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Surface Chemistry of Plastics Reinforced by Strong Fibers

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ABSTRACT

A critical and up-to-date review has been made on the present knowledge of the surface chemistry and related polymer science involved in the reinforcement of thermosetting and thermoplastic materials by glass or other strong fibers. Although the emphasis is basically on the behavior of glass-reinforcing fibers and particles, wherever possible the discussion and conclusions have been presented to allow their extension directly or by analogy to other strong reinforcing solids. A selected bibliography has been compiled of the most significant scientific work published to date. The treatment of the subject has been as fundamental as the scope and reliability of the available data permit. In many instances, available knowledge has been interpreted using the reviewer's judgment. Where significant gaps or conflicts have been noted in the literature, they have been discussed constructively. In the concluding sections numerous highly specific recommendations have been made to stimulate or guide future research and development in this complex field.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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SURFACE CHEMISTRY OF PLASTICS REINFORCED BY STRONG FIBERS

INTRODUCTION

One of the most troublesome problems in research and development of fiber-reinforced plastics is the achievement of optimum resin adhesion over the entire surface of each fiber. Even when regions of the resin medium are sufficiently continuous to be amply resistant to the action of water, there remains the difficulty of protecting the reinforcing fibers from loss of strength or resin adhesion wherever water has penetrated cracks and pores to reach the fibers. The object of this report is to summarize and interpret the more recent investigations of these two topics with an emphasis on the advances or problems concerning the surface chemical mechanisms and some related polymer mechanisms. Although attention here will usually appear to be focused on composites comprising a more or less continuous organic polymeric medium (the resin) in which are dispersed either a random or organized mass of a fibrous glass-reinforcing material, nearly all of the conclusions and interpretations will be extended frequently to include reinforcing materials other than glass.

CONDITIONS FOR OPTIMUM ADHESION OF RESIN TO FIBER

To obtain the fullest advantage in introducing the fibers in the resin, it is always desired to optimize W_A, the energy of adhesion per sq cm at the resin/fiber interface. In this way the fibers are made to distribute and carry as much of the stress load as possible, and their presence can also interfere most effectively with crack propagation through the surrounding resin. But thermodynamics shows that W_A cannot be greater than the equilibrium adhesive energy per unit area of the liquid form of the resin, except for the modest change which can arise through the solidification or density changes of the resin liquid contacting the adherend (1). Hence, a good guiding principle is to try to optimize the adhesion of liquid resin to the solid fibers. When the system solidifies, the essential (and sometimes difficult) practical problem then is to minimize the development of the mechanical stresses arising from thermal expansion differences of the resin and fiber or from crystallization of the resin, which may act to oppose attainment of the desired optimum adhesive strength (1).

At thermodynamic equilibrium the reversible specific work of adhesion of the liquid resin to the fiber surface is given by the following well-known relation derived from the early classic work of Young, Dupré, Bangham, and Razouk (1-3):

$$W_A = f_{SV^\circ} + \gamma_{LV^\circ}(\cos\theta + 1) \tag{1}$$

$$f_{SV^\circ} = \gamma_{S^\circ} - \gamma_{SV^\circ} . \tag{2}$$

Here γ_{LV° is the surface tension of the liquid resin, θ is the equilibrium contact angle, γ_{S° is the free surface energy of the solid fiber in a vacuum, γ_{SV° is the free energy of the solid in an atmosphere saturated with the vapor of the liquid, and f_{SV° is the free energy decrease on immersion of the solid in that saturated vapor. If adsorption of the liquid vapor can be treated as physical adsorption of an ideal gas, the term f_{SV° is given by

$$f_{SV^\circ} = RT \int_{p=0}^{p=p_0} \Gamma \, d(\ln p) \tag{3}$$

where Γ is the Gibbs' adsorption excess per unit area of the solid, p is the vapor pressure, p_0 is the saturation pressure, R is the gas constant, and T is the absolute temperature. Livingston and Boyd (3) later showed that f_{SV° is always a positive number.

To optimize W_A, f_{SV° should be made as great as possible; i.e., the vapor should adsorb so as to give the greatest possible free energy decrease to the solid surface. Unfortunately, there are no published data available on f_{SV° for polymeric liquids or even for their monomers. Only Harkins and coworkers (3-5) have given values of f_{SV° for a modest number of common organic and inorganic volatile solvents adsorbed on some metals and minerals. Furthermore, since f_{SV° is positive, the term $\gamma_{LV^\circ} \cos \theta$ in Eq. 1 should also be optimized. I have shown (1) that to a first approximation for many solid organic polymers this, in effect, means that θ should vanish. Thus, to obtain a maximum in W_A, the surface tension of the liquid resin should be as high as possible consistent with maintaining the contact angle at or close to zero. The former requirement can be restated to be more obvious, because letting $\theta = 0$ is tantamount to allowing the attractive molecular forces between liquid and fiber solid surfaces to work spontaneously to assure intimate contact of liquid resin and the entire surface of the solid. Since there is now a large body of data showing how the equilibrium value of θ varies with the nature of the liquid and the solid surfaces (1,6,7), there is much information available to help guide us in obtaining optimum or increased adhesion.

MECHANISMS WHICH DECREASE RESIN ADHESION TO THE FIBER SURFACE

Since ancient times, an adhesive has usually been applied to the solid adherends while it is in the liquid state, and solidification or polymerization is allowed to progress as soon thereafter as possible; hence, the viscosity increases rapidly during joint formation. This practice is the result of the common desire (or need) to speed up completion of the hardening, crosslinking (or "curing") of the joint. As predicted in earlier survey reports (1,8), all too frequently the adhesive will gel, or even solidify, during (or soon after) application to the joint; hence, it will soon cease spreading and will not fill completely all crevices and pores in the surface of the adherends. For this reason all the interfibrillar crevices in fiber-reinforced plastics are never filled completely, even when $\theta = 0$. This last difficulty has been well demonstrated experimentally by Bascom and Romans (9-11). The presence of only partially filled surface pores and crevices is a significant source of loss of strength and water resistance in composite materials; for example, if the reinforcing fibers are rough or are packed very closely, many unfilled narrow slits will remain. Bascom and Romans (11) counted as many as from 10^6 to 10^8 microvoids/cm^3 of a reinforced epoxy resin after resin impregnation and curing of an NOL glass-fiber-wound ring with an S-glass fiber coated commercially with HTS organosilane finish. Furthermore, the great majority of the voids were linear or slitlike in shape.

Voids and occlusions are regions of stress concentration; hence, the numerous elongated microbubbles or cavities found in nearly all resin-reinforced composite materials will be highly effective in encouraging the initiation and propagation of microcracks from bubble to bubble and so cause failure by splitting along the fiber-resin boundary. As Griffith proved in 1920 (12), the minimum stress F necessary for the propagation of a sharp crack in a brittle solid is

$$F = \left(\frac{4\gamma E}{\pi L}\right)^{1/2} \tag{4}$$

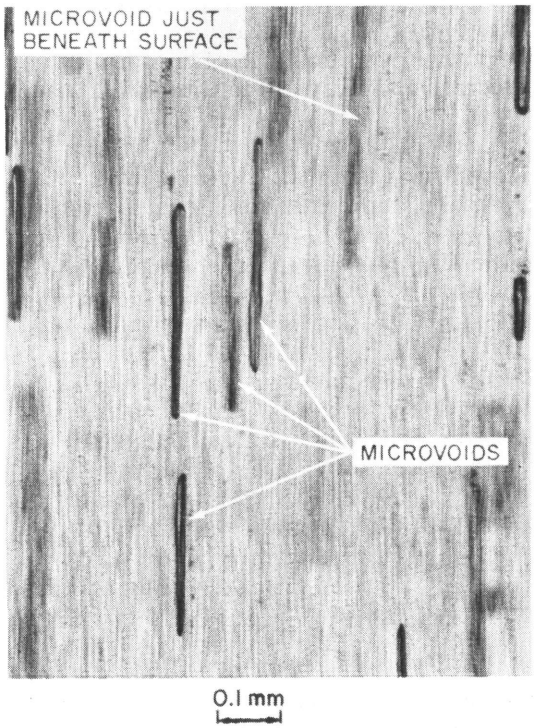

Fig. 1 - Photomicrograph of thin sections of an NOL ring

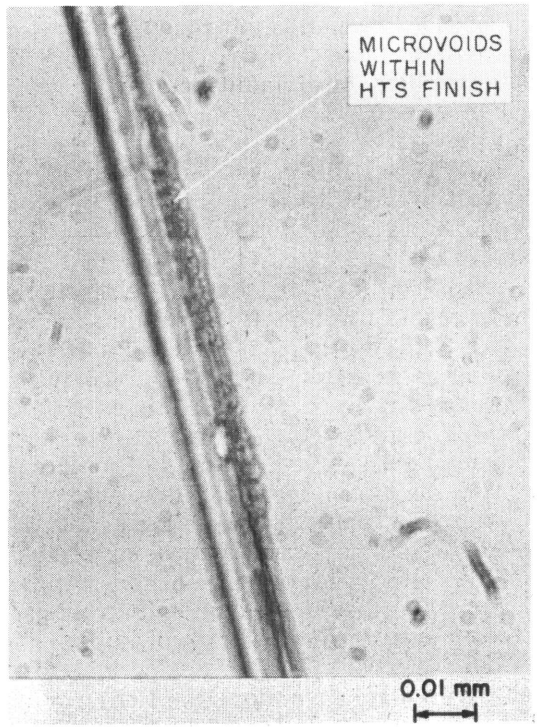

Fig. 2 - Photomicrograph of occluded voids in the HTS finish of an S-glass filament (1000X)

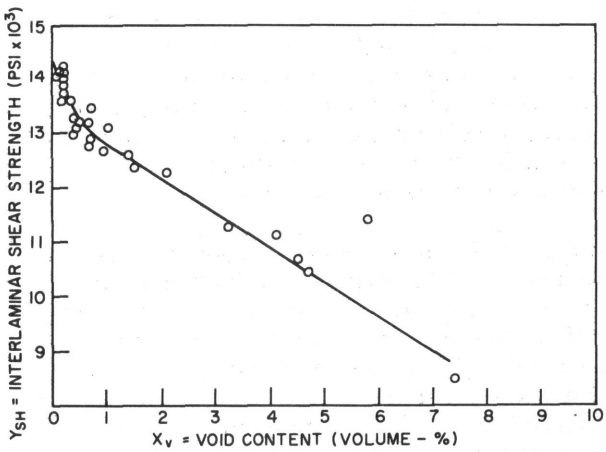

Fig. 3 - Interlaminar shear strength vs volume-percent void content of an NOL glass-fiber-wound resin impregnated ring (Ref. 14)

where γ is the surface energy of the newly formed surface, E is Young's modulus of elasticity of the resin, and L is the length of the crack. Examples of the incidence of large populations of slitlike microvoids in glass fiber-resin composites have been given by Paul and Thomson (13) and by Sands, Clark, and Kohn (14). Figures 1 and 2, taken from the latter investigation, are typical of the void problem in NOL test rings made from closely woven, glass-fiber rovings coated with an HTS finish and impregnated with an epoxy, amine-cured resin; Fig. 3 is a chart taken from the same reference. Very similar results were also found by Paul and Thomson (13). Conditions revealed in

Figs. 1, 2, and 3 are inevitable consequences of the existing methods of manufacturing glass-fiber-wound reinforced plastics. Such commercial products usually have void contents of from 3 to 5%. Hence, methods of impregnation need modification to obtain substantially lower incidence of microvoids and a significant increase in interlaminar shear strength.

A further difficulty resulting from the presence of the numerous linear voids in contact with the fibers is that permeation of water through the resin-fiber composite, especially via the glass/resin interface is an inevitable result. Laird and Nelson (15) have measured rates of diffusion of water which were 450 times greater along the glass/resin interface than those through the resin. Ashbee, Frank, and Wyatt (16), in their recent investigation of water damage in polyester resins, have proposed that water diffusion through the resin can give rise to high osmotic pressure buildup in cracks in the resin phase, which contains impurity inclusions, and that this mechanism can cause crazing, internal stress development, and crack growth, especially parallel to the glass surface. They also demonstrated that water cracking could be reduced by increasing dissolved amounts of ionic salts in the immersion water. From their calculations they concluded that saturated solutions of salts in cavities could have osmotic pressures capable of producing cracks in polyester resins. They proposed that this mechanism could cause debonding of resins to glass and would not be confined to polyester resins. A very recent, careful investigation by Romans and Sands (17) demonstrated that cyclic stressing of the reinforced plastic while it was kept submerged in water greatly accelerated the rate of failure of the material.

Void formation along the fiber surface is encouraged if the contact angle θ of liquid resin with the fiber is not zero, as confirmed in the valuable experiments of Bascom and Romans (11). In general, there are two types of mechanisms which could interfere with obtaining a zero contact angle, and each deserves mention here. The first mechanism arises from the presence on the fiber surface of organic contaminants or coatings which greatly decrease its surface energy. Less than a condensed adsorbed monolayer of many classes of common organic compounds is sufficient to cause a major increase in θ (1,6,8). Such films may happen to be a previous "size" or "finish" coating applied soon after drawing the fiber; they could be adsorbed unknowingly between the time of fiber extrusion, or coating with lubricants, sizes, or other finishing materials, until use of the fiber in the composite, or they may arise from unacceptable adsorbed impurities present (even if only in traces) in the atmosphere, in solvents, or in the resin during the fiber impregnation process. The influence on θ of the chemical constitution of such adsorbed organic films on solids has been extensively investigated (1,6,7).

The second mechanism of void formation results from the nonzero contact angle which can occur whenever a thin film of water adsorbs on the fiber and decreases its surface energy. We have recently proved that such water films need only be one molecule thick to have a significant effect on the surface energy, on the wetting properties, and on the contact angle exhibited by nonhydrophilic liquids on high energy surfaces. Such a mechanism can be especially troublesome whenever the resin (as applied) cannot react with, dissolve, or displace all of the adsorbed water on the fiber surface. An example of the effect of adsorbed water vapor on the critical surface tension of wetting γ_c of organic-free, soda-lime glass (18) is shown in several different ways by Figs. 4 and 5; nearly identical results were subsequently obtained on replacing the soda-lime glass by clean Pyrex, quartz, and sapphire (19). A variety of metals and metallic oxides behave just the same (20); the summary in Table 1 reveals a constant γ_c at each of two relative humidities.

As I pointed out earlier (8), any residual lubricant, size, or finish left on the glass fibers after having been drawn through the die and then coated with resin will limit (or even prevent) subsequent reaction of the coupling agent with the glass. James, Norman, and Stone (21) have given good evidence of such interferences by a residual layer of size

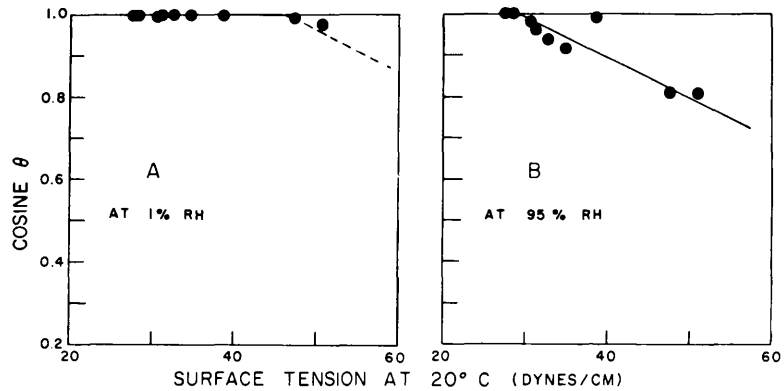

Fig. 4 - Comparison of the wettability by selected hydrocarbon and halocarbon liquids of soda-lime glass surfaces at two different relative humidities (Ref. 18)

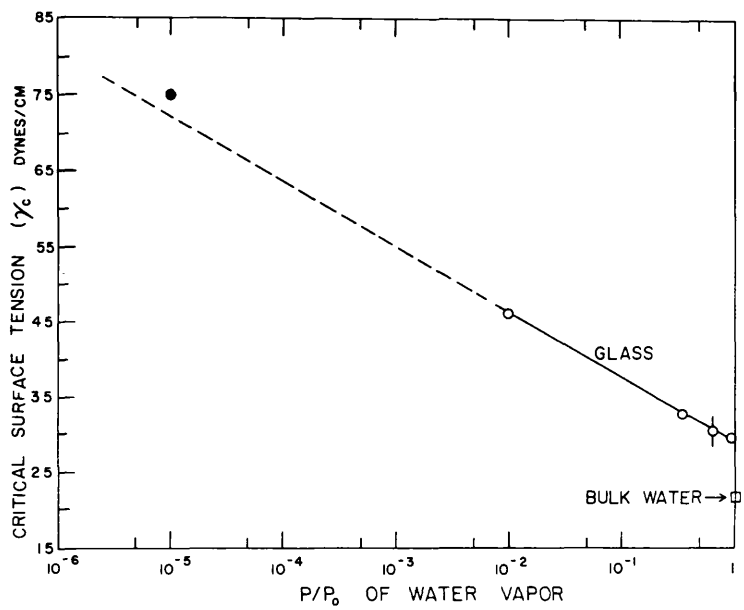

Fig. 5 - The effect of the partial pressure of water vapor on the critical surface tension of soda-lime glass (Ref. 18)

from their experiments using water contact angles on newly drawn glass fibers treated with vinyl silane or polyvinyl acetate (PVA) size alone and with standard commercial fibers treated with mixtures of vinyl silane and PVA. They concluded that the PVA covers much of the fiber surface and thereby reduced the number of chemical bonds formed between resin and adsorbed coupling agent. They suggested that changes were needed in the size coating used and also in the laminate curing conditions.

Another important cause of decreased adhesion with resins reinforced by metal-coated or metal oxide-coated fibers stems from the presence of a surface oxide which has either low cohesive strength or low adhesion to the metal substrate. The former aspect of the subject has been given much theoretical and some experimental attention, but it is doubtful that available data apply to the oxides as they are found in practice on

Table 1
Comparison of Critical Surface Tension of Wetting for 12 Metals*
(All Data Obtained at 20°C in Nitrogen)

Metal	Atomic Radius†	Crystal Structure	0.6% RH γ_c (dynes/cm)	95% RH		
				n-Alkanes γ_c (dynes/cm)	Aromatic Cpds. γ_c (dynes/cm)	Halogenated Alkanes γ_c (dynes/cm)
Nickel	1.24	cubic f.c.	45	26	38	36
Iron	1.26	cubic b.c.	46	27	37	36
Chromium	1.27	cubic b.c.	45	–	38	36
Copper	1.28	cubic f.c.	44	27	38	36
Germanium	1.37	diamond	46	27	35	36
Molybdenum	1.39	cubic b.c.	44	27	37	38
Tungsten	1.39	cubic b.c.	45	–	37	37
Aluminum	1.43	cubic f.c.	45	27	38	37
Gold	1.44	cubic f.c.	45	27	40	40
Niobium	1.46	cubic b.c.	44	–	38	38
Tantalum	1.46	cubic b.c.	42	27	37	37
Zirconium	1.60	hexagonal	45	–	37	37

*From Ref. 20.
†R.T. Sanderson, "Chemical Periodicity," New York:Reinhold, pp. 26-28, 1960.

the various metal fibers and surfaces of interest in producing composite materials. Especially interesting investigations of the cohesive energies in oxides are those of Livey and Murray (22), Hunter and Fowle (23), Benjamin and Weaver (24-26), Karnowsky and Estill (27), Eberhart (28), and Yatsimirskii (29).

In glass fiber-resin composites one is always confronted with the difficulty that the coefficient of thermal expansion of the commonly used organic resin for such systems is from 5 to 12 times greater than that of the glass-reinforcing material. Hence, large enough stresses can arise in the solidification of the system to cause crack and void formations at the interface as well as in the resin. Much has been written on the stress distributions developed under various simple assumed conditions. For many years some investigators of composite materials have emphasized the need for an elastic transition layer between the glass surface and the adjacent resin; however, there has been much argument and little illumination about the need and the most suitable mechanism for creating an acceptable transition layer.

COUPLING AGENTS

Increasing attention has been given during the past decade to improving adhesion and wet strength in reinforced plastics by coating the reinforcing fibers or particles with an adsorbed film of a "coupling agent." Such agents are compounds (or coatings) designed to interact with or link chemically the solid fiber or particle surface and the polymeric adhesive. At present, the most common classes of coupling agents are (a) various organosilanes (30-33) and (b) certain coordination compounds of chromium reaction products of basic chromyl chloride with carboxylic acids (34-36). Members of both classes of coupling agents have been used, and some have unquestionably given useful results in decreasing the loss of strength of glass-fiber-reinforced plastics during

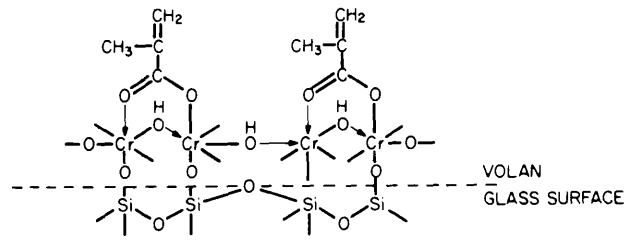

Fig. 6 - Structure proposed for Volan when chemisorbed on silica glass (Ref. 35)

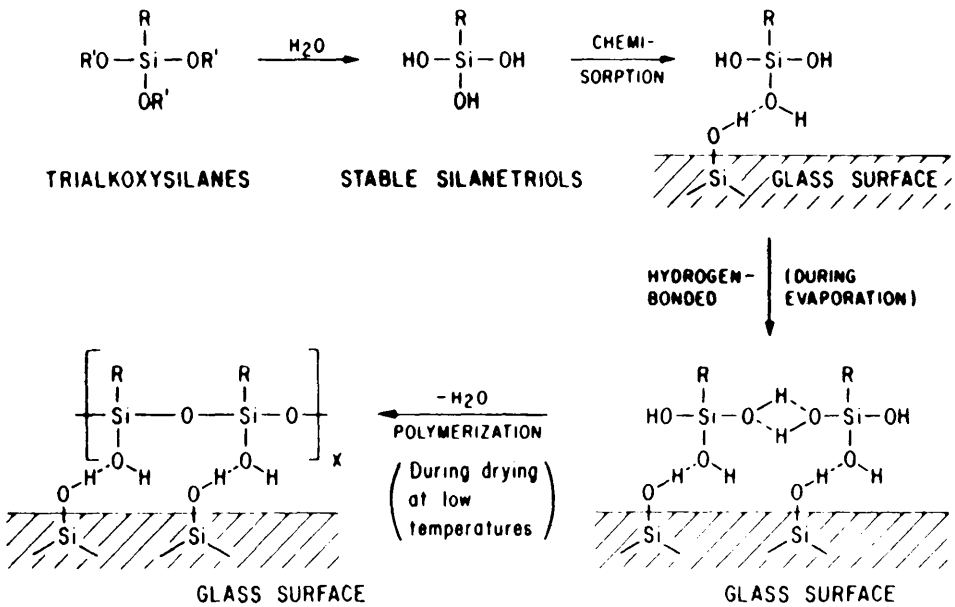

Fig. 7 - Formation of linear polysiloxanes on silicate glass surface (Ref. 37)

prolonged static immersion tests in hot water. There have been innumerable publications which have debated the resulting percentage improvement to the wet and dry strengths and also the function of such compounds. Various investigators have claimed reaction products that varied from adsorbed oriented monolayers to unspecified polymolecular films on glass. An example of a proposed monolayer structure for a film on glass of the chromium complex made from the reaction of chromyl chloride with monomeric acrylic acid is given in Fig. 6, and a recently proposed reaction mechanism and structure of a coupling film of a trialkoxyorganosilane on glass (37) are shown in Fig. 7.

Although our understanding of the mechanisms involved in adhesion, especially of the causes of weakness or failure in adhesive joints, have become clearer in the past decade and much importance is now generally assigned to obtaining a zero (or small) contact angle of the liquid resin with the adherend surface to have spontaneous spreading for optimizing joint strength (1), an as yet unanswered question is where and to what extent a chemical reaction at the joint interface is necessary or advantageous to form a strong joint. Another related question is whether or not it is essential that the opposite faces of the coupling agent layer or film need to react chemically with the adhesive and adherend, respectively.

Many physicists have long contended that intimate molecular contact of adhesive and adherend without surface chemical reaction is sufficient to develop adequately high strength to produce an effective adhesive joint. Because of the great difficulty of obtaining

such an intimate contact over the entire or "real" surface area comprising a macroscopic joint, liquid adhesives were introduced as the practical answer early in the history of adhesive technology. However, one must also recognize that if the joint is subsequently to be exposed to prolonged water immersion accompanied by water penetration through the joint, whether it be simple or composite, the resulting hydrolysis or corrosion at the solid/resin interface might be such as to necessitate use of a chemically reacted film of coupling agent between adhesive and adherend to prolong joint life.

Since many organic adhesives can be applied as solutions or dispersions having low surface tensions, it is often presumed that they would invariably spread spontaneously on hard, high-melting adherends, because they are presumed to have high-energy surfaces. Such is not invariably the case, because innumerable liquids, as commonly applied, do not spread spontaneously on the wide variety of high-energy solid surfaces which are able quickly to adsorb either water or one of many classes of atmospheric organic contaminants (1,6). Several methods can be used to minimize such potentially interfering effects. First, an adsorbed film of a coupling agent can serve as an adhesion promotor, if applied to the fiber surfaces early enough, because it can prevent the undesired contamination from adsorbing at the same sites; hence, it can serve as a "priming" or preliminary protective coating prior to application of the liquid adhesive. Second, the adsorbed film of coupling agent can prevent the adsorption of those contaminants often present in liquid adhesives which could decrease adhesion by interposing a weakly bound or "mold release" layer at the interface, thus introducing a plane of easy parting after resin solidification. Therefore, coupling agents have advantages in combating the interfering surface-energy-lowering effects of undesirable types of atmospheric or solution contaminants.

Generally, coupling agents presently used in fiber-reinforced plastics were designed to have an outermost exposed organic group which is supposed to react with molecules of the liquid adhesive, as for example by vinyl polymerization. The opposite end of the coupling molecule comprises one or more polar groups, each of which is more or less able to adsorb and react independently with a receptive site on the fiber surface. Consequently, there should result high resistance to the displacement of the coupling agent by solvents, other surface-active components, or heat. Since the small size of the molecule of water vapor, its high surface mobility, and the short relaxation time of the water molecule (ca. 10^{-12} sec) make moisture permeation a constant threat to the integrity and longevity of adhesive joints, it is advisable that the reacted film of the coupling agent be more hydrophobic in constitution than hydrophilic, as coherent and impermeable to water as possible, have minimum water solubility, and have optimum resistance to hydrolysis.

A limitation of many coupling compounds is that the critical surface tension of wetting γ_c of the solid surface when coated with an adsorbed condensed coupling film is too low relative to the surface tension γ_{LV} of the liquid adhesive to be applied; hence, spontaneous spreading of the adhesive cannot occur to give intimate molecular contact all over each film-coated solid fiber (1,8).

In the mass production of glass-fiber-resin composite materials and structures, coupling agents are most commonly applied to the fiber in aqueous solution; this procedure avoids fire and toxic hazards accompanying the use of most organic solvents. However, in one well-known industrial process the coupling agent is applied as a first coating in the form of a solution in a suitably thinned resin. This method is the "HTS finish" of Wong (38) in which 1/100 sec after drawing the glass fiber from the bushing, a first coating of the finish is applied as a dilute acetone solution of the hydrolyzed coupling agent, and shortly thereafter a second coating is applied of the coupling agent (such as γ-aminopropyltriethoxysilane) dissolved in a low-molecular-weight fraction of an epoxy resin. The resulting finished fiber is then made available for subsequent composite construction with an epoxy resin by the method of manufacture chosen by the product fabricator.

NATURE OF ADSORBED ORGANOSILANE COUPLING FILMS

The most commonly used coupling compounds for glass resin, and a variety of other composites, are derived from the silanes, especially the trialkoxyorganosilanes (30-33). When these compounds are effective as coupling agents, it is widely believed that they each hydrolyze on contact with the adsorbed water, coating the glass with a chemisorbed film. Because of the tetrahedral arrangement of silicon bonds and because there are only from 5 to 8.5 silanol groups available to react with these bonds per 100 $Å^2$ of amorphous quartz (39,40), it is not possible for all three OH groups of each molecule of adsorbed hydrolyzed coupling agent (Stuart Briegleb ball model cross-section area of about 27 $Å^2$) to react with the neighboring reactive silanol groups of the glass. Consequently, some R-Si-O-Si bonds form between the coupling compound and the silanol groups of the glass, and some Si-O-Si bonds must form between unadsorbed SiOH groups of adjacent adsorbed coupling molecules. Many years ago Fox, Solomon, and Zisman (41) showed that the Si-O-Si bonds in a polydimethylsiloxane are reasonably stable to hydrolysis, provided the pH is not below 2 or above 12. In Fig. 8 the effect of pH on the rate of hydrolysis in a Langmuir-Adam film balance of a pure dimethylsiloxane heptadecamer on water shows the drastic effect of very high or low pH on the rate of condensation of the area per molecule (A_L) due to scission of the Si-O-Si bonds. There is convincing radiotracer evidence that the organosilanol generated as a hydrolysis product from the trialkoxyorganosilane may adsorb as a monolayer on silica but forms a polymolecular layer on E glass (42).

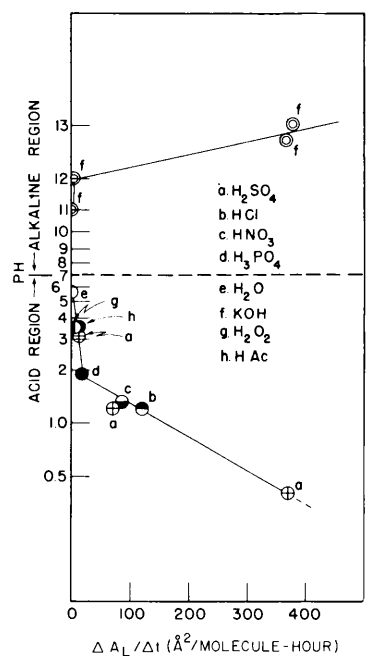

Fig. 8 - Time rate of change in area per molecule of a dimethylsiloxane heptadecamer adsorbed at the water/air interface as a function of pH of the aqueous substrate (Ref. 41)

Finally, the number of active adsorbing sites for the physical or chemical adsorption of resin to fiber may be temperature and history dependent. A well-established example shown in Fig. 9 reveals the marked decrease with rising temperature reported by Kiselev and coworkers (39) in the number of silanol groups present per sq cm of silica surface. This fact makes it probable that there is a loss in joint strength whenever the coupling agent or resin is applied too soon after quartz has been heated while being drawn as a fiber through the die or bushing. This problem would only be major if there were a long delay after fiber formation before the number of active adsorbing SiOH or other active sites, which had been destroyed or dehydrated by heat, had been restored to their maximum value. Other complications result, because the trialkoxyorganosilane molecules

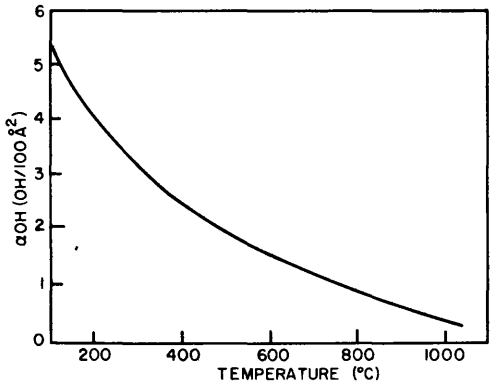

Fig. 9 - Change in the concentration of surface hydroxyl groups of silica with temperature of treatment in vacuum (Ref. 39)

commence to hydrolyze and polymerize as soon as they contact water in the aqueous solvent, or in the incompletely dried nonaqueous solvent in which it may be applied to the glass fibers, or even on contact with glass coated with adsorbed water. There is ample evidence (9,42) that complex polymeric products are gradually deposited on E-glass fibers in the form of thick films whenever the coupling agent is soluble enough to be applied from an aqueous solution. Therefore, it is difficult, if not impossible, to prepare on E glass an adsorbed monolayer of the simple structure postulated in Fig. 7.

An interesting variety of sound experimental information is now available about the nature of the coupling films formed by various trialkoxyorganosilanes on quartz, E glass, lead glass, stainless steel, and chromium. There is qualitatively good agreement between the recent investigations of four laboratories, and the relevant results will be discussed and compared briefly.

Tutas, Stromberg, and Passaglia (43) employed advanced optical ellipsometry techniques to measure the thickness of adsorbed organosilane films on lead glass and chromium. Their results in Table 2 were obtained with two common trialkoxyorganosilanes after adsorption on the flat, polished solid from dilute solutions in either water or water-free methylethyl ketone (MEK). The use of the ellipsometric method for determining film thickness on a surface capable of transmitting the light is complicated by the necessity of either measuring independently or estimating the refractive index of the adsorbed film. Nevertheless, the conclusions evident from Table 2 are (a) polymerization of the organosilane occurred either in the solution or very promptly at the glass/solution interface and (b) the resulting film adsorbed was from 60 Å up to 160 Å in thickness. However, it is remarkable that a film adsorbed on glass from a solution of the organosilane in dry MEK was only about 8 Å thick and also that a film adsorbed from aqueous solution on chromium was only 10 Å thick. These last two results deserve further investigation, since the deposited films were about the thickness of an adsorbed monolayer of the organosilane monomer.

Plots of film thickness vs time revealed that films of γ-aminopropyltriethoxysilane adsorbed on glass from aqueous solution were the same in thickness after a minute or an hour of contact (Fig. 10). Although the results in Fig. 10 can be interpreted as having been caused by a rapid rate of hydrolysis followed by polymerization of the organosilane when in contact with the wet glass, they could equally well be evidence that complex organosilane hydrolytic products had formed earlier in the aqueous solution, so that the time needed for the product polymer to adsorb on the glass was brief. The vinyl tri(2-methoxyethoxy)silane, on the other hand, either reacted slightly (or slowly) in the water solution; but on application of the solution to the lead glass surface, the polymerization reaction after adsorption on glass took place slowly, since Fig. 11 reveals that the thickness of the film deposited was increasing steadily with time and had not ceased even 100 minutes after contact between solution and glass.

Table 2
Thickness of Coupling Films on Lead Glass by Ellipsometric Measurements*

Finish	Surface	Solution	Film Thickness† (Å)	Adsorbance ‡ 10^{-4} (mg. cm^{-2})	Area Molecule§ (Å^2)
γ-Aminopropyltriethoxysilane	Glass¶	1% H_2O	60	5.7	6.4
	Glass¶	5% H_2O	150	14.1	2.6
	Chrome	1% H_2O	10	0.9	39.0
Vinyl-tris(2-methoxyethoxy)silane	Glass¶	0.1 to 1% H_2O	160**	16.5	2.8
		(initial thickness)	50††	5.1	9.1
	Glass¶	1% MEK	8	0.8	58.1

*From Ref. 43.
†A refractive index of 1.5 was used to calculate the thickness.
‡The density of amino silane is 0.943 g/ml, and the density of vinyl silane, is 1.029 g/ml.
§The values are based on the molecular weight of the original material.
¶Glass is composed of 26.23% SiO_2, 72.47% PbO, and 1.30% Li_2O.
**Average thickness after 240 min.
††Thickness of first measurement.

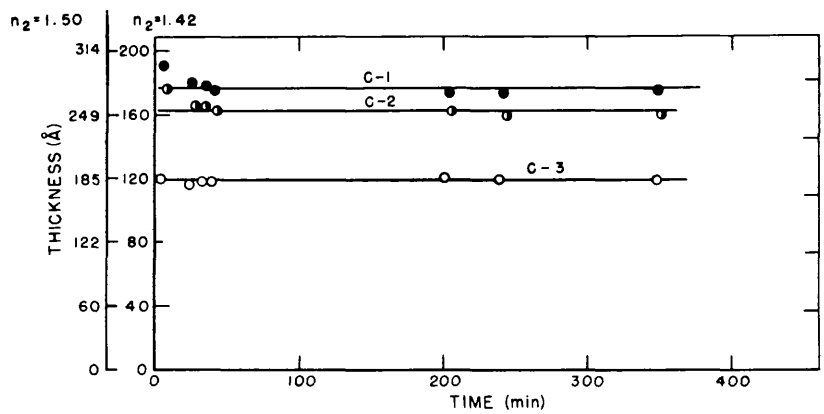

Fig. 10 - Thickness of γ-aminopropyltriethoxysilane adsorbed from a 5% water solution on glass (Ref. 43)

Two possible explanations of the difference in adsorption-vs-time behavior of Figs. 10 and 11 are (a) the alkaline amino group in γ-aminopropyltriethoxysilane may have had a catalytic effect on the rate of hydrolysis of the alkoxy groups leading to polymerization or (b) the mode of adsorption of this coupling agent is with both the amino group and a silanol group adsorbed on the lead glass after which rapid polymerization occurred. It is unfortunate that more experimentation was not done with the controlling chemical variables, metals other than chromium and organic solvents other than MEK.

Bascom (44,45) has reported several investigations using the contact angle method employing various chemical types of liquid sessile drops. He also used the ellipsometry method of measuring film thicknesses formed by the various trialkoxyorganosilanes and organotrichlorosilanes on clean polished plates of silica, Pyrex, α-alumina, gold, and 18/8 stainless steel. Both aqueous and nonaqueous solutions of the silanes were investigated. Of fundamental interest is his study (45) of films of $CF_3(CF_2)_6CH_2O(CH_2)_3$-$Si(OCH_2CH_3)_3$. This compound was not synthesized for use as a coupling agent but was investigated because when it adsorbed on glass or stainless steel from dilute solutions in α-chloronaphthalene (Table 3) a retracted film resulted (1) which adsorbed and behaved with respect to contact angle measurements like a well-oriented and reproducible monolayer. His consistent value of γ_c = 14 dynes/cm was strong evidence that the outermost composition of the adsorbed film was rich in closely packed $CF_3(CF_2)_6$- groups. Nevertheless, the ellipsometric determination of the thickness d_f of each film left no doubt that the film deposited was a polymolecular film about 400 Å thick. Even when

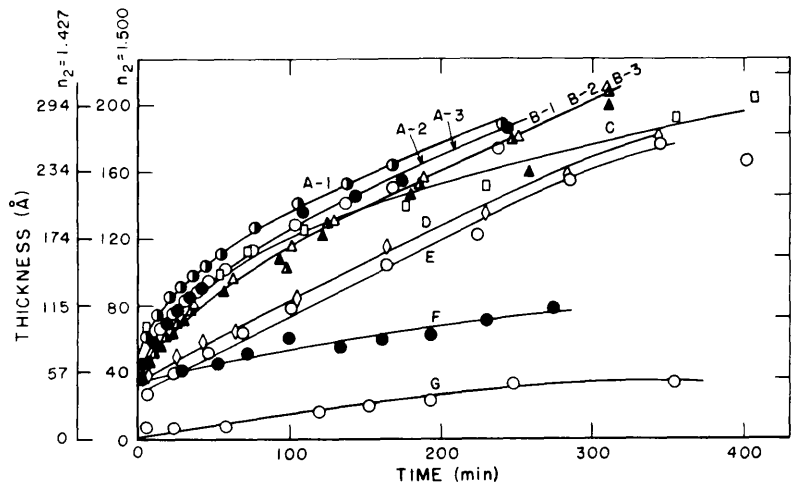

Fig. 11 - Thickness of vinyl tris(2-methoxyethoxy) silane adsorbed from a water solution on glass (Ref. 43)

		Conc.			Conc.
◐	Run A-1	1%	□	Run C	1%
○	Run A-2	1%	◊	Run D	1%
●	Run A-3	1%	○	Run E	0.1%
△	Run B-1	1%	●	Run F	0.5%
◭	Run B-2	1%	○	Run G	1%
▲	Run B-3	1%			

Table 3
Adsorbed Films on 18/8 Stainless Steel of
$CF_3(CF_2)_6CH_2O(CH_2)_3Si(OCH_2CH_3)_3$*

Property	Initial Film	After Rinsing in Freon TF
d_f (Å)	401	233
n_f (measured)†	1.34	1.23
γ_c (dynes/cm)	14	14
θ (degrees)‡	112	116

*The films were prepared by retraction at 25°C from a 0.25% solution in chloronaphthalene containing acetic acid catalyst in the ratio of 1 mole of acid to 10 moles of silane. The films retracted in air at 50% RH. An oriented close-packed monolayer would be 14 to 15 Å thick (45).
†Refractive index of the film.
‡Contact angle exhibited by water.

the purified fluorocarbon solvent Freon TF (CCl_2FCClF_2) was used to rinse these films, the residual adsorbed film was about 230 Å in thickness. The first conclusion was that hydrolysis had occurred. The necessary water could not have come from the small concentration of glacial acetic acid used in the organosilane solution employed. Therefore, the conclusion was unavoidable that either a trace of water was present in the α-chloronaphthalene or adsorbed water present on application of the solution to the surface of

Table 4
Adsorbed Films on 18/8 Stainless Steel of $Cl(CH_2)_3Si(OCH_3)_3$ and $p\text{-}ClC_6H_4CH_2CH_2Si(OCH_3)_3$ *

Property	Rinsed Film of $Cl(CH_2)_3Si(OCH_3)_3$ †	Rinsed Film of $p\text{-}ClC_6H_4CH_2CH_2(SiOCH_3)_3$ ‡
d_f (Å)	233	51-65
n_f §	1.35	1.4-1.6 (assumed)
γ_c (dynes/cm)	44	47
θ (degrees) ¶	84	85

*The films were prepared by adsorption at 70°C from a 0.25% solution in bicyclohexyl containing acetic acid catalyst in the ratio of 1 mole of acid to 10 moles of silane. Excess on the metal was rinsed off with acetone at 25°C and 50% RH (44).
†An oriented close-packed monolayer would be 7 Å thick.
‡An oriented close-packed monolayer would be 11 Å thick.
§Refractive index of the film.
¶Contact angle exhibited by water.

the steel was sufficient to cause extensive hydrolysis of ethoxy groups followed by polymerization of the resulting organosilanol groups. Clearly, the resulting adsorbed film cannot be at all like the simple monolayer proposed in Fig. 7.

Results of similar investigations by Bascom (44) of two different chlorinated trimethoxysilanes are summarized in Table 4. Since these solutions could not be separated from the adsorbed film on steel because such terminally chlorinated adsorbed molecules do not allow film retraction (6), excess solution was removed by rinsing the coated specimen with pure acetone at 25°C and 50% RH. Here the value of γ_c of the residual adsorbed film ranged from 44 to 47 dynes/cm, as would be expected of a well-oriented adsorbed organosilane molecule due to the outermost position of the chlorine atom in each of these two types of silane molecules (7,8). Despite the strong evidence of orientation of the outer portion of the film, Bascom found the film was polymolecular, because the thickness d_f was 233 Å for rinsed chloropropyltrimethoxysilane and from 51 to 65 Å for p-chlorophenylethyltrimethoxysilane.

Bascom's investigation (44) of the nature of the films adsorbed from organic solutions on silica glass by ethyltriethoxysilane and vinyltriethoxysilane revealed that the latter compound was more reactive with the silanol groups of the silica surface than was the former. The importance of acid or base catalysis for the promotion of these surface reactions was clearly demonstrated by the results of adding to the applied solution a small concentration of acetic acid or n-propylamine. Two possible modes of adsorption of these silanes on silica were proposed to explain the observed contact angles with various pure liquids. They are shown in Fig. 12. Although the films are probably more complex than indicated, structural diagrams a and b do give correct representations of the wetting characteristics of the portion of the polyorganosilane film most distant from the silica surface. Extraction studies on the resulting adsorbed films led Bascom to conclude that the "polymer films were formed so rapidly that the monomer, polymer fragments, amine catalyst, and solvent molecules were probably physically trapped in the adsorbed layer."

Adsorption of ^{14}C-labeled γ-aminopropyltriethoxysilane on clean Pyrex blocks was recently investigated by Schrader, Lerner, and D'Oria (46) using a 1% organosilane

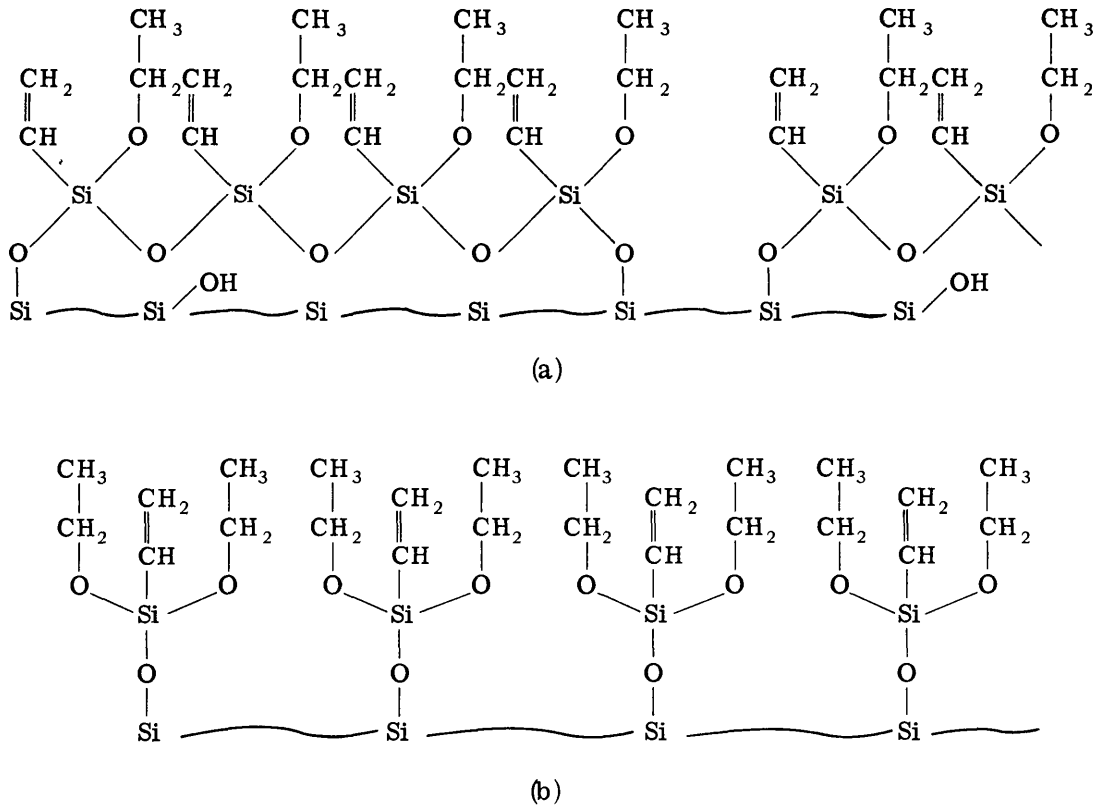

Fig. 12 - Two possible configurations of polymerized vinyltriethoxysilane suggested by the contact angle data (Ref. 44)

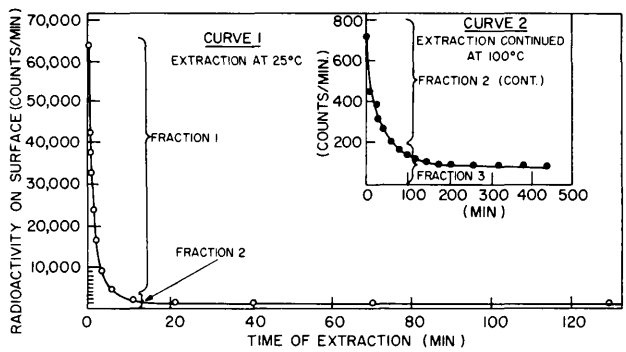

Fig. 13 - Amount of radioactive A-1100 remaining on a polished Pyrex surface after extraction with water. A-1100 was ^{14}C-labeled γ-aminopropyltriethoxysilane. ^{14}C is the γ carbon. The glass was treated with a 1% solution in benzene (Ref. 46).

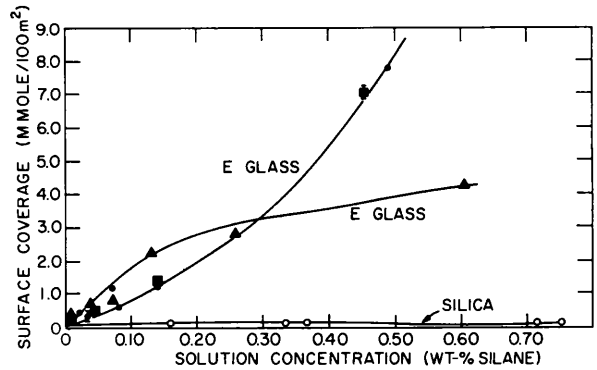

Fig. 14 - Coupling agent isotherms (Ref. 42). The coupling agent was applied from aqueous solutions containing 0.1% acetic acid. E glass and silica (Aerosil) were heat cleaned at 500°C for 4 hr.

- ● γ-(methacryloxy)propyltrimethoxysilane
- ■ 3-(2',3'-epoxypropoxy)propyltrimethoxysilane
- ▲ γ-(amino)propyltriethoxylsilane

solution in benzene. Their results (Fig. 13) proved that the film adsorbed on Pyrex was heterogeneous and polymolecular, because they could separate it into three fractions by a series of surface extractions with distilled water. About 97% (fraction 1 in Fig. 13) could be extracted with water at 25°C in 20 minutes, and it was proposed that this material consisted of a multilayer of hydrolyzed organosilane molecules linked to each other through hydrogen bonding. Fraction 2, which was extracted with water at 100°C for 150 minutes, was believed to be polymeric material bonded by intermolecular Si-O-Si linkages. The authors proposed that the remaining fraction 3 consisted of a monolayer of molecules bonded to the borosilicate surface by means of multiple siloxane linkages; the area per adsorbed molecule was estimated at 125 $Å^2$. It is worth noting here that extraction with hot water would leave Pyrex in the form of a rough hydrolyzed surface, which could cause the adsorbed film to be heterogeneous and polymolecular. These results convincingly agree with those of Tutas, Stromberg, and Passaglia (43), as well as those of Bascom (44,45), in one respect–all agreed that the films they had adsorbed on lead glass, quartz, and Pyrex, respectively, from dilute aqueous solution of the organosilane were all polymolecular in nature. Furthermore, the results of Schrader, et al. (46), agreed with those of Bascom on the effect of solvent extraction in decreasing the thickness of the adsorbed film as well as in the conclusion that the adsorbed organosilane film was much more complex in constitution than had been recognized.

Vogel, Johannson, Stark, and Fleischmann's investigation (42) of the behavior of the three very pure ^{14}C-tagged trialkoxysilanes adsorbed from solution on E-glass fibers and Aerosil (powdered SiO_2) has been invaluable. The exceptionally pure tagged compounds were γ-aminopropyltriethoxysilane, γ-(methacryloxy)propyltrimethoxysilane, and 3-(2',3'-epoxypropoxy)propyltrimethoxysilane. Solvents used were distilled water, 0.1% aqueous acetic acid, and anhydrous hexane. Organosilane solutions were always applied to a mat of heat-cleaned glass fibers placed in the top of a fritted glass filter. Each solution was allowed to contact the fibers for 1 minute or more, and then it was aspirated away from the fibers. The glass fibers so treated were then dried for 24 hours and assayed for radioactivity. Equilibrium amounts of coupling agent were adsorbed under these conditions within 30 seconds, and after that there was an extremely slow time-dependent buildup of coupling agent, which was believed to reflect some intermolecular silanol condensation occurring during the adsorption process. Therefore, they generally used a 60-second adsorption time in treating fibers with each organosilane solution.

Room-temperature adsorption isotherms for these three organotrialkoxysilanes on E glass and Aerosil are plotted in Fig. 14. Whereas the γ-(methacryloxy)propyltrimethoxysilane and the 3-(2',3'-epoxypropoxy)propyltrimethoxysilane showed no surface saturation and behaved identically in Fig. 14, the γ-(amino)propyltriethoxysilanes seemed to be approaching a surface saturation of the E glass and differed at essentially all concentrations from the former organosilanes. Vogel, Johannson, Stark, and Fleischmann (42) attributed these results to the adsorption of the γ-amino group on glass along with the silanol group. Another striking feature was that whereas multilayer adsorption on E glass of γ-(methacryloxy)propyltrimethoxysilane occurred at high solute concentrations,

less than monomolecular adsorption occurred on the Aerosil particles. Such large differences in adsorption behavior on E glass and silica were associated with two characteristics of the glass surface: (a) they stated that a catalytic effect occurred on polymerization on E glass and not on silica and (b) whereas strongly baked E glass rehydrates readily in bulk water, that was not true of the Aerosil surface.

In a much earlier investigation Sterman and Bradley (47) had given electron microscope evidence that organosilane coupling agents were distributed on glass surfaces as distinct islandlike deposits and had concluded from the amount applied that the remainder of the glass surface was uncoated. However, James, Norman, and Stone (21) used a selective dye adsorption technique as well as the water contact angle method to show that both methods gave results which agree that the coupling agent deposited on glass by Sterman and Bradley must have been a complete surface coverage and that probably an excess was deposited over that film in the form of agglomerates. Vogel, Johannson, Stark, and Fleischmann (42) found no evidence either of such islands from electron microscope photographs or from their radioactive counting data and concluded that their E-glass surfaces were coated uniformly with a thickness of about 10 monolayers. They identified the cause of disagreement in the electron microscope results as the method of application of the solution of coupling agent; whereas the Sterman and Bradley dip-coating technique left behind mechanically entrapped solution which evaporated to leave islands of organosilane products, the aspiration technique was believed to have avoided that difficulty.

Vogel, Johannson, Stark, and Fleischmann (42) also investigated the extraction of the organosilane finish adsorbed on glass by several methods. Extraction with hexane or toluene was used for several hours to remove any physically adsorbed coupling agent; however, that method was completely ineffective if the adsorbed film of organosilane had been air dried at room temperature for 24 hours. Exchange between ^{14}C-tagged and untagged coupling agent films with silane molecules in solution was investigated. Coupling films air dried on E glass for 24 hours at room temperature could exchange to some extent with the coupling agent in solution; hence, they concluded that extensive intermolecular silanol condensation had not occurred with such a coupling film. On curing the organosilane films at 100°C for 18 hours, silane exchange was prevented with the methacryloxy and glycidyl ether coupling agent films so that intermolecular condensation and chemisorption of the coupling compound on glass had already occurred, but some exchange still persisted with the similarly cured γ-aminopropyl agent. Like Schrader, Lerner, and D'Oria (46), they found that the application of boiling water to films cured on E glass rapidly displaced the adsorbed coupling film, the effect varying with time and the amount of initially cured coupling agent. However, they also measured the pH of the water and found it rose from 6.4 initially to 9.5 after a 2-hour extraction at 100°C. This fact and the subsequent roughened appearance of the glass-fiber surface revealed by electron microscopy were convincing evidence that catastrophic destruction of the glass surface had occurred; hence, the principal cause of the observed rapid extraction of the organosilane coating by boiling water was attack on the glass. Their conclusion is qualitatively in agreement with that of James, Norman, and Stone (21) about the attack of water on the glass which underlies an organosilane film. A similar rapid surface attack by boiling water did not occur on silane-treated Aerosil particles; hence, ions other than Si^{+4} and $O^{=}$ in E glass must be the cause of the remarkable surface attack by boiling water.

An investigation was made of the interaction of E glass treated with a coupling agent to which a monomeric mixture of 90% methyl ^{14}C-methacrylate and 10% styrene was applied. The resulting polyester had copolymerized with γ-(methacryloxy)propyltrimethoxysilane and also with the vinyltrimethoxysilane coupling film. However, the amount of resin reacted with the coupling agent was markedly greater when the coupling agent had not been heat cured. When using the uncured coupling agent, the data strongly suggested that the layer of adsorbed coupling agent was swollen by the monomer present in the

resin solution before final polymerization and that the monomer as well as the polymer may have been trapped in the coupling film by entanglement as well as by copolymerization. The amount of monomer retained to swell the film of a precured coupling agent was very much less than was observed with the uncured agent. A most indicative finding was that the rate of extraction by boiling water of resin-treated cured film from E-glass surfaces was greatly decreased when the film of the coupling agent had been coated with a thin layer of polyester resin containing 0.01% benzoyl peroxide resin and then had been cured for 18 hours at 90°C.

In a recent paper, Stark, Johannson, Vogel, Chaffee, and Lacefield (48) found that reactions between trimethylchlorosilane and either Aerosil or E glass occurred between hydroxyl groups as well as with silanoate structures on each adsorbent. Extensive bonding of trimethylsilanol to the adsorbents did not occur unless silanol condensation catalysts were present. Especially important was their finding that the reaction between trimethylchlorosilane- ^{14}C species and E glass is quite different from the reaction with Aerosil and that "the high coverages of sorbed trimethylsilyl species obtained during E-glass treatments plus the even higher ^{36}Cl uptakes observed suggest that chemical reaction is occurring during the treatment." They concluded that a reaction with the metal in the surface of the E glass, and not present in Aerosil, resulted in a chemisorbed trimethylsilanoate and that displacement of the trimethylsilylated structures from E glass by boiling water was consistent with destruction and solubilization of the glass underlying the trimethylsilylated surface.

EFFECT OF COUPLING COMPOUND ON SPONTANEOUS SPREADING BY LIQUID POLYMERS

In a previous section it was pointed out that the presence of an appropriate organic coupling agent or "finish," even if only as little as an adsorbed monolayer, was sufficient to modify the surface composition of the fiber so that spontaneous spreading by the liquid polymer could be assured. We have found it possible and illuminating to characterize the ability of liquids to spread, or not to spread, on a smooth solid surface by the equilibrium contact angle θ of the liquid with the solid, the surface tension γ_{LV} of the liquid, and the critical surface tension γ_c of the solid. One characteristic of γ_c is that any liquid with a surface tension γ_{LV} less than γ_c or equal to it will exhibit a zero equilibrium contact angle; if γ_{LV} is greater than γ_c, the contact angle will not be zero and will be greater, the greater $\gamma_{LV} - \gamma_c$. In a systematic series of investigations (6,49), we have shown how to measure γ_c for numerous organic solids and a variety of high-energy solids coated with organic films as thin as monolayers. It is sufficient to state here that γ_c was found to be determined essentially by the nature and packing of the outermost atoms of the solid surface and under some conditions could even be calculated (50). These results and their utility have been confirmed over the years by numerous independent investigators; especially of interest here are two extensive series of measurements of γ_c by Lee (51,52) covering elastomers and high polymers.

When the reinforcing fibers in a composite material are coated with a "finish," such as that formed by applying a film containing a coupling compound, it is helpful to know the value of γ_c to be assigned to the resulting coated surface. How γ_c varies, in general, with a variety of such surface coatings on Pyrex and silica glass according to Bascom (44,45) is summarized in Table 5. Lee (37) recently has published the values of γ_c in Table 6 for various commonly used organosilane coupling agents as they behaved when deposited on soda-lime glass slides from a methanol-water solution catalyzed with acetic acid. Note that the value of γ_c for vinyltrimethoxysilane is 25 dynes/cm in Table 6 whereas it is 30 in Table 5. The lower value must be caused by the greater surface density of adsorption sites on Lee's soda-lime glass than on Bascom's silica glass.

Table 5
Critical Surface Tensions of Various Silane Coupling Agents on Pyrex and Quartz Slides

Coupling Agent and Structure	Glass Substrate	γ_c (dynes/cm)	Refs.
3-(1,1-Dihydroperfluorooctoxy)propyltriethoxysilane $CF_3(CF_2)_6CH_2O(CH_2)_3Si(OCH_2CH_3)_3$	Pyrex	14	45
γ-Perfluoroisopropoxypropyltrimethoxysilane $(CF_3)_2CFO(CH_2)_3Si(OCH_3)_3$	Pyrex Silica	18 17	45 45
β-(p-Chlorophenyl)ethyltrimethoxysilane $p\text{-}ClC_6H_4(CH_2)_2Si(OCH_3)_3$	Pyrex Silica	40-45* 44	45 44,45
γ-Chloropropyltrimethoxysilane $Cl(CH_2)_3Si(OCH_3)_3$	Pyrex	43	45
Ethyltriethoxysilane $CH_3CH_2Si(OCH_2CH_3)_3$	Silica	26-33*	44
Vinyltriethoxysilane $CH_2{=}CHSi(OCH_2CH_3)_3$	Silica	30	44

*Depending on catalyst used.

Table 6
Critical Surface Tensions of Various Silane Coupling Agents on Soda-Lime Glass Slides*

Coupling Agent	γ_c (dynes/cm)
N(Trimethoxysilylpropyl)ethylenediamine	33.5
Methyltrimethoxysilane	22.5†
Vinyltrimethoxysilane	25.0
γ-Methacryloxypropyltrimethoxysilane	28.0
p-Methylphenyltrimethoxysilane	34.0†
γ-Glycidoxypropyltrimethoxysilane	
Non-Catalyzed	38.5
Catalyzed	42.5
γ-Chloropropyltrimethoxysilane	40.5
γ-Aminopropyltriethoxysilane	35.0
Bromomethylphenyltrimethoxysilane	39.5†
Phenyltrimethoxysilane	40.0†
γ-Mercaptopropyltrimethoxysilane	41.0
Bromophenyltrimethoxysilane	43.5†

*The films were deposited at room temperature from methanol-water solutions of silane. These were dried at 50°C for 1 hour. The solution hydrolysis was catalyzed with acetic acid (37).

†Data generously made available from a recent larger report to be published by L.H. Lee.

At present, there is a shortage of published data on the surface tensions γ_{LV} of chemically well-defined liquid polymers. This deficiency is created by the fact that γ_{LV} varies with the polymer molecular weight distribution, and special methods of measurement must be used with very viscous liquids. The temperature coefficient of γ_{LV} is needed also, since various investigators and industrial processers apply the liquid resins to fibers and other solid surfaces at different temperatures. It is well known that many classes of surface-active impurities can prevent obtaining reproducible and significant surface tensions in aqueous solutions or dispersions. However, a considerable body of research published in the past decade (53-60) will reveal that if the impurity concentrations are much below 1%, the error caused is not significant for organic liquid/gas interfaces, unless the impurities are of certain types of silicones or many classes of highly fluorinated compounds.

USE OF A NONCONJUGATED DIOLEFIN LIQUID TO IMPROVE PERFORMANCE OF COUPLING COMPOUNDS

An important variation in the use of organosilane coupling compounds as adhesion promoters has been reported by Vanderbilt and Clayton (61). On investigating methods of increasing the adhesion of polybutadiene-type rubbers to fibrous glass, they discovered that if they first coated the baked, silane-finished, glass fibers with a thin liquid layer of an unpolymerized nonconjugated diolefin, such as divinylbenzene containing 1% dicumyl peroxide, and then pressed and heat cured a layer of polybutadiene rubber placed in contact with the wet fibers, a major increase in joint adhesion resulted. They concluded that the vinyl group of the divinyl benzene had combined with a vinyl group in the silane coupling film and the other vinyl group had combined with the polybutadiene layer. Although a suitable polyolefinic monomer was highly effective in obtaining maximum adhesion between a peroxide-cured elastomer and glass fibers previously treated with an unsaturated silane, some adhesion was obtained on curing the elastomer directly in contact with the glass; this was particularly true of elastomers having vinyl side groups.

Rubbers which responded poorly to peroxides as catalysts or curatives could be bonded to glass by using an organo-substituted trialkoxysilane capable of entering into the vulcanization reaction of the rubber compound. Organosilane groups found effective with one or more types of elastomer cure systems were aminoalkyl, epoxyalkyl, mercaptoalkyl, and chloroalkyl types. Their good bonding combinations consisted of A, an elastomer containing an organic peroxide, plus B, a liquid, reactive, nonconjugated polymer, plus glass fibers coated with C, an unsaturated silane coupling agent. Examples of A are cis polyisoprenes, styrenebutadienes (SB), acrylonitrilobutadienes (NBR), ethylene propylenes (EPR), polyethylene, neoprene, chlorobutyl rubber, and any of the polybutadienes. Examples of B are divinyl benzene, ethylene dimethacrylate, vinyl fumarate, and trialkyl cyanurate. Examples of C are vinylsilanes, styrylethylsilanes, and allylsilanes.

Table 7 presents specific examples of their panel test adhesion results. The third line reveals the large increased adhesion possible with the Vanderbilt and Clayton system. The low adhesion obtained with ethyltrichlorosilane and Volan are probably due to wettability difficulties, since such coatings on glass have low values of γ_c (8,44).

NEED FOR GREATER COHESION IN COUPLING FILMS

There is now much good evidence that the films of common organosilane coupling agents deposited and baked on E glass are thin polymolecular coatings comprising a mixture of low- and higher-molecular-weight polymeric products besides some simpler chemisorbed organosilanes. However, it is improbable that the intermolecular cohesion of the coupling layer is always sufficiently high. Very commonly, cohesive failure and

Table 7
Use of Polyunsaturated Monomer Liquid With a Coupling Agent Precoated on Glass*

Coupling Agent Applied to Glass Cloth (No. 181 Fabric)	Peel Test Adhesion (lb/in.)		
	Natural Rubber	Nitrile Rubber	Chlorobutyl Rubber
None	2	2	2.5
Vinyl silane (A-172†)	28	35.5	13.5
Divinylbenzene + A-172	58	59.5	24.5
Divinyldichlorosilane	10	–	19.5
Allyltrichlorosilane	3.5	3.5	10.5
Ethyltrichlorosilane	2	2	7.5
Volan‡	4	3.5	6

*From Ref. 61.
†A-172 is vinyltris(2-methoxyethoxy)silane.
‡Volan is Werner-type compound in which methacrylic acid is coordinated with chromium to form a highly reactive complex.

associated water permeability in that coating will establish the limiting strength and/or durability of the composite glass-fiber system. Although it is very improbable that the cohesive strength can be made very high, that is probably one virtue, since the coating can better function also as a stress-relieving interlayer.

Bascom suggested recently (45) that molecules of the resin could penetrate into the loose structure of the silane coating and so form a more coherent (and perhaps a less water-penetrable) mixed film through vinyl polymerization. Good evidence for there being "greater resistance to water penetration depending on the extent to which molecules of the resin can diffuse through the film of coupling agent" has been recently given by Vogel, Johannson, Stark, and Fleischmann (42). However, the resulting resistance to water penetration must be highly dependent on (a) the ability of the liquid resin molecules to penetrate into the holes in the film of coupling agent, (b) the intermolecular cohesion developed in the resulting mixed film of resin chains and polyorganosilane chains, and (c) the extent to which any chemical reactions occur between adjacent resin and silane molecules. In the Vanderbilt and Clayton method (61), the liquid unconjugated polyene interlayer used may well have accomplished the above three objectives of obtaining a transition layer which could convert the entire coupling film into a stronger and more coherent material.

There is no evident reason why stronger and more coherent mixed films, or even merely films of coupling agent alone, could not be found or designed to have sufficient adhesion to glass, high enough cohesive strength, and sufficiently good wetting by and adhesion to the resin applied to it. The important step is to recognize clearly the mutually dependent physical and chemical qualities or requirements of coupling compounds and resin molecules. In short, their dependency involves more than the early recognized requirement that the resin chain terminals should be able to react chemically with the organic radical attached outermost to the adsorbed trialkoxy silane.

Erickson, Volpe, and Cooper (62) had proposed that the glass could adsorb the cross-linking agent or polymer catalyst used to form a strong resin coating. Under some special conditions this situation could happen. For example, Sands, Clark, and Kohn (63) investigated epoxy resins made from a diglycidyl ether of bisphenol A which

were cross linked with m-phenylenediamine and strengthened by dispersing in it various concentrations of Aerosil. They demonstrated that the Aerosil adsorbed significant amounts of the amine curing agent and so interfered with obtaining the desired cross-linking reaction with the epoxy resin. In other words, they were observing the kind of effect mentioned by Erickson, Volpe, and Cooper relative to uncoated pyrogenic silica. However, such processes are very unlikely to occur if the reinforcing agent has been precoated by an organosilane finish before addition to the liquid resin system, since adsorption sites for the amine curing agent would already have been occupied.

CONCLUSIONS

1. Although competent research has been done in the past 5 years on the behavior of organosilane coupling compounds and glass-resin composite materials, further, more carefully pointed research is needed, especially on the role of catalysts. Also, more attention should be given to the influence of any metallic ions in the glass-fiber surface in either promoting or interfering with the chemisorption of coupling compounds.

2. Further investigation is needed on the precise nature of coupling films made on glass (or other strong fibers) from Werner complexes of chromium with carboxylic acids. Much presented here about desired properties of the film could be helpful in guiding research on the most appropriate organic structures in forming the Werner complexes.

3. More effort should be expended to determine when liquid polymer or resin adhesion occurs by chemical coupling to the finish, through achieving better wetting, or through chemisorption of the finish with the polymer or resin. At present, too many investigators merely assume or claim that a chemical reaction has occurred between the coupling agent and the adjacent polymers. This is apparent in many recent investigations of thermoplastics and thermosetting resins reinforced with glass or other fibers. For example, a beneficial coupling action and also a strong reinforcing action for glass fibers and hydrocarbon polymers (thermoplastics) have been recently reported in valuable papers by Viventi, Plant, and Maher (64) and by DeVenuto, Stoltz, and Wiggill (65); yet the coupling action is not given adequate explanation in either paper.

4. There is an obvious need to try to increase the cohesive strength of the adsorbed film of the coupling agent; of particular promise is the search for methods of forming more coherent, mixed films of resin (or polymer) molecules with the thin adsorbed films of organosilane or other coupling compounds. Also, better research methods are needed for measuring the cohesive strength of the final coupled film produced on the adherend surface. We will report on this problem subsequently.

5. For long-term or severe conditions of water immersion of resins or thermoplastics reinforced by glass or other fibers, stronger fibers are needed having lower water susceptibility to surface erosion. In the case of glass fibers, we need to understand more about the surface reactions and how to promote or catalyze the reaction of organosilane or other coupling agents with the silanol groups as well as the metal ions in the glass surface so as to form more stable and water insoluble products. Such work is in progress at this laboratory.

6. Thermosetting resins or thermoplastics with lower permeability to water are preferred for systems exposed to long-term immersion in water. This problem is major when (a) the plastic is permeable to water because of the localized hydrophilic nature of some part of each monomer or the analogous problem in the cross-linking agents used for thermosetting resins, (b) the resin is overcured and hence becomes too susceptible to cracking, and (c) the glass surface readily forms water-soluble ionogenic deposits as a result of any reactions with water, ions extracted or adsorbed

from the resin, or carbon dioxide reaction products with glass surface constituents, since in each case there would be increased and detrimental osmotic pressure effects.

7. Presently used organosilane coupling compounds were synthesized for use with glass, and there is no reason that they should be the most suitable compounds for use with other fibrous or particulate reinforcing materials. Some organosilane compounds appear to be effective on a few classes of oxidized metal surfaces; examples are chromium and 18-8 stainless steel. Unfortunately, their limitations are not yet known. These aspects and the need for new types of coupling agents are areas of research which appear neglected in comparison with the major and extensive efforts in progress to produce new, stronger, or less water-susceptible fibers than glasses. Work is in progress at this laboratory on new or improved agents (8,66,67).

8. In developing plastics reinforced by metallic fibers, more information is needed about the cohesive strength of the oxide which usually coats the metal fiber (in the condition in which it is used) to be sure that the oxide is not the weakest joint of the completed composite material.

REFERENCES

1. Zisman, W.A., Ind. Eng. Chem. 55 (No. 10):18(1963)

2. Bangham, D.H., and Razouk, R.I., Trans. Faraday Soc. 33:1459 (1937)

3. Boyd, G.E., and Livingston, H.K., J. Am. Chem. Soc. 64:2383 (1942)

4. Harkins, W.D., and Loeser, E.H., J. Chem. Phys. 18:556 (1950)

5. Loeser, E.H., Harkins, W.D., and Twiss, S.B., J. Phys. Chem. 57:251 (1953)

6. Zisman, W.A., Advan. Chem. Ser. 43:1 (1964)

7. Shafrin, E.G., "Critical Surface Tension of Polymers" in "Polymer Handbook," J. Brandrup and E.H. Immergut, eds., New York:Interscience, pp. III-113, 1966

8. Zisman, W.A., "Surface Chemistry of Glass-Fiber-Reinforced Plastics," NRL Report 6083, June 9, 1964; Ind. Eng. Chem. 57(No. 1):26 (1965)

9. Bascom, W.D., "Wetting Behavior of Epoxy Resins on Glass Filaments," NRL Report 6140, Aug. 4, 1964

10. Bascom, W.D., "The Origin and Removal of Microvoids in Filament-Wound Composites," NRL Report 6268, May 24, 1965

11. Bascom, W.D., and Romans, J.B., Ind. Eng. Chem. Prod. Res. Develop. 7:172 (1968)

12. Griffith, A.A., Phil. Trans. Roy. Soc. (London) A221:163 (1920)

13. Paul, J.T., and Thomson, J.B., Proc. SPI Reinforced Plastics Div., Chicago, Ill., Sect. 12-C, p. 1, Feb. 2-4, 1965

14. Sands, A.G., Clark, R.C., and Kohn, E.J., "Microvoids in Glass-Filament-Wound Structures: Their Measurement, Minimization, and Correlation with Interlaminar Shear Strength," NRL Report 6498, Mar. 31, 1967; Ind. Eng. Chem. Prod. Res. Develop. 7:179 (1968)

15. Laird, J.A., and Nelson, F.W., SPE Trans., p. 124, Apr. 1964

16. Ashbee, K.H.G., Frank, F.C., and Wyatt, R.C., Proc. Roy. Soc. (London) A300:415 (1967)

17. Romans, J.B., and Sands, A.G., "Fatigue Characteristics of Filament-Wound Glass-Reinforced Plastics in Water," NRL Report to be published

18. Shafrin, E.G., and Zisman, W.A., J. Am. Ceram. Soc. 50:478 (1967)

19. Bernett, M.K., and Zisman, W.A., J. Colloid Interface Sci. 29:413(1969)

20. Bernett, M.K., and Zisman, W.A., J. Colloid Interface Sci. 28:243 (1968)

21. James, D.I., Norman, R.H., and Stone, M.H., J. Plastics Inst. 36(No. 121):21 (1968)

22. Livey, D.T., and Murray, P., J. Am. Ceram. Soc. 39:363 (1956)

23. Hunter, M.S., and Fowle, P., J. Electrochem. Soc. 103:482 (1956)

24. Benjamin, P., and Weaver, C., Proc. Roy. Soc. (London) A254:163 (1960)

25. Benjamin, P., and Weaver, C., Proc. Roy. Soc. (London) A254:177 (1960)

26. Benjamin, P., and Weaver, C., Proc. Roy. Soc. (London) A274:267 (1963)

27. Karnowsky, M.M., and Estill, W.B., Rev. Sci. Instr. 35:1324 (1964)

28. Eberhart, J.G., Trans. Met. Soc. AIME 236:1362 (1966)

29. Yatsimirskii, K.B., Russ. J. Inorg. Chem. 6:265 (1961)

30. Plueddemann, E.P., Clark, H.A., Nelson, L.E., and Hoffman, K.R., Mod. Plastics 39(No. 12):135 (1962)

31. Plueddemann, E.P., Proc. SPI Reinforced Plastics Div., Washington, D.C., Sect. 9-A, p. 1, Jan. 31-Feb. 3, 1967

32. Sterman, S., and Toogood, J.B., Adhesives Age 8(No. 7):34 (1965)

33. Sterman, S., and Marsden, J.G., Ind. Eng. Chem. 58(No. 3):33 (1966)

34. Iler, R.K., Ind. Eng. Chem. 46:766 (1954)

35. Hauserman, F.B., Advan. Chem. Ser. 23:338 (1959)

36. Yates, P.C., and Trebilcock, J.W., SPE Trans. 1:199 (1961)

37. Lee, L.H., J. Colloid Interface Sci. 27:751 (1968)

38. Wong, R., "Mechanism of Coupling by Silanes of Epoxies to Glass Fibers," in "Fundamental Aspects of Fiber Reinforced Plastic Composites," H. Schwartz, ed., New York:Interscience, pp 237-244, 1968

39. Davydov, V.Y., Kiselev, A.V., and Zhuravlev, L.T., Trans. Faraday Soc. 60:2254 (1964)

40. Boehm, H.P., Angew. Chem. Intern. Ed. Engl. 5:538 (1966)

41. Fox, H.W., Solomon, E.M., and Zisman, W.A., J. Phys. Colloid Chem. 54:726 (1950)

42. Vogel, G.E., Johannson, O.K., Stark, F.O., and Fleischmann, R.M., "The Chemical Nature of the Glass-Coupling Agent Interface," Proc. SPI (Reinforced Plastics Div.), Washington, D.C., Sect. 13-B, pp. 1-10, Jan. 31-Feb. 3, 1967

43. Tutas, D.J., Stromberg, R., and Passaglia, E., SPE Trans. 4:256 (1964)

44. Bascom, W.D., Adv. Chem. Ser. 87:38 (1968)

45. Bascom, W.D., J. Colloid Interface Sci. 27:789 (1968)

46. Schrader, M.E., Lerner, I., and D'Oria, F.J., Mod. Plastics 45(No. 1):195 (1967)

47. Sterman, S., and Bradley, H.B., Proc. SPI (Reinforced Plastics Div.), Section 8-D, p. 1, Feb. 1961

48. Stark, F.O., Johannson, O.K., Vogel, G.E., Chaffee, R.G., and Lacefield, R.M., J. Phys. Chem. 72:2750 (1968)

49. Shafrin, E.G., and Zisman, W.A., J. Phys. Chem. 64:519 (1960)

50. Bernett, M.K., and Zisman, W.A., J. Phys. Chem. 71:2075 (1967)

51. Lee, L.H., J. Polymer Sci. (Part A-2) 5:1103 (1967)

52. Lee, L.H., Advan. Chem. Ser. 87(Sect. 8):106 (1968)

53. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 60:416 (1956)

54. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 63:1121 (1959)

55. Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 63:727 (1959)

56. Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 64:150, 157 (1960)

57. Bernett, M.K., Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 66:328 (1962)

58. Kanner, B., Reid, W.G., and Petersen, I.H., Ind. Eng. Chem. Prod. Res. Develop. 6:88 (1967)

59. Jarvis, N.L., "Monomolecular Films of Polydimethylsiloxanes on Organic Liquids," NRL Report 6780, Nov. 15, 1968; to appear in J. Colloid Interface Sci., 1969

60. Bascom, W.D., Halper, L., and Jarvis, N.L., "Wetting of Low Energy Surfaces by Nonaqueous Dimethylsiloxane-Containing Surfactants," NRL Report 6808, Feb. 1969; to appear early spring of 1969 in Ind. Eng. Chem. Prod. Res. Develop.

61. Vanderbilt, B.M., and Clayton, R.E., Ind. Eng. Chem. Prod. Res. Develop. 4:18 (1965)

62. Erickson, P.W., Volpe, A., and Cooper, E.R., Mod. Plastics 41(No. 12):141 (1964)

63. Sands, A.G., Clark, R.C., and Kohn, E.J., "Microparticle and Fiber Reinforcement of Epoxy Resins," NRL Report 6403, Aug. 26, 1966

64. Viventi, R.V., Plant, H.T., and Maher, R.T., Proc. SPI Reinforced Plastics Div., Washington, D.C., Sect. 1-D, p. 1, Jan. 31-Feb. 3, 1969

65. DeVenuto, G., Stoltz, D.S., and Wiggill, J.B., Proc. SPI Reinforced Plastics Div., Washington, D.C., Sect. 2-A, p. 1, Jan. 31-Feb. 3, 1969

66. O'Rear, J.G., and Sniegoski, P.J., Advan. Chem. Ser. 87:10 (1968)

67. Shafrin, E.G., and Zisman, W.A., Advan. Chem. Ser. 87:20 (1968)

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13. ABSTRACT

A critical and up-to-date review has been made on the present knowledge of the surface chemistry and related polymer science involved in the reinforcement of thermosetting and thermoplastic materials by glass or other strong fibers. Although the emphasis is basically on the behavior of glass-reinforcing fibers and particles, wherever possible the discussion and conclusions have been presented to allow their extension directly or by analogy to other strong reinforcing solids. A selected bibliography has been compiled of the most significant scientific work published to date. The treatment of the subject has been as fundamental as the scope and reliability of the available data permit. In many instances, available knowledge has been interpreted using the reviewer's judgment. Where significant gaps or conflicts have been noted in the literature, they have been discussed constructively. In the concluding sections numerous highly specific recommendations have been made to stimulate or guide future research and development in this complex field.

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