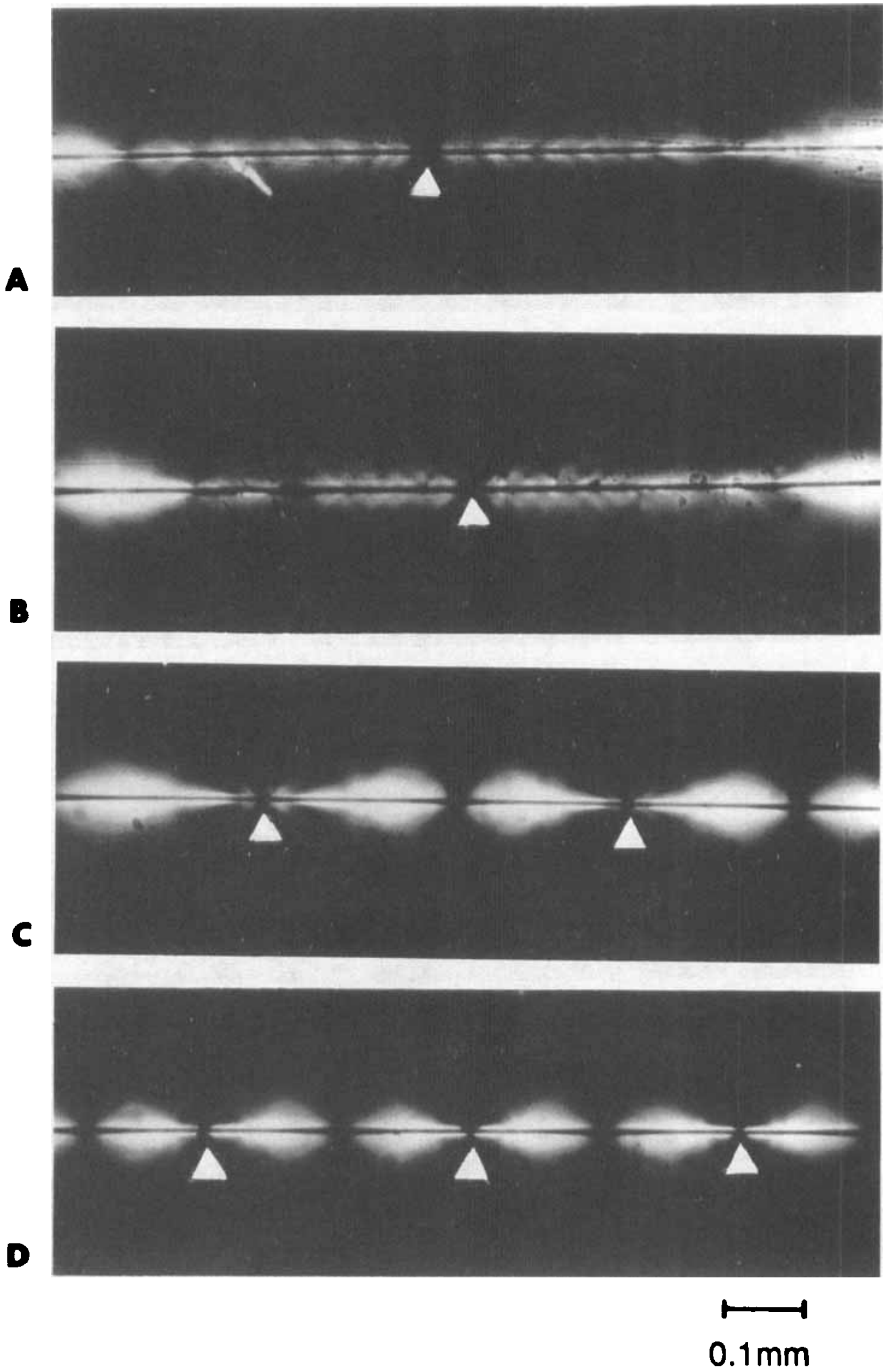

FIGURE 9 Stress birefringence at fiber breaks for AS1/polycarbonate after fiber plasma treatment in O_2 for 0 min (A), 1 min (B), 5 min (C) and 10 min (D). White arrows indicate fiber breaks.

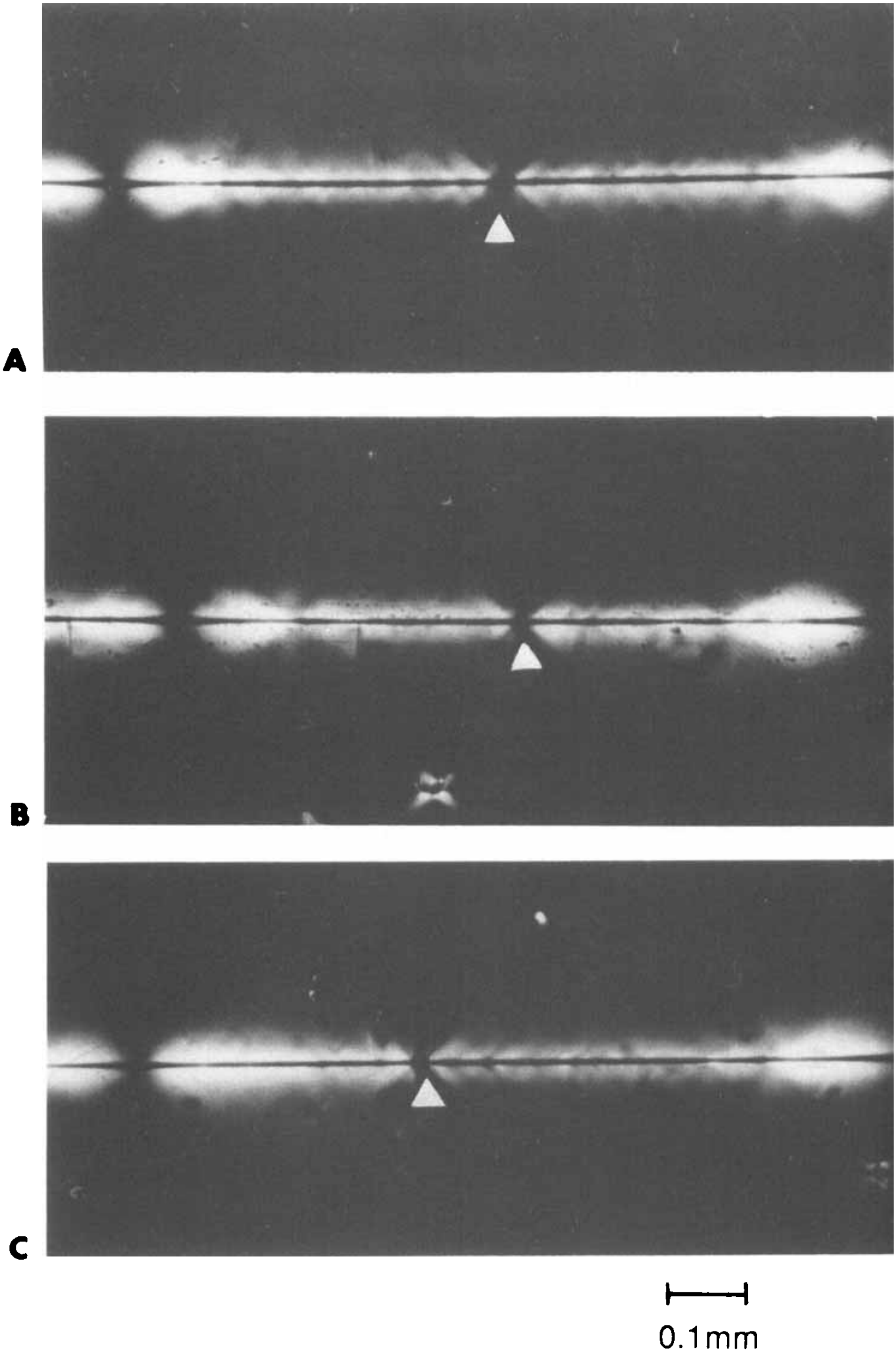

FIGURE 10 Stress birefringence at fiber breaks for AS1/polycarbonate after fibers treated (5 min) in ammonia (A), argon (B) and nitrogen (C) plasma. White arrows indicate fiber breaks.

TABLE IV
Critical lengths measured 7 days after treatment

AS1 in Polycarbonate

Treatment time (min)	0	1	3	5	7	10
Critical aspect ratio, l_c/d	123	123	123	119	116	113
Standard error on the mean	1.71	4.0	4.3	3.0	2.5	2.8

AS4 in Polycarbonate

Treatment time (min)	0	1	3	5	7	10
Critical aspect ratio, l_c/d	109	107	101	100	93	90
Standard error on the mean	1.68	2.8	2.6	1.77	2.0	1.69

and for AS4 in polycarbonate after treatment with NH_3, Ar and N_2. In Figures 8 and 9, the stress birefringence changed progressively from that characteristic of weak adhesion to that of strong adhesion with increasing exposure time to the O_2 plasma. These results are consistent with the change in the critical aspect ratio (Figures 5 and 6). The stress birefringence observed for AS1 fibers after 5 min exposure to NH_3, Ar and N_2 plasmas (Figure 10) are characteristic of weak adhesion and so are also consistent with the high critical aspect ratios in Figures 7.

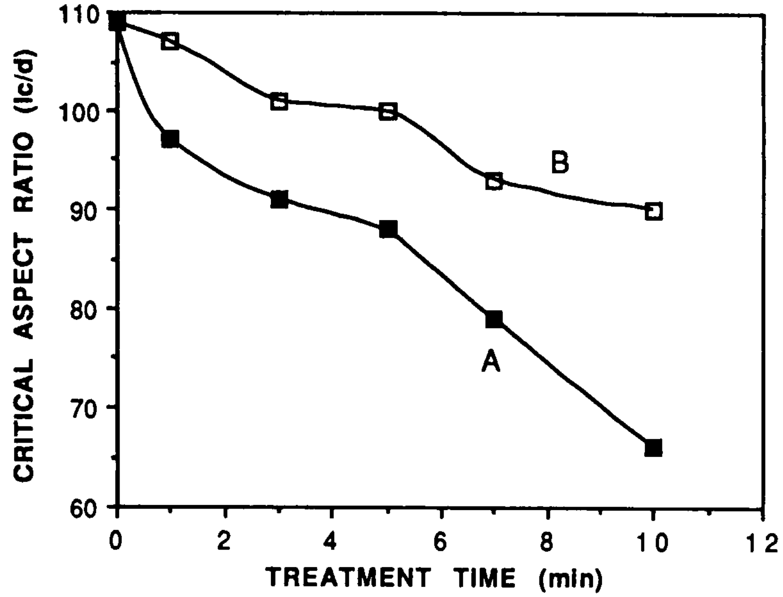

FIGURE 11 Critical aspect ratios of AS4 in polycarbonate after plasma treatment in O_2 tested within a few hours (A) and after storage of the treated fiber for 7 days (B).

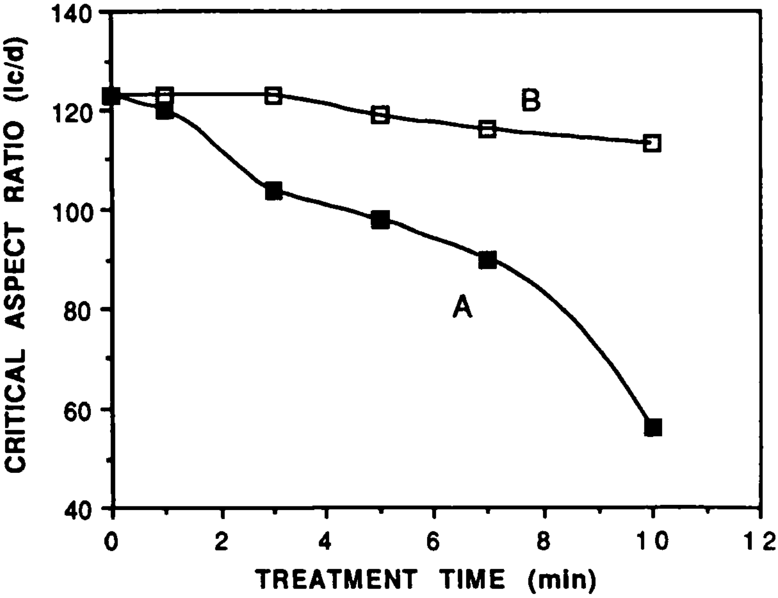

FIGURE 12 Critical aspect ratio of AS1 in polycarbonate after plasma treatment in O_2 and tested within a few hours (A) and after storage of the treated fiber for 7 days (B).

The possible loss in the effectiveness of the plasma treatments on the critical length was examined by storing treated fibers in a closed, clean glass container for 7 days before preparing and testing tensile specimens. The results of these experiments are presented in Table IV and Figures 11 and 12 for fibers treated in O_2 and then tested in polycarbonate. Quite clearly, there is a significant loss in the effect of the plasma treatment on the AS4 fiber (Figure 11) and a nearly complete loss in the case of the AS1 fiber (Figure 12).

Scanning electron microscopy photomicrographs of the untreated and treated fibers are shown in Figures 13–16. In Figure 13, the striations on the untreated AS1 fiber are the result of the spinning process used to produce the polyacrylonitrile (PAN) precursor. The PAN used to produce AS4 is smooth so that the resulting fiber has an essentially featureless surface (Figure 13). Treatment in NH_3 plasma for 7 min had no evident effect on the appearance of the AS4 fiber (Figure 14A). On the other hand, treatment in O_2 for 7 min resulted in speckling (small granules and pock marks) on the AS4 surface (Figure 14B). Treatment of the AS1 fiber in ammonia and in O_2 produced slightly speckled surfaces for both gases (Figure 15). Finally, Figure 16 shows that Ar and N_2 treatment of AS4 had no effect on the surface appearance. Examination of AS1 fibers treated with Ar and N_2 also showed no effect on the surface topography.

The effect of plasma treatment on the surface chemistry of the fibers was examined using XPS. The results are presented in Tables V and VI. Plasma treatment in O_2 resulted in a significant increase in the surface oxygen, especially in the case of the AS1 fiber. Plasma treatment in N_2 and Ar had no significant

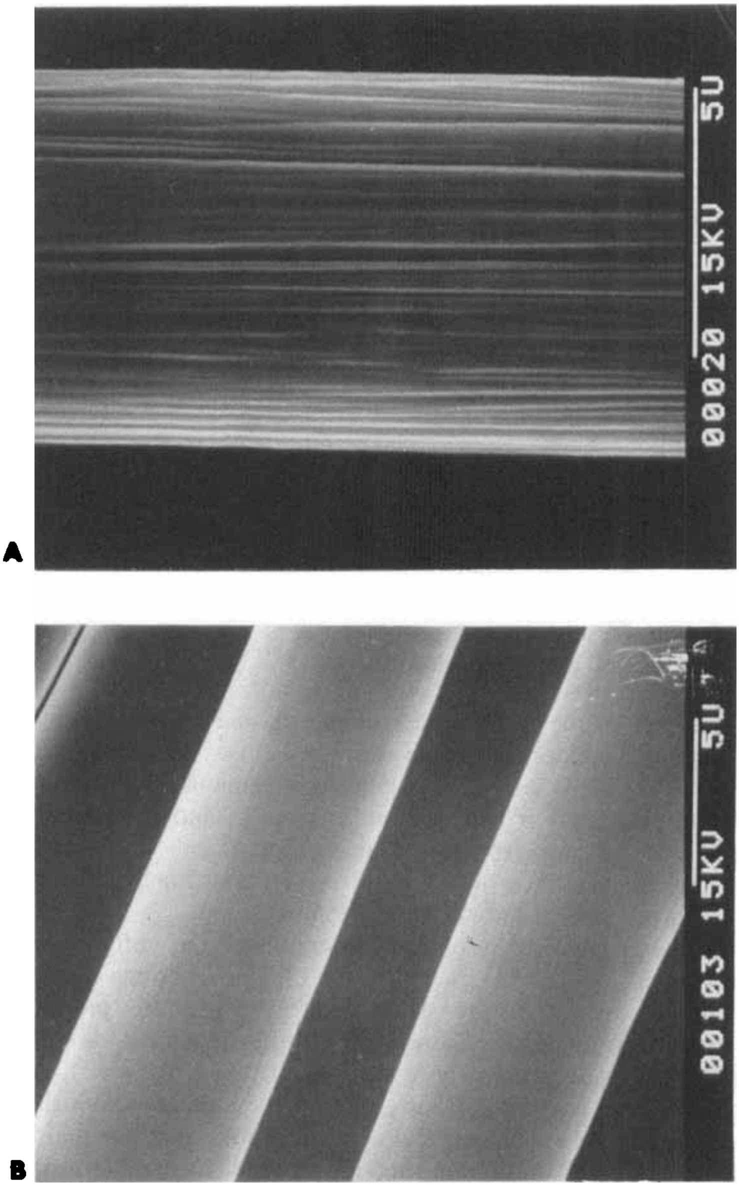

FIGURE 13 SEM photomicrographs of untreated AS1 (A) and AS4 (B) fibers.

effect on the XPS analyses of either fiber. Ammonia plasma treatment resulted in an increase in the nitrogen surface composition on both fibers.

In Table VII, the XPS analyses are compared for untreated AS4, AS4 treated in O_2 plasma and analyzed within a few minutes, and after 7 days storage. Note that storage of the treated fiber resulted in no measurable change in the atomic percent composition.

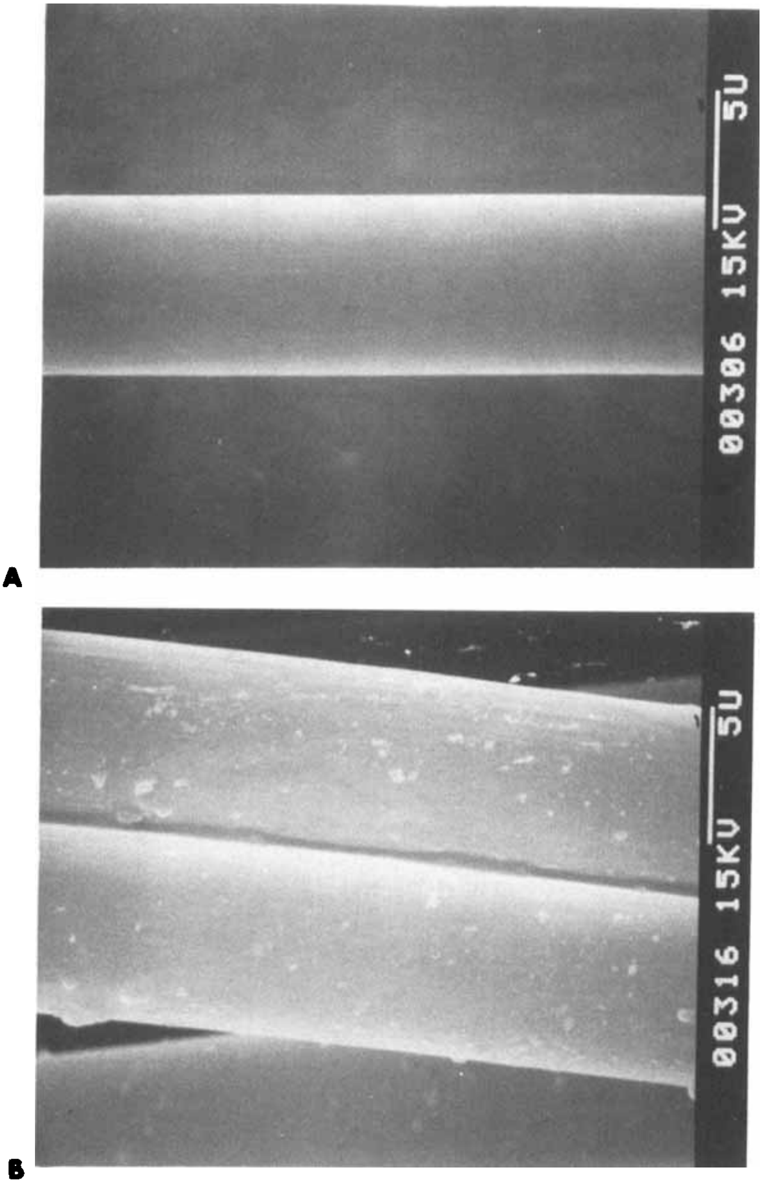

FIGURE 14 SEM photomicrographs of AS4 fibers after 7 min treatment in ammonia (A) and oxygen (B) plasmas.

The XPS C_{1s} spectra for untreated AS4, O_2 plasma treated AS4 fiber immediately after treatment and O_2 plasma treated AS4 fiber after 7 days of storage were obtained by computer least squares curve fitting (Surface Science, Mountain View, CA) in an effort to determine differences in the detailed chemical compositions. The results are presented in Table VIII. The O_2

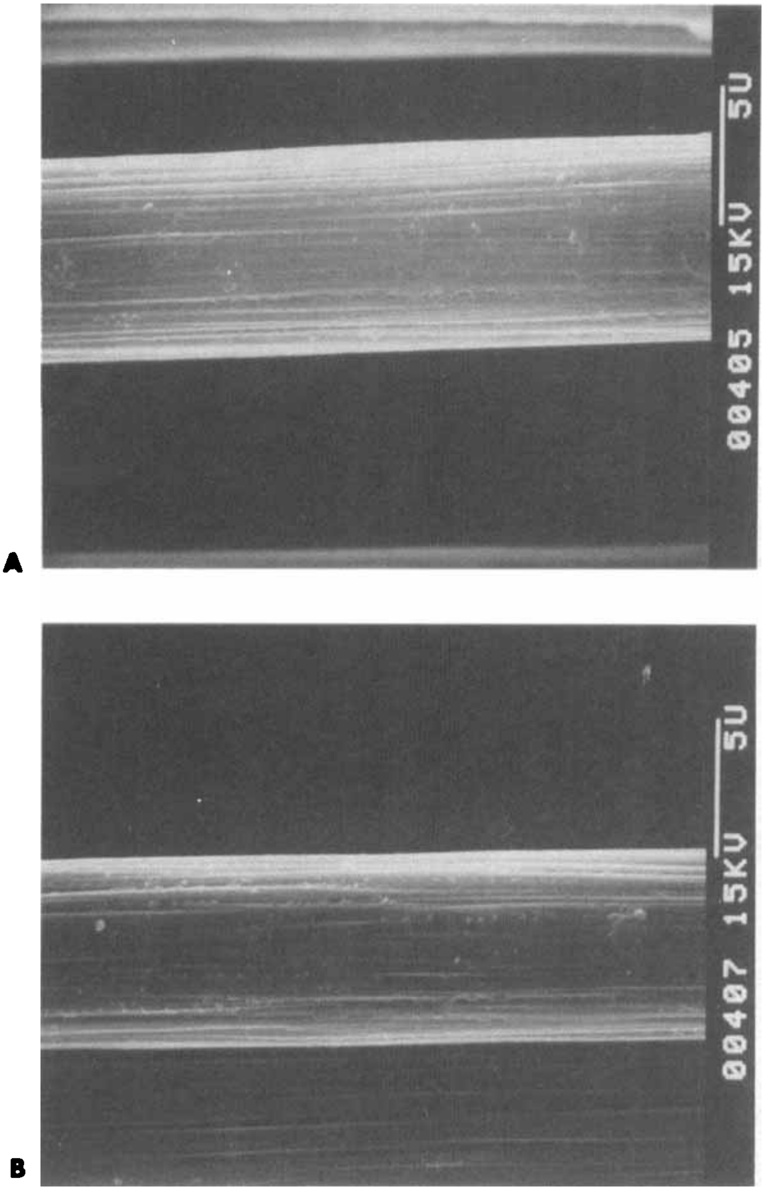

FIGURE 15 SEM photomicrographs of AS1 fibers after 7 min treatment in ammonia (A) and oxygen (B) plasmas.

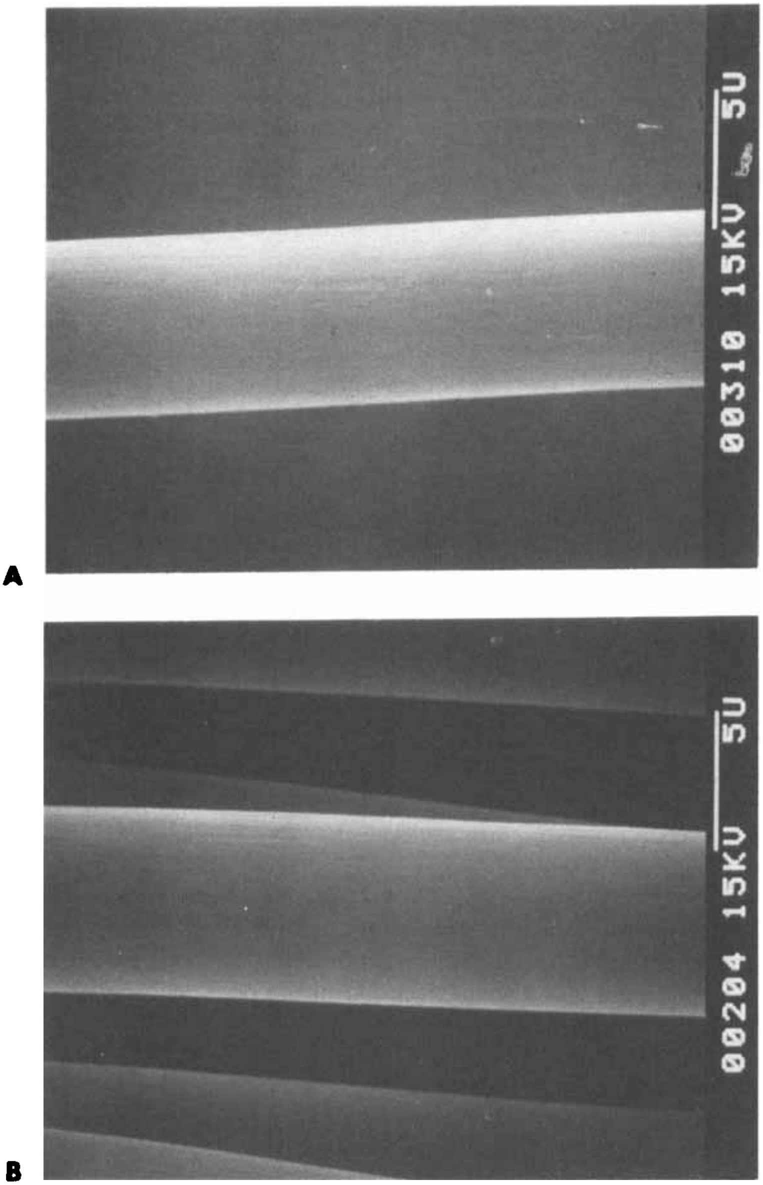

FIGURE 16 SEM photomicrographs of AS4 fibers after 7 min treatment in argon (A) and nitrogen (B) plasmas.

TABLE V
XPS analysis

AS4 Fibers after O_2 plasma treatment

Treatment time (min)	Composition (atom %)		
	C	N	O
0	91.0	3.7	5.3
3	84.8	2.5	12.7
7	83.5	3.2	13.3

AS4 Fibers after N_2 plasma treatment

Treatment time (min)	Composition (atom %)		
	C	N	O
0	91.0	3.7	5.3
3	85.2	7.6	7.2
7	90.1	5.2	4.7

AS4 Fibers after NH_3 plasma treatment

Treatment time (min)	Composition (atom %)		
	C	N	O
0	91.0	3.7	5.3
3	90.3	3.8	5.9
7	83.4	11.6	5.0

AS4 Fibers after Ar plasma treatment

Treatment time (min)	Composition (atom %)		
	C	N	O
0	91.0	3.7	5.3
3	85.4	4.6	10.0
7	83.4	7.8	8.8

treatment affected all of the spectral components. However, the only difference between the fibers tested immediately after treatment and those tested 7 days after plasma treatment was a small decrease in the peak at 286.9 eV.

DISCUSSION

It is clear that O_2 plasma treatment reduces the critical aspect ratio for AS4 and AS1 in polycarbonate and for AS4 in polysulfone. That this decrease in l_c/d corresponds to an increase in fiber matrix adhesion is supported by the systematic change in the stress birefringence from patterns indicative of low adhesion to patterns indicating strong adhesion. The improved adhesion was probably the result of increased oxygen functionality on the fiber surfaces.

The decrease in the critical aspect ratio could, of course, be simply the result of a decrease in the fiber tensile strength (Eq. 1) due to the surface damage observed on the fibers treated in the O_2 plasma (Figures 14 and 15). However,

TABLE VI
XPS analysis

AS1 Fibers after O_2 plasma treatment

Treatment time (min)	Composition (atom %) C	N	O	Na
0	83.7	4.6	10.3	1.2
3	80.8	1.6	14.6	2.4
7	76.9	0.9	16.4	4.7

AS1 Fibers after N_2 plasma treatment

Treatment time (min)	Composition (atom %) C	N	O	Na
0	83.7	4.6	10.3	1.2
3	83.1	5.7	9.7	1.2
7	85.4	4.9	8.0	1.2

AS1 Fibers after NH_3 plasma treatment

Treatment time (min)	Composition (atom %) C	N	O	Na
0	83.7	4.6	10.3	1.2
3	83.8	5.8	8.8	1.3
7	78.0	14.0	7.3	0.4

AS1 Fibers after Ar plasma treatment

Treatment time (min)	Composition (atom %) C	N	O	Na
0	83.7	4.6	10.3	1.2
3	83.4	4.7	10.5	1.0
7	82.3	5.8	10.6	1.2

TABLE VII
Effect of storage time after 3 min of plasma treatment in O_2

Storage time	Composition (%) C	N	O
Untreated fiber	91.0	3.7	5.3
>10 min	84.10	3.6	12.3
7 days	84.4	3.5	12.1

TABLE VIII
C_{1s} spectral peaks

Peak energy (eV)	Atom composition (%) Untreated	Immediate	7 days storage
283.9	85.43	76.12	76.99
285.6	10.76	14.72	14.76
286.9	1.71	3.64	2.70
287.8	2.10	5.52	5.56

this argument is dismissed based on the fact that after seven days storage the critical aspect ratios increased to values close to that for the untreated fiber.

As expected, XPS analysis of the O_2 plasma treated fibers indicated a significant increase in the surface oxygen content. However, this increase in %O did not decrease on the fibers stored for 7 days even though the adhesion of the stored fibers had diminished significantly. Curve fitting of the C_{1s} spectra peak revealed no significant difference between the fibers tested immediately after treatment and those tested after storage.

One possible reason for the loss in the effectiveness of the plasma treatment after 7 days storage is that the adhesion depends upon active chemical groups on the outer fiber surface. Exposure of these high energy sites to air for extended periods of time would result in surface reorganization to reduce the overall surface energy. However, since the sampling depth of XPS is 5–10 nm, this surface reorganization would have little effect on the spectra intensities. This explanation assumes, of course, that the chemical effect of the plasma extends to at least 5 nm in the fiber, about which we have no evidence except that there was visible surface roughening (Figures 14B and 15) which at least suggests chemical modification below the outer surface.

Studies of the effect of plasma treatment on carbon fibers have revealed major changes in the surface composition. Wesson and Allred,[9] for example, have investigated IM-6 fibers treated in O_2 plasma and have reported an increase in the surface oxygen from 7.9 atom % to 13.8 atom %. They also report an increase in the C_{1s} peak at 288.7 eV from 2.6 to 6.5, a 60% increase in acid sites and a 134% increase in surface polarity. They conclude that the treatment produces significant increases in surface carbonyl groups. Su *et al.*[6] also report a significant increase in surface oxygen (from 8.3 atom % to 14.6 atom % after 15 min treatment). However, they conclude that the major chemical change is an increase in the $=C-O-$ moiety.

In the work reported here, comparable increases in the %O were observed as well as significant changes in the C_{1s} peak intensities.

CONCLUSIONS

The effects of treating carbon fibers with RF plasmas on their adhesion to thermoplastic polymers were determined using the single embedded filament adhesion test. Treatment in an O_2 plasma significantly increased the adhesion of AS1 and AS4 to polycarbonate and polysulfone. Treatment in ammonia and nitrogen plasmas did not improve adhesion but treatment in argon plasma resulted in a slight improvement in the adhesion of AS1 to polycarbonate. The effect of the O_2 plasma treatment on adhesion dissipated when the fiber was stored for a week before testing. Surface analysis using XPS revealed a large increase in the atom % oxygen for fibers treated in oxygen. However, the C_{1s} spectra were identical for the fibers tested either immediately after treatment or after a week of storage in air. It is possible that the chemical state of the surface oxygen was not related to the improvement in adhesion. However, storage of the fibers in air would tend to reduce the surface energy with the loss of the reactive sites necessary for adhesion. Since the sampling depth of XPS is 5–10 nm, chemical rearrangement on the surface would have negligible effect on the XPS spectra intensities.

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