Recent Aspects of Glass Fiber-Resin Interfaces

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The recent developments in Auger spectroscopy have been used to define the composition of two glass fiber surfaces. The effect of fiber surface area on the interlaminar shear strength was also investigated. The chemistry of several silane "coupling agents" has been studied from the standpoint of its chemical form when it is applied to the glass fibers, and has in part been determined using a gas chromatographic technique. The relative thermal stability of some silanes in high temperature resin matrices was determined. A comparison of a treatment of glass fibers with aqueous and non-aqueous systems is made.

INTRODUCTION

This paper is a survey of some of the most recent activities being carried on in our laboratory to help develop the science of the glass fiber–resin interface. The detailed technical papers on each of the subjects covered will be published when the work in each phase is completed. In these studies essentially three phases are considered: (1) the glass fiber, (2) the interface, and (3) the resin matrix. Of these, the best understood is the resin matrix phase and, therefore, these studies have been concentrated at present on the other two.

Definitive work on the glass fiber–resin interface phenomenon has been hampered by the lack of convenient or suitable instrumentation to identify clearly the species, their structures, and orientations at the interface. Techniques commonly employed on materials having relatively large specific surface areas cannot be used on glass fibers which have extremely low specific surface areas. Thus the chemical constitution and structure of the glass fiber

surfaces have not been concretely established. The use of coatings and treatment materials on glass fiber surfaces to obtain improved interface properties has been well demonstrated and found necessary in commercial practice, but the complete elucidation of the phenomenon which occurs at the interface remains to be done. The technology in this field has advanced far ahead of the science.

RESULTS AND DISCUSSION

Auger Spectroscopy-Fibre Surface Analysis

The chemical composition of the glass fiber surface is of extreme importance in any application since it directly affects the strength and durability of the fiber itself as well as governing the interactions with sizes and resin binders. It has long been suspected that the surface composition can be very different from that of the fiber interior due to the effects of surface energy, vaporization, etc., in the forming of the glass fibers. To date, however, there has existed no experimental means of determining to what degree this occurs nor how deep this surface phase is present.

Auger electron spectroscopy is currently being investigated by our laboratory to fill this critical need. In this technique the sample is bombarded by an electron beam, and the energy distribution of the secondary electrons emitted by the sample is analyzed. These secondary or Auger electrons arise from a series of electronic transitions and their energy is characteristic of the atom where they originate. The technique is attractive for our application for two reasons:

1) Although the primary beam penetrates deeply into the surface, the Auger electrons detected arise from the very surface; typical escape depths are on the order of 10 Å.

2) The Auger transitions predominate for the lighter elements making it most attractive for glass constituents.

The preliminary work has been directed at demonstrating feasibility and the applicability of the technique to glass fiber surface analysis.

Two glass compositions have been investigated, E- and S-glass, both in bulk (fracture surface) and fiber form. The samples were analyzed at three preselected levels: the very surface, after removing 150 Å of material by sputtering, and again at the 600 Å level. The bulk fracture surface was used to establish the sensitivity of the technique to the various elements known to be present.

This technique has been found to be feasible for glass fiber surface analysis as indicated by the results in Tables I and II. Qualitatively this analytical technique is excellent and the use of external standards has shown good quantitative agreement with theoretical compositions. The fiber surface of

TABLE I

Auger Analysis of an E-Glass Surface—
Sensitivities based on a fracture surface of the bulk glass

Si = 1   O = 7.05
B = 5.29   F = 7.65
Ca = 23.1   Mg = 2.23
Al = 1.90

	Phase	Composition per 10 atoms of "glass"						
		B	Ca	O	F	Mg	Al	Si
Bulk	Surface	0.45	0.64	6.18	0.032	0.23	0.58	1.88
	150 Å	0.33	0.73	7.09	0.01	0.10	0.41	1.32
	600 Å	0.35	0.92	6.50	0.01	0.18	0.60	1.44
Fiber	Surface	0.34	0.19	6.12	0.14	0.06	0.70	2.43
	150 Å	0.20	0.15	6.55	0.032	Trace	0.44	2.44
	600 Å	0.22	0.18	6.64	0.022	Trace	0.94	2.00
Theoretical		0.45	0.64	6.18	0.032	0.23	0.58	1.88

TABLE II

Auger analysis of an S-Glass surface—
Sensitivities based on a fracture surface of the bulk glass

Si = 1   Mg = 1.61
O = 8.62   Al = 1.61

	Phase	Composition per 10 atoms of "glass"			
		O	Mg	Al	Si
Bulk	Surface	6.22	0.49	0.94	2.14
	150 Å	7.16	0.44	1.05	1.46
	600 Å	6.54	0.51	1.22	1.74
Fiber	Surface	5.20	1.72	1.27	1.81
	150 Å	6.04	0.41	1.83	1.71
	600 Å	5.66	0.24	2.71	1.39
Theoretical		6.22	0.49	0.94	2.14

S-glass is magnesium and aluminum rich when compared to the fracture surface. E-glass exhibits a surface that is low in magnesium, boron, and

calcium, but high in fluorine, silicon, and aluminum. We are currently attempting to correlate these differences with known variations in bulk glass structure. The differences in analysis at the various levels are not easily interpreted due to the significant differences noted in sputtering the fracture surfaces. It appears the sputtering is selective and is altering the surface composition.

As with any new technique, one must proceed cautiously. For example, it was found in the course of this investigation that the heat generated by the electron beam at higher beam currents can build up on the glass fibers to the point that structural rearrangements can occur. This led to an early, erroneous conclusion that aluminum accounted for 90% of the metallic ions in an S-glass surface. However, we are confident that more detailed work will enable us to completely define the glass surface and determine those interactions important to its formation.

Surface Area-Shear Strength Correlations

The acid leaching of glasses whereby certain glass constituents are selectively removed leaving a porous silica network has been known and studied by many investigators. Bulk glass applications of the leached material include porous sieves, ion exchange media, or intermediates in the production of novel glass composition as in the Corning Glass "Vycor" process. Investigations of leached glass in fibrous form have been limited and largely directed at using leaching as an intermediate step in the production of glass fibers of compositions unattainable by conventional forming methods; e.g., H. I. Thomson's use of leached E-glass fabric as an intermediate in the production of "Refrasil", a high temperature reinforcement. Little effort has been made to exploit the characteristics of this unique material.

Reinforcement is a particularly attractive area considering the large specific surface areas that can be developed upon leaching.

1) For a given fiber diameter, a greater specific surface could allow a larger degree of interfacial bonding and more efficient load transfer per unit length of fiber.

2) The pure silica structure left after leaching may be more receptive to silane coupling agents than the original glass surface.

3) In the absence of chemical bonding (thermoplastics), mechanical interlocking of resin to glass can play an important role in interlaminar shear strength.

However, three factors must be demonstrated:

1) The fibers must retain sufficient strength after leaching so they can be handled and offer reinforcement properties.

2) The leached layer must be strong and remain firmly attached to the unleached glass if stress transfer is to take place.

3) The accessibility of the interfacial area to resin and coupling agent must be known.

Work in these areas has progressed as follows:

1) It was shown that, under suitable conditions, E-glass filaments can retain 80% of their pretreatment strength after being leached to the extent that their specific area is 150 times the original.

2) Some early electron microscopy studies revealed that under some leaching conditions severe stresses can be built up along the leaching front to the degree that the porous layer actually spalls or flakes off upon drying. This condition must be avoided in any work directed at utilizing this porous structure. It appears to be most prevalent at intermediate leaching conditions; i.e., in a light leach the porous structure is maintained by the close proximity of the bulk glass structure; in a strong leach the porous layer is sufficiently thick that the stresses can be relieved by the restructuring without the spalling. Electron microscopy is being used to characterize the morphology of the leached layer and to determine if the spalling phenomenon is absent.

3) The surface areas discussed in this paper were determined by gas phase adsorption techniques and represent an upper limit in the amount of surface available to the resin matrix. In the case of a finely pored structure, the krypton probe molecule (effective molecular diameter $\approx$ 5 Å) could "see" a substantial amount of area that the bulky, polymeric molecules could not. Complete pore size distributions and characterizations are being obtained, but dye penetration of the porous layer indicates the pores should provide a degree of accessibility to the coupling and resin molecules.

The NOL short beam test was chosen as the test method in this study as it is widely accepted as being most sensitive to interfacial conditions between fiber and matrix. E-glass fibers were used throughout. The leaching treatment consisted of passing the strand through a 6N HCl bath at room temperature followed by a water wash. Coupling agent (A-1100, 1%) was applied immediately following the wash bath. Bare, unleached fibers and fibers treated with a 1% A-1100 solution in forming were used as control samples. NOL rings were fabricated using standard procedures. DER-330 epoxy resin and m-phenylene diamine curing agent were used in the ratio of 100 to 14. The cured rings were tested in the dry condition and after a 24-hour water boil.

The effects of acid leaching as it relates to interlaminar shear strengths are readily apparent, as shown in Table III.

TABLE III

NOL shear ring strengths

Test condition	Sample			
	Leached, bare psi	Unleached, Bare psi	Leached, C.A. psi	Unleached, C.A. psi
Dry	11,800 12,000	9,400* 11,400	9,600 9,700	8,000 7,800
Wet	4,000 4,300	900 1,200	7,200 6,800	6,600 7,100
Fiber surface area	0.516 M²/gm.	0.125 M²/gm.	0.516 M²/gm.	0.125 M²/gm.

* Ring had an extremely low resin content.

Bare Fiber

The bare, leached fiber dry strength is only slightly higher than the unleached control; however, in the wet test condition the shear strength of the test ring is four times that of the control. It could be argued that a lack of alkali on the leached surface is responsible for this effect although the findings of Nelson and Laird[1] seem to indicate this is not the overriding consideration. At the present time it seems most likely that the larger surface area simply takes a longer time to debond. If this were the sole consideration, it appears that all the surface is available for bonding since the specific surface area of the leached fibers is also four times that of the control.

Treated Fiber

Here the contribution of leaching to interlaminar shear strength is more evident in the ring dry strength; the improvement amounting to more than 20%. However, the moisture resistance of these rings seems to be governed by the coupling agent as an absolute wet strength of 7,000 psi is retained in each case. The amount of coupling agent per unit area is approximately the same for the leached sliver and control.

Aqueous and non-aqueous sizing systems

Experiments have shown that in some special non-aqueous systems containing silane coupling agents and epoxy film formers that the interlaminar shear strengths were 10–20% higher than in the analogous aqueous systems.

It was found that the type of non-aqueous solvent used had gross effects on the interlaminar shear strengths obtained. It was observed that the ketone and ketone-alcohol solvents yielded higher results than when less polar solvents such as toluene, benzene, or chlorinated solvents are used. These solvents affected not only the shear strengths, but also the compatibility of the size on the filaments with the epoxy matrix or impregnating resins.

When γ-aminopropylsilane is applied to glass fibers from an aqueous medium, the orientation of the molecule appears to be different from the same silane when applied from a polar non-aqueous solvent solution. Titration with dilute HCl of the amine groups of this silane applied from an aqueous medium is reported to require 2–3 minutes for complete neutralization, whereas the neutralization is instantaneous when the silane is applied from a polar non-aqueous solution.

The quantity or surface concentration of the ingredients in a size also affects the properties at the interface of glass-resin composites. Optimum concentration ranges occur for optimum laminate properties and the chemical reactivity of the glass treatment materials at the interface affect these properties. This effect is illustrated in Figure 1.

The thermal stability of the interfaces of glass fiber-polybenzimidazole and glass fiber-polyimide composites were studied using various silane coupling agents. It was observed that the existing aliphatic functional silanes all displayed poor heat-aging characteristics at the interface, and aromatic silanes displayed considerably better heat-aging properties. The most suitable silane from this standpoint for the reinforcement of polybenzimidazole resins was a carboxy phenylpolysiloxane (AF-CA-314) and for polyimide resins, chloromethyl phenyltrimethoxysilane (AF-CA-334) as shown in Table IV.

Rate of hydrolysis of silanes

A vapor phase chromatographic technique to determine the rate of hydrolysis of silanes in aqueous solutions has been developed. The results obtained by this method are quantitative. It has been found that γ-aminopropyltriethoxysilane (Union Carbide A-1100) and γ-glycidoxypropyltrimethoxysilane (Dow Corning Z-6040) solutions in deionized water require less than 10 minutes for complete hydrolysis, while γ-methacryloxypropyltrimethoxysilane (Union Carbide A-174) in deionized water requires about 30 minutes. γ-mercaptopropyltrimethoxysilane (Union Carbide A-189) takes about
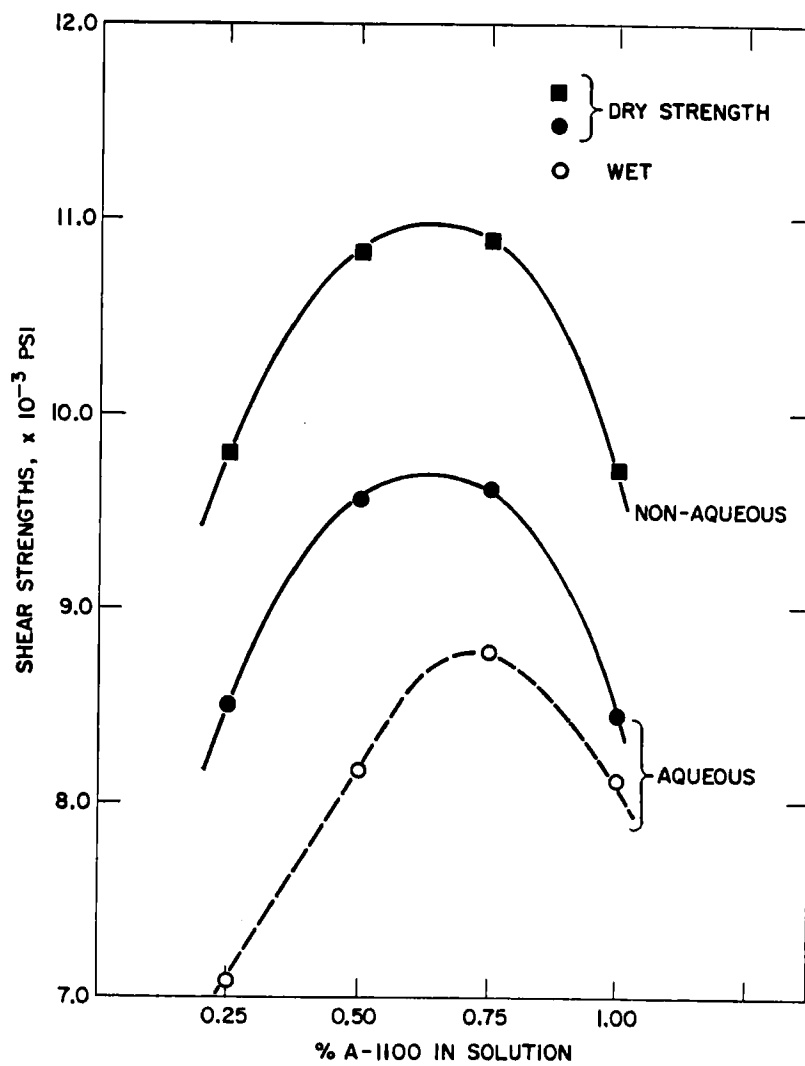
FIGURE 1   NOL short beam shear strengths epoxy resin-anhydride cure

25 minutes for the complete hydrolysis. γ-glycidoxypropyltrimethoxysilane and γ-methacryloxypropyltrimethoxysilane solutions in the presence of 0.2% acetic acid require only 1–2 and 15 minutes, respectively, for the complete hydrolysis.

TABLE IV

Flexural strengths of 14 ply, 181 style, S-glass,
skybond 700 polyimide laminates (43 % resin)

Structure	Room temperature	After 200 hrs. @ 600°F + 2 hrs. water boil
N_2H—$CH_2CH_2CH_2Si(OC_2H_5)_3$	45.5×10^3 psi	12.9×10^3 psi
HOOC—⟨⟩—$SiO_{1.5}$	43.7	15.4
H_2N—⟨⟩—$Si(OCH_2CH_2)_3N$	41.1	13.4
H_2N—⟨⟩—$SiO_{(3-n/2)}$ $(OH)_n$	41.4	13.3
$(CH_3O)_2CH$—⟨⟩—$Si(OCH_3)_3$	45.1	17.6
$ClCH_2$—⟨⟩—$Si(OCH_3)_3$	58.0	18.9

Reference

1. J. A. Laird and F. W. Nelson, *SPE Trans.*, April 1964, pp. 120–128.