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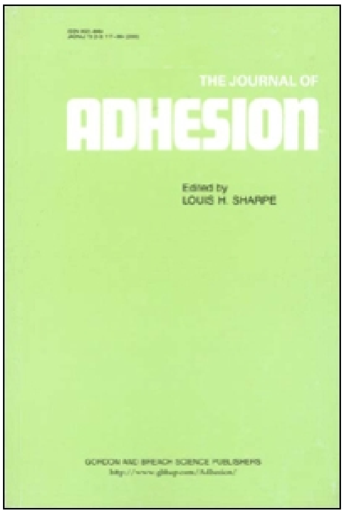

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Surface Aspects of New Fibers, Boron, Silicon Carbide, and Graphite

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ABSTRACT

A review of the literature for surface characteristics of boron, silicon carbide and graphite fibers was made. Some of the physical and chemical characteristics of the surfaces of these fibers are described. Surface properties that are unique as well as common to each fiber are discussed. Comparisons of these fiber surface properties to those of glass fibers are made in efforts to bring out differences and similarities. This report is an attempt to summarize the strength of the "bond" at the fiber-resin interface in high modulus fiber reinforced composites. The problems associated with defining the chemical and physical nature of the fiber surfaces which are most relevant to the development of composites with optimum mechanical properties are pointed out.

INTRODUCTION

ONE OF THE principal problems encountered in the use of new fibers in resin composites is how to establish an active fiber surface to achieve maximum adhesion between resin and fiber surface. An excellent review[1] of the bonding problems encountered in the glass fiber-resin system has recently been published. A current paper presents the evolution and present status of adhesion theory[2]. The purpose of the present report is to summarize the physical and chemical characteristics of the surfaces of boron, silicon carbide and graphite fibers and where possible attempt to relate these surface properties to the mechanical properties of composites prepared from these fibers.

PHYSICAL CHARACTERISTICS

The principal features of physical structure which are relevant to adhesive bond formation between a matrix material and a reinforcement fiber are the specific surface area and the extent of surface roughness. Both of these features of surface topography are relevant to adhesive bond formation inasmuch as they determine the extent of physical interfacial area available for formation of bonding between the fiber and matrix phases.

Topographical Features

The topographical features of each fiber surface as determined by optical and electron microscopy are shown in Figures 1, 2, 3, 4, 5, and 6. The surface of

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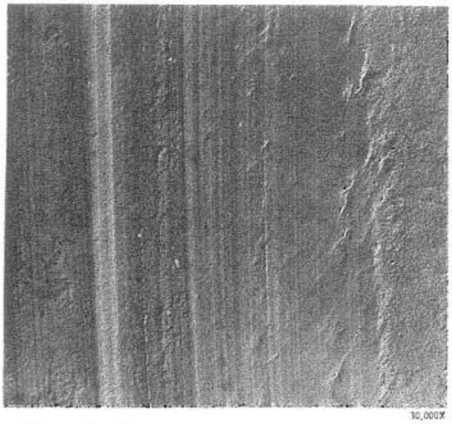


Figure 1a. Electron micrograph of s-glass (901) filament surface unfinished glass fiber.

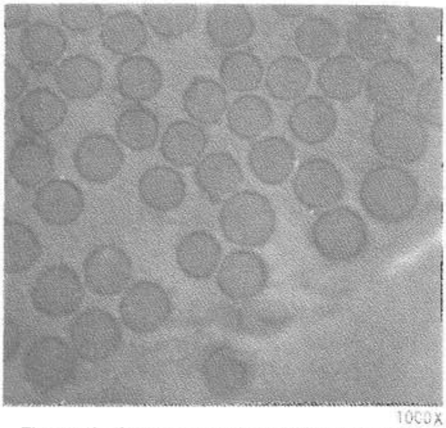


Figure 1b. Optical photomicrograph of s-glass (901) fibers (transverse cross sections)

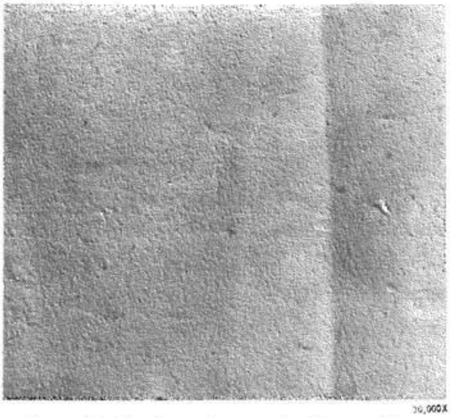


Figure 2a. Electron micrograph of boron fiber surface.

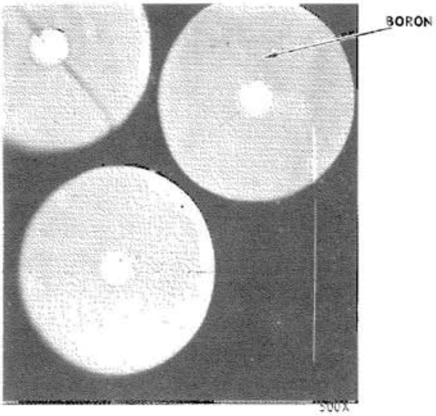


Figure 2b. Optical photomicrograph of boron fibers (transverse cross section).

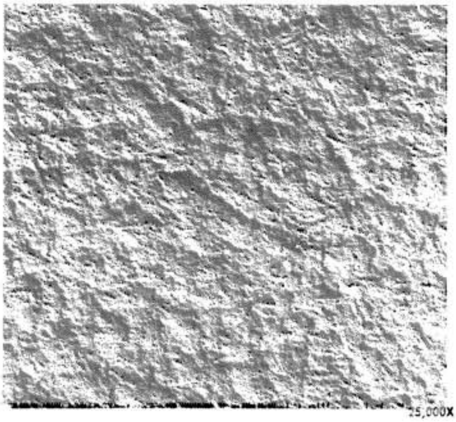


Figure 3a. Electron micrograph of a silicon carbide fiber surface.

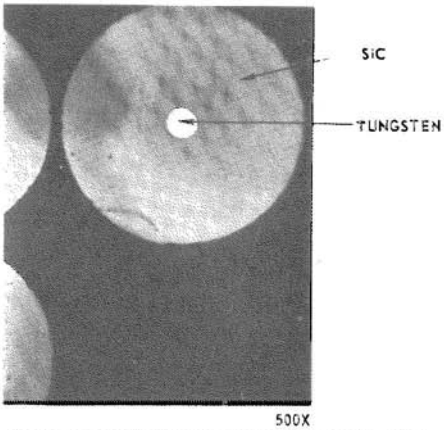


Figure 3b. Optical photomicrograph of the transverse cross section of silicon carbide fibers.

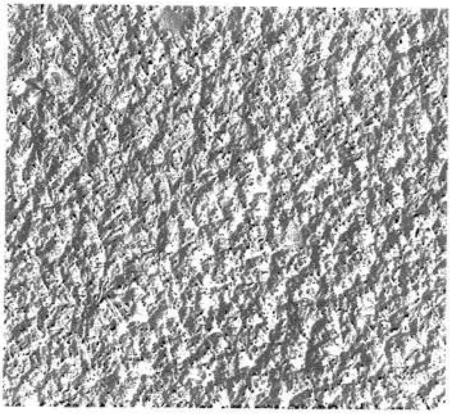


Figure 4a. Electron micrograph of a silicon carbide coated boron fiber surface (Borsic®).

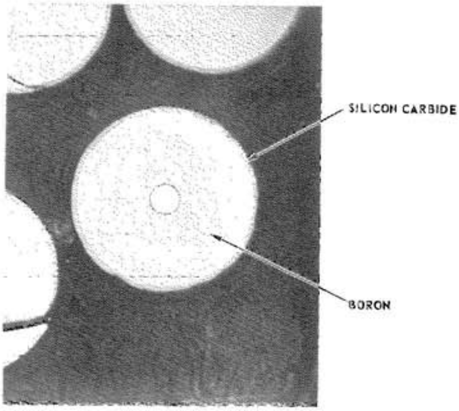


Figure 4b. Optical photomicrograph of silicon carbide coated boron fibers (Borsic®) (transverse cross (transverse cross section).

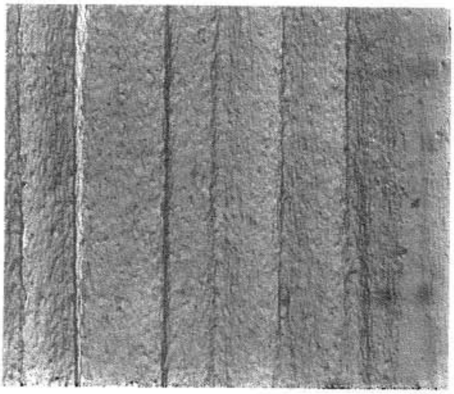


Figure 5a. Electron micrograph of a Hitco HMG-50 graphite fiber surface (untreated).

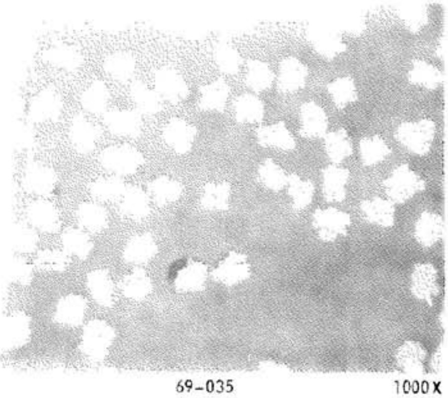


Figure 5b. Optical photomicrograph of Hitco HMG -50 graphite fibers (transverse cross section).

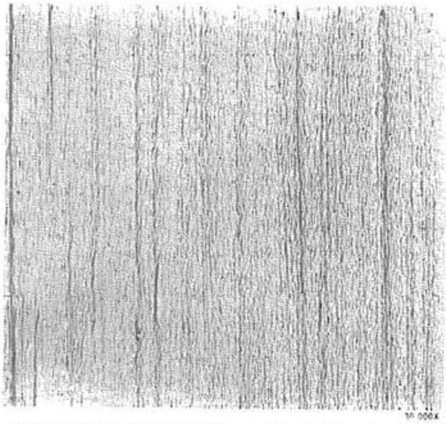


Figure 6a. Electron micrograph of a Courtaulds B graphite fiber surface (untreated).

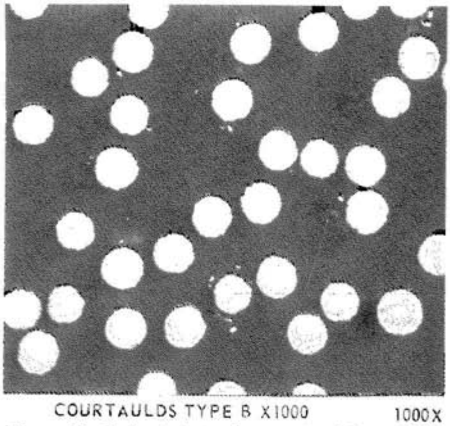


Figure 6b. Optical photomicrograph of Courtaulds B graphite fibers (transverse cross section).

S-glass fiber is smooth and relatively free of surface roughness (Figure 1a). The cross section shows a symmetrically round fiber (Figure 1b).

The surface of the boron has a corncob structure (Figure 2a). It is relatively smooth and one could expect a low surface area. The cross section (Figure 2b) reveals the internal composite structure (W_2B_5 and WB_4 inner core and boron outer core) and a geometry which is regular and round. The silicon carbide fiber (Figure 3a) reveals a surface that is grainy, but smooth. With the low order of surface roughness and relatively large fiber diameter (101.6 μ) a low specific surface area would be expected of this fiber. The micrograph of the cross section of the fiber (Figure 3b) shows a tungsten inner core and a silicon carbide outer core and a geometry which, like boron, is also regular and round. Silicon carbide coated boron filaments (BORSIC®) (Figure 4a) have a grainy surface structure similar to the silicon carbide fiber. Lower magnification shows corncob topography identical to the boron on which the silicon carbide is deposited. The cross section (Figure 4b) reveals the W_2B_5, WB_4 inner core, boron outer core and silicon carbide coating. The coating of the silicon carbide is of the order of 0.15×10^{-3} inches (3.8μ) in thickness.

Two common types of high modulus, high strength graphite filaments are represented by Figures 5 and 6. The electron micrograph of the surface of graphite fiber produced from a rayon precursor (Figure 5a) shows a smooth striated, fibrillar structure. Optical photographs of the cross section (Figure 5b) show a very irregular geometry and further reveal the striations seen in

Table 1 Physical Properties of Fiber Materials

Fiber	*Density g/cc*	*Diameter μ*	*Specific Surface Area, m²/g Exp(a)*	*Specific Surface Area, m²/g Calc*	*Total Surface Area in 100 cm³ Composite With 60 vol. % fiber, m²*
S-Glass	2.50	10	0.13	0.16	19.5
Boron	2.70	101.6	(b)	0.015	3.1(c)
Silicon Carbide	3.5	101.6	(b)	0.012	1.8(c)
Silicon Carbide Coated Boron (BORSIC®)	2.80	105.4	(b)	0.014	2.16(c)
Thornel 50	1.63	6.6	0.55	0.37	54.0
Hitco HMG-50	1.71	6.8	0.87	0.34	89.0
Morganite I	1.99	7.5	0.11	0.26	31.2
Courtaulds B	1.93	7.5	0.31	0.27	34.8

(a) Measured by low temperature adsorption of Krypton (Reference 3).

(b) Measured values of 0.01 or less were obtained. These are outside of the capability of the experimental technique.

(c) The calculated value of the specific surface area was used.

electron micrographs of the surface (Figure 5a). Electron micrographs of the surface of a carbon fiber prepared from a polyacrylonitrile (PAN) precursor also show fibrillar structure (Figure 6a) but the striations are not as pronounced as in the rayon based fibers. The overall effect is a more smooth and regular surface. This is also borne out by surface area data which are shown in Table 1. The light micrograph (Figure 6b) of the PAN based fiber is round and regular with some surface roughness noticeable on a microscale.

Specific Surface Area

The surface area data determined by low temperature adsorption of krypton[3] are presented in Table 1. The surface areas are consistent with what was expected from the fiber size and from observations of the electron micrographs of the fiber surface. Boron, silicon carbide and Borsic have low specific surface areas and the micrographs also showed very little surface roughness. In contrast, the specific surface areas of Thornel 50, Hitco HMG-50 and Morganite I are much greater, which is consistent with the fiber size and surface roughness revealed by electron micrographs. The calculated surface areas based on fiber size and density are very close to the experimental values which indicate the low order of surface roughness. Thornel and Hitco fibers, which have irregular cross sections and some surface roughness, show the greatest departure from experimental values as expected. The total fiber surface area in a composite (100 cc) containing 60 volume percent fiber is listed for comparison. These areas take into account density differences for each fiber and are more meaningful in terms of the total interfacial area available for adhesive bond formation.

CHEMICAL CHARACTERISTICS

Chemical Composition

The chemical composition and structural features of fiber surfaces determine the magnitude of the surface free energy. This latter property governs fiber wettability and chemical reactivity which are relevant to surface treatments, formation of chemical bonds between fiber and matrix materials, and vulnerability to reaction with the environment (O_2, H_2O, organic contaminants, etc.). The chemical composition of bulk fiber and of the surface for each fiber system is shown in Table 2. Except for glass fiber, the chemical composition of the surface does not resemble that of the bulk fiber. It is significant to note that oxygen is common to each fiber surface and if the concentration of oxygen per unit area were sufficiently high, each surface would most likely be hydrophylic.

The presence of hydroxyl groups and water on glass surfaces has been established by several investigators[4-8]. The presence of boron oxide on the surface of boron fibers has been demonstrated by reaction of the surface with methanol[9]. Removal of the oxide layer from boron, as will be shown later, results in improved dry and wet flexural and shear strengths. These workers

Table 2 Composition of Fibers

		Surface	
Fiber	Bulk	Analysis	Probable Functional Groups or Oxide
E-glass	Si, O, Al, Ca, Mg, B, F, Fe, Na(a)	Si, O, Al(f)	-Si-OH(f) Si-O-Si
Boron	W_2B_5, WB_4(b) (inner core) B (outer core)(b)	B_2O_3 as methyl borate(g)	B-OH B-O-B
Silicon Carbide	W (inner core) Si, C (outer core)(b) O, N(c)	Si, O(c)	Si-O-Si Si-OH
Graphite	C(d), O, N, H(e) metal impurities(e)	C, O, H(e)	$-CO_2H$, C-OH(h) C = O

(a) Reference 61
(b) Reference 62
(c) Reference 10
(d) Reference 63
(e) Reference 11
(f) References 4, 5, 6, 7, 8
(g) Reference 9
(h) References 12, 13, 14, 15

showed that exposure of the methanol-washed and oxide-free boron to air results in spontaneous oxidation to the oxide. Electron microprobe analysis of the surface of silicon carbide filaments qualitatively revealed the presence of surface oxides[10]. Thermodynamic calculations for the reaction $SiC(s) + \frac{3}{2}O_2(g) \rightarrow SiO_2(s) + CO(g)$ show that formation of SiO_2 from SiC is favored at room temperature, which is in complete agreement with electron microprobe analytical results[10]. The most common surface species on graphite other than carbon are hydrogen and oxygen. Electron microprobe analyses of high modulus carbon fibers have shown qualitatively the presence of oxygen at depths of 3μ[11]. Other workers have differentiated the types and concentration of oxygen containing functional groups on the graphite fiber surface[12]. Surface functional groups which have been identified on carbon and charcoal surfaces include carboxyl, $(-CO_2H)$, aromatic and aliphatic alcohols (-C-OH), carbonyl ($>C = O$), and lactone $(-\underset{\underset{O}{|}}{C}=O)$[13-15].

Surface Reactivity

The elemental composition, functionality, and crystallographic structural features of the fiber surface must determine surface reactivity. Studies to determine the chemical reactivity and nature of the surface seem to be logical means by which optimum materials combinations and modifications can be made to develop strong bonds in composite materials. The chemisorptive capability of a surface has been used as a measure of the surface chemical reactivity. Numerous examples of this are recorded in the literature and are reviewed by Zettlemoyer and Narayon[16].

Studies of the reactivity of E-glass fiber surfaces have led to a differentiation between silanol acid sites and other acid sites by titration with aqueous or alcoholic solutions of alkali hydroxides[17]. The glass fiber surface normally covered principally with hydroxyl groups has been shown to provide surface reactivity via the labile hydrogen[4,18]. High temperature surface treatments, however, can lead to dehydroxylation[4,19,20] and hence diminish surface reactivity and wettability. Glass surfaces have been shown to react with thionyl chloride[21-23], epichlorohydrin and alcohols[24,25]. The chemical adsorption of various coupling agents on glass surfaces for the improvement of the bond between the resin and glass surface is well documented in the literature[26-29]. For example, adsorption-desorption studies of C^{14}-labeled γ-methacryloxypropyltrimethoxysilane on E-glass fibers showed that the silane was not desorbed after toluene and ethyl acetate rinse. However, boiling water desorbed most of the material, leaving 0.236 of a monomolecular layer on the surface[29]. The retention of coupling agent by the glass exposed to boiling water has been ascribed to the formation of a chemical bond to the glass surface[28]. There is some evidence, however, that siloxane polymer formation on the glass surface[30-33] is responsible for the improvement in bond strength. The effectiveness of silane coupling agents in improving wet strength properties is well documented, but the mechanism by which the improvements occur is still a subject of considerable controversy.

Adsorption of oxygen, carbon dioxide, carbon monoxide, ammonia, nitrogen and ethylene oxide on boron filaments was studied[34] in efforts to determine if adsorbed gases were responsible for decreasing the bond strength of boron-epoxy resin composites. Adsorption in each case was very weak and found to be unrelated to composite shear strength. Efforts to enhance the reactivity of boron fibers toward epoxy resin by treatment of the boron with boron trichloride, chlorine[34], triphenylarsine, nitrogen and ammonia treatment[35] at elevated temperatures (800 to 2200° F) were ineffective based on shear or flexural strength. However, methanol has been shown to activate or clean the boron fiber surface[36]. This was found to be due to a removal of surface boron oxide or boric acid by reaction with methanol to form the volatile methylborate ester.

In the case of the graphite fibers the surface composition which consists of appreciable quantities of oxygen and traces of hydrogen and nitrogen is in part due to the nature of the precursor fiber (rayon or polyacrylonitrile) and in part due to the reactive nature of carbon. Extensive investigations of the reactivity of carbon blacks and graphitized carbon blacks indicate that oxygen on carbon surface are complicated species and evidence has been obtained that both acid and base sites due to oxygen adsorption can be present simultaneously[4, 13-15]. The adsorption capacity of carbon powder surfaces for water, oxygen and organic and inorganic materials has been adequately demonstrated by several investigators and recently reviewed[37, 38].

Recent progress directed toward determining the reactivity of graphite fiber surfaces has been made in our laboratories[39]. One approach to evaluation of surface reactivity involves use of chromatography. The reactivity of the carbon fiber surface has been measured in terms of adsorptive capability of carbon fibers for certain organic vapors using the fiber as a substrate in a gas phase chromatographic column. The retention time required for the vapors to transverse the graphite fiber column gave a measure of the adsorption coefficient or reactivity of the surface. The results (Tables 3 and 4)[11, 39] indicate that the reactivity of the surface toward n-decane, n-octylamine and isobutyric acid vapors has been increased by treatment of the graphite surface with nitric acid. Reactivity of Thornel 25 graphite yarn with

Table 3 Adsorption of Vapors on Hitco HMG-50 Graphite Fibers[a]

	Adsorption Coefficient at 547°K	
Vapors	*As Received*	*Oxidized*
n-decane	400	600
n-octylamine	1000	1500
isobutyric acid	700	1700

(a) Reference 39

Table 4 Adsorption of Vapors on Thornel 25 Graphite Fibers[a]

	Adsorption Coefficient at 422°K	
Vapor	*As Received Water Sized*	*H_2 Treated at 1200°C, Exposed to Air*
Water	200	1900
Toluene	100	1400
Pyridine	300	1600

(a) Reference 39

Table 5 Dye Adsorption on Hitco HMG-50 Graphite Fibers[a]

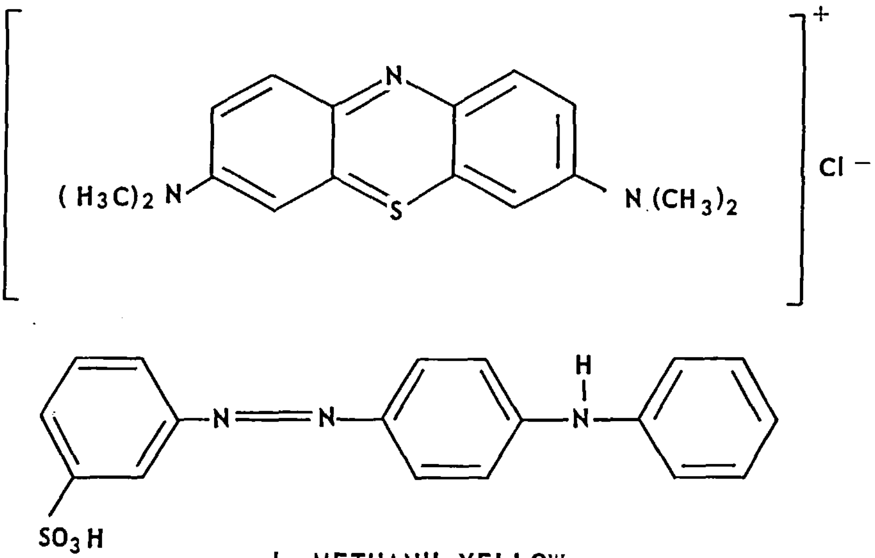
Surface Treatment	*Specific Surface Area m^2/g*[b]	*MB*[c] *Adsorbed μmole/g fiber*	*MY*[d] *Adsorbed μmole/g fiber*	*MB Adsorbed μmole/m^2 fiber*	*MY Adsorbed μmole/m^2 fiber*	*MB-MY μmole/g*
None	0.87	1.39	1.38	1.60	1.60	0.01
Oxidation	3.40	4.62	2.05	1.36	0.60	2.57
Oxidation	7.30	13.58	5.66	1.86	0.78	7.92

(a) Reference 40

(b) Measured by low temperature adsorption of Krypton (Reference 3)

(c) MB = methylene blue

(d) MY = metanil yellow



b. METHANIL YELLOW

Figure 7. Structural formulas of dyes used in adsorption studies.

the vapors listed in Table 4 was increased considerably by treatment in hydrogen at 1200° C. In both cases the fibers were exposed to the atmosphere before the adsorption experiments. The results of studies on Thornel 25 in terms of surface reactivity can be summarized as follows: Hydrogen treated Thornel 25 $>$ argon treated 1200°C Thornel 25 $>$ evacuation (1200°C) Thornel 25 $>$ as received Thornel 25.

Another approach we have used in studying the reactivity of the surface of graphite fibers is the adsorption of a cationic basic dye, methylene blue (MB) (Figure 7a) and an anionic acidic dye, metanil yellow (MY) (Figure 7b) from aqueous solution ($\sim 10^{-4}$ molar)[10]. This procedure has been used to characterize the surface acidity of activated carbon powders[11]. From the adsorption results (Table 5) it is apparent that the increase in surface area increases the adsorption capability of the fiber surface per gram of fiber for both methylene blue and metanil yellow. For example, methylene blue and metanil yellow were adsorbed to the extent of 1.39 and 1.38 μ moles per gram respectively on "as received" untreated HMG-50 fiber. However, oxidation increased the adsorption of the cationic dye to 13.58 μ moles per gram compared with an adsorption of 5.66 μ moles per gram of the anionic dye. The tenfold increase in the amount of cationic dye adsorbed corresponds to the increased surface area of the fiber measured by krypton adsorption. Oxidation does not increase the number of MB dye adsorption sites per m^2. It is significant that for the oxidized fibers, the adsorption capacity for MB increases to more than twice that for metanil yellow. The cationic methylene blue carries a positive charge and two basic amino groups which should be attracted by any acidic groups on the carbon surface. The metanil yellow, as an acidic anion in solution, should be attracted toward basic groups on the carbon surface, and tend to be repelled by acidic groups on the carbon surface. Inhibition of the adsorption of the anionic dye can be attributed to an anion exclusion effect resulting from an increase in the number of negatively charged sites relative to the number of positive sites. Any difference observed between the adsorption capacity of the cationic MB dye and the anionic MY dye for a given fiber provides a measure of the buildup of anionic sites on the graphite surface.

Further evidence[10] that the oxidation treatments actually incorporate acidic adsorption sites on the graphite fiber surface is provided by adsorption studies using a strong inorganic base, sodium hydroxide (Table 6). The increase in the number of μ mole of sodium hydroxide adsorbed per unit area (m^2) of oxidized fiber over that for untreated fiber shows that oxidation increases the number of acidic sites per m^2. This increased reactivity is most likely related to the improved shear properties of graphite fiber reinforced-epoxy resin composites. This is discussed in the last section of this report. These results are consistent with published results obtained for carbon blacks activated by oxidation[11].

Table 6 Sodium Hydroxide[(a)] Adsorption on HMG-50 Graphite Fibers[(b)]

Surface Treatment	*Specific Surface Area m^2/g[(c)]*	*NaOH Adsorbed*	
		μ mole/g fiber	*μ mole/m^2 fiber*
None	0.87	0.066	0.076
Oxidation	7.3	3.04	0.416
Oxidation	24.2	5.90	0.244

(a) $\sim 10^{-4}$ molar solution

(b) Reference 40

(c) Measured by low temperature adsorption of krypton (Reference 3).

SURFACE ENERGY AND WETTABILITY

An important condition for formation of a good adhesive bond is that the liquid adhesive adequately wets the surfaces to be bonded in order to obtain complete and intimate contact. A large interfacial area of intimate contact by the adhesive is a prerequisite whether the adhesive bond is due primarily to van der Waal's physical adsorption forces or to chemical bond formation.

A high surface energy solid surface offers the most conducive thermodynamic condition for good wetting, especially if the adhesive materials are polar organics with surface tensions in the range of 35 to 45 dyne/cm. The solid surface energy should exceed 45 dyne/cm for spontaneous spreading to occur. The fiber materials boron, silicon carbide and carbon as manufactured have appreciable surface oxides which are conducive to high surface energy. However, even with surface oxides the presence of contaminants, notably adsorbed water vapor, can produce conditions such that there is incomplete wetting by polar adhesives with surface tensions of about 40 dyne/cm. Zisman[12] has shown that water on glass surfaces of high energy need be only one molecule thick to have a pronounced effect on the surface energy, wetting properties, and contact angle exhibited by polar organic liquids. He further showed that surfaces free of adsorbed moisture are almost completely wetted by water, while those surfaces containing adsorbed moisture are partially wetted by water.

Because of the geometry and, in the case of graphite and glass fibers, the very small fiber diameter, contact angles between fiber and liquids have been difficult to measure with adequate accuracy and as a result critical surface energy data is not readily available. Direct contact angle measurements have been made on glass[13], boron fibers[14], and graphite fibers[15, 16] but in only one case[16] have contact angles been used to determine the critical surface tension, γ_c, of wetting using Zisman's procedure[17]. Some of the contact angle results on fibers are shown in Table 7. The decrease in the contact angle between the boron surface and epoxy resin most likely results from removal of impurities

Table 7 Contact Angles Between Several Liquids and Boron and Graphite Fibers

Fiber	*Treatment*	*Liquid Phase*	*Contact Angle Degrees*	*Method*
Boron	untreated	epoxy resin EPON-828	27-30	Goniometer(a)
Boron	5 min. wash at 70°F in acetone	*ibid*	11	Goniometer(a)
Boron	5 min. wash at 70°F in trichloroethylene	*ibid*	14	Goniometer(a)
Boron	5 min. wash in boiling ethanol	*ibid*	7	Goniometer(a)
Graphite Thornel 25	untreated	H_2O	36	Photomicrograph(b)
		epoxy resin ERLA-0400	12 ± 7	
		epoxy resin ERL-2774	32 ± 8	
Graphite Thornel 25	heated in 2 cm^3/min. O_2 stream for 15 min. 500°C followed by thermal desorption.	H_2O	38 ± 8	Photomicrograph(b)
		epoxy resin ERLA-0400	4.3 ± 0.6	
		epoxy resin ERL-2774	5.4 ± 0.7	

(a) Reference 44 (b) Reference 45

from the surface. In the case of boron fibers[44], direct measurement of the angle was made using a goniometer[48]. The contact angle between water and graphite fiber is 36° and is not altered by treatment for 15 minutes at 500° C in an air stream. However, the wettability of the graphite fiber for ERLA-0400 epoxy resin and ERL-2774 epoxy resin appeared to improve considerably by this treatment[45].

A flotation method has been suggested as a means of measuring the critical surface tension of fiber materials[49]. In this procedure the surface tension of the solid is determined by establishing the surface tension of the liquid which just permits the fiber to sink. This is considered to be the critical surface tension of the fiber surface. The fiber density must always exceed the density of the flotation liquid. Estimates of γ_c for organic polymeric fibers and some fibers coated with polymers appear compatible with estimates of γ_c employing more conventional procedures[47] (Table 8). The large difference in the critical surface tension for silicon carbide fibers and for silicon carbide coated coupons by the two techniques points out the difficulties in interpreting the results of the flotation method. The geometry of the samples influence the results in each method. Even more difficulty has been encountered in applying this procedure to graphite single filaments. The irregular surface structure, small filament diameter and small difference in density between filament and flotation liquids all add to the difficulty of obtaining unequivocal estimates of γ_c on graphite fibers by flotation.

The wetting properties of glass surfaces have been studied extensively with the view of determining the influence of silane coupling agents in preserving the bond at the glass-coupling agent interfaces. Although most of the wetting studies have been performed on glass microscope slides[28, 50-52], there are a few reports on the wetting properties of untreated and surface treated glass fibers[13, 53, 65].

Johannson has shown how surface treatment has a pronounced effect on the wetting properties[28] of E-glass surfaces (Table 9) in the form of microscope slides. Freshly cleaned E-glass is almost completely wetted by water, while glass that has been contaminated, or contains surface water is incompletely wetted and becomes hydrophobic. In earlier studies, Zisman showed that the moisture content of the atmosphere has a profound effect on the wettability of glass[42]. A silane treated surface of glass fibers[43] (Table 10) dried at room temperature appears to have about the same water wettability as a heat cleaned glass surface (Table 9). However, treatment of the fiber glass-silane system at 120° C does create a more hydrophobic surface (Table 10). The high contact angles between water and heat treated silane coated E-glass (70°) or between epoxy resin and heat treated silane coated E-glass fibers (55°) indicates that the silane is not easily wetted by resins or water. Furthermore, studies[51, 52] also show that adsorption of silane coupling agents on high energy surfaces such as glass, alumina, and steel (Table 11) reduce the critical surface tension of these surfaces to values between 25 to 45

Table 8 Fiber Wettability by the Flotation Method

Fiber	*Surface Treatment*	*Critical Surface Tension From Flotation Liquid γ_c, dyne/cm* *Float*	*Sink*	*Contact Angle Method γ_c, dyne/cm*
Boron[a]	Dried 1½ hrs in air 150°C	39.8	37.7	—
Boron(b)	None	28	26.1	—
Silicon carbide[a]	Dried 1½ hrs in air 150°C	42.1	39.8	52 ± 5[e]
Silicon carbide coated boron[a] (BORSIC®)	Dried 1½ hrs in air 150°C	50.5	52.1	—
Graphite[c] (Thornel 50)	Water sized	25.7	22.9	—
Saran[d]	None	39.5	38.4	39-40[f]
Nylon[d]	None	42.3	40.3	42[f]
Polyethylene[d] coated glass	None	32.1	28.7	31[f]
Silicone coated[d] glass	None	23.7	20.6	23[f]
Silicone coated[d] rayon	None	23.9	21.1	23[f]
Thornel 25	(g)	—	—	46[g]

(a) Reference 11
(b) Reference 34c
(c) Reference 40
(d) Reference 49
(e) Reference 10
(f) Reference 47b
(g) Reference 46. It was not reported whether or not the surface was sized with PVA or treated in some other manner.

Table 9 Contact Angles Between Water and Treated E-Glass Slides[a]

E-Glass Surface Treatment	*Water Contact Angle, degrees*
None	45, 50, 60
Heat cleaned, cooled to room temperature	16
Acid cleaned	0-8
Acid cleaned, aged overnight	16

(a) Reference 28 measured in dry box in nitrogen atmosphere, 20% RH dyne/cm, which are much lower than the γ_c of a clean oxide or metal surface.

Studies of the wetting properties of silicon carbide fibers were made by studying the behavior of silicon carbide coupons prepared in the same manner as the fiber material, namely by the thermal decomposition of dichloromethylsilane[10]. As prepared silicon carbide has the same wettability toward water as silicon carbide treated in air at 500° C for 24 hours (Table 12). Treatment of silicon carbide surface at 500° C for 24 hours followed by boiling

Table 10 Contact Angles Between E-Glass Fibers and Liquids- Water and Epoxy Resin[(a)]

E-Glass Fiber	*Contact Angle, Degrees*	
	H_2O	*Epoxy Resin*
1. Coated with γ-aminopropyltriethoxysilane, dried 15 min. at room temperature	20	~25
2. 1 after drying 15 min. 125°C	70	55

(a) Reference 43

Table 11 Wettability of High Energy Solids as Modified by Adsorbed Silane Coupling Agents

Substrate	*Coupling Agent*	*γ_c Critical Surface Tension of Wetting dyne/cm*	*Water Contact Angle deg.*
Pyrex[(a)]	γ-chloropropyltrimethoxysilane	43	80
α-Al_2O_3[(a)]	γ-chloropropyltrimethoxysilane	45	81
Stainless steel[(a)]	γ-chloropropyltrimethoxysilane	45	82
Glass microscope slides[(b)]	γ-methacryloxypropyltrimethoxysilane	28	
ibid[(b)]	γ-glycidoxypropyltrimethoxysilane	38.5 to 42.5	
ibid[(b)]	γ-aminopropyltriethoxysilane	35	
ibid[(b)]	vinyl trimethoxysilane	25 to	42
Pyrex glass[(c)]		>72	
α-Al_2O_3[(c)]		>>>72	
Stainless steel[(c)]		>>>>72	
Glass microscope[(c)] slides		>72	

(a) Reference 51 (b) Reference 52

(c) γ_c of these were assumed to be greater than 72 because they are wet by water

Table 12 Contact Angle Between Water and Treated Silicon Carbide Surfaces[a]

Surface Treatment	*Cosine of Contact Angle Cos θ After Boiling Water Rinse (5 min) then Air Dry*	*Contact Angle (deg)*
As prepared	0.88	28
Oxidized in air 500°C, 24 hrs.	0.88	28
Oxidized in air 500°C, 24 hrs. Boiling water treatment, 8 hrs.	0.97	14
Oxidation-boiling water-γ-glycidoxypropyltrimethoxysilane	0.84	33

(a) Reference 10

water treatment affects both adsorption capability of the surface and water wettability. The data shows that air oxidation followed by hydration decreases the contact angle between the oxidized-hydrated silicon carbide surface and water. Apparently, exposure to air at 500°C and water at 100°C provided favorable conditions for hydration of surface silicon oxide to silanols. The oxidized-hydrated silicon carbide surface adsorbs γ-glycidoxypropyltrimethoxysilane strongly since even after boiling water treatment, poor water wettability was observed which is what is also observed for silane treated glass surface.

SURFACE AND MECHANICAL PROPERTY RELATIONSHIPS

The degree of surface interaction of fiber with resin has a marked influence on the mechanical properties of the composite. The problem becomes one of defining the surface interaction required for maximum bond strength. A low specific surface area does not necessarily mean that little interfacial interaction will take place between fiber and resin. For example, Table 14 shows that although untreated glass, boron, and silicon carbide fibers have low total surface area available for adhesive bonding, these fibers have been fabricated into composites with high shear strengths, while the untreated graphite fibers, which have a large bonding area, have yielded composites with low shear strengths. Flexural and shear strength data before and after boiling water treatment have been used as a measure of the strength of this interaction. Flexural and shear strength data for glass, boron, silicon carbide and graphite fiber-epoxy resin composites prepared from untreated and treated fibers are shown in Tables 13 and 14. It is apparent that for glass, silicon carbide and boron fibers, hot water weakens the bond at the fiber-resin interface. The one property that these fiber surfaces have in common is easy hydration of the surface oxide. Glass is strongly susceptible to hydrolytic degradation, while the boron oxide on boron is readily dissolved. The graphite-epoxy resin composite, although containing surface oxygen, apparently is not readily attacked at the interface during boiling water treatment of the composite, judging from the flexural and shear strength data. This suggests that the carbon-oxygen linkage on the carbon surface apparently is less susceptible to hydrolytic degradation than are the oxides on the boron, silicon carbide, and glass surfaces. Data shown in Table 15 offer more evidence for the stability of the fiber-resin adhesion bond. Therefore, glass, silicon carbide and boron fibers required some surface modification to develop a strong fiber-resin interaction, thereby preventing attack of the interface by hot water. Silane treatment of glass fibers proved to be effective in strengthening the interface in glass-resin composites[26-29]. Similarly, air oxidation followed by coupling agent adsorption improved the bonding capability of silicon carbide fibers in epoxy resin[54]. A boiling methanol treatment of boron fibers was necessary to improve the dry and wet flexural and shear strengths of boron-epoxy resin composites[36]. As already mentioned, hydrolytic instabil-

Table 13 Flexural Strengths of Unidirectional Fiber Reinforced Epoxy Resin Composites

Fiber	*Surface Treatment*	*Fiber Content Vol%*	*Flexural Strength 10^3 psi Dry*	*Wet(h)*	*% Retention*
E-glass(a)	Heat cleaned	55	73.6	53.5	75
E-glass(a)	A-1100	55	81.0	75.0	93
S-994 glass yarn(b)	HTS	75	229	269	>100
Silicon carbide(c)	None	71	137.8	90.8	66
Silicon carbide(d)	None	62	260.0	—	—
Silicon carbide(d)	Thermal oxidation + silane Z-6020	65	319.0	—	—
Boron(e)	None	75	283.0	208(i)	73
Boron(e)	Boiling methanol 1 hr	75	373.0	330(i)	88
Graphite-Thornel 40(f)	None	50	80.3	77.3	97
Graphite-Thornel 40(g)	N_2-1100°C	51	81.0	92.4	>100

(a) Reference 26, 181 glass cloth
(b) Reference 60
(c) Reference 35
(d) Reference 54
(e) Reference 36
(f) Reference 56
(g) Reference 57
(h) After 2 hr water boil
(i) After 6 hr water boil

ity of the interface in graphite fiber-resin composites does not appear to be a problem. In these composites fiber-resin interaction is poor initially, leading to low interlaminar shear strengths (3500-4000 psi)[55-57] so that early studies on the high modulus fibers were focused on increasing this interaction.

Application of a silane coating to heat treated[57] or to oxidized fiber[64] was found to be ineffective in improving the interlaminar shear strength. However, studies by several investigators have shown that oxidation and heat treatments of the fiber surface markedly improves the shear strength of composites prepared from the activated filaments[12, 46, 57-59, 66] without the aid of a coupling agent.

Table 14 Shear Strengths of Unidirectional Fiber Reinforced Epoxy Resin Composites

Fiber	*Treatment*	*Fiber Content Vol%*	*Short Beam Shear Strength psi*		*% Retention*
			Dry	*Wet*	
S-glass(a)	None	60	12,000	3,000	25
S-994 Glass yarn(b)	HTS	75	12,000	11,400	95
Silicon carbide(c)	None	71	5,290	2,360	45
Silicon carbide(d)	Thermal oxidation + silane Z-6020	65	14,500	—	—
Boron(e)	None	—	8,000	3,800	48
Boron(e)	Boiling ethanol 20 minutes	—	9,500	9,200	97
Graphite-Thornel 40(f)	None	50	4,100	3,900	95
Graphite-Thornel 40(f)	N_2-1000°C	51	>6,100	>6,650	>100
Graphite-Thornel 50(g)	Oxidation	43	7,400	6,800	92

(a) Reference 40, water boiled 2 hrs
(b) Reference 60, water boiled 6 hrs
(c) Reference 35, water boiled 2 hrs
(d) Reference 54
(e) Reference 44, water boiled 2 hrs
(f) Reference 57, water boiled 2 hrs
(g) Reference 58, water boiled 168 hrs

Oxidation of graphite fibers affects the specific surface area[12, 58], surface activity[12, 58], and shear strength of composites[12, 46, 58, 59] prepared from the treated filaments. The tensile strength of the fiber is decreased if the oxidation is carried out for extended time periods in concentrated nitric acid[12] or in air at elevated temperatures[46, 58, 59]. A study of the effect of various fiber surface treatments on the shear strength of composites revealed that nitric acid oxidation gave the best composite shear strength (Table 15)[46]. Other

Table 15 Effect of Oxidation on Shear Strength of Thornel 25/2256-0820 Epoxy Resin Composite[a]

Treatment	Short Beam Shear Strength, psi Dry	After 6 hour water boil
none	4100	4100
PVA	3600	3500
nitric acid oxidized	7200	6600
air oxidized (400°C)	5900	6400
oxidized in RF heating	5800	6200
sodium hypochlorite	5400	5600
oxidized in ozone	5000	4800

(a) Reference 46

workers have shown that air oxidation also provided large improvements in shear strength but at the sacrifice of the tensile strength of the fiber and composite[59].

The effect of carboxyl group concentration per gram of carbon fiber and specific surface area on composite shear strength was compared and it was concluded that chemical functionality was much more important in influencing composite shear strength than was surface area (Table 16)[12]. However, when the data for concentration of carboxyl groups is calculated on a unit area basis the relative importance of surface activity and surface area becomes difficult to assess. The decrease in reactivity on a unit area basis for both the oxidized and oxidized-hydrogen treated fibers tends to reduce the influence of chemical functionality and increase the influence of surface area for the improvements in shear strength observed. This is further shown by comparing our results on the shear strength of a composite prepared from oxidized graphite fiber with that of a composite prepared from a portion of the oxidized fiber which was treated in hydrogen at 600° C (Table 17). The hydrogen treatment caused an increase in surface area compared with the oxidized sample which is difficult to explain unless carbon as well as oxygen had been volatilized from the surface. Data on surface functionality concentration is required for a more direct comparison with data in Table 15. The significant point is that in this case hydrogen treatment of the oxidized fiber did not lead to a decrease in shear strength, contrary to what has been reported (Table 16)[12].

Studies on higher modulus HMG-50 graphite fibers gave similar results (Table 18)[40]. Increasing oxidation exposure of the fiber caused a steady increase in the surface area with a very gradual increase in shear and transverse tensile strength. For example, the results in Table 18 indicate that there is a definite correlation between the surface properties (specific surface area and the concentration of acid sites per unit area of fiber based on sodium

Table 16 Effect of Fiber Properties on Shear Strength of Carbon Yarn WYB-85½/Epoxy Resin Composites[a]

Treatment	*-CO_2H meq/g*	*-CO_2H[b] meq/m^2*	*Specific Surface Area m^2/g*	*Fiber Volume %*	*Short Beam Shear Strength (psi)*
60% HNO_3	0.013	5.4×10^{-4}	24	51	5700(c)
60% HNO_3 H_2 at 500°C	0.002	0.9×10^{-4}	23	55	3500(c)
none	0.001	10×10^{-4}	1	55	3250(d)

(a) Reference 12
(b) Calculated by the authors
(c) Tensile failure
(d) Shear failure

hydroxide adsorption) and the observed increases in shear strength. The concentration of acid sites/unit area falls off as the surface area increases to 24 m²/g, but it is still greater than the untreated fiber. Therefore, both increased surface area and surface reactivity appear to be contributing to the improvement in shear strength of the composites, but a quantitative correlation is difficult to obtain.

It would be of interest to compare the shear strength with specific surface area, surface reactivity and wettability of graphite fibers from various sources with composites prepared from the fibers. Surface reactivity and wettability of the various graphite fibers have not been measured as yet but surface areas and composite shear strengths of some systems have been and these are compared in Table 19. For the series of untreated fibers and fibers treated by Hitco, Courtaulds, and Morganite, it is apparent that the large increases in

Table 17 Effect of Surface Treatment on Short Beam Shear Strength of Unidirectional HMG-50/2256-0820 Epoxy Resin Composites[a]

Treatment	*Yarn Specific Surface Area m^2/g[b]*	*Composite Short Beam Shear Strength[c] (psi)*
none	0.87	4400
oxidation	5.34	5930
oxidation, then H_2 at 600°C 3 hrs, atmospheric pressure	8.75	5870

(a) Reference 58
(b) Measured by low temperature adsorption of krypton (Reference 3)
(c) ~55 vol. % fiber, measured at a span to depth ratio of 5/1, cure cycle 2 hrs @ 80°C (80 psi) and 2 hrs @ 150°C

Table 18 ***Correlation Between Surface Properties and Composite Shear Strength for Hitco HMG-50 Graphite Yarn and Unidirectional HMG-50/Epoxy Resin Composites***[a,b]

Treatment	Specific[c] Surface Area m²/g	MB-MY[d] Adsorbed μmole/g	NaOH Adsorbed μmole/g	NaOH Adsorbed μmole/m²	Short Beam Shear Strength[e] psi	Transverse Strength[f] psi	Fiber Vol %
none	0.87	.011	0.066	.074	4490	—	64
oxidation	3.4	2.57	2.04	—	5600	1800	64
oxidation	7.3	7.92	3.0	0.41	6090	2790	59
oxidation	10.5	3.54	3.60	—	6500	3080	65
oxidation	24.0	17.1	5.9	0.25	7000	—	64

(a) Reference 40

(b) Cure cycle 2 hrs @ 80°C (200 psi) + 2 hrs @ 150°C, 2256-0820 epoxy resin

(c) Measured by low temperature adsorption of krypton (Ref. 3)

(d) MB-MY = Methylene blue – Metanil yellow

(e) Span-to-depth ratio 5/1, average of 3 samples

(f) Average of 3 samples

composite shear strengths are not due to increases in surface area, and most likely are highly dependent on the surface reactivity of each fiber system.

Obviously, several parameters contribute to the strength of the final adhesive bond. Surface properties such as specific surface area, surface reactivity and wettability (surface energy) are perhaps the prime variables. Other factors such as fiber contamination, variability in fiber quality, fabrication parameters, and composite composition also affect the adhesive bond strengths which must be reflected in the observed shear strengths. Even when these parameters are considered, it must be determined if failure occurred in the matrix, in the fiber or at the fiber-resin interface before a quantitative assessment of the role of surface area, and surface reactivity and wettability in adhesive bond formation can be made.

PROBLEM AREAS AND POSSIBLE APPROACHES

The principal problem areas in studying the surfaces of new reinforcing fibers and in determining the requirements for bonding of these fibers to resin matrices are as follows: (1) development of adequate characterization methods to define surface reactivity, hopefully in terms of functional groups, (2) development of reliable methods for measurement of wettability and surface energy, (3) definition of the surface treatments, environmental conditions and limits of contamination that are necessary for formation of strong adhesive bonds between the fiber and resin matrix, and (4) establish

Table 19 Comparison of Fiber Surface Areas and Composite Shear Strengths[a]

Fiber	Treatment	Fiber Specific Surface Area[b] m^2/g	Composite Short Beam Shear Strength[c,d] psi
Thornel 50	H_2O size	0.55	3700
Thornel 50	PVA size	0.59	4000
Thornel 50	Oxidation	2.5	7000
Hitco HMG-50	None	0.87	4800
Hitco HMG-50	By manufacturer	0.66	6500
Hitco HMG-50	Oxidation	7.3	8500
Morganite I	None	0.11	4000
Morganite I	By manufacturer	0.13	9000
Courtaulds B	None	0.31	4000
Courtaulds B	By manufacturer	0.39	9000

(a) Reference 40

(b) Measured by low temperature adsorption of Krypton (Reference 3).

(c) Unidirectional graphite fiber—2256-0820 epoxy resin composites, ~55 vol. % fiber, cure cycle, 2 hrs. @ 80°C (200 psi) + 2 hrs. @ 150°C.

(d) Shear strength measured at a span to depth ratio of 5/1.

whether or not coupling agents are required to obtain optimum adhesive bonds between fiber and resin.

Gas phase chromatography using the fiber materials as the chromatographic column appears to have some promise in determining surface reactivity of untreated and treated fiber materials. Solution adsorption and titration methods using radiotracer adsorbates and dye adsorbates are also sound approaches toward determining surface reactivity. New techniques for evaluation of fiber wettability, relevant to composite fabrication, such as the applicability of the flotation procedure for determining γ_c or adaptation of standard techniques for measuring contact angles to small diameter fibers (5 to 10 μ) should be investigated.

SUMMARY

A review of the surface characteristics of boron, silicon carbide and graphite fibers and comparison of the surface properties of these materials with those of glass fibers was made. Electron micrographs of the surfaces and surface area measurements indicate that glass, boron, silicon carbide and silicon carbide coated boron fiber surfaces are smooth and relatively free of surface roughness while high modulus graphite fiber surfaces, prepared from rayon precursors are not as smooth and exhibit surface roughness. However, the surfaces of high modulus graphite fibers prepared from polyacrylonitrile precursor are smooth and relatively free of surface roughness. A common characteristic of glass, boron, silicon carbide, and graphite is the presence of oxygen on the surface in the form of an oxide. In the case of graphite, these oxides exist as carboxyl, alcohol and ketone groups while for the other fibers, they exist as an inorganic oxide.

Glass surface reactivity has been linked to surface silanol groups but no detailed studies have been made with silicon carbide, boron, or graphite fibers or on bulk forms of these same materials that are more easily handled. Adsorption of various gases such as oxygen, ammonia and ethylene oxide on boron surfaces is very weak and appears to be unrelated to boron-epoxy resin composite shear strength. Efforts to enhance the surface reactivity of boron fibers by treatment with BCl_3, Cl_2, C_6H_5As, N_2 and NH_3 were unsuccessful. Methanol treatment of boron fibers was found necessary to prevent degradation of the flexural properties of boron-epoxy resin composites by boiling water. It is well known that silane coupling agent treatments of glass fibers are required to prevent loss of flexural strength of glass fiber-resin composites by boiling water treatment. In both cases the loss in strength has been attributed to a weakening of the fiber-resin interface. Studies on silicon carbide coupons which were prepared in a manner similar to silicon carbide fibers showed that oxidation-hydration improved the adsorption capability of the surface. Other studies of a more practical nature showed that air oxidation-silane treatment of silicon carbide fibers improved the flexural and shear strength of silicon carbide-epoxy resin composites prepared from the treated fibers relative to the properties of composites prepared from untreated fibers. Gas and solution adsorption studies revealed that the surface reactivity of graphite fibers can be increased by oxidation and by heat treatments at elevated temperatures in gases, such as hydrogen, nitrogen, and argon. Shear strengths of graphite fiber-epoxy resin composites prepared from untreated fibers are low (~4000 psi) but significant improvements have been made by fiber surface treatments (7000 to 9000 psi) such as oxidation. Graphite fiber-epoxy resin composites do not suffer significant degradation in the flexural and shear properties due to boiling water treatments. This is a marked difference from what was observed with glass and boron fiber composites and suggests greater resistance of the graphite fiber-resin interface to hydrolytic attack.

Practical experimental techniques to measure surface energy, surface reactivity and wettability for these high modulus fiber systems, particularly graphite, are necessary to characterize the surfaces. For graphite fiber systems, gas and solution adsorption techniques require further refinements to obtain more meaningful results.

REFERENCES

1. W. A. Zisman, *Ind. Eng. Chem. Prod. R & D,* **8,** 98 (1969).
2. N. J. DeLollis, *Adhesive Age,* December 1968, p. 21.
3. R. A. Beebe, S. B. Beckwith, J. M. Honig, *J. Am. Chem. Soc.,* **67,** 1554 (1945).
4. H. P. Boehm, *Angewandte Chemie,* **6,** 533-622 (1966). A review article.
5. T. E. White, "A Study of the Reactions of Surface Hydroxyl Groups of Silica by Means of Infrared Spectroscopy", *SPI,* Section 3-B (1969) p. 1.
6. B. J. Todd, *J. Appl. Phys.,* **26,** 1238 (1955).
7. B. J. Todd, *J. Appl. Phys.,* **27,** 1209 (1956).
8. H. P. Leftin and M. C. Hobson, Jr., "Advances in Catalysis", Academic Press, Inc. New York, N.Y., **14,** 127-128 (1963).
9. General Electric Co., "Research on Improved High Modulus High Strength Filaments and Composites Thereof", Tech. Report AFML-TR-66-98, April 1969.
10. C. S. Brooks, M. A. DeCrescente and D. A. Scola, *J. Coll. & Interface Sci.,* **27,** 773 (1968).
11. D. A. Scola and C. S. Brooks, "Investigation of the Physical and Chemical Nature of the Surfaces of Recently Developed Fibers", Tech. Report TR-67-28, Part II, Oct. 1968.
12. J. W. Herrick, "Resin-Fiber Interactions in Graphite/Fiber-Epoxy Resin Composites", 23rd Annual Tech. Conf. SPI Reinforced Plastics/Composites Division, Section 16-A, Feb. 1968.
13. J. V. Hallum and H. V. Drushel, *J. Phys. Chem.,* **62,** 110 (1958).
14. H. P. Boehm, E. Diehl and W. Heck, *Colloq. Nationaux Centre Natl. Rech. Sci. (Paris)* No. **24,** 91 (1963).
15. J. B. Donnet, *Carbon,* **6,** 161 (1968).
16. A. C. Zettlemoyer and K. S. Narayon, "Adsorption from Solutions by Graphite Surfaces", Chemistry and Physics of Carbon, **II,** Philip L. Walker, Jr. Ed., Marcel Dekker, New York (1966) pp. 177-224.
17. W. J. Eakins, "Studying the Reactivity of Various Fiber Clean Surfaces as Formed after Heat Soaking and after Melt and Leaching", Proc. 19th Ann. Tech. Conference, Reinforced Plastics Div., *SPI,* Section 10-C, Feb. 1962.
18. H. P. Boehm, "Chemical Identification of Surface Groups", Advances in Catalysis, Academic Press (1966).
19. G. I. Young, *J. Coll. Sci.,* **13,** 67 (1958).
20. A. V. Kiselev and V. I. Lyggin, *Kolloidnyi Zh.,* **21,** 581 (1959).
21. H. P. Boehm and M. Schneider, *Z. Anorg. Allg. Chem.,* **301,** 326 (1959).
22. H. P. Boehm, M. Schneider and F. Arendt, *Z. Anorg. Allg. Chem.,* **320,** 43 (1963).
23. J. Wartmann and H. Deuel, *Chimia,* **12,** 82 (1958).
24. R. K. Iler, "The Colloid Chemistry of Silica and Silicates", Cornell University Press, Ithaca, N.Y. (1955), p. 257.
25. K. Gutfreund and H. S. Weber, "Interaction of Organic Monomers with Fiber-Glass Surfaces", Proc. 16th Ann. Tech. and Management Conf., Reinforced Plastics Ind., *SPI,* Inc., Section 8-C, Feb. 1961.
26. S. Sterman and H. B. Bradley, Proceedings of the SPI Reinforced Plastics Division, Section 8-D, Feb. 1961, p. 1.
27. E. P. Plueddeman, H. A. Clark, L. E. Nelson, and K. R. Hoffman, "New Silane Coupling Agents for Reinforced Plastics", *Modern Plastics,* **39,** 135 (1962).
28. O. Johannson, F. Stark, and R. Baney, "Investigation of the Physical-Chemical Nature of the Matrix-Reinforcement Interface", Tech. Report AFML-TR-65-303, Part I, Sept. 1965.
29. O. Johannson, F. Stark, and G. Vogel, "Investigation of the Physical-Chemical Nature of the Matrix-Reinforcement Interface", Tech. Report AFML-TR-65-303, Part II, July 1966.
30. G. E. Vogel, O. K. Johannson, F. O. Stark, and R. M. Fleishmann, "Chemical Nature of the Glass-Coupling Agent Interface", Proceedings of the SPI Reinforced Plastics Div., Section 13-B, Washington, D. C., Jan. 31 - Feb. 3, 1967, p. 1.
31. D. J. Tutas, R. Stromberg, and E. Passaglia, *SPE Trans.,* **4,** 256 (1964).
32. M. E. Schrader, "Radioisotope Study of the Role of A-1100 in Glass-Resin Interface". Presented at Fourth Annual Symposium on High Performance Composites, April 8-9, 1969, St. Louis, Mo., sponsored by ARPA Research Project.

33. W. D. Bascom, "The Structure of Silane Adhesion Promoters on Glass and Metal Surfaces", Presented at Fourth Annual Symposium of High Performance Composites, April 8-9, 1969, St. Louis, Mo., sponsored by ARPA Research Project.
34a. K. Gutfreund, D. Kutscha, and L. J. Broutman, "Investigations of Interfacial Conditions in Boron-Fiber Reinforced Plastics", 23rd Annual Tech. Conf., *SPI,* Section 16-C, Feb. 1968.
34b. K. Gutfreund and D. Kutscha, "Interfacial Investigations in Advanced Fiber-Reinforced Plastics", AFML-TR-275, Sept. 1967.
34c. D. Kutscha and K. Gutfreund, "Investigation and Development of New Finishes and Coupling Agents for High Modulus Fibers", First Quarterly Progress Report, AFML Contract No. F33615-67-C-1821, Sept. 1967.
35. Whittaker Corp., "Research on High Modulus, High Strength, Collimated Boron Filaments and Composites", Sixth Quarterly Report, Contract No. AF33(615)-2150, Aug. 1966.
36. General Electric Company, "Research on Improved High Modulus, High Strength Filaments and Composites Thereof", Tech. Report AFML-TR-66-98, April 1966.
37. H. P. Boehm, "Chemistry of Heteroatoms on the Carbon Surface", Ninth Biennial Conf. on Carbon, June 16-20, 1960, Summary of Papers, p. 127.
38. R. Didchenko, "Carbon and Graphite Surface Properties Relevant to Fiber Reinforced Composites", Tech. Report AFML-TR-68-45, Feb. 1968.
39. C. S. Brooks and D. A. Scola, "Examination of the Surface Reactivity of Graphite Fibers by Gas-Solid Chromatography", presented at the 43rd National Colloid Symposium, Journal of Colloid and Interface Science, **32**, 561 (1970) Symposium on Carbon Surfaces, Case-Western Reserve University, Cleveland, Ohio, June 23-28, 1969.
40. C. S. Brooks and D. A. Scola, unpublished results.
41. D. Graham, *J. Phys. Chem.,* **59**, 896 (1955).
42a. E. Shaffrin and W. A. Zisman, *J. Am. Ceramic Soc.,* **50**, 478 (1967).
42b. M. K. Bernett and W. A. Zisman, *J. Coll. Interface Sci.,* **28**, 243 (1968).
43. W. D. Bascom, "Some Surface Chemical Aspects of Glass-Resin Composites", Part I - Wetting Behavior of Epoxy Resins on Glass Filaments. Proceedings of the SPI Reinforced Plastics Division, Section 15-B, Feb. 1965.
44. W. C. Jones and M. C. Porter, "Measurement of Contact Angles on Filaments to Indicate the Effects on Surface Treatments", *SAMPE,* **10**, E-17 (1966).
45. R. J. Bobka and L. P. Lowell, "Integrated Research on Carbon Composite Materials", AFAPL-TR-66-310, Part I, Oct. 1966.
46. J. C. Goan and S. P. Prosen, "Interfacial Bonding in Graphite Fiber-Resin Composites". Presented at the 71st ASTM Meeting, Session on "Interfaces in Composites", June 23-28, 1968, San Francisco, Calif.
47a. M. K. Bernett and W. A. Zisman, *J. Phys. Chem.,* **63**, 1241 (1959).
47b. W. A. Zisman, Advances in Chem. Series No. 43, Am. Chem. Soc., Washington, D. C., (1964) p. 1.
48. T. Fort, Jr. and H. T. Patterson, *J. Coll. Sci.,* **18**, 217 (1963).
49. J. P. Mutchler, J. Menkart and A. M. Schwartz, 153rd Natl. Mtg., Am. Chem. Soc., Miami, Florida, April 1967. Div. Colloid and Surface Chem. Abstract 59A.
50. E. Shaffrin and W. A. Zisman, *J. Am. Ceramic Soc.,* **50**, 478 (1967).
51. W. D. Bascom, Symposium on the Interface in Composites. 42nd Natl. Colloid Symposium, IITRI, Chicago, Illinois, June 19-21 (1968) p. 363 preprints.
52. L. H. Lee, ibid., p. 367 preprints.
53. P. E. Throckmorton and M. F. Browne, "The Effect of Surface Tension and Strength of Glass Fiber Reinforced Fiber", Proceedings of the SPI Reinforced Plastics Division, Section 15-A, Feb. 1965.
54. H. P. Materne and R. J. Kuhbander, "Silicon Carbide Filament Reinforced Epoxy Resin Composites", Tech. Report AFML-TR-66-383, May 1967.
55. R. Bacon, A. A. Palozzi, and S. F. Slosonck, "Carbon Filament Reinforced Composites", Proceedings 21st Annual Tech. Conf., SPI Reinforced Plastics Div., Section 8-E, Feb. 1966.
56. R. J. Dauksys, N. N. Pagano, and R. G. Spain, "Graphite Fiber/Epoxy Resin Composites", Tech. Report AFML-TR-67-3627, April 1968.

57. S. Steingiser and R. A. Cass, "Graphite Fiber Reinforced Composites", Tech. Report AFML-TR-68-357, Part I, Nov. 1968.
58. D. A. Scola, "Studies to Improve the Shear Properties of Graphite Filament Reinforced Composites", United Aircraft Corporation, July 1969 (Unpublished work).
59. R. C. Novak, "Investigation of Graphite Filament Reinforced Epoxies", Final Report, Prepared under contract N0019-67-C-0354, May 1968.
60. F. R. Barnet, "NOL Rings for Composite Materials Research and Development", *Trans. J. Plastics,* **33,** 107 (1965).
61. R. A. Schoenlamb, U. S. Patent 2,334,961, Nov. 23, 1943.
    R. L. Tiede and F. V. Tooley, U. S. Patent 3,571,074, Oct. 1951.
62. F. Galasso, "High Modulus Fibers and Composites", Gordon and Breach, New York, N.Y. (1969).
63. M. Jang and R. Bacon, *Carbon,* **2,** 211 (1964).
64. B. Harris, P. W. R. Beaumont, *J. Materials Sci.,* **4,** 432 (1969).
65. G. Mozzo, R. Chabird, "Contribution to the Study of Glass-Resin Adhesion", Proceedings of the 23rd Annual Tech. Conf. SPI Reinforced Plastics/Composites Division, Section 9-C, Feb. 1968.
66. E. L. McKaque, "Graphite Filament Epoxy Matrix Interface Study", *SAMPE,* April/May, 49 (1969).