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13. ABSTRACT

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The characteristics of the fiber surfaces were found to be related to the type of fiber with high-modulus fibers having a graphite-like surface and lower-modulus fibers exhibiting a carbon-like surface. The nature of the surface carbon determines to a large extent the reactivity of the surface to matrix resins and the resulting composite shear strength. Carbon-like surfaces are important for the development of high composite shear strengths. Several other factors, such as surface area, functionality, and wettability, were found to play less important roles in composite shear strengths.

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NOLTR 71-165 **29 October 1971**

Carbon Fiber Surface Treatments

This report describes the treatment of carbon fiber surfaces by oxidation, vapor deposition, and solution-reduction. The surfaces of treated and untreated fibers are also characterized by various techniques. The method of resin coating the fibers and then pyrolyzing the resin is the first method known to give high shear strengths on high-moduli fibers. Thus it represents a scientific break-through in this field. Further development is now needed to optimize the method and make it commercially feasible. Its further use in R & D on advanced composites for aircraft and other military hardware should be started at once.

This project was funded by the Naval Air Systems Command under Task A32 520/292/70 F 51-544-201. The work reported herein was conducted between September 1969 and July 1971. Portions of this report are taken from the Doctoral Thesis of the principal author submitted to the Chemical Engineering Department at the University of Maryland. The thesis work was directed by Professor Theodore G. Smith in conjunction with the staff of the Non-Metallic Materials Division at NOL.

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By direction

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INTRODUCTION

Carbon fibers are one of the most promising new materials of recent years. Currently there is considerable interest in these high-modulus, high-strength filaments in developing technology for their use in reinforced plastics composites. The attractiveness of carbon fiber composites can be seen when their specific properties (modulus and tensile strength) are compared with those of conventional engineering materials (Figure 1). At the present time, the relatively high price of the fibers (one to several hundred dollars per pound) has limited their use to applications where weight saving is at a premium. Price projections, however, for large-scale production of the fibers have been as low as five dollars per pound (21). At lower prices, the fibers could profitably be used in many conventional applications such as sports equipment, cables, commercial buildings, bridges, and even automobiles.

Other properties of carbon fibers which are of particular interest are their thermal and chemical stability, electrical conductivity, low coefficients of friction and thermal expansion, high strength retention in tensile cyclic fatigue, and resistance to moisture. Carbon fibers offer one other distinct advantage. They are available with a range of mechanical strengths so that fibers with specific desirable properties can be chosen to advantage for a particular application. The fiber tensile strengths range from 200,000 psi to over 450,000 spi while the moduli range from 25 million psi to over 80 million psi. Experimental fibers of 550,000 psi tensile strength and 110 million psi modulus have been fabricated (21). A reasonable goal which is theoretically obtainable based on early work with graphite whiskers (5) would be a fiber having 1 million psi tensile strength and 100 million psi modulus (39).

High-modulus, high-strength fibers are produced by the pyrolysis of relatively inexpensive, commercially available polymeric textile fibers. Two precursor fibers which are most frequently used are Rayon (cellulose) and polyacrylonitrile (PAN). The Rayon-based carbon fibers are commercially sold in continuous yarn form consisting of 1440 filaments each of which is approximately seven microns in diameter. PAN-based carbon fibers generally come in tow form (a tow is a large bundle of filaments without twist) consisting of 10,000 filaments. Recently PAN-based fibers have been introduced in the form of a hank (a large tow) containing 40,000 filaments and a small tow of 5,000 filaments. Fibers made from other precursor materials such as

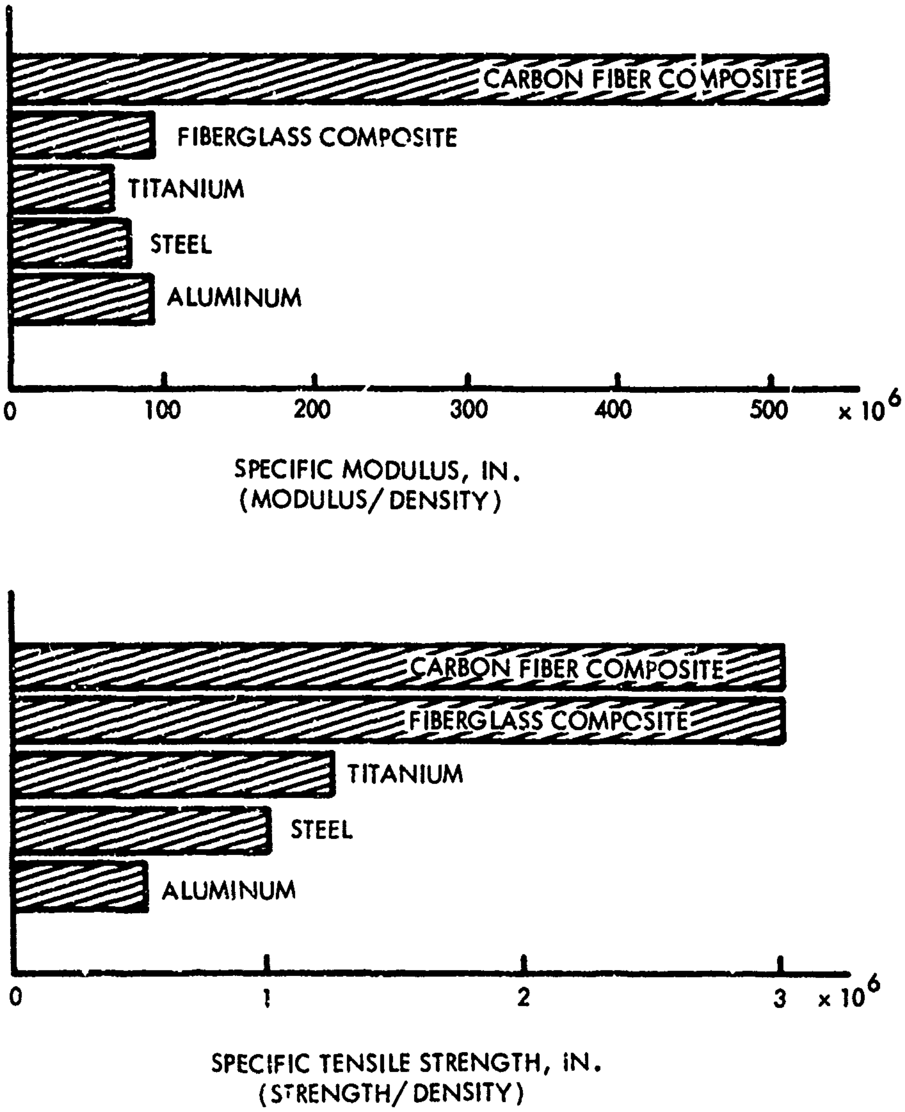


FIG. 1 COMPARISON OF CARBON FIBER COMPOSITE PROPERTIES WITH OTHER ENGINEERING MATERIALS

pitch (2), polybenzimidazole (21), polyvinyl alcohol (50), and phenolic fibers (KYNOL) (37) offer some promise but are not yet commercially available.

In spite of the interest in carbon fibers, the promise they hold, and the technology developed so far towards their use in composite materials, several problem areas still remain. The most significant of these has been associated with the interface area and the development of strong fiber-resin bonds. The weak bond achieved between the matrix resin and the carbon fibers has been the subject of many investigations but still the role of the many interacting factors is not fully understood and is the subject of much debate. Typically interlaminar shear strengths, which are a measure of the fiber-resin bond, in untreated carbon fiber-epoxy resin composites are around 3500 psi. This compares with values of over 15,000 psi for other reinforcing fibers (glass and boron) (25). The general approach to the shear strength problem with carbon fibers has been through fiber surface treatments.

To date the surface treatment approach most widely used has been oxidation of the fiber surface by a variety of processes. Such treatments have produced various desirable and undesirable results. Most of the oxidation treatments require long exposures to the oxidative environment which, on occasion, cause reductions in the fiber tensile strengths along with the increased composite shear strengths.

The objective of this study was to develop further understanding concerning the structure and surface of high-modulus, high-strength carbon fibers and with this understanding investigate new approaches to fiber surface treatments. The criteria for evaluation of the treatment effectiveness were: 1) increased composite shear strengths (equivalent or superior to those of manufacturers), 2) little or no decrease in fiber tensile strengths, and 3) short processing times required to achieve the desired results.

The fiber structure was analyzed using scanning electron microscopy, transmission electron microscopy, and light microscopy (polarized and sensitive tint). This work is reported in NOLTR 71-166 . Fiber surfaces were analyzed using Raman spectroscopy, gas chromatography, energy dispersive X-ray, and measurements of the fiber wettability, surface energy and surface area. Fibers were surface treated using oxidation, vapor deposition, and solution-reduction techniques. The effects of the treatments on the fiber were investigated using Raman spectroscopy, gas chromatography, and measurements of the surface energy and surface area. The intent of this research was to improve the overall performance of carbon fiber composites through better understanding of the shear strength problem and specific methods to overcome it.

BACKGROUND

A) FIBER SURFACE AND SURFACE CHEMISTRY. Work concerning the fiber surface, surface chemistry, and surface treatments was initiated because of the low interlaminar shear strengths developed in carbon fiber composites. This work has now branched into many areas and disciplines.

Early work concerning the fiber surface consisted of the measurement of fiber surface areas. The results showed the area measured by BET nitrogen adsorption for untreated fibers to be 0.25 to 1.0 m^2/gm. (18,46,47). Various treatments produced two to ten-fold increases in the surface area (47). These increases were often accompanied by increases in composite shear strengths. Degassing of certain fibers at elevated temperatures produced increases in the measured surface areas but no increases in shear strengths of composites fabricated from degassed fibers were observed (40). This would lead on to conclude, and it has been verified by several investigators, that surface area of the fiber is not the only contributing factor towards composite shear strengths (25,28). One reason the relationship between surface area and shear strength may not hold true is that the measured increase in surface area is a result of pores having diameters of 6 to 20 Å (40). Such pores are too small for resin molecules to enter and, therefore, the effective surface area is much lower than the measured area.

Scanning photomicrographs of fiber surfaces reveal a surface which is fairly rough on a microscale (46,47). The surface of the fibers appears to be somewhat smoothed by treatment in certain cases even though the surface area is increased. Again this is the case of area increases in very small pores. In high-magnification micrographs, the appearance of the surface is somewhat rougher (46).

Chemically the fiber surface contains one or more types of oxygen-containing function groups. Carboxyl and hydroxyl groups have been measured in low concentrations on untreated fiber surfaces (30). Other functional groups which have been identified on carbon surfaces include carbonyl and lactone groups (28,47). Increased shear strengths in composites have been attributed to increased functionality on the fibers through surface treatments (28). However, investigators have treated fibers and shown increased shear strengths along with increased functionality, then destroyed the functionality, and still retained the improved composite shear strength (16).

A new technique has recently been employed for characterizing fiber surfaces. This technique involves the use of Raman spectroscopy. From the Raman spectrum of a fiber, the form in which the carbon is present on the surface of the fiber, whether graphite or carbon, can be determined (55,56). The apparent crystallite size and the relative amount of edge dislocations, vacancies, and crystal edges can be calculated. A correlation between these and composite shear strengths for untreated fibers has been shown (56).

The final question concerning the fiber surface is its wettability by the resin matrix and the reactivity between the matrix resin and the fiber surface. To date these factors have not been fully explored or quantitatively assessed. Investigations of fiber surface reactivity using gas chromatography have shown that the fiber has an increased affinity for various adsorbent vapors (37,38). Certain treatments increased while others decreased the adsorption coefficients. The adsorption coefficients were not correlated with fiber or composite properties.

The wettability of carbon fibers has been a difficult problem because of measurement techniques. Early work was done indirectly by using graphite coupons rather than the fibers themselves (13,46). The degree to which a graphite coupon models the fiber surface is questionable. Direct measurements of contact angles have been attempted (47,62), but these results have not been conclusive. One value which has been reported is 46 dynes/cm. (51). This value is very near the value for the surface tension of common epoxy resins (44 dynes/cm.). Another new method, that of calculating contact angles from wicking rate measurements offers some promise (17). The difficulties in obtaining reliable measurements of the critical surface tension of carbon fibers arise from the small diameters of the filaments, the irregular surfaces, and the inherent limitations of the methods themselves.

3) SURFACE TREATMENTS. Fiber surface treatments have been aimed at developing higher composite shear strengths through altering the fiber surface. In the past, many of the treatment methods have been guarded with utmost secrecy. The most frequently used methods can be classed as oxidation treatments of two types--liquid and gaseous. The liquid oxidations can double the composite shear strengths with slight reductions (4 to 6%) in fiber tensile strengths (24). A doubling of shear strength represents an increase from around 4000 psi for an untreated high-modulus fiber to 8000 psi. Common liquid oxidation treatments are nitric acid boil, electrolytic oxidation with sodium hydroxide, and the British treatment with sodium hypochlorite (1,24,53). The gaseous oxidations affect the fiber differently in that in some cases the fiber tensile strength is significantly reduced (12 to 25%) while the composite shear strength is not always improved (24,53). Typical gaseous oxidation treatments include air and ozone.

While a reasonable amount of success has been achieved by the manufacturers using oxidation treatments, the treatment times are usually quite long (from several hours to several days). A graph of shear strength versus treatment time for the sodium hypochlorite oxidation is shown in Figure 2. Similar results have been shown for other oxidation treatments (41).

Other approaches to fiber surface treatment have been investigated. Many of these have been based on the addition of material to the fiber surface. Coupling agents, similar to those used on glass fibers were not effective (28). Polymer coatings and metal coatings have also been tried with little success (28,42). One successful approach has been that of growing silicon carbide whiskers of the fibers (48). With this method, increases in composite shear strengths and transverse tensile strengths have resulted.

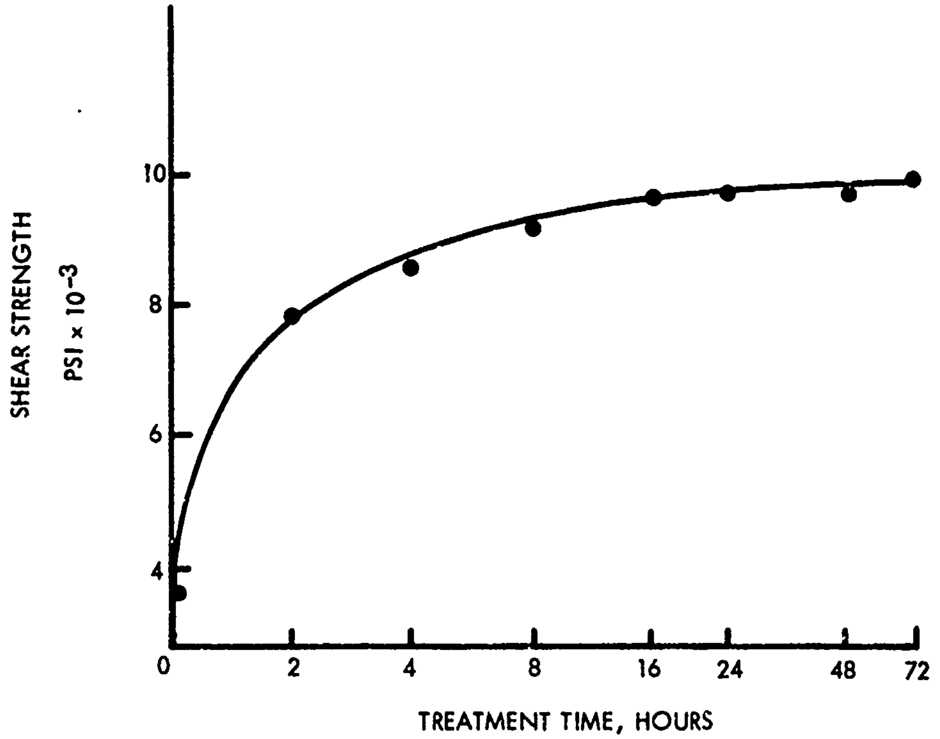


FIG. 2 SHEAR STRENGTH VS. TREATMENT TIME FOR THE SODIUM HYPOCHLORITE OXIDATION TREATMENT (1)

EXPERIMENTAL APPROACH

A) INTRODUCTION. The fibers used in this investigation are listed in Table 1 along with their mechanical strengths. Not all of the fibers were used in each phase of the study.

The size and orientation of crystallites within a fiber determine, to a great extent, the mechanical properties of the fiber. More important, the crystallite orientation at the surface along with pores, vacancies, and dislocations determine the condition of the surface with respect to resin bonding. Since most attempts at shear strength improvement are based on improved resin bonding through modification of the fiber surface, it is important that the surface be as well defined as possible. With a better understanding of the fiber surface, approaches to more effective treatments become evident. Our experimental approach has been based on this philosophy.

B) SURFACE TREATMENTS

1. Introduction. Surface treatments of three basic types were investigated; oxidation, vapor deposition, and solution reduction. The oxidation treatments were generally of the batch type and required long exposures. The other treatments were made as continuous as possible in order to arrive at treatments which could be a part of a continuous fabrication process with a minimum residence time. The fibers used for treatments were untreated as received from the manufacturers.

2. Oxidation Methods. Oxidation treatments can be divided into liquid and gaseous treatments. The three liquid methods investigated were the nitric acid boil, sodium hypochlorite, and electrolytic NaOH. The first two use essentially the same procedure. The fibers were wound on glass spools and immersed in the oxidizing solution at elevated temperatures for a period of time. In the nitric acid boil, the fibers were immersed in 60% aqueous nitric acid at 120°C refluxing temperature for periods of 3 to 60 hours. The fibers were then washed to remove all traces of the acid. Since previous work had been done using this method (24,41), fibers were treated only to analyze the effects of the oxidation to the fiber surface. In the sodium hypochlorite treatment, solutions of 5.5% to 10% (ph 5.5) have been studied by other investigators (16,24). Exposures up to 72 hours are required at 45°C to achieve sufficient oxidation of the surface. Addition of acetic acid to form hypochlorous acid reduces the time (1).

TABLE 1

CARBON FIBERS AND THEIR MECHANICAL PROPERTIES

(Manufacturer's Stated Values)

Fiber	Tensile Modulus psi x 10^{-6}	Ultimate Tensile Strength psi x 10^{-3}	Composite Shear Strength psi
HMG 50 treated* (Rayon)	45-53	200-275	7000
untreated	45-53	230-330	4000
Thornel 50 treated* (Rayon)	45-55	175-220	7500
untreated	45-55	230-285	3500
Courtalds HMS* (PAN)	50-60	250-350	8500
HM	50-60	250-350	3000
HTS*	32-40	300-400	14000
HT	32-40	300-400	6500
Modmor I treated* (PAN)	55-65	200-300	8000
I untreated	55-65	200-300	3000
II treated*	35-45	350-450	15000
II untreated	35-45	350-450	7000
Fortafil 6T treated* (PAN)	60	400	8000
Thornel 75S treated* (Rayon)	75	400-425	6000
VYB untreated	6	170	13000

*Treated in this case refers to the as-received fibers with the proprietary surface treatments of the manufacturers

Since this process is used commercially, manufacturer treated fibers were used for the investigation of the treatment effects on the fibers.

The electrolytic NaOH treatment differs from the other two liquid oxidations in that it is a continuous method. A 5% NaOH electrolytic solution was used with a three minute residence time. With this residence time, currents up to 1.0 amps were required to achieve sufficient current densities. An optimum current density had been suggested by other investigators (53). A schematic of the electrolytic oxidation apparatus is shown in Figure 3. The pull-through rate was 10.5 feet per minute with a residence time of 25 seconds in the drying tube at 150°F. Electrolytic oxidations were evaluated for effects on the fiber surfaces and the fiber mechanical strengths.

Gaseous oxidations using air, ozone, and RF plasma have been investigated (24). Generally these treatments have not been as successful as other methods because of the resulting decreases in the fiber tensile strengths. Therefore, they were not considered in this program. Recent information, however, indicates that moist air oxidations can effectively increase shear strengths without reducing the fiber tensile strengths (60).

3. Vapor Deposition Methods. Three vapor deposition treatments were investigated. The first two (SiC and FeC) were accomplished using a gas generator while the third (CH_4) was done directly from the gas phase. The gas generator used was merely a flask partially filled with solution into which a carrier gas, nitrogen or argon, was bubbled. The solutions were silicon hydride for the SiC treatment and iron pentacarbonyl for the FeC treatment. The exit gases from the flask passed into a resistance treater (Figure 4). The fibers passed continuously through the treater where they were heated to the desired temperatures (400-1600°C) by applied current across the graphite pulleys. For fiber yarns 1.5 to 3.0 amps were required while tows required 15 to 20 amps. The fiber temperature was measured using an optical pyrometer. Pull-through rates of fibers through the treater were 10.5 and 5.25 feet per minute giving residence times of 6 seconds and 12 seconds respectively. Various treatment temperatures and gas flow rates were also investigated. For the methane treatments, the methane gas was introduced directly into the carrier gas stream and the methane decomposed upon contact with the hot fiber (1200°C). Fiber tensile strengths and composite shear strengths were measured for vapor deposition treated fibers.

4. Solution-Reduction Methods. The solution-reduction treatments were generally two-step methods where the fiber was passed through a solution and dried in the first step. In the second step, the fiber was heated and the material which had been deposited on the surface was thermally decomposed forming decomposition products which could react with the carbon fiber. The equipment utilized to accomplish the two steps was the treatment section shown in Figure 5 and the reaction section previously shown in Figure 4. In the treatment section, the fiber was passed through the solution then through a heated drying tube to remove the solvent. Warm air passed through the tube

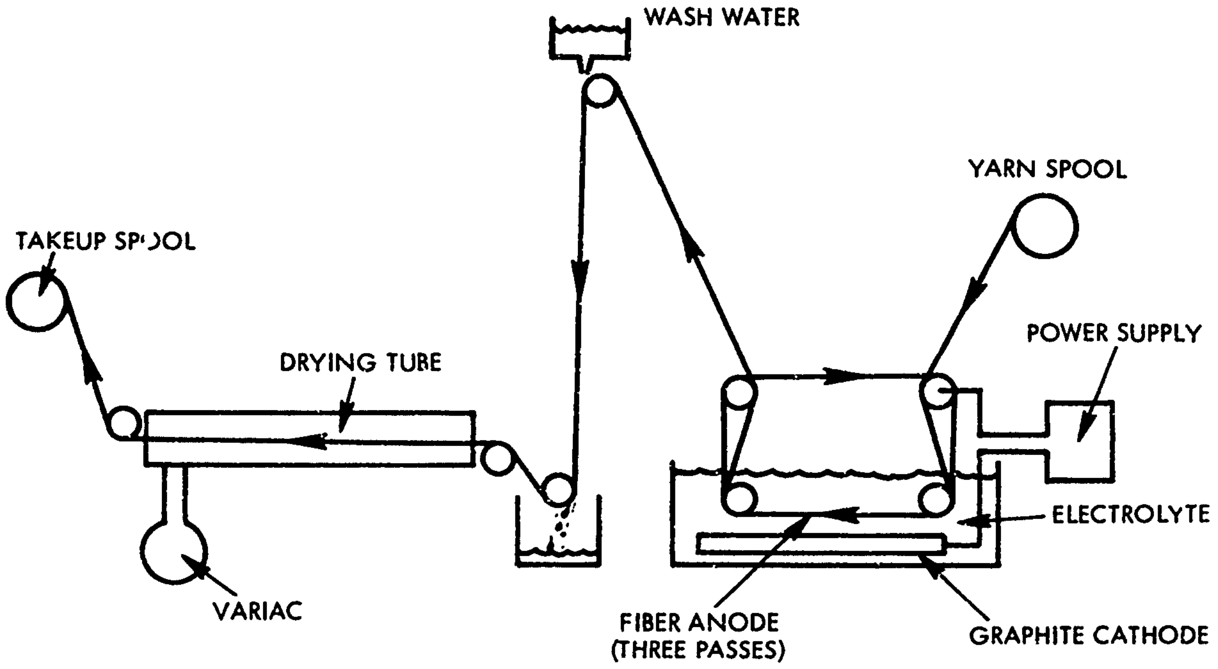


FIG. 3 SCHEMATIC OF APPARATUS FOR ELECTROLYTIC OXIDATION OF CARBON FIBER SURFACES

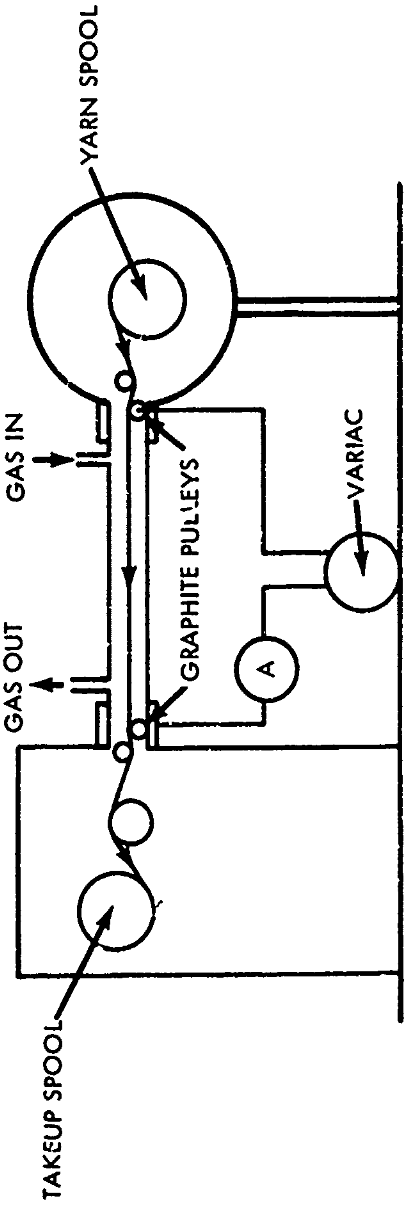


FIG. 4 SCHEMATIC OF RESISTANCE FIBER TREATER

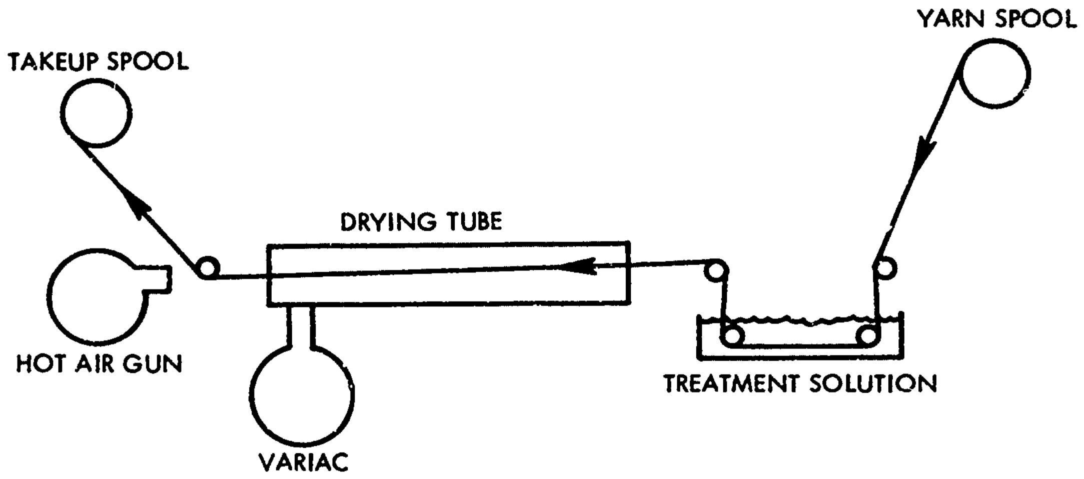


FIG. 5 SCHEMATIC OF SOLUTION TREATMENT APPARATUS

countercurrent to the direction of fiber travel. (See Appendix E for details of treatment parameters). In the reaction section, the process was similar to the vapor deposition treatments except an inert carrier gas was used. The gas was introduced at 3 liters per minute for 10 minutes prior to treatment in order to purge the oxygen from the system. The solution treatments which were successful were ferric chloride (1% to 5% in benzene and in water), ferrocene (1% to 3% in toluene), and phenylated polyquinoxaline (PPQ) (0.1% in chloroform). Other treatments which were not as successful were ammonium ferrocyanide, ferric oxalate, ferric citrate, ferrous ammonium sulphate, and chromium acetylacetonate. The successful treatments were evaluated for effects on the fiber and composite.

C) CHARACTERIZATION OF TREATED AND UNTREATED FIBERS

1. Introduction. Various methods were used to characterize the physical, chemical, and surface properties of fibers and the treatments applied to them. The methods were aimed at gaining a broad understanding of the fiber surface and the effects which could be measured from treatments to the surface.

2. Surface Area. Surface areas were determined from krypton adsorption isotherms. A standard volumetric apparatus for making such measurements, located at the Naval Research Laboratories, Washington, D. C., was used for these measurements. The surface areas were calculated using the Brunauer, Emmett, and Teller (BET) equations (45). A detailed explanation of the method is given in Appendix A. Comparisons were made between surface areas of treated and untreated fibers.

3. Surface Wettability. In order for strong bonds to form between the carbon fibers and the resin matrix, it is essential that the liquid resin adequately wets the fibers, producing a large interfacial area of intimate contact. Such a condition will occur spontaneously when the surface energy of the fiber exceeds that of the liquid resin (63). Determination of the liquid resin surface tension is a straight forward procedure. A Cenco-du Nouy Tensiometer ring method was used (14). Several different standard methods were attempted for measuring the critical surface tensions of the fibers. Because of the small diameter of the carbon filaments (7-10 microns), the standard contact angle method is difficult to use (47). Measurements using this method vary from 12° (10) to 72° (62). Critical surface tensions estimated from these values would range from 40 dynes/cm. to 25 dynes/cm. A floatation method has been suggested as a means of determining fiber critical surface tensions (47). Problems associated with this method arise from the small differences between the fiber density and the floatation liquid densities, the irregular fiber surfaces, and the large area to volume ratio of the fibers.

A new method was developed to measure the critical surface tension of carbon fibers. It is similar to the ring method of determining surface tensions of liquids where a platinum ring is used which is completely wet by the liquids. To determine the critical surface tensions of fibers, a small strand of fibers was mounted to a wire fixture such that it formed a triangle (Figure 6). This ring of fiber was then calibrated with liquids of known surface tensions using the standard torsion balance ring procedure for surface tension determinations. A calibration constant was determined for liquids which have low enough surface tensions to wet the fibers. (See Appendix B for a complete discussion of the method). Surface tensions of other liquids and matrix resins were then measured using the fiber ring and the measured values were plotted against the known values. Such a plot is linear to the point where the liquid does not spontaneously and completely wet the fiber, at which point there is a change in the slope of the line. There are several difficulties with this method: the fiber must be cleaned and dried after each measurement as moisture or solvent of the fiber surface drastically affects the measurements; it is somewhat tedious to mount the fibers on the wire fixture; and the plane formed by the triangle of fibers is difficult to align parallel to the surface of the measurement liquid. These difficulties, however, are not insurmountable. It was found that the slope of the line on the wettability plot in the region where the liquid does not wet the fibers is a function of the type of fibers being measured. The wettabilities of treated and untreated fibers were compared.

4. Surface Morphology. Fiber surface morphologies of treated and untreated fibers were determined using scanning and transmission electron microscopy. Since much work has previously been done on untreated fibers, the bulk of the effort was concentrated on the fiber surfaces after treatment. Fibers were prepared for SEM viewing by mounting on a stub with conductive silver paint and depositing by vapor evaporation first a thin layer of carbon and then a thin (200 Å) layer of gold on the fibers to render them conductive. The carbon layer is necessary since the fiber surfaces are irregular and of small diameter. Carbon migrates into areas where the gold will not. The fibers were then viewed in an Ultrascan SM-2 SEM using standard techniques (35). Fibers were prepared for TEM viewing by replication. Cellulose acetate was applied to the fiber surface, stripped, and shadowed with chromium and then carbon backing. The coated plastic was placed on a microscope grid and the plastic dissolved with acetone leaving the thin replicate for viewing.

5. Gas Chromatograph Reactivity. One method of measuring the reactivity of a fiber surface is to use the fiber as packing in a gas chromatograph column. Various vapors are passed through the column, and the affinity of the fiber packing for these adsorbate vapors can be measured by the pulse retention time represented by the peak base width (11). (See Appendix C for details). The adsorption coefficient, K, calculated from the peak width is a measure of the retention volume or time it takes a vapor flowing at a given rate to adsorb onto the fibers and subsequently desorb. Columns of glass six feet long and eight millimeters in diameter were packed with seven grams of fiber. The continuous fibers were packed into the column using vacuum suction on one end. The measurements of reactivity were made using an F&M 720 Dual Column gas chromatograph. Six adsorbate vapors consisting

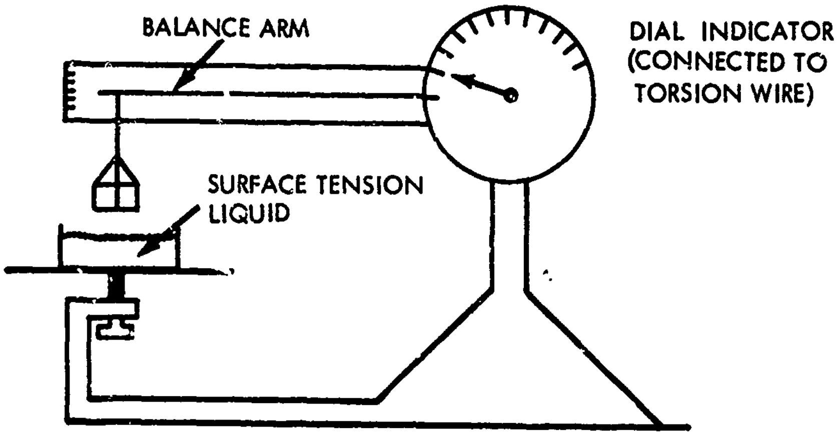


FIG. 6a SCHEMATIC OF TORSION BALANCE WITH FIBER RING

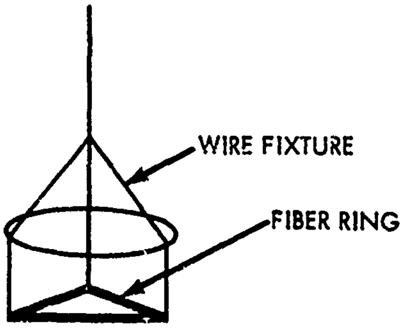


FIG. 6b DETAIL OF WIRE FIXTURE HOLDING FIBER

of compounds containing no oxygen groups; n-hexane, and compounds containing different kinds of oxygen bound groups; methyl alcohol, ethyl ether, acetic acid, ethylene glycol, and water, were injected in 1 microliter pulses into the column. The adsorption coefficients at room temperature, 120°C and 220°C for treated and untreated fibers were calculated and compared.

6. Energy Dispersive X-Ray. Wavelength dispersive X-ray has been a standard method for analyzing fiber structure. Energy dispersive X-ray is a similar method of materials analysis in which the energies of the characteristic X-rays are analyzed rather than the wavelengths at which they are produced. Energy dispersive X-ray analysis was used in conjunction with the scanning microscope using the electron beam in the microscope as the X-ray exciter. Surfaces of treated fibers containing detectable elements, (elements below Na are not detectable) especially Fe and Si, were examined. The output from the Nuclear Diodes EDAX 504-A X-ray analyzer was fed back into the microscope electronics to be displayed on the CRT to determine the distribution of the elements of interest on the fiber surface.

7. Raman Spectroscopy. Raman spectroscopy has been shown to be a useful tool for identifying carbon in its various forms (55). The advent of the laser as a powerful light source has made the Raman spectroscopy of carbons and graphites possible. Materials which are completely graphitic, natural graphite single crystals, exhibit a single Raman peak at 1575 cm.$^{-1}$. Other forms of graphites and carbons exhibit a second peak at 1355 cm.$^{-1}$ with the intensity of this peak proportional to the amount of non-graphitic carbon in the specimen and inversely a function of the graphite crystal size (55). From the relative intensities of the two peaks, the average apparent crystal size on the specimen surface can be calculated. (See Appendix D for a more detailed discussion). Since the laser beam does not penetrate deeply into the specimen due to the high extinction coefficient of graphite, a thin surface layer is the only contributor of signal. For carbon fibers, the intensity ratio of the two peaks has been related to the crystal size on the surface and the amount of crystal boundary, edge dislocations, and vacancies on the surface (56). Treated and untreated fibers were mounted on special holders which would hold the fibers stable in the laser beam. The fibers were mounted such that they were in the plane formed by the beam, the specimen, and the spectrometer. They were placed at a low angle (20°) to the incoming beam (Figure 7). The light source was a 1000 mW Coherent Radiation Ar-ion laser with a Spex 1401 double monochrometer spectrometer monitoring the radiation from the specimen. A large bundle of fibers (1000-2000 filaments) was used and the laser power had to be adjusted so as not to burn the fibers. A rejection filter of 4880 Å light (the wavelength of the laser beam) was used at the entrance slits of the spectrometer to eliminate background "ghosts" in the region of interest. It was essential that the surface of the fiber be located at the focal point of the objective lens and that the signal be focused on the slits of the spectrometer. Spectra were run for treated and untreated fibers of several different types.

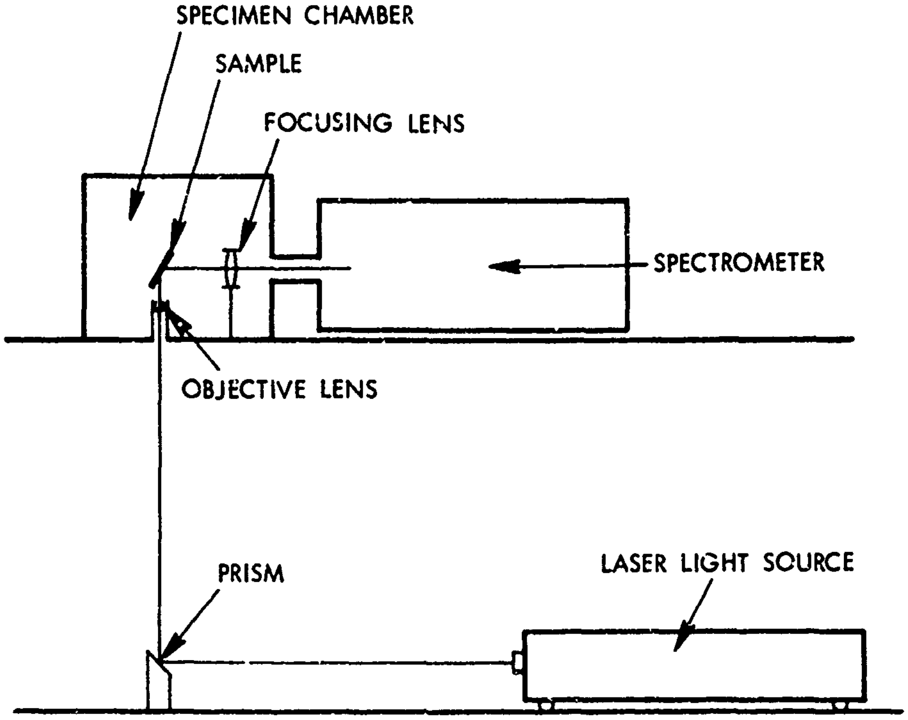


FIG. 7a SCHEMATIC OF LASER RAMAN INSTRUMENT SHOWING SAMPLE POSITIONING

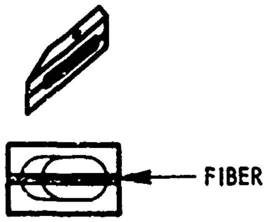


FIG. 7b DETAIL OF FIBER SPECIMEN HOLDER (TWO VIEWS)

D) TESTING

1. Tensile Strengths. Fiber tensile strengths were determined from a standard strand test (3). The fiber yarn or tow was dipped into a resin bath, removed and drained, and cured under tension. (See Appendix F for resin formulations and curing cycles). The cured strands were cut into 8-inch long sections. Cardboard tabs were bonded on the strands to form the desired guage length (2 inches) and to permit better gripping of the strands in the testing equipment. Seven to ten replicates of each specimen were tested in an Instron testing machine. Fiber tensile strengths were calculated from the fiber cross-sectional area (determined from the fiber density and weight per unit length) and the breaking load.

2. Shear Strengths. Composite interlaminar shear strengths were measured using the short beam method on specimens cut from NOL rings (32). Specimens 0.25 inches wide were machined to a 0.5 inch guage length and 0.125 inches thick. This gives a span/depth ratio of 4:1 rather than the usual 5:1. Such a ratio was necessary to prevent flexural failures in the specimen and to insure true shear breaks. In composites where the shear strengths were above 11,000 psi, flexural failures often occurred anyway. For these cases, the true shear strengths are higher than the calculated values. The specimens (5 replicates of each) were tested under three-point shear loadings in a Baldwin testing machine (32). The shear strengths were calculated from the breaking loads and the cross-sectional areas of the fibers (shear strength = 3/4 load/area). Surface treatments were first evaluated for their effects on composite shear strengths.

3. Fractography. Studies were made of shear failures in composites to determine the location of failure, whether in the matrix resin, in the fiber-resin interface, or within the outer layers of the fibers. Fractured specimens were examined in the SEM to determine if any traces of resin remained bonded to the fibers as is often seen in glass fiber composite shear fractures (35). Specimens were also prepared such that under tensile loading the fiber bundle would shear or pull out of the surrounding resin tab. The shear surface of the resin was then examined using Raman spectroscopy to determine if any thin layers of carbon or graphite remained bonded to the resin, thus indicating failures within the fibers themselves.

RESULTS AND DISCUSSION

A) SURFACE TREATMENTS

1. Oxidation Methods. Oxidation treatments were among the first approaches attempted by early investigators in solving the composite shear strength problem. In this study, oxidation treatments were investigated primarily to determine their effects on the fiber surface. Results of these treatments as related to effects on mechanical properties are given in Table 2. With the liquid oxidations, a doubling of shear strengths was achieved accompaned by only slight decreases in the fiber tensile strengths. The opposite was true for the gaseous oxidations. Only small increases in composite shear strengths were achieved accompanied by large decreases in fiber tensile strengths. One explanation for the differing effects from the two types of oxidations is in the manner in which the fiber is attacked by liquids and by gases. Liquid oxidations are generally restricted to the near surface while gaseous oxidations penetrate more deeply into the fiber especially at flaws and defects on the fiber surface (Figure 8). This penetration is most likely the cause of decreased fiber tensile strengths due to local reductions in the fiber cross-sectional area through increased flaw sizes. Decreased fiber strengths have also been related to increased treatment temperatures for various oxidation treatments (52). At the elevated temperatures (above 1200°C), a degradation of the fiber occurs even in the presence of inert environments. It is possible but has not yet been determined that this is due to some annealing effects in fibers graphitized under stress.

Oxidation treatments have a significant effect on the fiber surface morphology. The fiber surface is somewhat smoothed on a macro scale yet pitted on a micro scale. This pitting of the surface can be seen in Figure 9 for intermediate modulus PAN-based fibers but is not so evident for the Thornel fiber shown. The pitted fiber surface indicates that a selective oxidation occurs, probably at sites where edge planes, dislocations, vacancies, or other breaks in the basal plane surface structure are in evidence. This pitting produces an effective increase in the edge plane exposure on the surface and a decrease in the crystallite size by creating breaks in the large graphite layers. It is believed that only at the exposed edge planes can activation occur to produce effective resin bonding. The oxidation produces an increase in the oxygen containing functional groups on the fiber surface. These groups can act as reactive sites for the resin, reacting with epoxy, aminc, or other chemical groups in the resin to form high-strength chemical bonds.

TABLE 2

OXIDATION TREATMENT RESULTS

Oxidation Method	Average Tensile Strength Effect	Average Shear Strength Effect
Liquid		
HNO_3 Boil	-6%	+100%
Electrolytic NaOH	-4%	+120%
Sodium Hypochlorite*	-	+100%
Gaseous		
Air**	-23%	+ 0.6%
RF Plasma	-12%	+ 10%

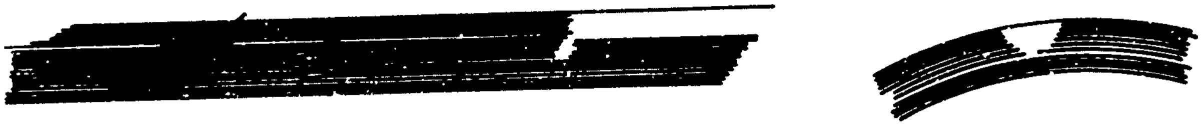
* Manufacturer treatment

** Better results have been obtained by other investigators using air oxidations

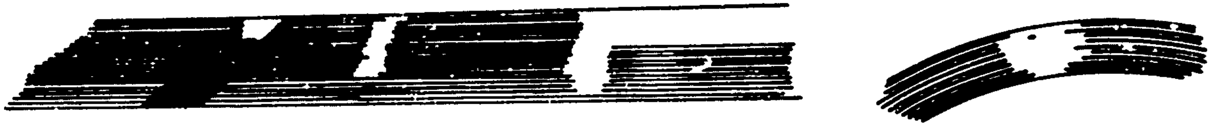
Notes: The above results are based on the following untreated fiber properties for HMG-50 and Thornel 50 fibers--

Tensile Strength	265,000 to 285,000 psi
Composite Shear Strength	3800 to 4200 psi

SCHEMATIC OF UNTREATED FIBER SURFACE



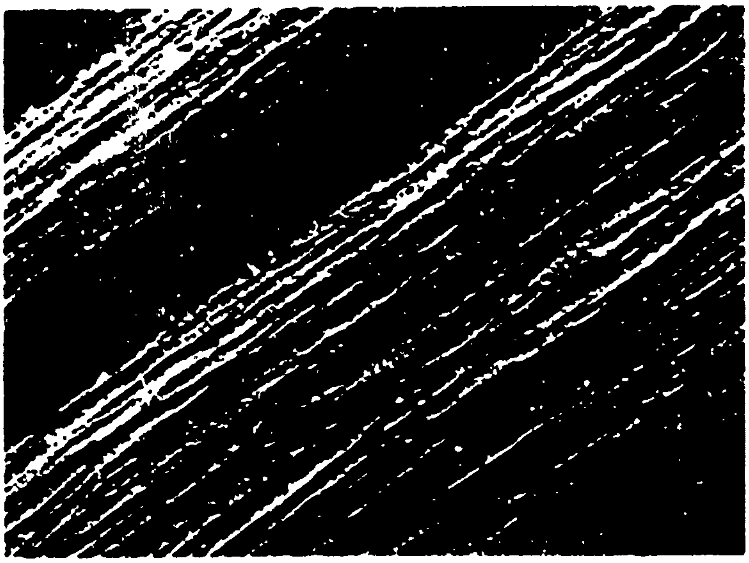
LIQUID OXIDATION ATTACK



GASEOUS OXIDATION ATTACK

FIG. 8 OXIDATION OF FIBER SURFACES (PROPOSED MECHANISM) (53)

a. Surface of Intermediate Modulus PAN-Based Fiber Oxidation Surface Treated by the Manufacturer



b. Surface of Thornel Fiber Surface Treated by the Manufacturer

FIGURE 9 . MICROGRAPHS OF FIBER SURFACES SHOWING OXIDATION (40,000 X)

Both the nitric acid boil and the electrolytic sodium hydroxide treatments produced around 5% decreases in the fiber tensile strengths. The air and plasma oxidations produced even greater strength decreases (over 10%) and only slight increases (less than 10%) in composite shear strengths. The manufacturer oxidation treatments of high-modulus fibers (50-75 million psi) produce essentially the same results as the liquid oxidations studied; i.e., doubling of composite shear strengths with little or no decrease in fiber tensile strengths. With the intermediate-modulus fibers, the manufacturer oxidation treatments are more effective. In the first place, the untreated fiber composites exhibit higher shear strengths (around 6000 psi) than the high modulus fibers (around 3500 psi). After treatment, the intermediate-modulus fibers can exhibit composite shear strength values of 14,000 to 16,000 psi. These values are in the same range as glass and boron fibers and are considered adequate.

The results from oxidation treatments on high-modulus fibers are not considered to be good enough. Part of the problem lies in the lower tensile strengths of some high-modulus fibers. In composites the stress needed to produce shear failures in the 10,000 to 15,000 psi range would also produce tensile stresses in the fibers above their ultimate tensile strengths and, therefore, failures would be tensile rather than shear. The 8000 psi shear strengths exhibited by treated high-modulus fibers lie somewhat below the point where tensile failures occur first and, therefore, an increase in the shear strengths to over 10,000 psi could be effective in improving the composite performance. This is especially true in compressive applications where compressive strength (which is very low in carbon fiber composites) is proportional to the shear strength.

Oxidation treatments have one further shortcoming; that of lengthy residence time requirements (up to 72 hours) which practically necessitates batch processing. One factor in the high cost of the fibers is certainly the time required to produce the fibers and effectively treat them. Considerable reductions in the treatment time should effectively reduce the cost of the fibers. Oxidation treatments, therefore, could be considered impractical as far as improved processing is concerned. When the effectiveness of the treatments in improving composite shear strengths is considered, oxidation treatments can be classed as marginally effective.

2. Vapor Deposition Methods. Other treatment methods investigated were aimed at introducing a coupling agent on the fiber surface which bonds to the fiber and to which the resin matrix can bond. Vapor deposition and solution-reduction treatment results are presented in Table 3. The silicon and iron vapor deposition treatments along with the $FeCl_3$ solution-reduction treatment were partially based on the assumption that relatively weak Van der Waals forces exist between layer planes. Even if good bonding was achieved to outer layers, the inherent shear strength within the fiber itself may be so poor that shear failures between layer planes could easily occur. Iron and silicon were deposited on the fiber surface so that they could react with the fiber such that the outer layers would be pinned together.

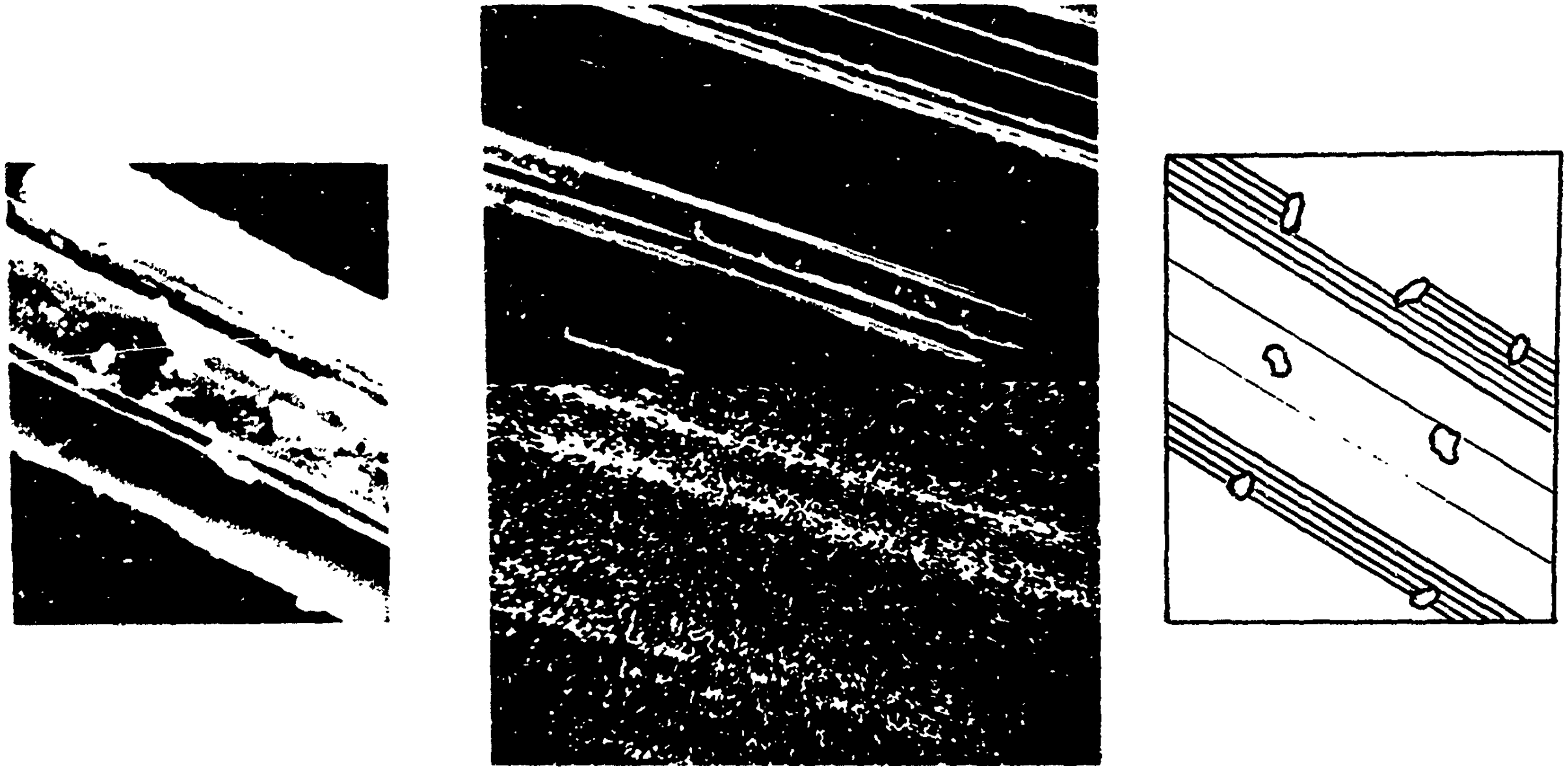
At the same time, the SiC or FeC formed on the fiber provides active areas for mechanical and perhaps chemical bonding (Figure 10). The results shown in Table 3 indicate that such an approach produces up to 10% reductions in the fiber tensile strengths (probably from the reaction penetration into the fiber) and increases in composite shear strengths. The shear strength increases, however, are not equivalent to those achieved through oxidation of the fiber surface. Therefore, the pinning of layers either is not achieved by vapor deposition; and subsequent reaction with the fiber or failure between layer planes is not the most prevalent failure mechanism in the composite. This point will be discussed later.

It can be seen in Figure 10 that treatments based on the deposition of silicon or iron on the fiber surface produce an uneven coating (even globules) on the fiber surface. The X-ray distribution scan of the iron treated fiber shows the globules are high in iron content. This uneven distribution of the metal or the metallic carbide on the fiber surface is not desirable because any beneficial effects produced by the formation of the carbides through reaction with the fiber are concentrated in local areas rather than distributed over the fiber surface. This also may explain the only moderate increases in composite shear strengths using this approach.

The methane treatments were based on the decomposition of the gas upon the hot fiber as is done in the fabrication of carbon-carbon composites. The philosophy of adding thin layers of carbon to the surface is the same as for several of the solution-reduction treatments and will be discussed under that section. The methane treatments, however, produced significant increases in composite shear strengths; but these increases were accompanied by decreases in the fiber tensile strengths. The mechanism by which the tensile strength decreases occur is probably similar to that of gaseous oxidations. The decreases would not be expected to be as severe since carbon is being deposited on the fiber which could heal some of the surface flaws and defects.

Vapor deposition treatments on the whole are not considered to be as successful as oxidation treatments. Shear strength improvements of less than 100% (doubling) were achieved. These treatments, however, were not optimized as to treatment parameters and further improvement may be possible. Vapor deposition does offer the advantage of a quick one-step treatment process. To become more effective, the uniformity of the deposition on the fiber surface must be improved.

3. Solution-Reduction Methods. Solution-reduction treatments have been the most successful treatments investigated to date. The philosophy of these and the other carbon-depositing treatments (ferrocene, methane, and PPQ) was that since the surface of high-modulus fibers consists of essentially graphite basal planes, it would be desirable to chemically attach carbon to the fiber thus making the surface more carbon like. Figure 13 shows that high shear strengths are achieved with fibers having more carbon-like surfaces. Untreated VYB carbon fibers, for example, exhibit shear strengths of 13,000 psi. Apparently epoxy resins bond more readily to carbon



a. Vapor Deposited SiC on Thornel 50

Solution Deposited FeC on HMG-50 X-ray Scan Showing Fe Distribution (below)

c. Schematic of Layer Pinning

FIGURE 10. THE LAYER PINNING THEORY

TABLE 3

VAPOR DEPOSITION AND SOLUTION-REDUCTION TREATMENT RESULTS

Vapor Deposition Treatment	Average Tensile Strength Effect	Average Shear Strength Effect
SiC	- 5%	+ 60%
FeC	-10%	+ 80%
CH_4	- 5%	+100%
Solution-Reduction Treatment		
$FeCl_3$	- 7%	+100%
$Fe(C_5H_5)_2$	+28%	+ 80%
$Cr(C_5H_7O_2)$	+18%	+ 50%
PPQ*	0%	+170% +200%**

* Phenylated Polyquinoxaline
** Results with Courtaulds HM fibers

Note: The above results are based on the following properties for untreated HMG-50 fibers--

Tensile strength	205,000 to 285,000 psi
Shear strength in composite	3800 to 4200 psi

surfaces because of the presence of more reactive sites. On graphitic fibers, the thin carbon layer on the surface acts as a coupling agent between the fiber and the epoxy resin much like the silane coupling agents for glass fibers. The results of the carbon depositing treatments shown in Table 3 bear this out. With the PPQ treatment, (PPQ is an acronym for phenylated polyquinoxaline resin - reference 4) shear strengths of 11,000 psi were achieved with HMG-50 fiber and 12,000 psi with Courtaulds HM fiber. These are among the highest shear strength values reported for high-modulus carbon fibers. PPQ has a high char yield upon thermal decomposition. The formation of this char on the surface modifies both the chemistry and structure of the fiber surface.

Table 4 shows the changes in carbon, hydrogen, and oxygen produced with the PPQ treatment. With both fibers, the oxygen content is substantially increased by the treatment. The oxygen, bound in functional groups, may not be reactive to epoxy resins. Investigators have shown that increased functionality does not necessarily mean increased composite shear strengths. In the table, the values for oxygen and hydrogen are compared with values for VYB low-modulus carbon fiber. The increased oxygen on the fiber surface may be related to improved resin bonding and higher shear strengths, but it is apparent that oxygen or hydrogen content alone do not account for the improvement. The VYB fiber, which contains 15 times more oxygen and 8 times more hydrogen than either of the treated fibers, exhibits only slightly higher shear strengths. The untreated fibers, on the other hand, contain only about 1/8 the amount of oxygen as the treated fiber yet exhibit about 1/3 the shear strengths. Of course, oxygen content may be essential in the forming of bonds only up to a given level, above which increased oxygen content does little good.

The PPQ treatment was generally done by applications of the resin from dilute (0.1%) solutions in chloroform. Concentrations other than the 0.1% were investigated, but the results were not as satisfactory. A 0.2% solution produces bridges between the fibers after decomposition, thus forming a kind of carbon-carbon composite. The result was a reduction in fiber tensile strengths and composite shear strengths. The reduction in tensile strengths may be due to too much reaction between the decomposing polymer and the fiber. The decreases in composite shear strengths occur because the bridging between fibers prevents the resin matrix from penetrating the fiber bundle. A 0.05% solution treatment did not achieve shear strength improvements equivalent to the 0.1% solution. With such a dilute solution, the carbon coverage of the fiber surface is probably not adequate.

The organometallic complexes (ferrocene and others) were tried as another attempt to introduce carbon onto the fiber surface, this time in the presence of a catalyst. The results obtained with this approach showed moderate increases in composite shear strengths accompanied by significant increases in the fiber tensile strengths. This was the first time that increased tensile strengths resulted from fiber treatments and can be explained by the flaw sensitivity of the fibers. The reaction of the carbon on the fiber surface,

TABLE 4

CHEMICAL COMPOSITION CHANGES WITH SOLUTION-REDUCTION TREATMENTS

	C%	H%	O%*
HM Untreated as received	99.7%	0.17%	0.1%
HM PPQ treated	99.1	0.15	0.7
HMG-50 Untreated as received	99.8	0.10	0.1
HMG-50 PPQ treated	98.9	0.18	0.9
VYB Untreated as received	82.9	1.43	15.7

* Oxygen by difference

especially in the presence of the metallic catalyst, evidently acts to smooth and heal some surface flaws and defects. This flaw healing is apparently opposed by the degradation of the fiber with increased treatment temperature. Treatments made above 1200°C did not produce increased tensile strengths. Those below 800°C, the decomposition temperature of ferrocene, had no significant effect on the shear or tensile strengths. All organometallic complex treatments at temperatures above 800°C produced increased composite shear strengths. The increases, however, were not as great as with the PPQ polymer treatment. These complex treatments, however, are attractive where high tensile strengths along with moderate shear strengths are required with a high-modulus fiber. Resultant changes in the fiber surface structure from these and other treatments are discussed later.

The methane method of depositing carbon, being a vapor treatment, resulted in reduced fiber tensile strengths similar to those exhibited by the gaseous oxidations. The doubling of shear strength was equivalent to several other treatment methods, but the reduced tensile strength is not desirable.

B) FIBER SURFACE CHARACTERIZATION

1. Surface Structure. As can readily be seen from Figures 6, 16, and 21, the arrangement of crystallites at the surface of carbon fibers is parallel to the fiber surface. It has been shown by other investigators that the crystallites are also parallel to the fiber axis (13,23). Thus the fiber presents primarily a basal plane surface. It therefore becomes evident that the smaller the crystallites, the greater will be the number of edges which are available for resin bonding (resins cannot bond well to basal surfaces). Also, with large crystallites, some of the surface areas are held to the fiber core by relatively weak interlayer forces. This presents the problem that even when good bonding to the outer layers is achieved, composite shear strengths may be low due to interlayer failures. It would be desirable to have more bridges bonding the outer layers to the inner fiber core. This can be most easily achieved when the crystallites are smaller.

a. Raman Spectroscopy. Raman spectroscopy is one method of determining the crystallite size on carbon fiber surfaces. Typical spectra of treated and untreated fibers and graphites are shown in Figure 11. The increase in Raman activity at 1355 cm.$^{-1}$ (induced by crystal edge effects) is evident for the less graphitic, more carbon-like specimens. The relationship of the intensity ratio of the two peaks shown in these spectra to apparent crystallite size on the surface of the specimen is shown in Figure 12 (55,56). Growth in the 1355 cm.$^{-1}$ peak intensity reflects a decrease in apparent crystallite size. Large differences in crystallite size as measured by Raman spectroscopy were found between fiber types with a range from 42 to 220 Å (Table 5). The spectra of high-modulus fibers are similar to those of commercial graphite indicating a graphite-type surface structure. Intermediate and low-modulus fibers exhibit spectra similar to carbon. With high-modulus PAN-based fibers, there was a significant decrease in apparent crystallite size (from over 200 Å to

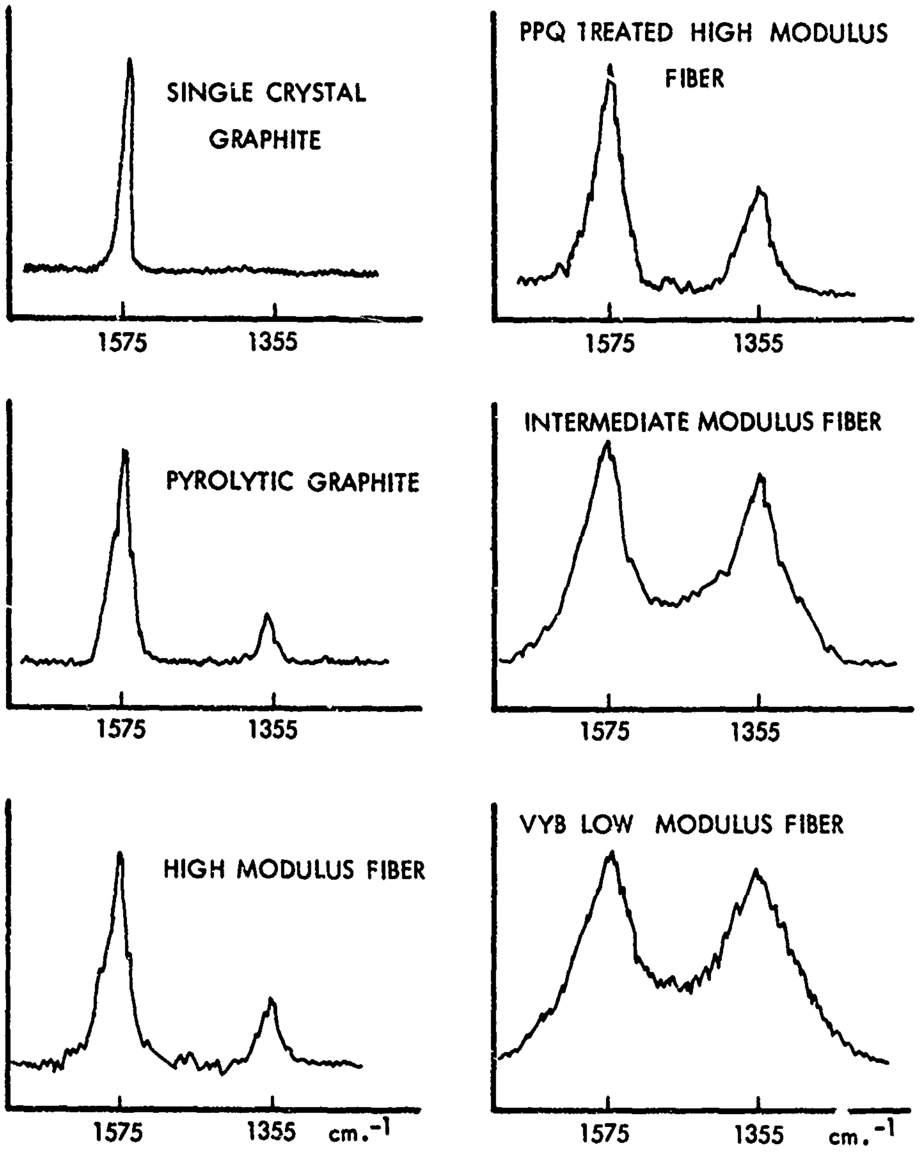


FIG. 11 COMPARISON OF RAMAN SPECTRA OF VARIOUS GRAPHITES AND CARBONS

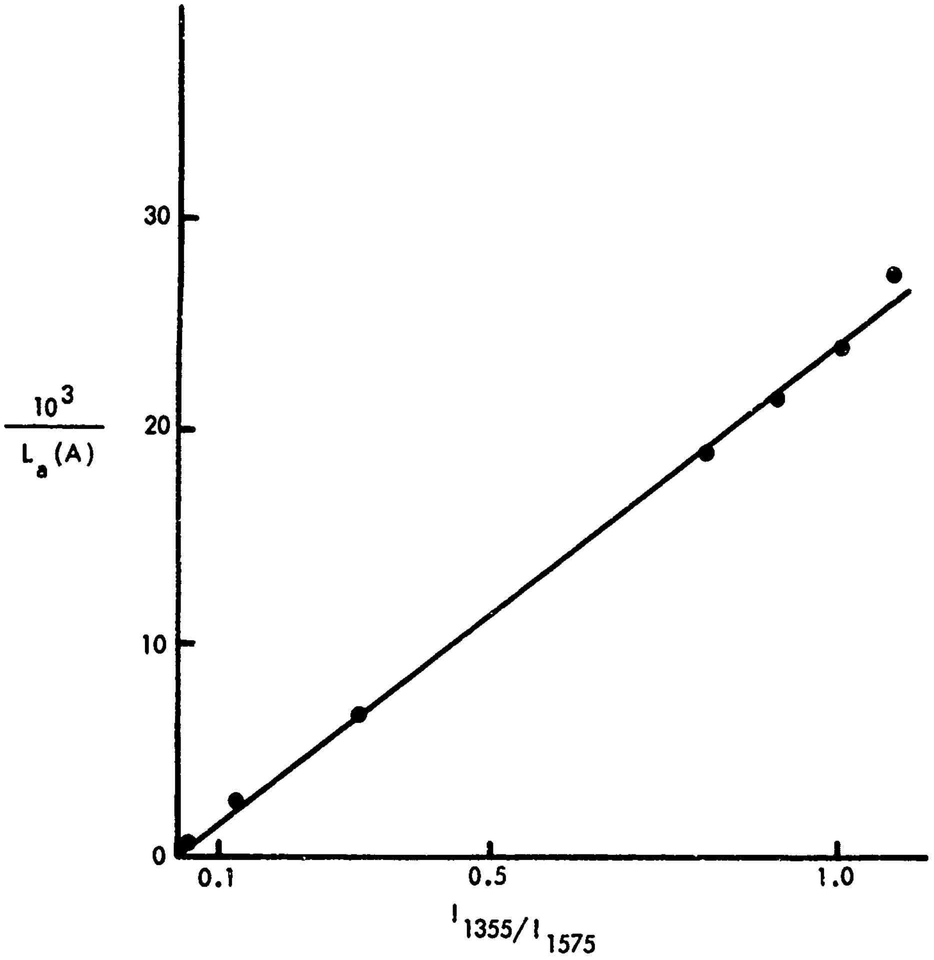


FIG. 12 X-RAY CRYSTALLITE SIZE VS. RAMAN INTENSITY RATIO (55)

TABLE 5

RAMAN INTENSITY RATIO (I_{1355}/I_{1575}) FOR VARIOUS CARBON FIBERS AND GRAPHITES

Material	Intensity Ratio	Calculated Crystallite Size, Å
Natural Ticonderoga Graphite	0 (No 1355 peak)	
Synthetic General Electric Graphite Single Crystals	0 (No 1355 peak)	
Pyrolytic Graphite Basal Exposure	0.12	500
Pyrolytic Graphite Edge Exposure	0.22	220
Commercial Graphite	0.22	220
Modmor I Untreated	0.22	220
Courtaulds HM Untreated	0.22	220
HMG-50 $FeCl_3$ Treated	0.25	190
Modmor I Treated*	0.30	150
Courtaulds HMS Treated*	0.32	145
HMG-50 Untreated	0.38	120
HMG-50 Ferrocene Treated	0.41	110
Courtaulds HM PPQ Treated	0.44	100
HMG-50 PPQ Treated	0.48	85
Courtaulds HT Untreated	0.80	55
Modmor II Untreated	0.82	50
VYB Untreated (Carbon)	0.89	45
Courtaulds HTS Treated*	0.93	42

* Manufacturer Treatments

less than 100 Å) when the outer surfaces of the fibers were removed by severe oxidations. This helps to reinforce the theory of a radial orientation in the fiber center which becomes exposed as the circumferential layers are removed. The radially oriented center with the exposed edge planes would produce a lower apparent crystallite size. The center of the fibers may also be less crystalline than the surface and this would also produce the same effect.

Treatment of the fiber surface by oxidation or carbon deposition decreased the apparent crystallite size. The mechanism by which the decrease is achieved is related to the type of treatment. Oxidation treatments probably "break up" large crystallites by pitting and etching the large layers. Carbon depositing treatments produce the same effect by introduction of smaller carbon crystallites on the surface. In terms of increased peak intensity ratio, the manufacturer oxidation treatments are only half as effective as the PPQ treatment. They also are about half as effective in the shear strength improvement as the PPQ treatment. The PPQ treated high-modulus fibers exhibit intensities in the 1355 cm.$^{-1}$ peak half as strong as carbon and twice as strong as graphite or the untreated fibers. This change in the carbon nature of the fiber surface is believed to be one major contributor towards the high shear values obtained from this treatment. Other treatments produced similar decreases in crystallite size except for the $FeCl_3$ treatment. In this case, the thick coatings of iron on the surface of the fibers, even though they are localized, perhaps reduce the edge effects contributing to the 1355 cm.$^{-1}$ signal. The improved shear strength achieved from this treatment method may be a result of mechanical bonding to the roughened surface created by the iron carbide rather than bonding to activated crystal edges.

The correlations between Raman peak intensity ratio and composite shear strength are given in Figure 13. Figure 14 shows a similar relationship between fiber modulus and composite shear strength. Since the curve for the R of untreated fibers versus shear strength in Figure 13 is almost identical to the curve for the fiber modulus versus shear strength in Figure 14, a good correlation can be made between R for untreated fibers and the fiber modulus. As the fiber modulus increases, the intensity ratio (R) decreases. This would be expected since the fiber modulus has been shown to be a function of the crystallite size in the fiber with higher-modulus fibers having larger crystallites, i.e., lower R values. Raman peak intensity ratios for treated fibers do not fall on the same curve as the untreated fibers as was previously thought (56). As seen in Figure 13, effective treatments of the fiber surface reduce the apparent crystallite size (increased R) but not in proportion to the increases achieved in shear strength. For example, the manufacturer oxidation treatment of high-modulus PAN-based fibers produced a 1/3 reduction in crystallite size (50% increase in R) and a doubling (100% increase) in the composite shear strengths. Similar oxidations of Rayon-based fibers produced a 1/2 reduction in crystallite size and a 70% increase in composite shear strengths (56). With the PPQ treatment, a 1/2 reduction in crystallite size (doubling of R values) produced a 3-fold increase in shear strengths. Therefore, while the apparent crystallite size as measured by Raman spectroscopy may indicate trends

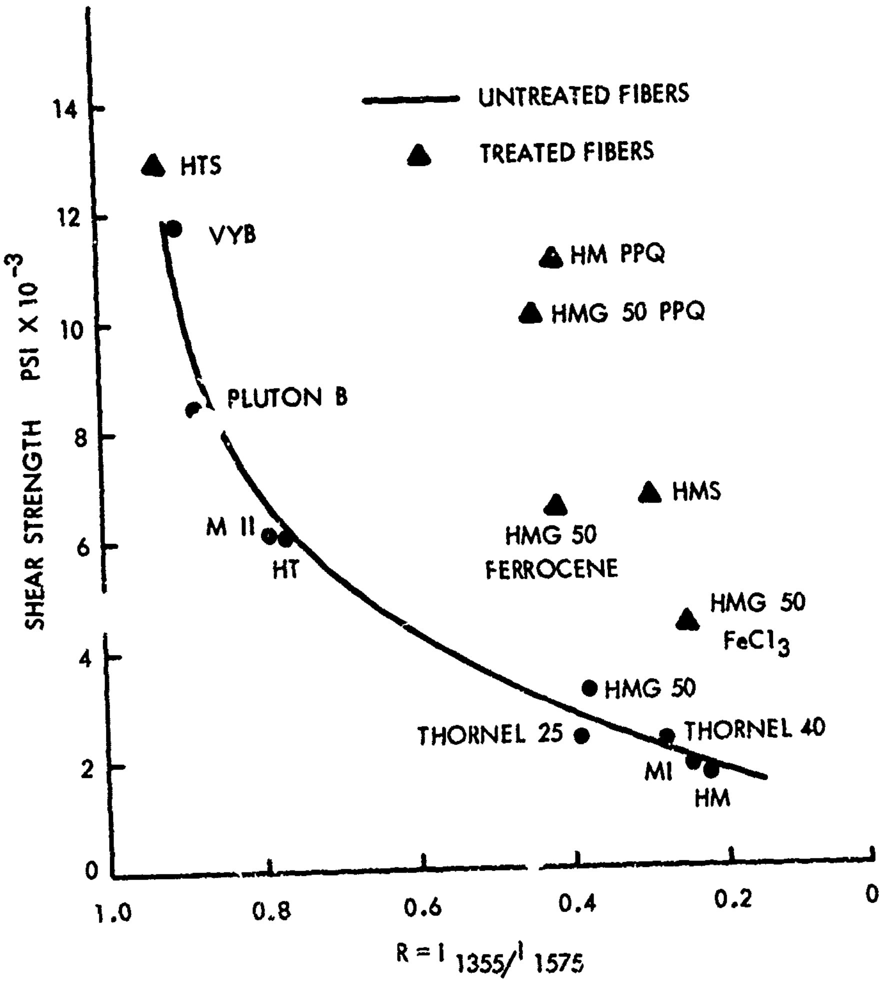


FIG. 13 RAMAN PEAK INTENSITY RATIO (R) VS. COMPOSITE SHEAR STRENGTH

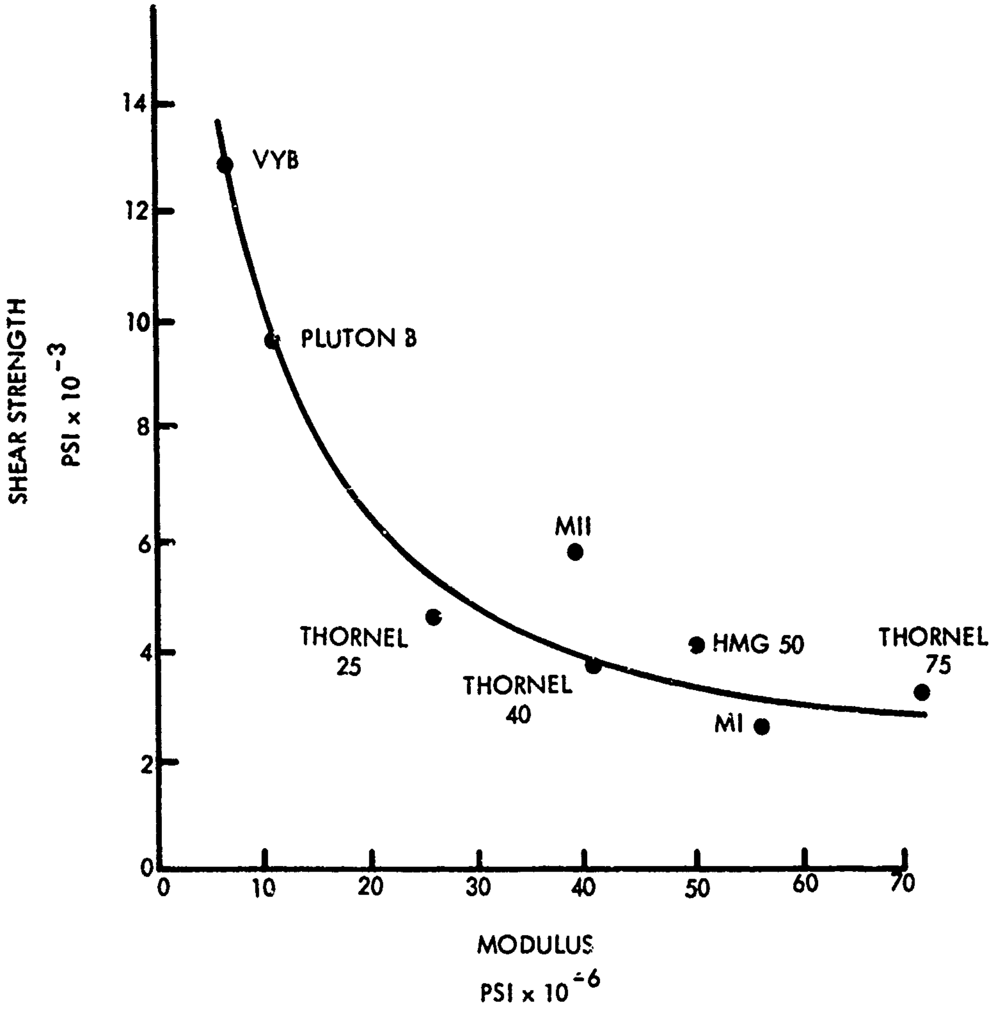


FIG. 14 SHEAR STRENGTH VS. FIBER MODULUS (51)
(UNTREATED FIBERS)

in composite shear strengths produced by fiber treatments; it by no means can be used to predict the composite shear strengths. The shear strengths of untreated fiber composites, on the other hand, are closely reflected by the R values. Good correlation exists between crystallite size (hence R values) and composite shear strengths for the untreated fibers.

The changes in composite shear strengths which are produced by surface treatments are reflected by relatively small changes in the R values. The nature of the surface actually may be modified more extensively and be more carbon like than reflected by the changes in R values. The PPQ treatment produces a verv thin carbon layer on the fiber which may not be continuous. Such thin layers may be penetrated by the laser beam, thus Raman signal would be generated from the more graphitic regions below as well as from the carbon surface. The Raman spectra would then reflect a semi-graphitic, semi-carbon surface while the surface would actually be more carbon like. Therefore, high shear strengths can be achieved by two mechanisms; 1) low-temperature treatment (1500°C) of the fiber in fabrication such that an essentially carbon fiber is produced, or 2) treatment of a graphitic fiber by modification of the surface making it more carbon like.

b. Surface Area. Measurement of fiber surface areas was one of the early methods of characterizing fiber surfaces. While surface area alone cannot be correlated with shear strengths, it does give an indication of the condition and morphologv of the surface.

Fiber surface areas are functions of the type of precursor and the type of processing the precursor undergoes in the graphitizing process. HMG-50 fibers, which are fabricated by electrical resistance heating, have a surface area of 0.9 m^2/gm. while Thornel 50 fibers, also from a Rayon precursor and fabricated by heating in a furnace, have a surface area of 0.55 m^2/gm. (Table 6). It has also been shown that outgassing the fiber in vacuum at elevated temperatures produces significant increases in the fiber surface area (41). Therefore, the surface area of fibers as produced can exhibit large variations and is not a true reflection of the fiber properties.

Surface treatments of the fibers produce varied changes in the fiber surface area. On Thornel fibers, nitric acid oxidation treatments produced large increases in the fiber surface area while gaseous oxidations increased the surface area by relatively small amounts. Heat treatment in an inert environment also increases the fiber surface area (40). Increases in composite shear strengths, however, are not proportional to surface area increases. Some of the increases in area are attributable to small pores which are too small for resin molecules to enter. Pore diameters of 8 Å have been measured (45). For the manufacturer treatments of fibers from both precursor types, increases in shear strengths of 100% (doubling) were achieved with little increase (less than 20%) in the fiber surface area. It should be noted from Table 6 that surface areas of the same fibers measured by different investigators can differ significantly.

TABLE 6

SURFACE AREAS OF CARBON FIBERS - TREATED AND UNTREATED

Fiber and Treatment	Area (m^2/gm.)
HMG-50 Untreated	0.90
Oxidation Treated	3.4 - 24.0[a]
Manufacturer Treated	0.66[a]
PPQ Treated	5.38
Thornel 50 Untreated	0.55[a]
Air Oxidation	1.4[b]
HNO_3 Boil	11.3[b]
Courtaulds HM Untreated	0.35
Manufacturer Treated	0.43
PPQ Treated	3.55
Modmor I Untreated	0.11[a], 0.38[c]
Manufacturer Treated	0.13[a]
HNO_3 Boil	1.64[c]
HNO_3 Boil + Outgass at 900°C	4.26[c]
Modmor II Manufacturer Treated	0.24[c]
VYB	0.47

[a] Reference 46 [b] Reference 24 [c] Reference 41

This may be due to differences in equipment or the measurement methods. Treatments which deposit carbon on the fiber significantly increase the surface area. Values of treated fibers run well over 3.0 m^2/gm., over six times the values for the untreated fibers. That these high surface areas are not necessary for high shear strengths is seen with the VYB carbon fiber whose surface area is 0.47 m^2/gm. and whose composite shear strength typically is 13,000 psi. Thus, the measurement of surface area serves only as a method to characterize the change in surface morphology produced by surface treatments and the surface area is not the most important contributing factor to shear strength.

2. Surface Reactivity. Carbon fiber surface reactivity can be estimated by various methods among which are surface energy, wettability, and gas chromatograph reactivity.

a. Gas Chromatograph Reactivity. Investigations of fiber reactivity using gas chromatography have shown increased affinity of treated fibers for various adsorbent vapors. Nitric acid oxidation, which increases the surface area, was not as effective in increasing the adsorption coefficients as was H_2 or air oxidations. For high-modulus fibers, only small differences could be discerned between the reactivity of treated and untreated fibers for 6 adsorbent vapors at three temperatures; room temperature, 120°C, and 220°C. It was expected that the fibers tested would exhibit the greatest differences in reactivity between treated and untreated fibers because they showed the greatest shear strength improvement after treatment. This, however, was not the case as is shown in Figure 15, where a comparison of treated and untreated fiber reactivity is presented. There is a tendency for greater reactivity of both treated and untreated fibers with vapors containing oxygen groups, the more available the oxygen the higher the reactivity. Classification of the reactivity of the 6 vapors tested for treated fibers is as follows: ethylene glycol > acetic acid > water > methyl alcohol > ethyl ether > n-hexane. The same order holds true for untreated fibers except the reactivity of ethylene glycol and acetic acid are about the same. One of the most reactive vapors, ethylene glycol, is a reactive component of ERLB 4617 epoxy resin systems. This indicates that the fiber reactivity with the resin may be quite high.

Differences in the reactivity between treated and untreated fibers, however, were not significant enough to be used as indicators of treatment effectiveness. The coefficient for water was 2500 at 220°C for both treated and untreated fibers. This compares with similar values for water of other investigators (11). Acetic acid showed the greatest change in reactivity between one treated and untreated fiber at 220°C, almost doubling. For another fiber which exhibited equal shear strength improvement upon treatment, the acetic acid reactivity was the same for the treated and untreated fiber. Based on the small differences observed in reactivity between treated and untreated fibers and the rather random increases in reactivity for treated fibers with some vapors and decreases in reactivity for others at various temperatures, this method is not useful for

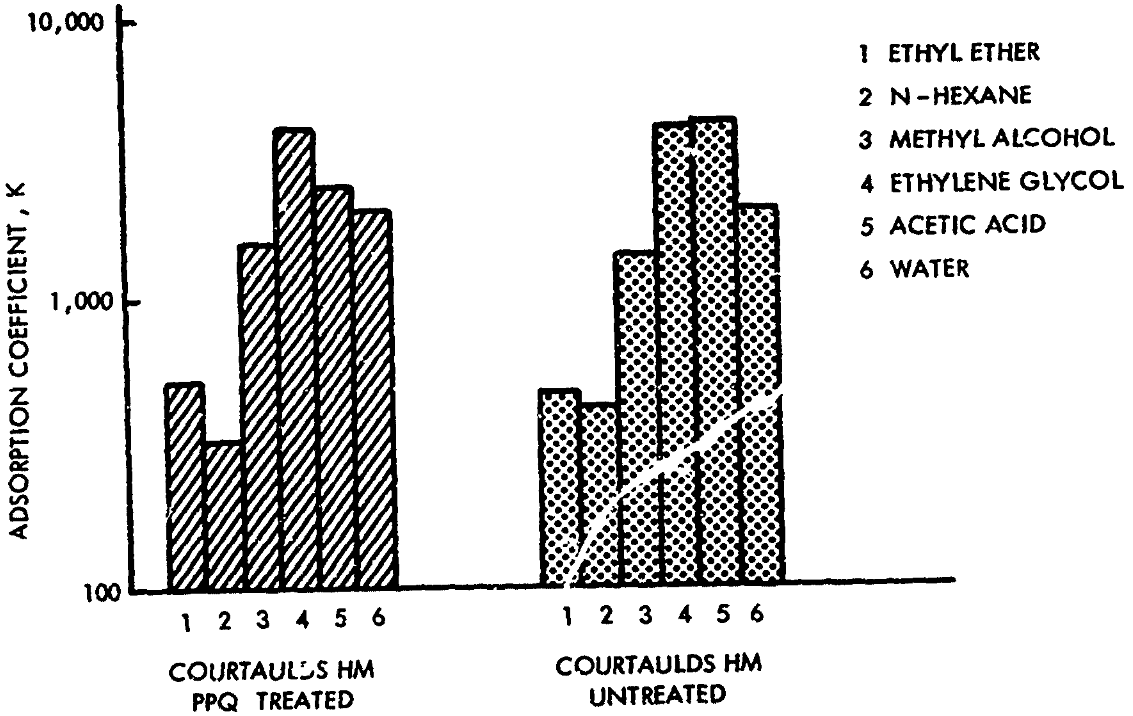


FIG. 15 GAS CHROMATOGRAPHIC REACTIVITY OF TREATED AND UNTREATED CARBON FIBERS

treatment evaluation. Of course, the sensitivity of the method may not be great enough to measure subtle differences between fibers. The information obtained may be of some theoretical use but to date is of little practical value to investigators of fiber treatments.

b. Wettability and Surface Energy. The measured surface tensions of treated and untreated fibers measured by the fiber ring method (Appendix B) differed only slightly with the treated fibers having critical surface tensions of 44 dynes/cm. and the untreated fibers having critical surface tensions of 43 dynes/cm. Standard epoxy resins have surface tensions of 40 to 45 dynes/cm. Wetting of the fibers by the resins, therefore, should in most cases be spontaneous. This doesn't occur in all cases, however, because of the irregular, rough nature of the surface. In the case of ERLB 4617 epoxy resin, the measured surface tension was 45 dynes/cm. and it would appear that wetting could be marginal. When the other factors (surface roughness, adsorbed gases, and contamination) are considered, the wetting properties of the surface could change drastically.

In most cases, resins are applied to fibers from prepreg solutions. The resins are diluted with solvents which have significantly lower surface tensions than the resins themselves, and these dilute solutions readily wet the fibers without difficulty. Therefore, the problem of wetting the fibers with the resin, previously considered to be serious, can be substantially overcome using preimpregnation techniques. The other factors of adhesion play more important roles in the fiber-resin bond, and it is for this reason that further studies of wettability were not pursued. One factor which has not been considered and is beyond the scope of this study is the change in the surface tension of the resin while curing and the effects this may have upon the bond formed between the resin and the fiber. Other factors of adhesion also have not been considered.

Scanning microscope examinations of shear fractured carbon-fiber composites have revealed that little or no resin remains bonded to fibers along the shear fracture plane. Fractures perpendicular to the fiber direction often reveal separations of up to 1 micron in the region of the fiber-resin interface. This indicates that failure is not occurring in the resin but at the resin-fiber interface or within the outer layers of the fiber. Experiments using Raman spectroscopy of resin areas where fibers had sheared out were not conclusive in determining the presence of thin fiber layers bonded to the resin. The fluorescence induced by the laser in the resin was so great that it would be impossible to detect by this means any thin layers of graphite bonded to the resin. Other investigators have shown the presence of these layers using diffraction techniques (56). The shear strength between the layers of pyrolytic graphite was measured at less than 2000 psi. For commercial graphite, it was less than 3000 psi. Therefore, it is very possible that failure is occurring within the outer layers of the fiber; but further work is needed to substantiate this.

CONCLUSIONS AND RECOMMENDATIONS

This investigation has encompassed many areas involving the structure, surface, and surface treatment of carbon fibers. The objectives were 1) to determine the structure and surface properties of the fibers, (NOLTR 71-), 2) to relate these properties to composite shear strengths, and 3) to devise new effective treatment methods which would improve the composite shear strengths of high-modulus carbon fibers without degrading the fiber tensile strengths. The need for such a study arose from the lack of understanding of the fiber structure and the nature of the surface, and from the low composite shear strengths achieved with high-modulus carbon fibers. It was postulated that some correlation exists between the fiber surface structure and the low shear strength values.

The greatest improvement in composite shear strengths resulted when the number of oxygen containing groups on the surface was increased and also when the average surface crystallite size was decreased. Such surfaces are more carbon like and less graphitic in nature and may be considerably different than the fiber interior. The composite shear strength is related to the carbon-like nature of the fiber surface.

Effective surface treatments using oxidation, vapor deposition, and solution-reduction methods were investigated. Of these, the solution-reduction treatments were the most effective and easiest to process (requiring residence times of less than one minute in continuous fabrication). This in itself has significant commercial application and a patent has been applied for. Shear strengths of 11,000 and 12,000 psi were achieved with high-modulus (50-60 million psi) Rayon and PAN-based fibers respectively. These values are the highest reported to date and compare with the 8000 psi values obtained by the manufacturers with the currently used lengthy oxidation treatments.

The most attractive approach achieved a carbon-like surface by solution coating the fiber with a polymer and the subsequent thermal decomposition of the polymer. This totally new approach to fiber treatments can be contrasted with surface oxidations which achieve similar yet less effective results.

The nature of carbon on the fiber surface and its crystallite size can readily be determined by using Raman spectroscopy. This in itself does not characterize the surface and cannot be used to predict composite shear strengths. However, when used in conjunction with known fiber properties, a fair indication of the composite performance can be obtained.

Future work is recommended in the study of fiber structure related to the surface condition and processing of the fibers. A study of the changes in fiber structure with varying low-temperature oxidation times from very short to very long should be made. The investigation of the fiber surface chemistry for surface reactivity needs to be pursued in greater detail. It has been suggested that this can be accomplished using Raman spectroscopy at highly oblique angles. Further study of the fiber-resin bond also needs attention. Finally the treatments which have been shown to be successful should be optimized as to the treatment parameters. Action should be taken then to introduce solution-reduction treated fibers into Navy programs such that the benefits of the improved shear strengths can be realized.

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APPENDIX A

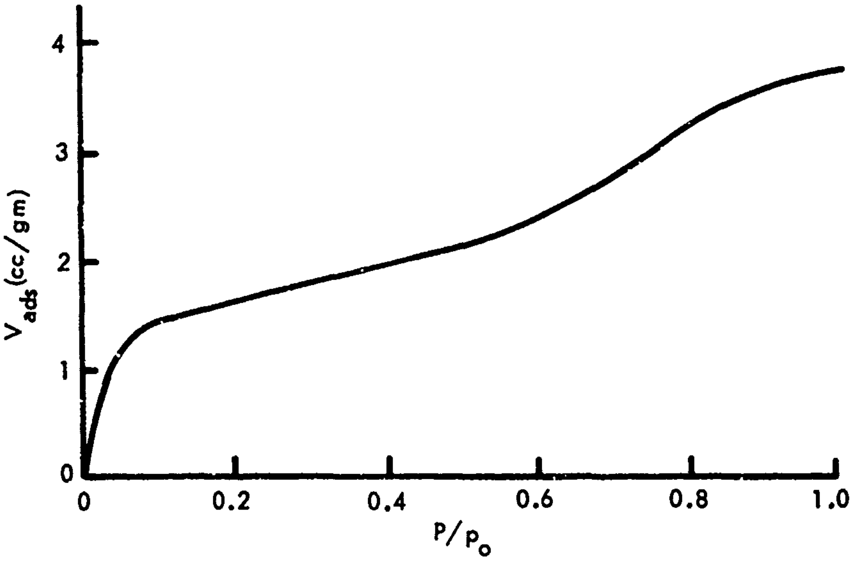
SURFACE AREA MEASUREMENT

A-1. A method for the determination of surface areas of solids by low-temperature krypton or nitrogen adsorption was devised by Brunauer, Emmett, and Teller in 1937 (12). The method consists of determining the volume of a gas necessary to complete an adsorbed monolayer, V_m, at liquid nitrogen temperature. If the volume adsorbed is plotted versus the relative pressure P/p_o (P is the pressure and p_o is the vapor pressure of the gas at the temperature T), adsorption isotherms as shown in Figure A-1 result. To these S-shaped isotherms two equations, (A) and (B), or more complex forms of these equations are applied giving plots of $P/V(p_o-P)$ versus P/p_o which are linear with slopes of $(C-1)/V_mC$ and an intercept of $1/V_mC$. The slope is a constant approximately equal to $e^{E_1 - E_2/RT}$.

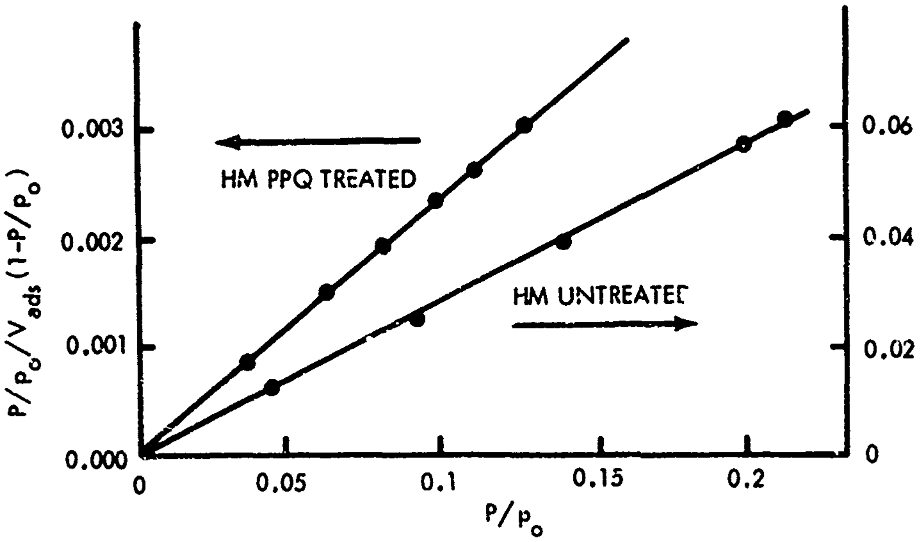
$$\frac{P}{V(p_o-P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC}\,\frac{P}{p_o} \qquad \text{(A)}$$

$$V = \frac{V_mCx}{1-x}\;\frac{1-(n+1)\,x^n + nx^{n+1}}{1+(C-1)\,x - Cx^{n+1}} \qquad \text{(B)}$$

From the value V_m obtained from the plot, the number of molecules required to form the monolayer is calculated. This number is multiplied by the average area occupied by each molecule to obtain the value for the surface area of the adsorbent solid.



A. TYPICAL ADSORPTION ISOTHERM



B. BET PLOTS OF TREATED AND UNTREATED FIBERS

FIG. A-1 SURFACE AREA MEASUREMENT

APPENDIX B

CRITICAL SURFACE TENSION BY THE FIBER-RING METHOD

B-1. Surface tensions of liquids are routinely measured by the ring method where $\gamma = (mg/2L)F$

γ = surface tension of the liquid

m = measured separation force

g = gravitational constant

L = circumference of ring

F = correction factor for the particular ring and liquid used

When performed correctly, such a method can be very accurate. A platinum ring is usually used and assumed to be completely and spontaneously wetted by the liquid (contact angle = 0).

B-2. Measurement of the critical surface tension of solids has been much more difficult. Contact angle measurements (the angle a drop of liquid makes with a clean flat solid surface) is the standard method. Various liquids of known surface tensions are used to obtain a plot of the cosine of the contact angles versus the liquid surface tensions. This is usually measured or extrapolated to the point where the contact angle equals zero which is defined as the critical surface tension of the solid. Moisture or other contaminants on the solid will greatly effect the contact angle measurements.

B-3. Measurement of contact angles of liquid droplets in contact with the irregular surface of small diameter fibers presents even greater problems. No really good method for doing this, especially with carbon fibers, exists. It was, therefore, proposed that a combination of the two methods be used to determine the surface tensions of fibers. A fiber ring instead of the usual platinum ring was used. This fiber ring was calibrated using very low surface tension liquids which were assumed to completely wet the fibers and the correction factor F was determined so that the surface tension values measured by the platinum ring and the fiber ring were equivalent.

B-4. Surface tensions of various liquids were then measured with the fiber ring and plotted versus the known surface tensions of the liquids. Such a plot (shown in Figure B-1) is linear as long as the liquid wets the fiber. The point where a sharp discontinuity occurs was assumed to be the critical surface tension of the fiber, since it was the point where the fiber no longer was wet by the liquid.

$$W = \frac{\text{SURFACE TENSION MEASURED BY FIBER RING}}{\text{SURFACE TENSION OF LIQUID}}$$

= 1 WHEN THE FIBER RING IS WET BY THE LIQUID

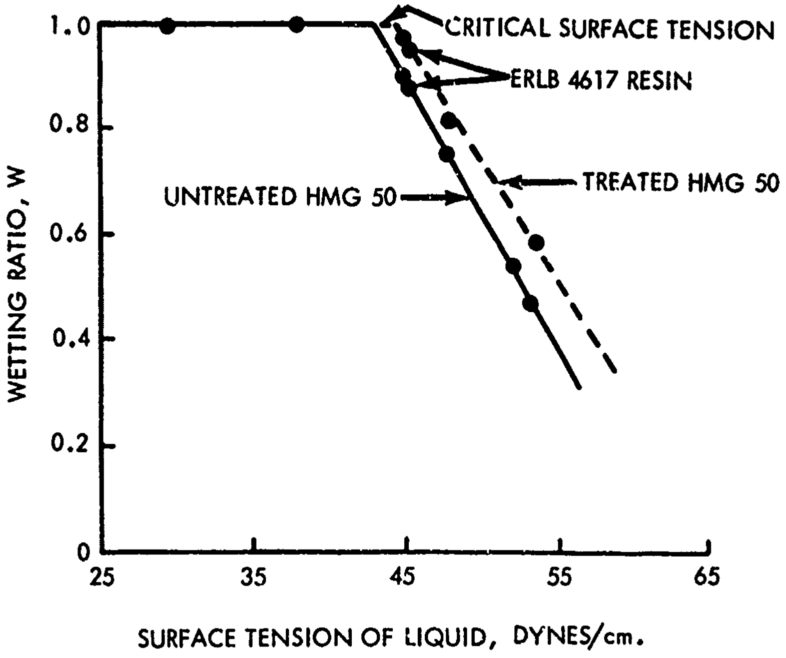


FIG. B-1 CRITICAL SURFACE TENSION OF FIBERS DETERMINED BY THE FIBER RING METHOD

APPENDIX C

GAS CHROMATOGRAPHY OF CARBON FIBERS

C-1. The surface reactivity of carbon fibers can be measured to an extent by the affinity the fibers have for various vapors and the length of time the vapors take to traverse a column packed with the fibers. The specific relationships of gas-solid chromatography can be used to calculate the retention volume (V_g) or the adsorption coefficient (K) from the pulse retention time (T_r) measured from the base width of the peak (11).

$$V_g = K = (T_r/T_m - 1)(V_m/W)$$

T_m = transit time for the carrier gas

V_m = total gas free volume in the column

W = adsorbent weight

The transit time is a function of the volume of the column, the amount of packing and its density, the gas flow rate, and the temperature of the column.

$$T_m = \frac{\pi r^2 L - W/\rho}{V(T_2/T_1)}$$

$\pi r^2 L$ = volume of column

V = volume flow rate of carrier gas

ρ = density of packing

T_1 = absolute temperature at flow meter

T_2 = absolute temperature of column

C-2. Since pulse retention times as conventionally measured would be too short for accurate determination, the peak base widths were used as a measure of the time required to adsorb and desorb the various vapors. With the greater affinity of the fibers for certain vapors, the peaks become very unsymmetrical especially when the desorption times are long. Great stability is required in the instrument to maintain a constant base line over such periods of time. In the author's judgement, this method may be of some significance to a pure researcher; but the information obtained does not show enough difference between treated and untreated fibers to be of practical significance for characterizing surface treatments.

APPENDIX D

RAMAN SPECTROSCOPY OF CARBON FIBERS

D-1. Raman spectroscopy can discriminate between different types of carbons and graphites. For the single graphite crystal, a single band is active at 1575 cm.$^{-1}$ from asymmetrical in-plane vibrations of the carbon layers in phase or in opposite phase. This active band contains two fundamental modes from the phasing, but the difference in energy between the two modes is small due to weak forces between layers and appears as a single band. The band does not depend on order between graphite layer planes as it appears at the same frequency in ordered and turbostatic graphites. For graphites and carbons other than single crystal graphites, an additional band becomes Raman active at 1355 cm.$^{-1}$. This additional activity appears from a particle size effect. The activity is attributed to symmetric ring stretching vibrations which in the infinite lattice are cancelled out due to the symmetry of the lattice. As the crystallite size becomes smaller (of the order of magnitude of the incident beam diameter), the symmetry is destroyed due to the crystal edges and Raman activity is achieved (55). The activity arising from the borders of the crystallites, due to this loss in translational symmetry is, therefore, a function of the amount of crystal boundary in the specimen or the average crystal diameter. Larger crystallites exhibit fewer boundary edges and from the intensity of the 1355 cm.$^{-1}$ activity the crystallite size can be calculated.

D-2. The Raman signal is generated in a thin surface layer (about 500 Å thick for graphite) and, therefore, reflects primarily the condition of the surface. Crystal size and orientation have certain effects on the intensity ratio (R) of the 1355 and 1575 cm.$^{-1}$ peaks. This ratio presents a fairly good estimate of the number of vacancies, edge planes, and crystal edges to which resin can bond. It also represents to a degree the proportion of carbon and graphite near the specimen surface.

APPENDIX E

SOLUTION-REDUCTION TREATMENT PARAMETERS

E-1. Several variables in the solution treatment of carbon fibers remain unexplored. The following variables are readily apparent:

1) Choice of solvent

2) Concentration of the solution

3) Residence time of fiber in solution (4 sec.)
(Fiber travel rate - 10.5 fpm)

4) Drying time and temperature (25 sec., 150°F)
(Air flow rate - 10 cfm)

5) Temperature of heater

6) Residence time in heater (6 sec.)
(Fiber travel rate - 10.5 fpm)

E-2. For various treatments, certain of these variables remained constant by design (3,4, and 6). Of the others, the choice of solvent is restricted somewhat by the type of treatment. With PPQ one is restricted to three or four convenient solvents. (Only one was used - chloroform). With the $FeCl_3$ treatment, three solvents (benzene, toluene, and water) were tried but not fully explored. Variations in the solution concentration were investigated with the PPQ treatment, and the results of these variations are discussed in the text.

E-3. The treatment temperature was varied on several of the treatments. Temperatures that are too high produce reactions which degrade the fiber tensile properties. At low temperatures, not enough reaction occurs between the fiber and the deposited material to achieve the desired results.

E-4. All in all, a much more thorough investigation of all these parameters would be necessary to optimize the most promising treatments.

APPENDIX F

RESIN FORMULATION AND CURE CYCLE

F-1. Treated and untreated fibers were fabricated into composites using one resin system. This resin was chosen for its high strength and modulus and its good bonding properties between the resin and the fibers. The resin formulation used contains curing agent in 5% excess of stoichiometry.

Resin:	ERLB 4617 (Union Carbide) cycloaliphatic epoxy resin	100 parts
Curing Agent:	MDA, methylene dianaline (Dow Chemical Company)	46 parts

Cure Cycle:	4 hours	85°C
	3 hours	120°C
	16 hours	150°C

Cured Resin Properties:

Tensile Strength	15,000 psi
Tensile Modulus	672,000 psi