

GAS PLASMA AND THE TREATMENT OF ADVANCED FIBERS

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INTRODUCTION

The unique properties and characteristics of fibers such as KevlarTM and SpectraTM and those of graphite fibers offer an opportunity to develop composites with strength to weight ratios never before attainable.

Cold gas plasma treatment technology was little more than an academic curiosity a decade ago. In recent years with the increasing demands on product performance, this technology is emerging as the preferred method for treating fibers to enhance interlaminar shear properties.

In order to improve the stress transfer at the interface and efficiently utilize the properties of the fiber, an intimate interaction between the resin matrix and the fiber appears to be a key requirement. Barriers to this interaction include surface contaminants, poor wetting, and the absence of chemical bonding between the fiber and the resin system. Plasma surface treatment affords an opportunity to minimize or eliminate these negative barriers by 1) removing surface contaminants and weakly-bound polymer layers 2) enhancing wettability by incorporating polar groups on the surface and 3) forming functional groups on the surface permitting covalent bonding between the fiber and the resin matrix. Since plasma treatment is a process of surface modification, the bulk properties of the fiber are maintained. Furthermore, the nature of the process is such that it can be precisely controlled.

PLASMA CHEMISTRY AND SURFACE TREATMENT

A gas plasma is created by the introduction of the desired process gas into a vacuum chamber and subsequent excitation of the gas using radio frequency (RF) energy. The energy applied dissociates the gas into electrons, ions, free radicals, and metastable excited species. The free radicals and electrons created in the plasma collide with the material surface rupturing covalent bonds. At this stage two possible events can occur: 1) surface contaminants and weakly bound polymer layers dissociate into volatile by-products that are removed by the vacuum system, and 2) free radicals are created on the material surface which may then combine with the active species in the plasma to provide thermodynamically preferred products on the surface. Since plasma surface treatment causes changes to a limited depth (several molecular layers), bulk properties of even the most delicate materials remain unchanged.

Several excellent papers and literature sources providing an in depth discussions of the nature of gas plasmas and their chemistries have been published (1,2,3). These sources describe the many chemical processes that can take place in a plasma environment.

EQUIPMENT

Spectra™ 900 and Spectra™ 1000, developed by Allied Fibers, were treated in a Plasma Science PS1010 continuous reactor. The PS 1010 allows continuous treatment of yarn in an air-to-air mode, i.e., the yarn is paid off from multiple bobbins or spools outside of the chamber and passes through transition zones to the reactor which is maintained at reduced pressure. After treatment the yarn exits through similar transition zones to a take-up reel that is outside the reactor chamber.

The reactor is powered by a 600 watt solid state generator. Dual vacuum pumping systems are employed where the first stage is a 280 cfm high pressure pump. The second pump which exhausts the reactor chamber is a 180 cfm oxygen plasma service pump which has the ability to reduce the chamber pressure from atmosphere (760,000 microns) to 20 microns within two minutes. Once the chamber is pumped down, process gases are introduced through mass flow controllers. During the plasma treatment of Spectra™ fibers, the chamber pressure was maintained at approximately 500 microns. Power level used for this series of experiments was 350 watts in order to limit the plasma temperature and prevent thermal damage to the fiber. Process gases used were a mixture of oxygen and tetrafluoromethane. Residence time of the fiber in the reactor chamber was varied by changing the line speed. Residence times of one minute and two minutes were used.

Experimental

Both plasma treated and virgin Spectra™ 900 were filament wound into flat unidirectional composites for mechanical property measurements. Un-impregnated fiber bundles were tested in accordance with ASTM Method D 2256 using a crosshead speed of 254 mm/min. Values are the average of at least 10 specimens at each condition.

Composites were prepared using a Bisphenol A Epoxy resin (Ciba-Geigy Araldite 6010) and a modified amine hardener (Ciba-Geigy HY 956). A ratio of 25 parts HY 956 to 100 parts Araldite 6010 was employed with a 5 hour cure at 100 C (no post cure) for all composites.

The flexural properties of reinforced composites were obtained from a three point bending test based on guidelines of ASTM Method D 790. The dimensions of the test specimen were 3.2mm x 12.7mm x 72.6mm. The support span was 50.8mm or 16 times the depth.

The International Shear Strength (ILSS) by the short beam method was obtained on flat specimens using guidelines of ASTM Method D 2344. The dimensions of the test specimen were 3.2mm x 12.7mm x 22mm. The support span was 15.9mm or 5 times the depth. In both the flexural and short beam shear tests, the crosshead speed was 1.3mm/min.

ESCA (Electron Spectroscopy for Chemical Analysis) which yields composition and chemical bonding information from up to 40 - 80Å of the outer layer was used to measure the amount of functional

groups on the surface. The functional groups were tagged by site specific derivatization. Using these methods, the amount of carbonyl, alcohol, and carboxylic acid groups present on the surface were quantitatively determined.

DISCUSSION OF RESULTS

The tensile and composite properties of Spectra™ 900 and Spectra™ 1000 after plasma treatment have been studied extensively (4,5). Although a modest reduction in tensile strength was observed for plasma treated fibers - less than 10% - this reduction was more than offset by the significant increase in composite properties.

Plasma treatment of Spectra™ 900 fiber showed a four-fold increase in interlaminar shear strength over untreated fibers and a two-fold increase over fibers treated with corona or a proprietary chemical surface treatment. Earlier studies have attributed these improvements in composite properties to improved wetting, mechanical interlocking, and bonding.

Using diffuse reflectance FTIR spectroscopy, earlier studies (5), have identified the presence of carbonyl, hydroxyl, and other oxygen containing groups on the surface of plasma treated Spectra™ fiber. However, the extent to which the fiber surface has been modified has not been measured until recently.

ESCA surveys of surface derivatized Spectra™ fibers that have been plasma treated show that almost the entire surface of the fiber has been oxidatively modified.

Careful examination of the data points up some interesting results. Untreated Spectra™ 900 appeared to have a higher degree of oxidation than the plasma treated fiber samples. The oxygen content of the untreated fibers, however, dropped significantly after sonication in hexane, suggesting the presence of loosely bound contaminants on the surface of the fibers. Spectra™ 1000 similarly contained loosely bound surface contaminants. The oxygen content of unwashed treated fibers (17-23%) was higher than those of derivatized fibers (10-15%). The common denominator for all derivatized samples was sonication in either hexane or ethanol. It appears that the oxidation of the fiber is occurring underneath the sizing. It also appears that a steady state oxidation level has been reached within one minute of process time, since the oxidation levels were the same for both residence times. The one and two minute residence times probably represent various stages of completeness in contaminant removal. These hypotheses appear to be confirmed by SEM photomicrographs of untreated and treated fibers. Note that the fibers exposed to two minutes of plasma appear to have a rougher surface which would aid in the mechanical interlocking of the fiber with the resin matrix.

The surface chemistry of plasma treated Spectra™ fibers also show some interesting results. The hydroxyl and carbonyl (ketone and aldehyde) groups each account for 6.8% of the total oxygen on the Spectra™ 900 samples. Carboxylic acid groups were not measured for this sample. Spectra™ 1000 showed similar levels of hydroxyl and carbonyl groups. In addition, the carboxylic acid groups accounted for 16.7% of the total oxygen. On the average it appears that one out of three to four oxygen

atoms is a reactive site containing either a hydroxyl, carbonyl, or carboxylic acid group.

Surface derivatization is site specific and only the reactive groups on the surface participate in the derivatization reaction. If we assume that the oxidation of the fibers occurs only on the surface, 25 to 30% of the fiber surface consists of reactive sites. This represents a high level of surface functional density. If the oxidation were to extend beyond the surface layer, the concentration of reactive sites on the surface would be even higher.

The high concentration of hydroxyl and carboxylic acid groups on the surface of plasma treated Spectra™ fiber can help explain the increase in interlaminar shear strength obtained with epoxy resin matrices. Evidence of these types of reactions were presented by Nguyen et al (5).

Wesson and Alfred (6), using ESCA techniques, similarly found increased concentrations of carbon-oxygen bonds, particularly at the assignment corresponding to carboxylic acid, on carbon fibers treated in an RF plasma. The presence of significant amounts of acid functionality on these fibers was confirmed by titrations for acid and basic groups. It is interesting to note that graphitized and unsized carbon fibers showed fair amounts of basic (alkali) groups on the plasma treated fiber surfaces.

CONCLUSIONS

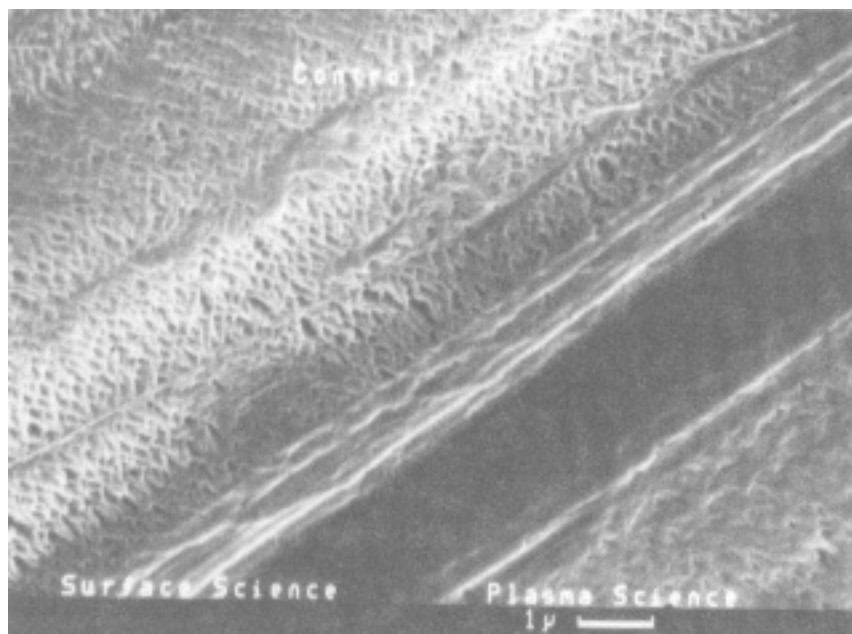
Plasma surface treatment has been shown to accomplish the three functions important to achieving maximum interaction between the fiber and the resin matrix:

- 1) The removal of surface contamination which requires a finite time and is dependent on the amount on the surface. The mechanics of contamination removal is mostly an ablation process.
- 2) The creation of polar groups on the surface that provide a high surface energy and that permit easy wetting of the fiber by the resin systems commonly employed.
- 3) The creation of reactive groups on the surface of the fiber, allowing covalent bonding between the fiber and the resin.

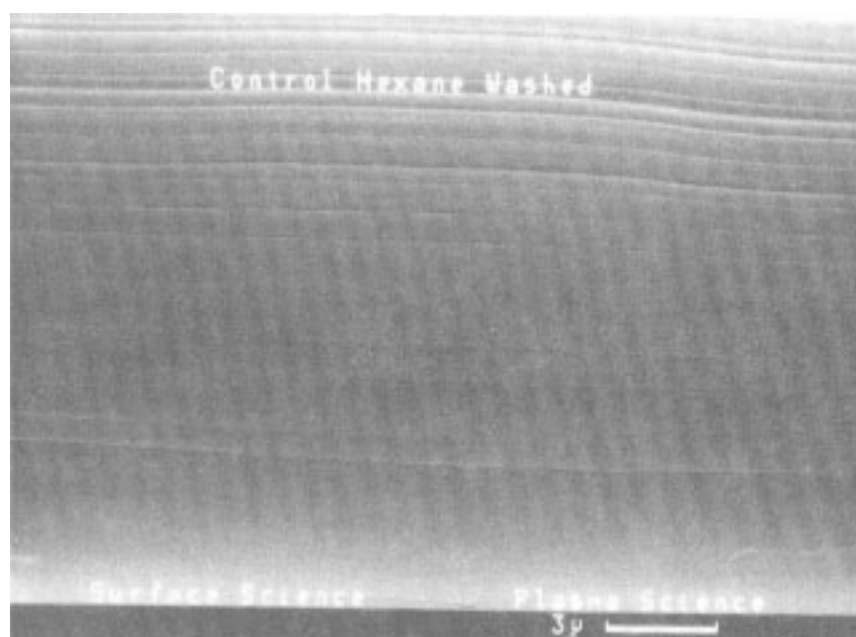
ESCA analysis using site specific surface derivatization has proven to be an effective tool in quantitatively determining the concentration of reactive sites on the fiber. The chemical analysis showed little difference in concentration of functional sites between the two residence times although experience has shown us that an increase in residence time improves interlaminar shear strength. The difference in shear strength behavior is attributed to mechanical effects such as an increased surface roughness and surface area in the case of fibers treated for longer times.

Spectra™ presents unusual problems for surface modification, not the least of which is a relatively modest transition or relaxation temperature. Plasma treated Spectra™ provided a 400% increase in interlaminar shear strength. This has resulted in effective use of this fiber in composite structural applications. The evidence presented in this study has shown that oxygen plasma treatment is

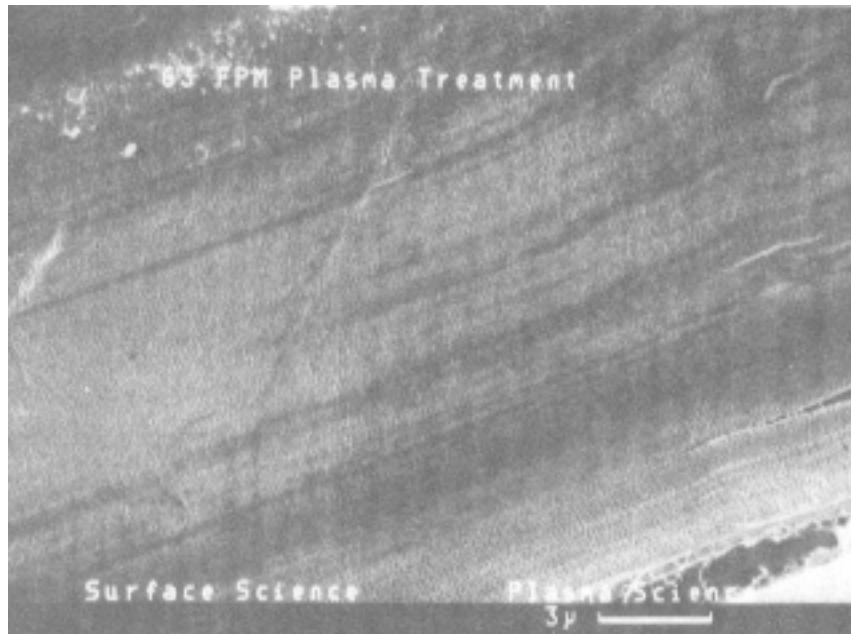
particularly effective in modifying the surface of Spectra™ fiber. Using surface derivatization techniques and ESCA analysis we have shown that the treatment has resulted in effective oxidation of the surface, and that this treatment has resulted in one out of three to four oxygen atoms being a reactive site consisting of either a hydroxyl, carbonyl, or carboxylic acid functionality.



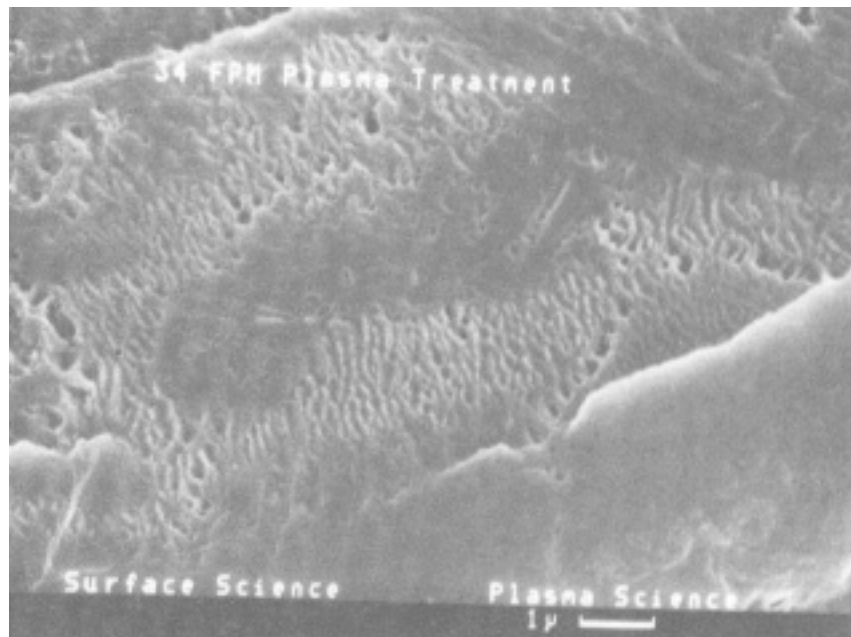
Untreated Spectra™ 900



Spectra™ 900 washed in Hexane



Spectra™ 900 1 minute in plasma



Spectra™ 900 2 minutes in plasma

Table I
Properties of Unidirectional Composites
Spectra™ 900/Epoxy

Surface Treatment Property	Plasma	Corona	Chemical	Untreated
Fiber Volume (%)	51	51	55	56
Flex Strength (MPA)	234	190	---	146
Flex Modulus (Gpa)	28	25	---	20
ILSS (Mpa)	31	18	20	8

Table 2
Oxidation Levels and Site Concentrations -
Plasma Treated Spectra™ 900

Derivatized for

	Unwashed % O	-OH % O	%O as -OH	-C=O % O	%O as -C=O	% O	%O as -COOH
Control	25	1.1	---	2.9	13.8	n m	nm
1 min. res. time	23	13	6.9	15	6.7	n m	nm
2 min. res. time	17	12	7.5	15	6.7	n m	nm

nm=not measured

Table 3
Oxidation Levels and Site Concentrations -
Plasma Treated Spectra™ 1000

Derivatized for

	Unwashed %	-OH		-C=O		-COOH	
	O	% O	%O as -OH	% O	%O as -C=O	% O	%O as -COOH
Control	6.1	0.9	---	---	---	3.4	14.7
1 min. res. time	17.0	13	6.9	9.8	7.1	9.8	17.4
2 min. res. time	20.0	14	5.7	12	7.1	10	16.0

nm=not measured

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