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Abstract

~~Recent unusual and demanding applications of glass fiber reinforced plastics, such as rocket cases and submarine hulls, have made evident the need for a better understanding of the mechanism of reinforcement by glass fibers, the conditions for obtaining the optimum ratio of strength to weight, the means of decreasing the rate of deterioration of strength with age or exposure to water, and any basis for recognizing or expediting the evaluation of the conditions limiting long-term or extreme applications. Glass fiber reinforced plastics are greatly affected by surface chemical mechanisms, such as spreading, wetting, adhesion, friction, adsorption, and desorption; this is not surprising because (a) glass has a highly adsorptive surface and (b) the glass fiber as now used in reinforcing plastics corresponds to a surface area from 3400 to 5500 square centimeters per gram of plastic. Various processes of molecular diffusion play an important part in long-term deterioration, and the ability to decrease the rate of diffusion of water involves recognition of the effect of polymer constitution on the cohesive and adhesive properties of the resin system. This report attempts to apply present knowledge of surface chemistry and polymer chemistry to explain many of the properties of glass fiber reinforced plastics and to point out ways to obtain improvements. In most respects, the analysis given also applies to any plastic reinforced by a fibrous solid material whose surface is hydrophilic.~~

## INTRODUCTION

Today's plastics reinforced with inorganic solids of high tensile strength, such as glass fibers, are the product of over two decades of increasingly intensive industrial research and development. A review of the published literature on the technology of the subject reveals, however, that in many particulars the chemical and physical mechanisms controlling important properties are still in doubt.

Recent unusual and demanding applications of glass-reinforced resin systems, especially several sponsored by the military, have made evident the need for a better understanding of the mechanism of reinforcement, the conditions for obtaining the optimum ration of strength to weight, the methods of decreasing the rate of deterioration of strength with age or with exposure to water immersion, and any basis for recognizing or evaluating the conditions limiting long-term or extreme applications. Examples are the U.S. Navy's developmental program on glass-fiber-wound cases for the Advanced Polaris rocket, and more recently a rapidly accelerating program on reinforced plastics for the external hull structures of

deep-submergence submarines. In the latter application, in addition to the question of how to obtain the optimum strength-to-weight ratio, there also is the problem of the long-term creep or deterioration caused by water permeation under high compression loads during many and long successive submergences to great sea depths. Developing and testing reinforced plastics for such an extreme application is costly and time consuming. More thoughtful consideration of and research on reinforced plastics is obviously necessary if such a demanding application can be made safely.

Glass-fiber-reinforced plastics are much affected by surface chemical mechanisms because (a) glass has a highly adsorptive surface and (b) the glass fiber as now used has diameters of from 0.00037 to 0.00022 inch, which in an 80% glass and 20% resin plastic corresponds to a surface area of from 3400 to 5500 square centimeters per gram of plastic. It is already widely recognized that strong adhesion of resin to glass is needed to obtain strong glass-reinforced plastics, and various surface treatments are widely used for increasing strength, especially for use under conditions of water immersion. Hence, it is no exaggeration to state that the surface chemistry of the glass-resin interface has a profound influence on the properties of glass-reinforced plastics. Because in the postwar year there have been many advances at the Naval Research Laboratory in the understanding of the surface chemistry of the solid-liquid

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interface, it is the purpose of this report to try to relate that knowledge to the current state of the art as indicated in technical publications and reports concerning the production and properties of glass-reinforced plastics; also to indicate areas of research where improvements may be expected.

### PRESERVING THE ORIGINAL TENSILE STRENGTH OF THE GLASS

Griffith proposed many years ago (1) that the tensile strength of glass fiber is greatly decreased by the development of microcracks in the surface of glass following drawing during the subsequent approach toward thermal and mechanical equilibrium. Although this explanation appears to be widely accepted, there is a paucity of reliable supporting data. It is very likely that other mechanisms also contribute to the observed loss in strength. It is well known there can be other causes of damage to the surface of glass; for example, many surface cracks develop whenever clean glass rubs against clean glass or other hard clean solids (2). Figure 1 illustrates a typical surface fracture pattern resulting from a single traverse of a plate of clean soda lime glass by a clean 1/2-inch-diameter steel ball sliding at a speed of 0.01 cm/sec under a 600-gram load. From the elastic deformation the estimated unit load on the glass is 42,000 psi. Such damage obviously must be avoided since the cracks, which run roughly at right angles to the friction path traversed, are precisely the kind capable of greatly decreasing tensile strength. Similar results are

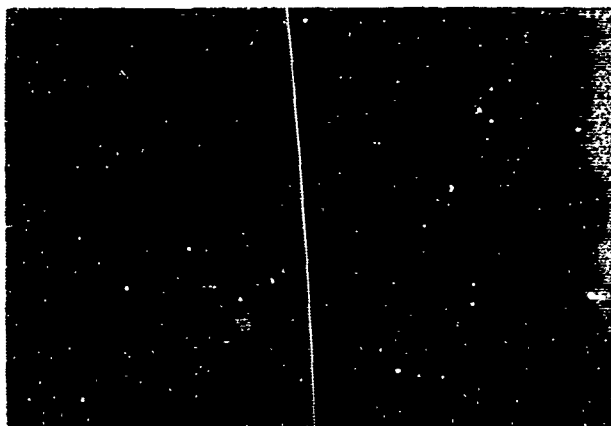


Fig. 1 — Friction-track steel ball sliding on glass (one traverse at 0.01 cm/sec with 1/2-inch steel ball and 600-gram load)

found when a clean glass ball is used. Therefore, in the manufacture of glass bottles and glass fiber, a common practice is to coat the glass surface with a lubricating film immediately after it has cooled. For the development of optimum adhesion of the resin to glass fiber, most boundary lubricating coatings should be removed from the fiber before applying the resin. Obviously, at no time thereafter during processing or later use of the reinforced plastic object should there be any opportunity for the glass fibers to rub against each other.

Prolonged contact of glass by some aqueous solutions can result in surface erosion and roughening. Such effects are exemplified by Trichane and Carrier's findings (3) that some commonly used aqueous cleaning solutions erode and roughen the surface of glass but that aqueous solutions of ethylenediamine tetraacetic acid, sodium citrate, or phosphoric acid have a remarkable leveling and smoothing effect. Although their findings were based on electron microscope studies on soda lime glass and different effects may be observed on other kinds of glass, their results focus attention on the need for examining the effect on surface structure of any aqueous solution used in cleaning or in prolonged contact with glass fibers.

Many publications have discussed the effect of water on the tensile strength of Owens Corning E glass fibers, and it would appear that at ordinary temperatures after continuous contact with water for not over a few weeks, the loss of strength does not exceed from 10% to 20%. Several investigators have suggested that the loss of tensile strength may be greater if the water is in contact with the glass while it is under large tensile stresses, but no reliable and convincing data have yet been published. Fox (4) has pointed out that under the appropriate conditions, water may weaken stressed glass analogously to the embrittling effect of liquid metals (such as mercury) when in contact with tensile-stressed metals (such as aluminum) (5). When bulk water reaches a microcrack in a clean glass surface, it will creep up the crack through capillary action and so lower the surface energy. The combined effect may be sufficient to cause extension of the crack. A smaller effect should result if the available water is not bulk water but merely that adsorbed in the crack resulting from molecular diffusion through the resin, or through any protective coating on the glass fiber, or by surface diffusion along the glass-resin interface.

It is especially important to realize that even though the glass fiber may be coated with a protective adsorbed film which is very "water-repellent" or hydrophobic, unless that film is very thick or is much more coherent than any presently used materials, it cannot prevent molecules of water vapor from diffusing to the glass surface (6). However, if the hydrophobic film is uniform, it will not allow *bulk* water to reach the glass. This inability of the film to prevent water vapor penetration may be understood from Fig. 2, which represents the spiral arrangement of the carbon-carbon chain in each molecule of a close-packed adsorbed monolayer of a fatty acid or primary amine of high molecular weight. Such monolayers are very permeable to individual molecules of water because of the many parallel spiral stairwaylike passages through the film. Permeation by water molecules can only be stopped by compressing the monolayers laterally with forces which are much greater than those normally existing in adsorbed monolayers (7,8). Despite the penetration by water vapor, bulk water cannot pass through because such films commonly exhibit water contact angles of around 90 degrees (9).

Condensed films of these and other similar polar-nonpolar compounds will prevent bulk water from contacting microcracks in the glass surface; hence, they may decrease greatly the probability that sufficient water will penetrate into a microcrack to decrease the surface energy enough to promote crack propagation and loss of tensile strength. Inasmuch as some of the

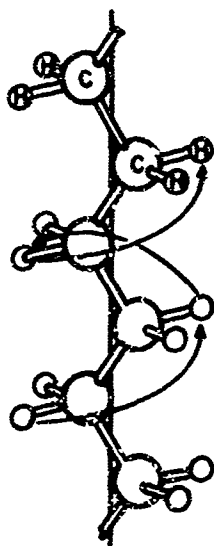


Fig. 2 - Spiral structure of paraffin chain

coupling agents used in manufacturing plastics reinforced with glass fiber have the property of forming adsorbed hydrophobic films on the glass, it is possible that if they coat each fiber uniformly they may help decrease any susceptibility of the reinforced plastic to stress failure under prolonged water immersion.

### OBTAINING OPTIMUM ADHESION OF RESIN TO GLASS

Much of the mystery about adhesion and the effect of chemical constitution has disappeared in the past decade. It has long been known that adhesion is caused by the forces between the molecules in or near the surface of the two contacting materials. The forces involved are short-range forces of the type described in the classic work on nonideal gases by van der Waals and the later discussion of intermolecular forces between nonpolar molecules by London (10). Characteristically, these attractive forces between any two atoms are insignificant in intensity when they are more than 3 to 10 angstroms apart. Therefore, significant adhesion between two solids or between a solid and a liquid does not become apparent until the surface molecules are practically in contact. Since a liquid drop resting on a solid conforms quickly to the hills and valleys of the surface, its adhesion is considerable and readily observed. In other words, every liquid adheres to some extent to any solid. However, when two dry solids are pressed together, they will not adhere perceptibly because the rigidity and surface roughness of the two solids allows only a small percentage of the surface atoms of the solids to come close enough together to make a significant contribution to the total adhesion.

Numerous investigations during the past two decades, especially the classic work of Bowden, Tabor, and coworkers (2) on the nature of the friction between clean, dry, rubbing solids, have revealed that sliding friction is the result of the forces needed to overcome the strong adhesion developed between the two solids at the contacting prominences or "asperities." Nearly all such solids adhere strongly enough at the contacting asperities to require shearing these "cold-welded" joints; this is the principal cause of wear. The concepts involved here are illustrated in Fig. 3 where it is seen that the force of friction ( $F$ ) is approximately equal to the product of the total

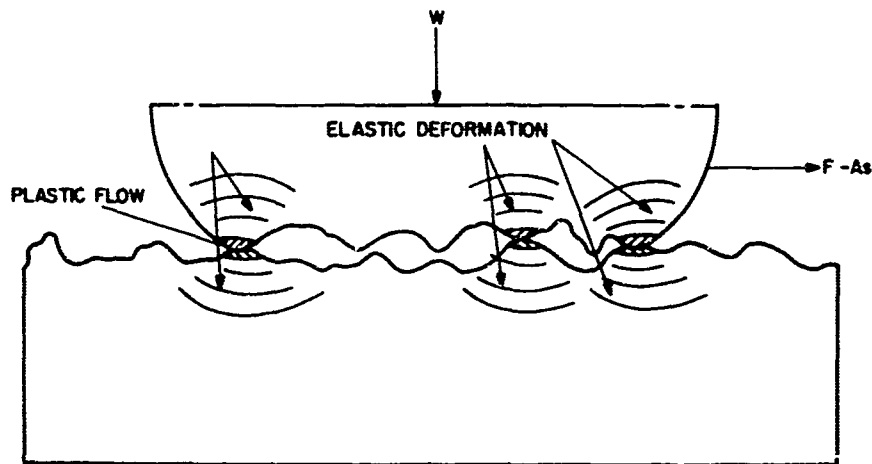


Fig. 3 - Contact of two solids

area (A) of contact of the contacting asperities of the rubbing solids and the average shear strength (S) of the resulting adhesive joints formed. The cracking and surface damage to glass caused by sliding the steel ball shown in Fig. 1 is an example of this process.

A long-term program of research on the adhesion of liquids and solids has enabled us to show that adhesion is determined essentially by the nature of the atoms in the surface of each solid and not by the material deeper within (11, 12). This experimental result is an expression of the highly localized nature of the forces of attraction between the molecules. Therefore, it follows that an adsorbed film only one molecule thick can radically change both the wetting and the adhesive properties of solid surfaces. This conclusion has been well verified in a variety of ways. For example, the wetting and adhesive properties of two pieces of steel or glass coated with a close-packed monolayer of polyethylene differ little from those of two pieces of bulk polyethylene. Thus, in producing a reinforced plastic, major changes in the adhesion of the resin to the glass fibers can result from the presence of an adsorbed film only one molecule thick.

In manufacturing a reinforced plastic, the more intimate the contact the liquid resin makes with every hill, valley, and crevice in the surface of the glass fiber or flake, the greater the strength of the final adhesive joint. Furthermore, as the area of contact approaches its maximum, the strength of the joint formed between the solidifying resin and the glass surface becomes greater than the

tensile strength of the solid resin. This conclusion is true even when the attractive forces acting across the joint interface are only the physical adsorption forces. In other words, where there is complete wetting and filling-up of cavities in the glass surface by the resin at the time of application, the adhesion is so great that later rupture under external mechanical stresses will occur in the resin rather than at the glass-resin interface. This conclusion means that it is not *necessary* that the molecules of resin should form a chemical bond with surface atoms or ions in the glass. Surface chemical reaction may be desirable for some uses in order to increase resistance to chemical attack or to the deteriorative effects of water through long use or submersion; however, such a need is not firmly established in the literature.

Internal stresses developed during resin solidification and also the stress concentrations occurring during applications of such adhesive joints have been given much attention. Important photoelastic studies by Mylonas (13) and Mylonas and deBruyne (14) led to the conclusion that in a lap joint poor wetting of the adherend tends to produce a greater stress concentration at the free surface of the adhesive where failure is most likely to be initiated. As the contact angle of resin to adherend becomes larger, the maximum stress concentration increases and moves toward the lineal boundary where the adhesive and atmosphere make contact with the adherend; in the process the stress concentration factor increases from about 1.2 to 2.5. Of especial importance here is Griffith's conclusion that failure of

the adhesive may occur at a relatively small applied stress if there are air bubbles, voids, inclusions, or surface defects (!); it occurs because stress concentrations result which are much higher than the mean stress applied across the specimen.

Consider this last result in terms of the probable effect of poor wetting by the liquid resin on the development of air (or vacuum) pockets at the glass-resin interface. It has already been pointed out that if the liquid resin spreads spontaneously on the glass (*i.e.*, the contact angle  $\theta$  is zero), and if all hills and valleys on the glass surface are filled with resin, the theoretical joint strength far exceeds the tensile strength of the resin. In practice the theoretical joint strength is never attained; two major causes are the development of stress concentrations during solidification of the resin and incomplete contact of resin and glass. Even when  $\theta = 0$ , gas pockets at the glass-resin interface may remain unfilled if the resin is too viscous when applied or it cannot penetrate all of the accessible surface pores and cracks before polymerizing. Of course this situation is aggravated if  $\theta \neq 0$ . Around each such surface gas pocket, stress concentrations will build up when the reinforced plastic is subjected to external forces.

If these surface occlusions are all nearly in the same plane and not far apart (as on the upper adherend of Fig. 4), there can occur crack propagation from one pocket to the next; and the joint may break as if it has a built-in "zipper." Therefore, if surface roughness must be accepted, the kind of roughness shown on the lower adherend of Fig. 4 would be preferable because crack propagation along a plane would be less probable. In producing reinforced plastics, especially with glass-fiber-wound rocket bodies or with glass-cloth-impregnated materials, the difficulties of avoiding surface voids or gas pockets are numerous. This

factor is responsible in practice for a substantial loss of tensile and shear strength. Therefore, it is advantageous to apply the liquid resin to the glass surface while it is as smooth as possible. For the same reason, in treating the glass fiber with sizes, lubricants, or coupling agents, it is helpful to avoid leaving rough deposits rather than a uniform film. Therefore, if the coupling agent can be dissolved in the resin, it would be better to apply it to the glass in that way rather than by a separate application followed by a coating of the liquid resin.

### THE PROBLEM OF SPREADING THE RESIN AND WETTING THE GLASS

Solids can be conveniently separated into two classes: high surface energy solids which are hard at ordinary temperatures and have high melting points; and low surface energy solids which are much softer and have much lower melting points. Examples of the high surface energy solids are diamond, quartz,  $\alpha$ -alumina, silicate glasses, most metals, and various metallic oxides and nitrides. Examples of the low surface energy solids are solid organic polymers, resins, waxes, and nearly all organic compounds. These two classes of solid surfaces also differ greatly in their wetting properties. Uncontaminated high energy surfaces are wet completely by all but a special class of pure liquids, *i.e.*, the contact angle  $\theta$  is usually zero. Low energy surfaces are not wet completely ( $\theta > 0$ ) by many classes of pure liquids. As the subject of wettability and constitution has been fully reviewed in recent publications (11, 12, 15), only several essential conclusions will be discussed here.

Whenever a liquid cannot spread on a high-energy solid surface, it means that  $\mathcal{W}_c$ , the work

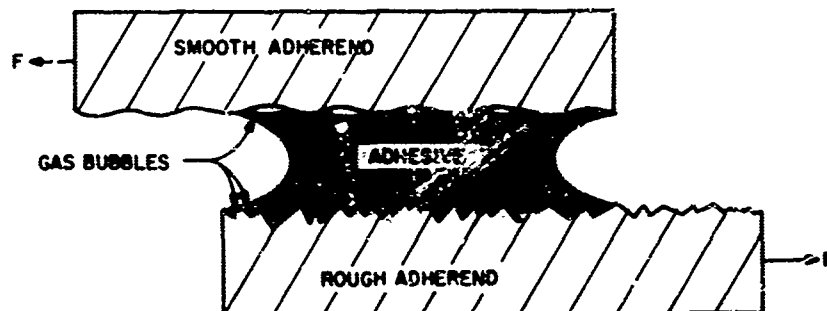


Fig. 4 - Effect of surface roughness on coplanarity of gas bubbles

of cohesion of the liquid ( $W_c =$  twice the liquid surface tension), is greater than  $W_A$ , the work of adhesion of liquid to solid. This thermodynamic criterion of Harkins (16, 17) simply expresses the fact that the liquid will exhibit a nonzero contact angle and not spread spontaneously whenever its tendency to cohere into a drop is greater than its tendency to adhere to the solid. Harkins' criterion is not easy to use because it does not explicitly relate the effect of the chemical constitution of solid and liquid; however, much has been revealed about this aspect of the problem as the result of our postwar research. We have shown that whenever a liquid cannot spread on a high-energy solid surface, a film has been formed on the solid which lowers its surface energy enough to make it behave like a low energy surface. This result can occur through one of the following several processes:

1. A volatile compound from the atmosphere, or an additive in the liquid, can adsorb on the high energy surface to form a physically or chemically adsorbed monolayer which lowers the surface energy of the solid.

2. The liquid itself can adsorb on contact with the high energy surface to deposit a monolayer on which the bulk liquid cannot spread; *i.e.*, the liquid cannot spread on its own monolayer. Such liquids have been named "autophobic" liquids.

3. Diffusion to the surface of some constituent of the solid can result in forming a surface film of lower energy.

As will be shown, in manufacturing reinforced plastics wetting problems can be introduced unintentionally by using (a) glass fiber, (b) room air, or (c) resins contaminated with chemicals having the above properties. As will be shown, many chemicals used in coating glass with a hydrophobic film can increase the contact angle with some organic materials and so hinder spreading of the resin on the glass.

The wetting properties of each solid surface can be described to a good first approximation in terms of the critical surface tension of wetting ( $\gamma_c$ ). Some values of  $\gamma_c$  are given in Table 1. The composition of each solid surface is characterized by indicating the nature of the atoms or organic radicals composing the surface. In Table 2 are values of  $\gamma_c$  for surfaces of various well-known polymeric solids. If the value of  $\gamma_c$  is known, it is possible to predict from knowledge of the surface tension ( $\gamma_{LV}$ ) of a liquid whether or not it will spread on that surface. If  $\gamma_{LV}$  is less than  $\gamma_c$ , the

TABLE I  
Critical Surface Tensions of  
Low Energy Surfaces  
(at 20° C)

Surface Constitution	$\lambda_c$ (dynes/cm)
Fluorocarbon surfaces	
- CF <sub>3</sub>	6
- CF <sub>2</sub> H	15
- CF <sub>2</sub> and - CF <sub>2</sub> -	17
- CF <sub>2</sub> - CF <sub>2</sub> -	18
- CF <sub>2</sub> - CFH -	22
- CF <sub>2</sub> - CH <sub>2</sub> -	25
- CFH - CH <sub>2</sub> -	28
Hydrocarbon surfaces	
- CH <sub>3</sub> (crystal)	20-22
- CH <sub>3</sub> (monolayer)	22-24
- CH <sub>2</sub> - CH <sub>2</sub> -	31
= CH = (phenyl ring edge)	35
Chlorocarbon surfaces	
- CClH - CH <sub>2</sub> -	39
- CCl <sub>2</sub> - CH <sub>2</sub> -	40
= CCl <sub>2</sub>	43

contact angle  $\theta$  will be zero and the liquid will spread spontaneously over the solid (the rate being determined by the viscosity of the liquid and the smoothness of the solid). If  $\gamma_{LV}$  is greater than  $\gamma_c$ , the liquid will not spread but will exhibit an equilibrium contact angle  $\theta$  which will be greater, the greater the difference between  $\gamma_{LV}$  and  $\gamma_c$ . A graph of cosine  $\theta$  against  $\gamma_{LV}$  will be a straight line intercepting the line  $\cos \theta = 1$  at  $\gamma_{LV} = \gamma_c$ . Typical graphs for various fluorinated polymeric solids are given in Fig. 5. Tables 1 and 2 are made more useful by the fact that  $\gamma_c$  is not sensitive to moderate variations in the temperature.

Returning to the subject of reinforced plastics, any film or coating on the glass which causes its critical surface tension of wetting to be lowered substantially will limit greatly the variety of liquid

TABLE 2  
Critical Surface Tensions of  
Various Polymeric Solids  
(at 20°C)

Polymeric Solid	$\gamma_c$ (dynes/cm)
Polymethacrylic ester of $\Phi'$ -octanol <sup>a</sup>	10.6
Polyhexafluoropropylene	16.2
Polytetrafluoroethylene	18.5
Polytrifluoroethylene	22
Polyvinylidene fluoride	25
Polyvinyl fluoride	28
Polyethylene	31
Polytrifluorochloroethylene	31
Polystyrene	33
Polyvinyl alcohol	37
Polymethyl methacrylate	39
Polyvinyl chloride	39
Polyvinylidene chloride	40
Polyethylene terephthalate	43
Polyhexamethylene adipamide	46

<sup>a</sup> $\Phi'$ -Octanol is  $CF_3 \cdot (C_2F)_6 \cdot CH_2OH$ .

resins capable of spreading spontaneously on that surface. For example, if a surface-active compound like octadecyl amine (9) or Quilon S, the chromium complex of stearic acid (18), is adsorbed as a monolayer on the surface of glass, as the film approaches closest packing it forms an outer surface of close-packed  $-CH_3$  groups having a value of  $\gamma_c$  of from 22 to 24 dynes/cm (Table 1). The only polymeric liquids able to spread spontaneously on such a surface are the dimethyl silicones and the highly fluorinated polymers. In fact, such films function as adhesives, antistick or release agents (14); other examples of such films are given in Table 3. But if the outermost portion of the adsorbed monolayer consists of aromatic rings or covalent chlorine atoms (Fig. 6),  $\gamma_c$  will be from 35 to 43 dynes/cm, and a much larger variety of common polymeric liquids (like polyethylene and polyvinyl chloride) will spread upon it.

If the adsorbed compound is such as to have a larger value of  $\gamma_c$  than the surface tension  $\gamma_{LV}$  of

the liquid resin, there will result spontaneous spreading and excellent adhesion; hence, such a compound would increase wettability of the glass and function as a kind of wetting agent. It should now be obvious that any compound adsorbed or deposited on the surface of the glass fibers during the manufacturing process should not lower the value of  $\gamma_c$  of the surface below the  $\gamma_{LV}$  of the liquid resin at the time of application. For example, a chromium carboxylic acid complex with one or more terminal benzene (or chlorine) substituents would have a higher value of  $\gamma_c$  than would Quilon S, and hence it should be more suitable for use as a coupling agent with the most common resins. It is worthy of note that in processing such an "active" surface as clean glass through manufacturing operations prior to resin impregnation, it would be better to coat the surface with an agent which will increase  $\gamma_c$  sufficiently so that accidental adsorption of undesirable organic contamination would be prevented. Since a "size" and a boundary lubricant are applied to glass fiber in the early manufacturing operation, it is now obvious that such coatings should be removed completely before applying the resin or else these agents should be selected so that they will not lower excessively the critical surface tension of wetting if allowed to remain on the glass.

#### PROBLEMS ARISING FROM HYDROPHILIC NATURE OF GLASS

When free from organic contamination, the glass used as reinforcing material is always wet completely by water (*i.e.*,  $\theta = 0$ ). Unlike high energy hydrophilic surfaces such as the metals, aluminum oxide, or certain silicate minerals, glass will react with many materials since on the surface there are many silanol ( $-\text{SiOH}$ ) groups. Because of that fact as well as the hydrogen-donating ability of the silanol group and the ability of the many oxygen atoms in the surface to be acceptors of hydrogen bonds, it is difficult to remove all of the adsorbed water from glass. Long heating above 350°C is required to dehydrate the surface; if prolonged, chemically bound water is split off by the condensation of nearby SiOH groups. At ordinary temperatures, depending on the relative humidity (R.H.), adsorbed water may cover the surface of clean glass with a film varying from one monolayer to 20 or more. The lower limit is encountered between 30% and 50% R.H.,



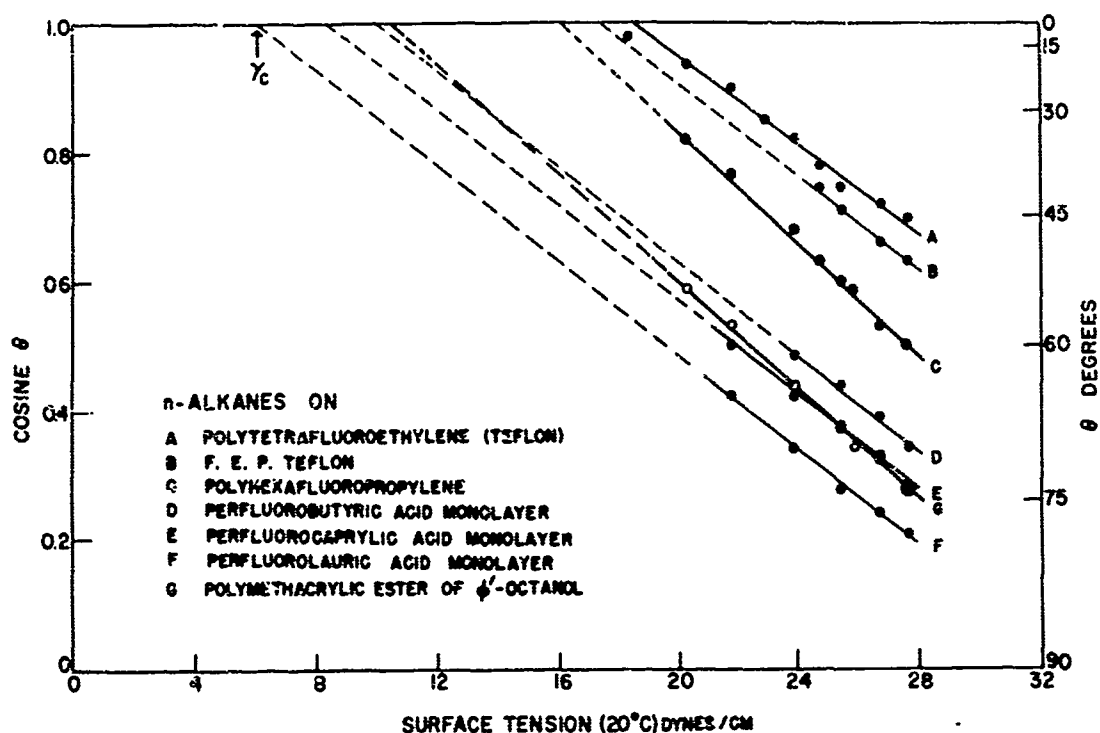
Fig. 5 — Cos  $\theta$  vs  $\gamma_{LV}$  for various fluorocarbon surfaces

TABLE 3  
Critical Surface Tensions of Wetting of  
Surfaces Coated with Adhesives  
(at 20°C)

Coating Material (All Condensed)	$\gamma_c$ (dynes/cm)
Polymethylsiloxane film	24
Fatty acid monolayer	24
Polytetrafluoroethylene film	18
$\text{HCF}_2 \cdot (\text{CF}_2)_4 \cdot \text{COOH}$ monolayer	15
Polymethacrylic ester of $\phi'$ -octanol*	10
Perfluorolauric acid monolayer	6

\* $\phi'$ -Octanol is  $\text{CF}_3 \cdot (\text{CF}_2)_4 \cdot \text{CH}_2\text{OH}$ .

and the higher values develop above 90% R.H. as the relative humidity approaches 100% (19). However, much more water may be present if hygroscopic materials (such as NaCl or NaOH) are left on the surface of the glass through improper cleaning or chemical attack. Modifications of the chemical composition of the glass fibers used at present in reinforced plastics may alter chemical resistance, but they do not appear to change greatly the

hydrophilic character of the surface. Although it is possible to treat glass with inorganic or organic reagents to decrease its tendency to adsorb water, such surface treatment also affects the wetting and adhesive properties with respect to liquid resins. The preceding discussion is indicative of the results of using organic compounds; the effects of inorganic treatments are not well covered in the literature.

Surprisingly little information has been published on the effect of the thickness of an adsorbed film of water upon the ability of organic liquids to spread upon glass. When the adsorbed water is many molecules thick, as at 20°C and high relative humidity, any liquid polymer free from hydrophilic substituents would not be expected to spread spontaneously over the glass unless highly diluted with a spreading solvent. This conclusion results from the fact that the Harkins spreading coefficient (16,17) on bulk water of any hydrocarbon liquids of high molecular weight is always negative. One can also predict that the greater the extent of chlorination or the more aromatic the polymer, the more negative will be the spreading coefficient. However, when the adsorbed film of water is only one or a few molecules thick, the spreading properties of the liquid polymer upon glass cannot be predicted from in-

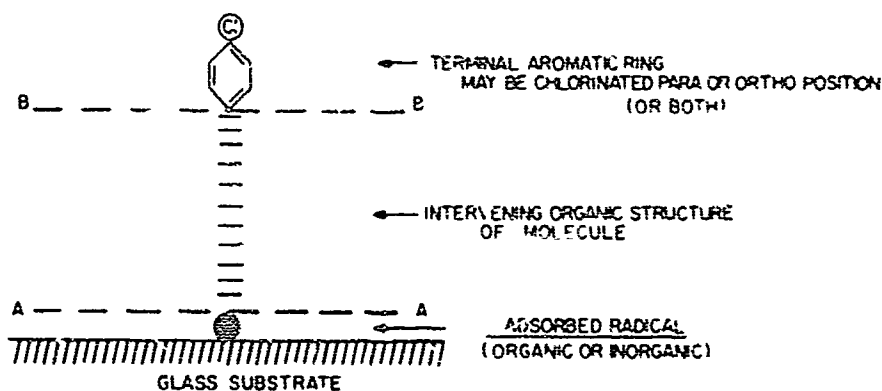


Fig. 6 - Some synthetic improvements in coupling agents for glass-reinforced plastics

formation in the literature. However, some simple experiments have indicated that at 20°C when the relative humidity is around 50% or less, the high-boiling aliphatic and naphthenic liquid hydrocarbons spread freely on borosilicate glass and quartz. If the liquid polymer contains enough hydrophilic substituents per molecule to have a positive spreading coefficient on water, good spreading on glass may occur even at high relative humidities; however, no information is available on the spreading coefficients of the liquid resins now being used.

Certain liquid polar-nonpolar compounds have the ability to displace water from the surface of hydrophilic solids such as glass and metal. The essential mechanism and the properties of these materials have been described in NRL reports (20,21). Good examples of this large group of compounds are found among the liquid alcohols, ketones, acetates, acetoacetates, and ether-alcohols. Figure 7 shows how a drop of butyl alcohol placed on a soaking wet high energy surface displaces the water layer. Because of its large spreading coefficient and low viscosity, the drop of butyl alcohol spreads rapidly over the surface of the water. The hydroxyl group of each butanol molecule contacting the water

surface forms hydrogen bonds with molecules of water beneath, and so numerous water molecules are dragged along with the spreading butanol. Because of this transfer of momentum to the water layer, there forms a circular depression with a ridge or mound surrounding it (shown in profile in Fig. 7). If the water layer initially is not thicker than a few millimeters, one small spreading drop of butyl alcohol readily displaces all of the water, and the depression deepens to form a hole reaching down to the dry solid surface beneath. Before the butanol drop has evaporated, a hole, 1 or 2 cm in diameter, can be formed by one drop. Once the butanol has evaporated, the water mound collapses and fills in the hole.

The above-mentioned surface chemical mechanism is being applied widely by the Navy in displacing water from metal surfaces in connection with salvaging operations (21), and there have been numerous other applications. Because there are many water-displacing agents among the lower boiling, polar-nonpolar, hydrophilic organic compounds, it is possible that in the application of some liquid resin systems to glass fibers, an addition agent, impurity, or a solvent may function as a water-displacing

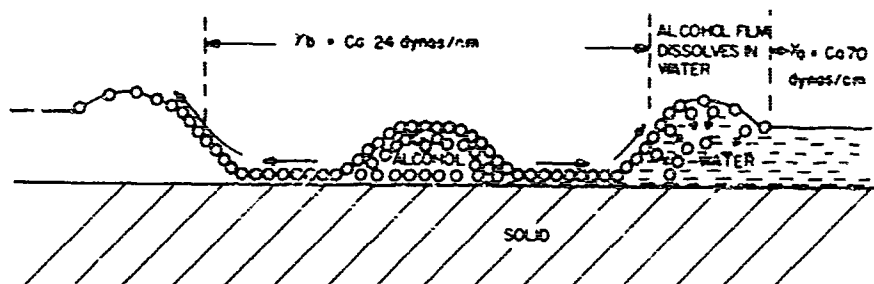


Fig. 7 - Mechanism of water displacement by butyl alcohol

agent. When such an agent is used, it may be possible to obtain good wetting and adhesion by the resin even if the relative humidity is high. However, if any hydrophilic groups are added to the resin molecules in order to give it a positive spreading coefficient and some water-displacing ability, the substitution should not be carried too far because then the resin will become more susceptible to water permeation and to the effect of water in displacing adsorbed compounds from glass.

### WATER PENETRATION THROUGH REINFORCED PLASTICS

If water seeping through macroscopic cracks or holes in the resin is ignored, water can penetrate into a submerged reinforced plastic by three molecular diffusion processes: (a) diffusion through the resin phase, (b) diffusion along the glass-resin interface, and (c) diffusion through any protective film coating the glass. Each of these processes deserves discussion.

Even after polymerization has been completed, many resins are permeable to water molecules by a mechanism which is well exemplified by the behavior of a sheet of low-density polyethylene. Two related mechanisms permit diffusion through such a solid, the first being the "helical stairway" between adjacently adlined aliphatic hydrocarbon chains (Fig. 2). Usually this stairway is wide enough to allow the passage of individual molecules of water; this process is only hindered when the paraffinic chains or chain segments of the neighboring molecules are pressed together by strong intermolecular cohesive forces such as occur in single crystals. The other mechanism is prominent only when the resin is above its glass transition temperature ( $T_g$ ) and statistical fluctuations in the density and alignment of small segments of the polymer chains allow water molecules to pass through.

Water diffusion through such hydrocarbon polymer resins would be accelerated if some hydrogen atoms in the hydrocarbon chains were replaced by hydrophilic groups. However, if enough hydrogen atoms were replaced by chlorine atoms, there would result increased intermolecular cohesion due to the stronger dispersion forces between neighboring chlorine atoms and the rate of water diffusion would be decreased greatly. It is for this reason that the polyvinylidene

chloride plastics are so much less permeable to water than the polyvinyl chloride or polyethylene plastics. Since the work of intermolecular cohesion of a liquid ( $W_c$ ) is twice its surface tension, it follows that any substituent for hydrogen that raises the surface tension of the liquid polymer will help decrease the permeability to water, provided that it doesn't result in an increase in the number of hydrophilic groups present. However, if one attempts to decrease greatly the water permeability of the resin phase through the chemical modifications indicated above, mechanical limitations develop. As the intermolecular cohesion of the resin increases, it becomes more brittle and decreases in impact strength. Therefore, chlorination can be used only within limits to decrease the water permeability of reinforced plastics.

As indicated in the section "Preserving the Original Tensile Strength of the Glass," adsorbed monolayers or thin polymolecular films are not effective barriers to water diffusion because of their low intermolecular cohesion. Therefore, it is not sufficient to rely upon even the most condensed adsorbed films, such as those of coupling or waterproofing agents, to increase the water resistance of glass-fiber-reinforced plastics.

Rates of molecular diffusion of water can be much greater along the glass-resin interface than through the resin. Laird (22) has recently reported that the rate of diffusion of water along the glass-resin interface of an epoxy resin bonded to E. glass was 450 times faster than through the resin. Of course, this ratio will vary considerably with the nature of the resin and with the glass finish or coupling agent used. Evidently, such easy pathways for water penetration need to be minimized. For example, it appears undesirable to use laminated glass-resin systems for submarine hulls because the sheets of glass cloth will offer such excellent paths for water diffusion wherever they come near the external surface of the hull. The reinforcing glass should be arranged in a more random way and possibly the length or arrangement of the individual glass fibers employed may need restriction.

### EFFECT OF WATER ON ADHESION

Although the subject has been discussed widely, not much is known about the extent to which water reaching the glass-resin interface affects

the adhesion of the resin. Any polar groups in the molecule placed there to increase adhesion of resin to the glass may subsequently be displaced from the glass surface by the penetrating water molecules through a competitive adsorption mechanism. Although the implication is that resin molecules containing polar constituents be avoided, that is impractical, it is suggested that instead the polar substituents be such as to have the ability to adsorb on the kind of glass used in order to compete with the adsorbing tendency of water. The desorptive action of water could also be combated by chemically reacting the resin molecules with the glass surface; obviously, the chemical bond formed should not only be resistant to hydrolysis but also to any acceleration of hydrolysis which might result if contact of water molecules with the glass surface should leach from it enough alkali or acid to alter significantly the pH in the locality. It is evident that the mechanisms of water interaction at glass-resin interfaces need investigation.

A more radical way to decrease water displacement at the glass-resin interface would be to seek a reinforcing material whose ability to hold on to physically adsorbed (or chemisorbed) molecules of resin despite competition with water of diffusion would be much greater than presently used glasses. However, it is not firmly established how urgently such an approach is needed. A more long-term investigation would be involved; nevertheless, an effort is needed because many new types of strong inorganic fibers are beginning to appear at various laboratories. There seems to be widespread industrial and governmental interest in obtaining improved reinforced plastics; hence, much activity in this area of research can be predicted.

### CONCLUSIONS

This survey of the surface chemical properties of glass-reinforced plastics has led to the following conclusions and recommendations which it is hoped will stimulate and guide productive discussion and research:

1. Experimentation with better defined organic materials is needed not because it is evident that purer materials are needed in production, but in order to learn more about the factors controlling the manufacture, quality control, strength, and behavior in extreme environments of the reinforced plastics.

2. In order to increase the strength of glass-fiber-wound rocket bodies, there needs to be greater freedom from the entrapment of gas bubbles (or voids), especially at the glass-resin interface. This would require (a) application of the resin in as low a viscosity state (low cure) as possible and (b) avoiding treatment of glass fibers with any sizes, lubricants, or coupling agents which roughen the surface or leave any residual film on the glass which decreases spreading by the liquid resin.

3. An effort is needed to decrease the rate of water permeation into the reinforced plastics through preferred pathways along the glass-resin interface; this is particularly important in developing reinforced plastics for submarine hulls.

4. Experiments are needed to decide whether water decreases significantly the strength of glass fiber while it is under tensile stress. The effects during submersion of cyclic loading in tension and in compression both deserve attention.

5. More care is needed in making the proper choice of surface treatments such as coupling agents in relation to the spreading properties of resin materials used with them. Possible pathways to improve present practices have been outlined.

6. As regards presently available reinforced plastics, more reliable information is needed on the life expectancy and possible longtime creep in physical properties of the materials under various conditions and especially under conditions of deep immersion in the sea. In this connection, it is questionable whether any presently used accelerated tests are sufficient.

7. Longer term research seeking improved reinforcing materials is desirable for use in the more extreme applications.

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