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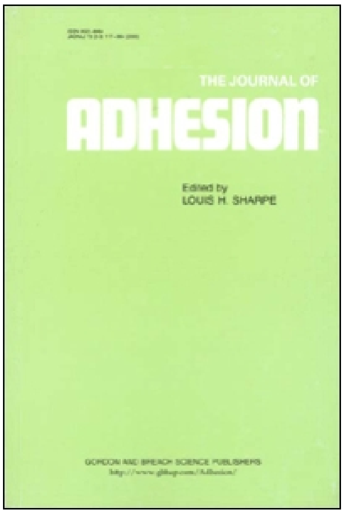

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Historical Background of the Interface—Studies and Theories

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ABSTRACT

This paper is a historical review of the many theories of the interface which were proposed during the period 1947 up to 1964. The evidence for and against these theories are discussed.

INTRODUCTION

REINFORCED PLASTIC STRUCTURES are required to perform under many types of loading and a variety of environmental conditions. Even now in 1970, the best quality fabricated glass fiber composites do not perform too well under bending loads for long periods of time in a moist and/or hot environment. A great deal of progress has, however, been made since Oleesky reportedly made the first polyester-glass fabric laminate for use in a radome in the middle or late 1940's.

A quality-fabricated high-strength, high-performance glass fiber reinforced plastic is primarily dependent upon the three factors: a) strength of the glass fiber, b) strength of the resin and, c) strength and permanency of the bonding between the glass and the resin. The advent of the S-glass fibers during this period was a substantial advance. The appearance of epoxy resins in the early 1950's was also an important milestone for glass reinforced plastics (GRP). Progress was slower in the area of the interface however.

Parameters of the interface were more difficult to study and critical experiments were not set up to gain fundamental understanding. Substantial progress was, however, made during these years in developing effective treatments for glass fibers. These came about largely as a result of development work being carried out by many investigators based on theories which had not or, perhaps, could not then be tested scientifically. Applied development work rather than the scientific approach was, in fact, forced upon the industry by the military and others in the rush for getting GRP into structural applications. The fact remains that many glass fiber treatments developed during this period of "no understanding" are still with us in 1970 and doing very well.

There were two events in 1963 which deserve mention and which had a significant impact on subsequent interface investigations. Prior to that year, the efforts that led to commercial treatments were of an empirical nature. The first event was the formation of "The Ad-hoc Committee on the Interface Problem in Fibrous Composites" by the Materials Advisory Board.

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This committee was charged with investigating the problem in depth, to define problem areas, and to come up with recommendations on what sort of research should be sponsored. University, government and industry were represented by persons from many disciplines. The committee report (MAB-214-M) was published in 1965. A most important finding was that the principles of surface chemistry, as related to the problem, had been virtually ignored for about 15 years. A major recommendation was that research efforts be scaled up to a 50 senior investigator level for a period of five years.

The second event to have an impact on the type of research done was a two-day meeting by invitation only on the interface problem at the Naval Research Laboratory in Washington. This was attended by about 75 persons, also from government, universities and industry. The proceedings were not published, but this meeting had an impact on the type of interface research which the government at least sponsored in the succeeding years. Surface chemistry investigations began in earnest on exploring basic phenomena at the interface. The Air Force followed by sponsoring interface research using radioisotope methods.

Many over the past several years have been puzzled by an occasional very high laminate strength result. The usual explanation is that, "For once everything was optimum: good finish, glass, and resin and the best fabrication procedure." Such "best ever" indicate targets to strive for. In Table 1 several "best evers" are shown which were observed at the U. S. Naval Ordnance Laboratory (NOL) over several years. Actually, data from state-of-the-art laminate strengths in 1970 or present military specification requirements for that matter do not even come close to these values.

Table 1. The Strongest Ever (NOL)[a,b]

	Polyester	*Melamine*	*Epoxy*	*Phenolic*
Tensile Str., dry, psi	75,000	60,000	77,600	75,000
Tensile Mod., dry, psi $\times 10^{-6}$	4.6	5.2	5.0	5.0
Tensile Str., wet, psi	70,400	61,600	76,700	68,800
Tensile Mod., psi $\times 10^{-6}$	3.6	4.6	4.5	4.2
Flex. Str., dry, psi	120,500	112,300	129,200	130,200
Tensile Mod., wet, psi $\times 10^{-6}$	6.2	5.5	6.0	7.9
Flex. Str., wet, psi	104,000	93,600	150,000	121,000
Flex. Mod., wet, psi $\times 10^{-6}$	7.0	5.3	5.0	5.7
Shear Strength, psi	23,300	—	23,200	21,000
Compressive Strength, dry, psi	67,700	76,300	64,300	89,800

a. Satin weave, "E" glass fabric laminates.

b. Values shown were obtained from a single specimen; strength and corresponding modulus value were not necessarily obtained from the same specimen.

The solution to the problem of the interface in terms of basic knowledge which can be exploited to design new finishes is still not here. This is clearly evident from the one or more sessions on the interface over the past six years. The subject has been and still is highly controversial. We are still using, for the most part, glass fiber treatments which were developed on a "cut and try" basis in the 1950's.

SIZES AND FINISHES

A distinction should be made between the two types of glass fiber treatments which are in use. Much of the glass fiber made for filament winding is given a single and final surface treatment at the time of forming. Such a treatment is correctly called a size. The treating solution used is a mixture of many things, the more important of these being lubricant, binder, and coupling agent. The first of these provides surface lubricity, which prevents abrasive damage during handling. A binder is necessary for strand integrity, since the single filaments normally do not pack well due to static electricity and perhaps other factors. The coupling agent presumably improves the bond between the glass surface and the resin matrix in a laminate.

The other type of treatment is called a finish. Glass fibers which are to be given a finish are also given a size at the time of forming. This size contains ingredients which provide surface lubricity and binding action but no coupling agent is usually present. These fibers in the sized condition can be plied and woven into fabric without any important damage to the fibers. To remove this size, which is necessary before the finish is applied, the fabric (or roving) is heated in air circulating ovens to burn the size away. The finish is then applied from solution to the heat cleaned fabric to complete the treatment. The chemical in the finish treatment is a coupling agent, but many finishes also impart a large amount of lubricity to the glass surface.

It is obvious, therefore, that fiber treatments may be quite different. All sizes contain ingredients which might be likened to a release agent. This would certainly militate against good bonding between the resin matrix and the glass. Another difference between sizes and true finishes is that the amount of loading (% by weight) for most finishes is much less. The measured strength of a finished single filament also is less than that of one which has been given a size. One reason for this is that the strength of a glass filament is severely reduced by heat cleaning. Thomas has shown that the filament strength is reduced by 50% when heated for only four hours at temperatures commonly used for much longer times to ignite the No. 630 size off glass fibers[1]. In spite of this, though, the measured strength of composites with finished fibers is often greater than from those using fibers treated with the coupling agent containing sizes. On a per-pound-of-glass-fiber basis, those with coupling sizes cost less than those with finishes. In determining whether sized or finished fibers will be used in an application, many factors are considered and often a trade-off in properties against cost will be made.

THEORIES ON MECHANISMS AT THE INTERFACE

There was in 1963 no complete picture of processes or mechanisms at the interface which could explain the beneficial effects from treatments on fibers. Many theories had been proposed. There was scientific evidence for every one of these theories. There was also equally good evidence against many of them. A treatment probably does many things at the interface, all of which are important but, perhaps, to different degrees. Irrespective of theories, a requirement for high strength laminate properties under loading conditions is effective transfer of stress in all parts of the composite from fiber to fiber across the resin-glass interface. Stress transfer must be efficient under a wide variety of environmental conditions, often for long periods of time. Fiber treatments somehow played a part in not only strengthening but maintaining this interfacial bond.

The Chemical Bonding Theory was the oldest and still the best known. The coupling agent contained chemical functional groups which could theoretically react with silanol groups on the glass. Attachment could thus be made to the glass by covalent bonds. The coupling agent, in addition, contained at least one other different chemical functional group which could theoretically coreact with the laminating resin during cure. Assuming that this all occurred, the coupling agent acted as a vehicle to bond the glass to the resin with a chain of primary bonds. This should theoretically lead to the strongest interfacial bond (50-100 Kcal/mole).

The first reference to the idea of the Chemical Bonding Theory, as far as I can determine, occurs in an October, 1947, report prepared by Dr. Ralph K. Witt, et al., from Johns Hopkins University. Dr. Witt had at that time a contract with the Navy Bureau of Ordnance to investigate the problem, "Development of a High Strength, Low Radar Reflectancy Material." This work was classified "Confidential" until October 16, 1963, when it was finally declassified. Exerpts from pages 39 and 40 of this report state, "Treatments of the glass surfaces with different chlorosilanes . . . . hydroxyl groups, OH, which are present on the glass surface react with R_2SiCl_2 . . . The silane for treating glass surface could be monoallyltrichlorosilane or diallyldichlorosilane . . . so that the 'R-groups' in this case would be allyl groups which could copolymerize with the resin during the curing process." Dr. Witt was referring to an unsaturated polyester resin in this case.

This group, over the next two years, applied many treatments to glass fabric and mat and made as well as tested a large number of laminates. They evaluated various chlorosilanes such as methyltrichlorosilane (MTS), dimethyldichlorosilane (DMDS), ethyltrichlorosilane (ETCS), and mono- and diallyl alkoxy and chlorosilanes. They also investigated surfactants and polymeric silicones. The results showed that the monoallylalkoxy silane gave laminate strengths almost twice those obtained with treatments where the "R-group" was unable in theory to coreact with the resin. This treatment also gave results which were somewhat better than those obtained on laminates

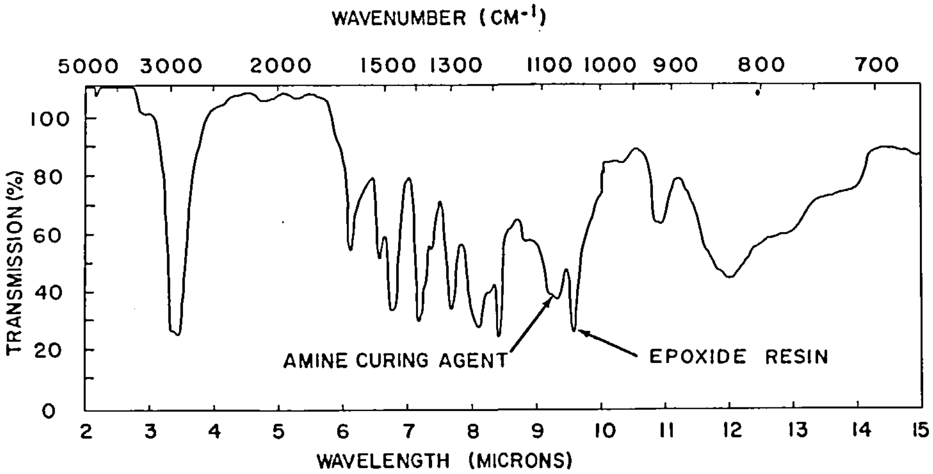

Figure 1. Infrared spectrum of resin-hardener mixture before contact with A-172 treated glass[a].
a. Curing agent A and epoxide resin.

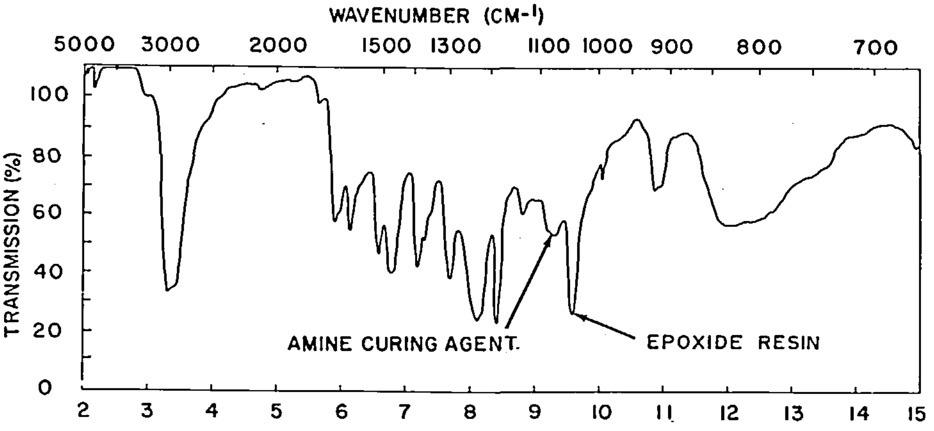

Figure 2. Infrared spectrum of resin-hardener mixture after contact with A-172 treated glass[a,b].
a. Same system as in Fig. 1.
b. Spectrum taken on the first few drops coming through the glass packed column.

made with fabric having the finish "14", which was presumably an early chrome complex treatment.

It is interesting to note that Dr. Witt was strongly interested in a surface chemistry approach to the problem of the interface. In his December 1949 report he mentions that results from surface tension and contact angle measurements had been inconclusive. He states then, "Because the Bureau of Ordnance was desirous at that time of results of a more practical nature that could be translated into design applications, this earlier more theoretical approach was discontinued in favor of a program that would show directly the effect of improvement of interfacial bond between resin and glass on the laminates themselves."

This is perhaps the first time that this early work of Dr. Witt, Miss Raskin and Mr. Carson has been publicly recognized because of the military classification problem.

Dr. Johan Bjorksten and Mr. Luther Yaeger are generally thought of as originators of the "Chemical Bonding Theory." The Bjorksten organization had been given a contract by the U. S. Air Force in about 1949 (AFTR 6220) to explore the effect of glass fabric treatments on polyester laminate wet strength properties. A total of 2000 compounds was screened. The best of these, and still good by today's standards, was a nonaqueous solvent treatment (BJY) based on an equimolar adduct of vinyltrichlorosilane and beta-chloroallylalcohol.

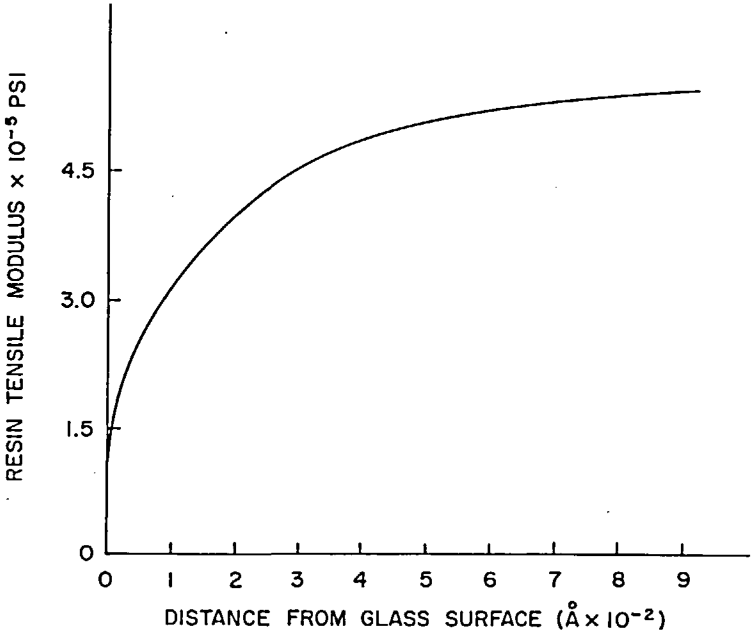

Figure 3. Deformable resin layer at interface: proposed model.

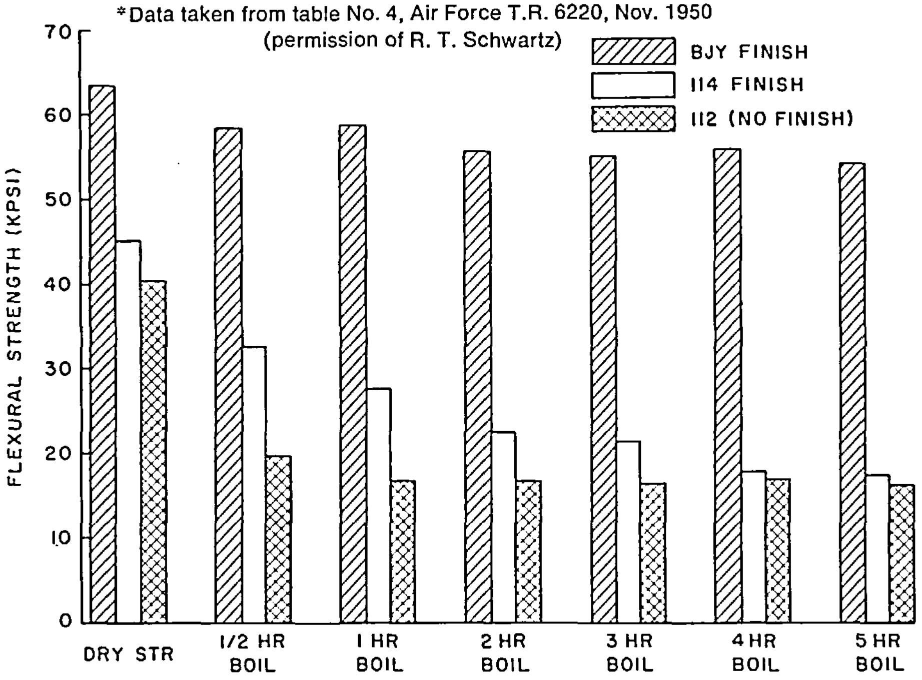

Figure 4. Polyester laminate strengths in 1950*

Polyester laminate strength data obtained by the Bjorksten group using their BJY treatment is shown in Figure 4. Laminates with treatments 114 and 112 (no finish) are also shown for comparison. After 5 hours in boiling water, the flexural strength of the BJY laminate was still above 55,000 psi and was, in fact, substantially greater than the original *dry* strength of the other laminates. Polyester laminate dry strengths up to 90,000 psi with only a 10% loss on two hour boiling were obtained by us at NOL in 1952 in evaluating this finish.

On pages 22 and 23 of AFTR 6220, the authors propose that the unusual benefit from their treatment could be due to, "integral chemical unification between the glass and resin." The Bjorksten group was probably unaware of the earlier work of Dr. Witt's group for the Navy. Dr. Witt does in fact also mention vinyltrichlorosilane in one of his reports and stated that they intended having some synthesized.

The Chemical Bonding Theory whether rigorously proven or not must have had a tremendous impact on the direction of development work at the Union Carbide, DuPont and Dow Corning Corporations during the years 1950 through 1963. Almost every glass fiber treatment which was offered on glass fabric had at least the potential to chemically bind together the resin and the glass. There were, however, exceptions such as why should the Volan finish work with an epoxy resin when theory would indicate that it should not.

During these years a large number of meaningful (but not rigorous) experiments were caried out and reported which certainly favored the theory. Some of these also cast serious doubts on the theory. Table 2 shows laminate flexural strength data obtained with several pairs of closely related chemical structures, which were used to finish heat cleaned glass cloth. In terms of strength properties, vinyltrichlorosilane finished glass gives dry and wet polyester laminate strengths about 60% greater than ethyltrichlorosilane. Similarily, allyl trichlorosilane gives about 70% greater values than the saturated derivative, propyltrichlorosilane. Yates had reported that the chromium complex of isobutyric acid vs. that of methacrylic acid (Volan A) when used to finish glass fabric gave only about half of the polyester laminate strength found with the latter[2]. The two compounds in each pair differ chemically only by olefinic unsaturation. On the basis of the theory, an unsaturated polyester laminating resin should be able to copolymerize with olefinic groups in a finish.

Table 2. Polyester Laminate Strength Data[a]

	Flexural Strength, psi		*Retention*
	Dry	*Wet*	%
112 (heat clean)[b]	56,000	34,800	62
Ethyltrichlorosilane[b]	34,500	26,000	77
Vinyltrichlorosilane[b]	72,000	59,000	82
Propyltrichlorosilane[c]	34,500	26,600	77
Allyltrichlorosilane[c]	57,800	58,400	101

a. 181 Style Glass Cloth

b. Plueddemann, *Modern Plastics*, 39, 135 (1962).

c. Clark, Remarks at Session 8, 16th Annual Technical and Management Conference, Reinforced Plastics Division of S.P.I., Chicago, 1961.

The Naval Ordnance Laboratory carried out a study in 1961 to see if the Chemical Bonding Theory could be used to design very inferior finishes[3]. Two silanes, methyltrichlorosilane (MTCS) and dimethyldichlorosilane (DMDCS), neither of which have any organic functional groups were used to treat heat cleaned glass fabric. Laminates were made with this fabric as well as the original heat cleaned fabric (control). Flexural and compressive strengths were obtained on these laminates which were made with epoxy, polyester and phenolic resins.

Table 3 shows a part of these data which were obtained on the phenolic resin laminates. For comparison, similar data with 136, Garan and NOL-24 finishes are included. The vinyl groups in 136 and Garan finishes are not capable of coreaction with this resin. The NOL-24 finish was originally designed for use with a phenolic resin based on the validity of the Chemical Bonding Theory. The dry and wet laminate strengths with MTCS and DMDCS finished fabric are about the same as obtained with heat cleaned

Table 3. Phenolic Laminate Strength Data[a]

	Flexural Strength, psi	
	Dry	(?) Net
112 (heat clean)[b]	32,000	20,000
136[c]	35,000	27,800
GARAN[c]	44,600	47,200
NOL-24[b]	90,000	88,000
CH_3SiCl_3[b]	40,000	31,000
$(CH_3)_2SiCl_2$[b]	25,000	18,000

a. 181 Style Glass Cloth, BLL 3085 Resin.
b. NOL Technical Report 62-23.
c. NAVORD Report 3889.

fabric (control). The corresponding strengths obtained with 136 and Garan finishes are only slightly better than those from the heat cleaned fabric. The values from the NOL-24 finished fabric are two to four times greater than the control. The results, therefore, show that it is possible to design extremely poor as well as effective fiber treatments for a given resin system on the basis of this theory. This is dramatic evidence for but, of course, not scientific proof for the Chemical Bonding Theory.

Despite the above and other equally strong supporting evidence for the Chemical Bonding Theory, greater laminate strength properties should be realized if primary valence bonding at the interface does indeed take place. Several attempts were made using model systems to obtain more definitive evidence for covalent bonding. Gutfreund and Weber[4], tried to copolymerize styrene and vinyl siloxane on a glass surface onto which di-t-butylperoxide had been previously adsorbed. More rigorous conditions were used than in the curing of a polyester laminate. The styrene homopolymerized and could be removed by solvent extraction.

Another model compound study made by Vanderbilt gave results which seriously undermined the Chemical Bonding Theory[5]. An attempt was made to bulk-copolymerize vinyltriethoxysilane and diethylfumarate. The latter is similar in structure to an unsaturated polyester. There was virtually no evidence of copolymerization. In another experiment, a copolymer of the silane and styrene was obtained which confirmed the earlier work of Pike and Baily[6]. Styrene is a reactive diluent in polyester laminating resins. The conditions of reaction were in all cases much more rigorous than required in the curing of a laminate. Clark[7] reports attempting a similar experiment with the same silane and styrene but with different results. He hoped to obtain a copolymer which would be useful as a resin. The polymerization was carried out in an infra-red cell. After 15 hours, 98% of the silane remained unchanged, but 85% of the styrene had homopolymerized. We see, therefore, that the results from different workers with styrene and the unsaturated silane are not in agreement.

Yates[2] reports having directly copolymerized Volan A, which contains a methacrylate group, with a polyester resin. A chromium containing resin was obtained which was in part insoluble in acetone, whereas the resin obtained from exposing the chromium complex alone to the same conditions was soluble in acetone. These results support the Chemical Bonding Theory.

The nature of the bonding between the glass and the silane finish in 1963 was very much the subject of speculation. Rochow[8] had studied this with chlorosilanes. He found that glassy type surfaces had many monolayers of adsorbed water on them. Dimethyldichlorosilane reacted with this water on a molecule for molecule basis to produce hydrogen chloride. A strongly adhering coat formed on the surface which could not be removed by usual solvent extraction. The film had all the appearances of being chemically bonding to the surface.

All the silanes, as well as the chromium complex (Volan A), which were used to treat glass, contained hydrolyzable groups which could in theory react with hydroxyl groups (or adsorbed water) on the glass surface. There was evidence that all of these hydroxyls might not react with hydrolyzable groups on the finish molecule. Yates (Table 2 of ref. 2) had shown by titration that silica under certain conditions had 16 acidic hydroxyl groups per square millimicron. E glass had 7 acidic (silanol) hydroxyl groups per square millimicron and 5.7 other hydroxyl groups which were not silanol. Many had reported that the usual finishing chemicals used on E glass were not effective on silica. Perhaps the only effective finish coupling action to E glass might be made with hydroxyl groups on aluminum and/or boron atoms rather than silanol groups. The Naval Ordnance Laboratory had found that several chlorosilanes which react almost violently with aliphatic alcohols (and also water) reacted very sluggishly with phenolic hydroxyl groups, *which are also acidic.* In fact, Fothergill and Harvey[9] had infra-red evidence indicating that in the synthesis of NOL-24, allyltrichlorosilane reacted with the ring hydrogen of resorcinol rather than the phenolic hydroxyl groups. On the basis of the above, it seemed likely that chlorosilanes and probably also alkoxysilanes, as applied to glass fibers, reacted with both water and hydroxyl groups. The bonding to glass would most likely to be made through hydroxyl groups on either or both aluminum and boron atoms rather than silanol. Vanderbilt has suggested that the finish-glass bond is the weakest link in the interface[5].

Many other theories had also been proposed to explain the benefits from glass fiber treatments. In 1956, Dr. Hooper observing that fatigue properties of laminates were greatly improved by finishes on the glass reinforcement proposed the Deformable (Finish) Layer Theory[10]. He suggested that the finish was truly plastic in the interface. If one considers the amount of resin shrinkage on curing and also the relatively large differences in the coefficients of thermal expansion of the glass and the resin in a laminate, substantial interfacial shear stresses within a cured (unloaded) laminate would be expected under many circumstances. An important function of a finish then could be to provide a mechanism for local relief of these stresses. It would seem reasonable, therefore, that another required property for a finish could be sufficient relaxation properties, such that stresses between the resin and the glass might be relieved without rupture of the bonds. Once rupture had occurred in such a situation, there was no apparent self-healing mechanism to repair the damage. A minimization of these internal stresses would be expected to favor better laminate strength properties, particularly under unfavorable (wet) environmental conditions.

The Deformable Layer Theory was, however, short lived. Simple calculations showed that a typical finish if it had any solid character whatever was much too thin to relax in the amount required under favorable conditions.

The Preferential Adsorption Theory is a modification of the Deformable Layer Theory. This theory was advanced by the Naval Ordnance Laboratory and proposes that finishes on glass set the stage for the formation of a *deformable resin layer* at the interface. It has been shown here that glass surfaces with and without treatments exhibit chromatographic properties. A comparison of the infra-red curves in Figures 1 and 2 shows evidence for the ability of glass fibers treated with A-172 finish to alter the relative concentrations of an epoxide resin and its amine hardener in a liquid mixture of the two[21].

This new theory was based on the assumption that different finishes on glass fibers have, to different degrees, the power to deactivate, destroy or adsorb out of the uncured liquid resin mixture certain constituents necessary to the complete curing of the resin. This would lead to an upset in the optimum local material balance of the liquid resin mixture at the interface, as a result of what is termed "preferential adsorption." It was assumed that this effect was important only close to the surface since the separation process would be dependent on diffusion rates, which would be low in viscous resins. Carried to its logical conclusion, the above would imply that a finish would lead to an *interface resin layer* of *variable thickness* and *flexibility.* The generalized flexible properties of such a layer are shown in Figure 3. This postulated flexible layer was not dependent on finish thickness and could have a thickness much greater than 100 A. Such a layer would need, in addition, the properties of ductility and strength in order to provide respectively stress relaxation and effective transfer of stress between the fibers in load-bearing situations.

More evidence for the chromatographic effect was later obtained. It was found that silica (no finish) separated hexamethylenetetramine from a phenolic resin.

The Preferential Adsorption Theory was new in 1963. More work was anticipated with a greater variety of laminating resins and finishes. It was deserving of attention and study since it offered a reasonable explanation for the principal benefits from finishes which are improved laminate strength properties under adverse environmental conditions and fatigue. It was free of many of the limitations and unproven assumptions inherent in other theories. According to Zisman[11], the adhesive bond in a laminate is stronger than the resin and could be even stronger than the glass. The 5 to 10 Kcal/mole energy of hydrogen bonding may be more than adequate to maintain bonding at the interface. More work should have been done to test this theory. We are unaware of anyone having done any further work to test this theory, however.

The tendency for glass fibers to be damaged in handling was well-known. Much of this occurs because of fiber self-abrasion. Sizes and some finishes provide surface lubricity to different degrees which minimizes this damage. It had been proposed by Outwater that an important function of a finish could be to modify the coefficient of friction[12]. This theory was based on a model of a single filament which was embedded in a relatively large amount of resin. Upon curing, the resin shrinks onto the filament to put it into compressive stress. Loading such a system was assumed to lead to a relative motion between the resin and the glass. The resistance to this motion was further assumed to be dependent on the coefficient of friction between the glass finish and the resin. No adhesive or other strong bonding was required by this theory. The strength properties of a laminate were on the basis of this theory, a function of a coefficient of friction characteristic of each fiber surface treatment.

Anderson[13] had shown that long sections of a single filament could be pulled out of a cured resin matrix. This showed that, under certain circumstances of stress, there would be a relative motion between the fiber and the cured resin. Perhaps the resin did not seize the fiber to the degree suggested by Outwater. In an actual composite of yarns and resin, few if any filaments are individually surrounded by relatively large amounts of resin. The model assumed in the Coefficient of Friction Theory certainly did not fit the actual situation in a fabric laminate.

Many believed that an important function of a finish was to protect the glass surface from the effects of water. Otto and Charters had data to show that the strength of a glass filament was seriously degraded by the presence of moisture[14]. Thomas also indicated that damage occurred[1]. Silanes replace, perhaps, the bound water on the surface of glass filaments even when the treatments are carried out in water. The evidence, based on laminate data, was overwhelming that appropriate fiber treatments improved laminate wet strengths. An inconsistency about the Vapor Barrier Theory is that silicones which lead to high laminate wet strength retention as a class have high permeability to water vapor. This was an area which was ripe for a fundamental study.

According to DeBruyne, one of the three requirements for a good adhesive bond was that the adhesive must wet the substrate[15]. Adhesion at the interface certainly is an important factor in effective transfer of stress from fiber to fiber. Most fiber treatments, however, inhibited rather than promoted wetting by the liquid resins. Laird had shown that A-1100 treated glass was wetted poorly by an epoxy resin yet the interface bond life in the presence of water was over 200 times that with no treatment[16]. Whether a solid is wet or not by a liquid is determined by the respective surface energies of the two. Ordinarily a clean glass fiber will have a surface energy much greater than that of the liquid resin and spreading (wetting) occurs spontaneously. Application of a treatment may reduce the surface energy of the fiber to a value less than that for the resin and the fibers resist wetting. There was no doubt that wetting is important. More fundamental work needed to be done in 1963 to elucidate the role of surface energy as related to wetting, bond permanence, and bond strength.

In this connection and perhaps important to the interface problem, Zisman had reported two phenomena which involved wetting[17]. In general, wetting of a solid by a liquid occurs only when the surface energy of the former is greater than the latter. All hard or high melting solids have high surface energies ranging from 500 to 5000 ergs/cm^2. Most organic liquids including liquid resins have surface energies of 100 ergs/cm^2 or less. Zisman found that many high energy surfaces behave in respect to wetting, under certain circumstances, like low energy surfaces. Liquids such as highly purfied octanol-1, octanol-2 and 2-ethylhexanol-1 exhibit appreciable contact angles on several hydrophilic high energy surfaces. These solids include platinum, glass, and fused alumina. The explanation for this anomaly is that the high energy surface adsorbs a portion of the liquid to form an oriented film whose surface energy is less than that of the liquid itself. Adsorption of this film thus converts a high energy surface to a low energy surface. The liquid, in this case, seemingly cannot even spread on itself. Zisman had termed this phenomena "Autophobicity."

The second phenomena which Zisman at first found difficult to explain was that some liquid diesters spread on certain high energy surfaces and not on others. Bis-(2-ethylhexyl) sebacete spreads freely on metals but does not spread (wet) on fused silica or borosilicate glass. The explanation is that the adsorbed (and oriented) water molecules on the silica and the glass hydrolyze a small quantity of the ester. A film of the acid, resulting from the hydrolysis, is then immediately adsorbed. The formerly high energy surfaces now have surface energies which are less than that of the liquid ester. The metals studied do not have adsorbed water molecules on the surface, hence are wet by the diester. This phenomenon had implications to the wetting of glass fibers by polyester and anhydride cured epoxy resins both of which have hydrolyzable linkages.

Plueddemann had proposed a new theory to account for what appeared to be the ability of silane finishes to relieve local stresses at the interface[18]. This theory was in a sense a new Deformable (Finish) Layer Theory. He suggested that when the silicon atom in the finish is bonded by two or more oxygen linkages (siloxane) to the glass surface, the finish could move relative to the surface without interfacial delamination. When local stresses arose at the interface as a result of causes cited before with the Deformable Layer Theory, the finish could "walk" along the glass surface on the two or three siloxane legs between each silicon atom in the finish and the glass. He postulated that when stresses arose in the interface, many of these legs (bonds) were broken. As we understood this, there are always at any instant *at least one* unbroken leg to every silicon atom in the finish. The finish to glass linkage was therefore never completely broken (delamination). As the finish layer moved relative to the glass surface the broken bonds reformed at new positions.

The creep mechanism for stress relief was, therefore, based on the "musical chairs" idea in which the siloxane bonds could shift along the interface and thus lessen local stresses between the resin and the glass. The mechanism was likened to a rubber suction cup on a wet glass surface. The section could be moved about on the surface without "losing its grip."

The Special Project Office (POLARIS) funded an effort at the A. O. Smith Corporation in 1962 and part of 1963. The title of the task was "Effect of Glass Surface Chemistry on Wetting, Bond Strength and Bond Life of an Epoxy Resin;" Contract NOw 62-0679-c (FBM). The purpose was to study the three properties listed in the task title, all of which are important to laminate strength. Several important bits of information pertinent to the interface were developed or enlarged on in this study.

Glass surface variations included a virgin E glass surface formed by cleaving glass submerged in the resin, E glass with surfaces as-cast from the melt, chemically cleaned, degassed, contaminated, alkali deficient, alkali rich, polished and roughened. These surfaces were compared with and without such finishes as A-1100 and HTS.

Contamination of surfaces by adsorbed moisture and perhaps fatty acids from air exposure decreased wetting but was not detrimental to bond permanence or bond strength. As stated before, coupling agents inhibited wetting but were highly effective in increasing bond life in the presence of water. The effect of water temperature was an important factor in bond life.

A virgin E glass surface formed by fracturing the glass under the liquid resin showed poor bond permanence. In fact, these studies showed no difference in bond permanence when chemically cleaned, contaminated or virgin (fractured) glass surfaces (all without finish) are bonded to the resin. There are still many who believe that if a resin could be applied to the virgin fiber at the time of forming, the need for a coupling finish could be obviated. These results showed little encouragement for this view.

There were then as well as now special constructions such as in certain filament wound composites where stress transfer *across* the glass resin interface could be relatively unimportant to performance. In a properly designed filament wound internal pressure vessel, the filaments are laid down essentially parallel to the direction of expected stress. A high degree of fiber surface lubricity in situations such as this is probably more important than interfacial bonding since the fiber stresses are nearly 100% tensile. If, under stress the fibers moved longitudinally relative to the resin matrix, abrasive effects on the fibers could be, perhaps, nearly as damaging from the resin as from other fibers. The tensile strength of the reinforcing filaments would therefore be reduced. Outwater had cited data indicating that a finish protected glass fibers from the effects of resin[19].

Many believed that for such constructions, finishes (or sizes) should be selected for fiber surface lubricity rather than resin bonding properties. The filament wound high pressure spherical air bottles for aircraft in 1963 were in many instances, wound with glass roving having the 630 size[20]. This size gave high fiber surface lubricity and actually interfered with bonding to the resin.

The above generally summarizes the confusion on the state of the theories on the interface in late 1963. "Testing" of a theory was not much different in 1963 from that in 1947 when Dr. Ralph Witt was compelled to "show directly the effect of improvement of interfacial bond between the resin and glass on the laminates themselves." The method of testing theory was still to make and test laminates with new glass fabric treatments which entailed a host of additional often uncontrolled variables.

The major part of this historical review is based on a survey which was made on this subject by the author in September 1963 for the Department of Defense. This was given as a paper in October 1963 at a meeting attended by a small number of military persons from England, Canada and the USA.

It is easily possible that important work of many persons, particularly in private industry, has not been acknowledged in this survey. This survey does not extend into the patent literature. Another later survey entitled "Glass Resin Interface: Patent Survey, Patent List and General Bibliography" (PLASTEC Report No. 18, AD 609526, Sept. 1964) by Eakins does go into the patent literature and is an excellent review on the subject of the interface.

CONCLUSION

The Chemical Bonding Theory was the only viable theory in terms of successful treatments in late 1963. It was possible to predict finish structures with a good degree of success which would lead to effective treatments. As far as the author knows every successful commercial treatment, even in 1970 is based on this dual functionality concept.

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