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NRL Report 6140

Some Surface Chemical Aspects of Glass-Resin Composites

Part 1 - Wetting Behavior of Epoxy Resins on Glass Filaments

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August 10, 1964

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ABSTRACT

A study has been made of the wetting behavior of epoxy resins on glass filaments and its relation to the fabrication and the properties of filament wound glass-resin composites. The experiments were designed to determine how wetting is affected by the surface finish on the glass, the molecular structure of the epoxy liquid, and the presence in the liquid of a curing agent. Wetting behavior on freshly drawn E-glass fibers was compared with the wetting of commercial HTS-finished E-glass filaments and of glass fibers coated with hydrolyzed silane finishing agents. Three different types of epoxy liquids were used; an aromatic, a cycloaliphatic, and a fluoroaromatic, with and without the addition of amine curing agents. It was found that the HTS and the silane finished glass were poorly wet by all the epoxy liquids regardless of the chemical structure of the liquid or the presence of amine. For instance, the aromatic epoxy monomer bisphenol A diglycidyl ether had advancing contact angles of 70 to 80 degrees on the HTS-finished filaments and 60 degrees on a coating of hydrolyzed aminosilane compared with 25 to 30 degrees on uncoated E-glass. The wettability of the finished glass was comparable with polyethylene, against which the aromatic epoxy has a contact angle of 53 degrees. Attempts to improve wettability by adding fluoroorganic surfactants to the epoxy liquids were unsuccessful, presumably because of adsorption of the fluoro additive onto the solid surface.

The wetting studies also provided other pertinent information: (a) the dynamic advancing contact angle formed against a fiber as it moves into the liquid was generally about 10 to 20 degrees higher than the static, equilibrium advancing angle, (b) the HTS and silane finished glass fibers were covered with a visible coating of the sizing material, and (c) the coating materials were only partially soluble in the epoxy liquids. The silane surface finishes were found to be coatings of siloxane polymers about one micron thick; the surface properties of these polymeric coatings are discussed in relation to the theories that have been proposed to explain the success of silane finishes in improving the wet strength of glass-resin laminates. In view of the observed thickness of both types of finish coatings, the theory that part of their usefulness is to create a deformable layer near the glass/resin interface is given some support. It has been claimed that this layer relieves internal stresses which occur during cooling of the cured resin to ambient temperature due to the different coefficients of thermal expansion of the glass and resin.

Observations of filament winding on pilot plant equipment, using some of the same glass-epoxy systems employed in the wetting studies, as well as the examination of segments of impregnated glass roving taken from the machine, revealed that air bubbles amounting to a significant portion of the total volume were entrapped in the glass-resin composite. It is known that such voids degrade the strength of the composite. Air entrapment results because of the viscous resistance to resin flow in the capillary spaces between filaments and the capillary resistance to flow due to poor wetting. It was estimated that the maximum possible capillary pressure available for axial flow between parallel filament was orders of magnitude too low to allow the resin to penetrate the glass yarn as it was pulled into the liquid. Penetration must therefore take place by lateral flow, perpendicular to the fiber axis from the sides of the yarn. This lateral flow will be opposed by a capillary pressure unless the contact angle is zero. A further reason for air entrapment is that the filaments are not uniformly spaced; hence as the resin flows

into the yarn, it will pass more readily into the larger spaces between filaments, bypassing the more narrow spaces. It was concluded that for optimum impregnation it is necessary that the resin wet the glass fiber at a zero contact angle and, since this condition alone will not eliminate air entrapment, mechanical means must be provided in the winding operation to minimize air entrainment and to release air bubbles from the roving.

PROBLEM STATUS

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

Manuscript submitted July 7, 1964.

SOME SURFACE CHEMICAL ASPECTS OF GLASS-RESIN COMPOSITES

PART 1 - WETTING BEHAVIOR OF EPOXY RESINS ON GLASS FILAMENTS

INTRODUCTION

Glass-resin composites have attracted attention for both military and nonmilitary applications because of the high strength, comparatively low cost, and the ease of fabrication that they offer. Particularly attractive for the construction of military hardware are the composites formed by the geodesic isotensoid winding of resin-impregnated continuous-glass filaments. These filament-wound materials offer a surprisingly high strength-to-weight ratio that can even exceed that of high strength steel. The Polaris rocket motor case is presently being constructed of glass-resin filament-wound materials and the Navy is investigating their utility in the construction of deep-submersible hull structures.

Although glass-resin composites have found a wide range of applications, they have shortcomings. One of the more important of these is a marked loss in strength when exposed to water. Furthermore, many questions remain unanswered concerning the mechanics of these materials and how their properties are related to the individual properties of the resin and glass. Much industrial, academic, and government research on glass-resin materials is now in progress. This wide interest reflects the high potential which these materials are believed to possess. There have been two excellent reviews published recently on the subject of composite materials in general (1) and glass-resin systems specifically (2).

There are three important surface chemical aspects to the technology of filament-wound glass-resin composites that are badly in need of experimental examination (3); they are (a) the impregnation of the glass yarn by resin in the winding operation, (b) the adhesion of the glass to the resin, and (c) the integrity of the glass/resin interface when exposed to water. All three of these topics will be studied in the course of this program. The subject of this initial report is the wetting behavior of glass-resin systems and how this affects the impregnation process. The importance of wetting is clear in view of the fact that in a typical winding operation thousands of filaments are simultaneously pulled through a relatively viscous resin at speeds in excess of 500 inches/min. Under these conditions it cannot be presumed that the resin completely displaces air from between the filaments; air pockets or voids left in the final composite can only degrade its mechanical properties. This report concerns work done to find the conditions for optimum impregnation and is restricted to the epoxy resins because these polymers appear to dominate present technical practice.

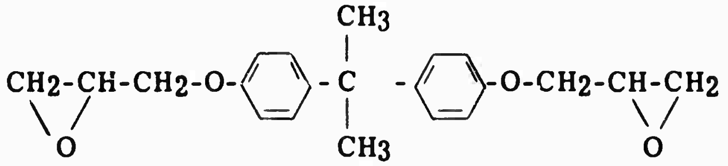
The adhesion of the resin to the glass and the effect of water on this adhesion are critical for the mechanical strength of the composite. It is generally believed that the glass filaments are the load carrying component and that the resin serves only to transmit load to the fibers and to prevent damage of the fibers by abrasion. However, the transfer of stress within the material requires that the glass-resin bond remain intact, so it is pertinent to inquire into the surface chemical conditions necessary for good adhesion between the glass and resin. It is also possible that the encapsulating resin can affect the strength of the glass itself. It has been repeatedly shown that the strength of any solid can be influenced by the kind of molecules adsorbed on its surface. Consequently, it is important that the resin not affect the strength of the glass adversely and that it protect the glass from agents such as water which are known to be harmful. The extent to which glass-resin composites are affected by long term submersion in water is particularly important if these materials are to be used in the construction of deep-submersible structures.

EXPERIMENTAL MATERIALS

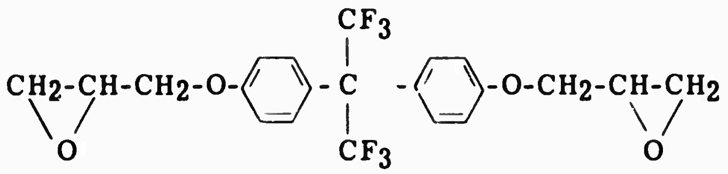
Epoxy Liquids and Curing Agents

A commercial epoxy monomer, the diglycidyl ether of bisphenol A (DER-332LC) of relatively high purity, was obtained from the Dow Chemical Co. The material was received as a waxy crystalline solid which was stated by the supplier to have a melting point of 40°C and an epoxy equivalent weight of 170 to 175 (theoretical–170). A cycloaliphatic epoxy monomer, the cis-trans isomer of bis(2,3-epoxycyclopentyl) ether was prepared by the Union Carbide Plastics Co. (4). This material had an approximate purity of 90%. A perfluoro analog of the diglycidyl ether of bisphenol A, [bis(trifluoromethyl)bis(4-hydroxyphenyl)methane diglycidyl ether, mp 70°-71°C] was synthesized and purified at this Laboratory (5). The structural formulas of these three compounds are given in Table 1. The epoxy compounds, 1,2-epoxy-3-phenoxypropane and 1,2-epoxydodecane, were obtained as reagent grade chemicals. All these materials were used without further purification.

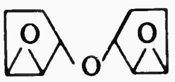
Table 1
The Structural Formulas of Epoxy Resin Monomers



Bisphenol A, diglycidyl ether



Trifluoromethyl bisphenol A, diglycidyl ether



Bis(2,3-epoxycyclopentyl) ether

The two amine curing agents used were a commercial grade of m-phenylenediamine, and m-aminobenzylamine which had been synthesized by Griffith at this Laboratory (6).

Silanes

Three organosilane esters were studied. Two of these, vinyl tris(2-methoxyethoxy) silane (vinylsilane) and aminopropyltriethoxy silane (aminosilane) were obtained from the Union Carbide Silicone Division in 93% and 95% purity, respectively. The third, propyltrimethoxy silane glycidyl ether (epoxysilane), was obtained from the Dow Chemical Co. and was of unknown purity. These materials were used as received.

Fluorocompounds

The perfluoroesters, bis(1H,1H pentadecafluorooctyl) n-octylsuccinate (mp 19°-20°C), bis(1H,1H heptafluorobutyl) adipate (bp 94°C at 0.8 mm Hg), and bis(1H,1H heptafluorobutyl(3-methylgluturate (bp 85°C at 0.5 mm Hg) were synthesized at this Laboratory (7). The other fluorochemicals used are listed in Table 6 along with their source. The only purification given to these compounds was a percolation through Florisil adsorbent to remove the more polar contaminants.

Glass

Marbles of E-glass were supplied by Dr. William Cass of the Owens-Corning Fiberglas Corp. This glass is formulated to have a composition of 54.6% SiO_2, 14.9% of Al_2O_3 and Fe_2O_3 combined, 17.4% CaO, 4.5% MgO, 8.0% B_2O_3, and 0.6% Na_2O. Short fibers of this glass were drawn from the marbles using a hydrogen-oxygen flame. Studies were also made on filaments of a commercially finished E-glass (HTS-finish, Owens-Corning Fiberglass Corp.).

EXPERIMENTAL METHODS

Three different methods were devised for determining the contact angle of liquids on the glass filaments. The ways in which the filaments were held relative to the liquid are schematically represented in Figs. 1-3. Short fibers of E-glass that had been drawn from marbles using a torch were sufficiently thick (1-2 mm in diameter) to be clamped as in Fig. 1. The clamp was mounted on a rack and pinion so that the fiber could be moved into and out of the drop of liquid. The intersection of the fiber with the liquid surface was photographed through a low power microscope and the angle of contact measured geometrically (Fig. 4A). The single filaments of commercial glass were only 0.0036 inch in diameter and so were too fine to be supported from the end and pushed through a liquid surface. One of the methods devised to handle these thin filaments was to place them across the inner of two concentric Teflon rings as indicated in Fig. 2. A drop of liquid was then touched to the filament; when the drop was pulled away the liquid that remained on the filament drew up into droplets which were viewed and photographed through a microscope (Fig. 4B). This technique was used to study the wetting of textile fibers (8) and Schwartz and Minor have shown that droplets always form even when the contact angle is zero (9). Only the receding contact angle can be measured by this method since the droplets left on the filament are formed by the liquid withdrawing from the surface. In order to measure the advancing angle the method represented in Fig. 3 was devised. A filament was held across the ends of two Teflon rods and this support was attached to a rack and pinion. A drop of the liquid was supported in a platinum inoculating loop. A thin slit was cut in the loop opposite the support wire and the glass filament was positioned in the drop by passing through this slit. This device permits determination of the advancing and receding angles (Fig. 4C) as well as observation of the dynamic contact angle the liquid assumes as the filament passes through the liquid surface. Many of the studies had to be done above room temperature and so it was necessary in all the above procedures to heat the drops by convection from small heating elements positioned nearby. The contact angles were essentially constant over the temperature range from 25° to 100°C.

Contact angle measurements were also made on flat pieces of linear polyethylene using a telescope goniometer. The polyethylene plates had been formed by compressing pellets to a compact that had a glossy, smooth surface (10). The plates were cleaned by washing in detergent solution, rinsing thoroughly with distilled water and drying.

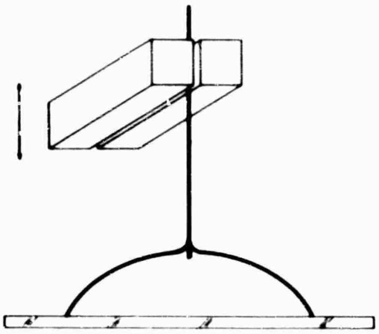


Fig. 1 - A schematic representation of the method used to determine contact angles by dipping fibers into a small pool of liquid

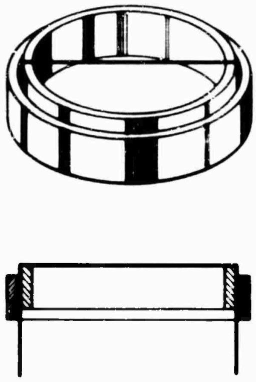


Fig. 2 - A schematic representation of the method used to determine contact angles by touching the liquid to a filament held across a ring

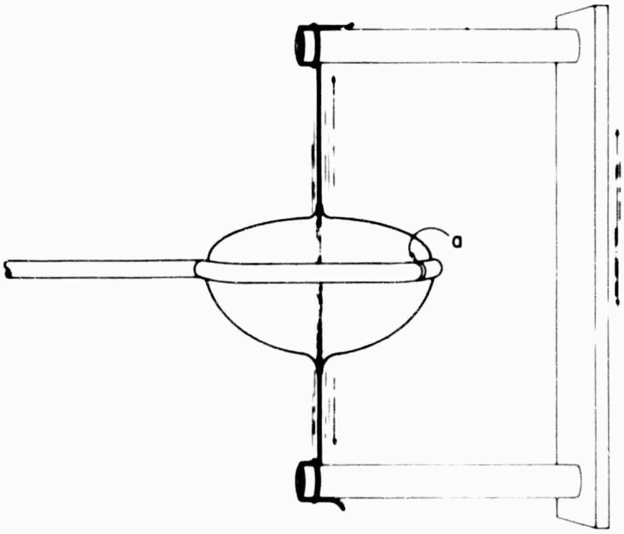


Fig. 3 - A schematic representation of the method used to determine contact angles by passing the filament through a drop held in a wire loop. The filament is positioned in the drop by passing it through a cut in the loop at a.

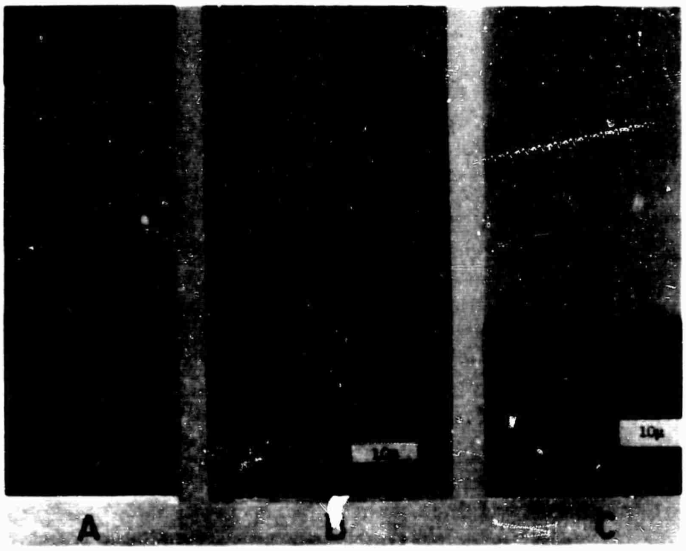


Fig. 4 - Typical photomicrographs used to determine contact angles against fibers: (A) A fiber supported in a small pool; (B) Droplets left on a suspended filament after touching with a larger drop; (C) A single filament passing through a hanging drop

Surface tension measurements were made by the duNouy ring method and by the drop volume method (11). All contact angle measurements and surface tension measurements were made in a room maintained at 25°C ± 2° and between 35% to 45% relative humidity.

RESULTS

Observation of an experimental filament-winding machine in use at this Laboratory showed that a significant amount of air was being trapped between glass filaments during resin impregnation. Impregnation in this particular machine is accomplished by pulling more than 6000 glass filaments simultaneously through a 2-inch layer of resin monomer and curing agent at speeds up to 500 inches/min. The resin in use at the time of observation was an amine-cured bisphenol A epoxy (diglycidyl ether of bisphenol A) and the glass was a commercial E-glass. The process is represented schematically in Fig. 5. Thirty strands of yarn (204 filaments each) enter the resin trough vertically and exit through a narrow slit or eyelet which removes excess resin. The filaments leave the trough as a narrow band of roving or parallel strands. During the winding operation the resin in the trough becomes turbid with air bubbles that have been displaced from between filaments by the resin. Inspection of the roving after it left the trough and was being wound on the mandrel revealed that tiny air bubbles were continually expelled from the resin.

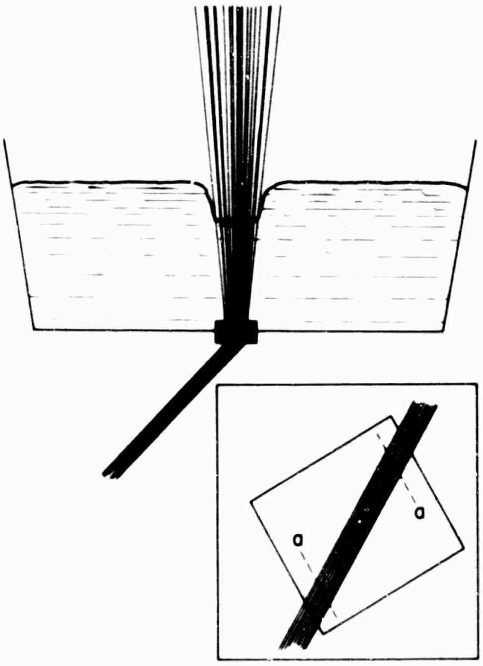


Fig. 5 - A schematic representation of the resin trough used for glass yarn impregnation. Insert: The manner in which the impregnated roving was clamped (a) to glass slides before cutting the section.

Microscopic examination of impregnated strands provided a more detailed picture of the entrapped air bubbles. Segments were cut from the band of filaments passing through the trough eyelet. The filaments are held under tension in the winding operation and in order not to release this tension in the sample segments the section of the band to be cut was first clamped to a microscope slide as indicated in the insert in Fig. 5. Examination of the cut segments revealed two types of air voids; interfiber bubbles and cross-fiber bubbles. The interfiber voids were thin, usually had a sausage shape and seemed to be trapped between glass fibers. The cross-fiber voids were generally larger than the interfiber bubbles and had filaments passing through them. Photomicrographs of the two types of voids are presented in Fig. 6. A typical interfiber bubble can be seen in Fig. 6A and the dark shadows out of focus are cross-filament voids. The filaments surrounding and passing through the larger cross-fiber voids distort their appearance as in Fig. 6B. The amount of void space was estimated to range from 5% to nearly 30% of the volume in the field of view at any one time. Curing of the resin at the appropriate temperature had no effect on the number or shape of the voids nor was any difference noted when the curing agent was changed from m-phenylenediamine to m-aminobenzylamine.

The penetration of a resin between the filaments is undoubtedly related to the degree to which the fibers are wet by the resin. Consequently, contact angles were measured for various epoxy liquids including some epoxy monomers and mixtures of monomer +

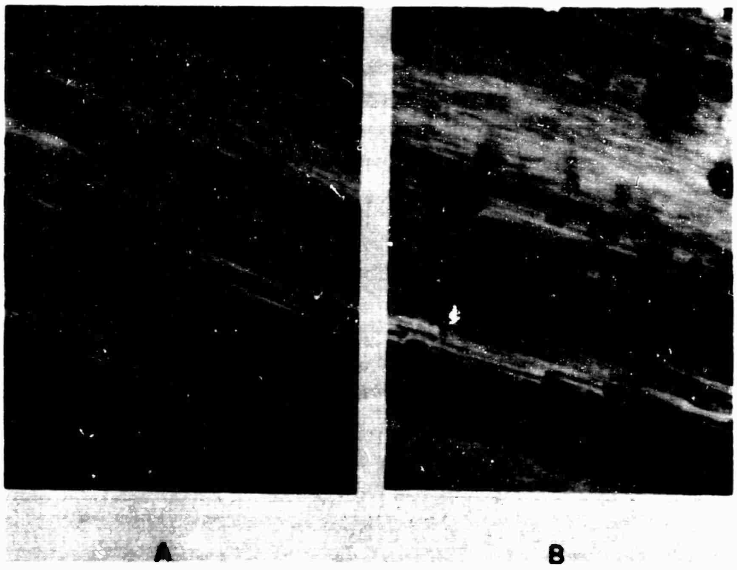


Fig. 6 - Photomicrographs of air bubbles trapped in impregnated roving: (A) an interfiber bubble; (B) cross fiber bubbles

curing agent on clean glass fibers, and on fibers to which different surface coatings had been applied. In these experiments attention was given to three specific questions; (a) how the surface coating on the glass affected wetting behavior, (b) how the wetting was influenced by the molecular structure of the epoxy liquid, and (c) what effect the curing agent had on wetting behavior.

The epoxy resin monomers and the surface coatings studied were chosen either because of their widespread use in glass-resin composite technology or to provide answers to specific research questions. The monomers were the diglycidyl ether of bisphenol A, its trifluoromethyl derivative, and a cycloaliphatic epoxy, bis(2,3-epoxycyclopentyl)ether (Table 1). The two glass finish coatings were the commercial HTS finish on E-glass and three typical hydrolyzed silanes. The HTS-finished glass was studied because in the present technology of filament-wound glass-epoxy materials this type of filament is used quite extensively. The manufacturer has not disclosed the chemical composition of the coating. The silane coatings studied are typical of the materials being extensively used to treat glass fabric for glass-resin laminate composites. They were formed from the esters of a vinylsilane, an aminosilane, and an epoxypropylsilane. E-glass fibers drawn from marbles were placed in 1% solutions of the silanes in water adjusted to pH 3 with acetic acid to hydrolyze the ester groups. The fibers were taken from the solution and dired in air or in an oven at 110°C.

The contact angles for the epoxy liquids on clean E-glass fibers, HTS finished E-glass filaments, and fibers coated with an aminosilane finishing agents are listed in Tables 2-4, respectively. For purposes of comparison, contact angles were also measured for these liquids on polyethylene. These results are listed in Table 5. Inspection of the data leads to three conclusions:

1. The epoxy liquids gave much higher contact angles on the coated glass fibers than they did on clean glass, the wettability of the finished fibers being closer to that of polyethylene than to that of clean glass. The bisphenol A diglycidyl ether monomer, for instance, had a contact angle of 28 degrees on clean glass but contact angles of about 80, 56, and 53 degrees on the HTS-finished glass, the amino-silane-coated glass, and polyethylene, respectively. Contact angles of about 50 degrees were also obtained for this epoxy liquid on the vinylsilane and the epoxysilane coatings.

Table 2
The Spreading Behavior of Various Liquids on Clean E-Glass Fibers

Liquid	Surface Tension (dynes/cm)	Advancing Contact Angle (degrees)
Epoxy monomers		
Bisphenol A, diglycidyl ether	42.5*	28*
Bis(2,3-epoxycyclopentyl) ether	42.0	8
Trifluoromethyl bisphenol A, diglycidyl ether	25.2*	25*
Epoxys with curing agent†		
Bisphenol A, diglycidyl ether m-phenylenediamine	41.9*	37*
Bis(2,3-epoxycyclopentyl) ether m-phenylenediamine	41.4	15

*Approximately 40°C.
†Stoichiometric proportions.
‡Zero receding angle.

Table 3
The Spreading Behavior of Epoxy Liquids on HTS-finish E-Glass Single Elements

Liquid	Surface Tension (dynes/cm)	Contact Angle (degrees)	
		Advancing*	Receding
Epoxy monomer			
Bisphenol A, diglycidyl ether	42.5†	80†	60†
Bis(2,3-epoxycyclopentyl) ether	42.0	60	60
Bis(trifluoromethyl) bisphenol A, diglycidyl ether	25.2†	80†	50-60†
1% bis(1H,1H heptafluorobutyl) 3-methyl glutarate in bisphenol A, diglycidyl ether	21.7†	80†	40†
Epoxy with curing agent‡			
Bisphenol A, diglycidyl ether m-phenylenediamine	41.9†		60†
Bisphenol A, diglycidyl ether m-aminobenzylamine	47		60

*Angles only approximate because of photographic difficulties and variations due to fiber coating roughness.
†Approximately 40°C.
‡Stoichiometric proportions.

Table 4
Wettability of Silane Hydrolysate Coatings on E-Glass Fibers
(Aminopropylsilane applied from 1 wt-% aqueous solution (pH 3))

Drying Temperature (°C)	Drying Time	Contact Angle (degrees)‡					
		H_2O		Epoxy*		Epoxy-amine†	
		Advancing	Receding	Advancing	Receding	Advancing	Receding
25	15 min	20	20	35	20	35	0
25	> 2 hr	30	20	45	31		
120	15 min	70	70	56	50	50	37

*Bisphenol A, diglycidyl ether.
†Bisphenol A, diglycidyl ether monomer + m-phenylenediamine in stoichiometric proportions.
‡Approximately 40° C.

Table 5
Spreading Behavior of Epoxy Liquids on Polyethylene

Liquid	Surface Tension (dynes/cm)	Advancing Contact Angle (degrees)
Bisphenol A, diglycidyl ether	42.5*	53*
1,2-epoxy-3-phenoxypropane	42.2	43
Bis(2,3-epoxycyclopentyl) ether	42.0	50
1,2-epoxydodecane	27.9	spreads
Trifluoromethyl bisphenol A, diglycidyl ether	25.2*	43*

*Approximately 40°C.

2. The fluoroepoxy monomer (trifluoromethyl bisphenol A, diglycidyl ether) formed contact angles comparable with those of the nonfluorinated aromatic and cycloaliphatic epoxy liquids even though the fluorocompound had a considerably lower surface tension. The bisphenol A epoxy monomer and the trifluoromethyl bisphenol A epoxy monomer differed by no more than 3 degrees on the clean glass and the polyethylene surfaces and showed no significant difference in advancing angle on the HTS-finished filaments.

3. Finally, the presence of the amine curing agents had relatively little effect on the advancing angle for the epoxy liquids on the different glass surfaces but did cause a marked contact angle hysteresis in some instances. Thus, the advancing angle for the bisphenol A epoxy containing a stoichiometric amount of m-phenylenediamine on the amino silane coating was 50 degrees while the receding angle was 37 degrees.

Some experimental difficulty was encountered in obtaining precise values for the contact angles of liquids on HTS-finished glass filaments. The values given in Table 3 are listed according to whether they were determined by bringing a filament through a hanging drop or by touching the liquid to a suspended fiber. The latter method gives only the receding angle whereas both advancing and receding angles could be measured in the hanging drop. Unfortunately, the present equipment does not permit satisfactory photomicrographs in the hanging drop method so that the data in Table 3 for the advancing angles are only visual estimates.

The wetting studies not only provide contact angle values but also some phenomenological information about the surface characteristics and wetting behavior of the coated fibers. These surface properties undoubtedly affect the function of the glass filament in composite materials. Considering the HTS-finished glass first, the most important observations were that the individual filaments were covered by a rather substantial amount of the finish, the finish material was only partially soluble in the resin, and the dynamic contact angle exhibited by a single filament as it was pulled through the liquid was substantially higher than the static, equilibrium advancing angle. Observation of the amount of coating was made by taking single filaments from a spool of continuous yarn and examining by dark field microscopy, which revealed that at many places the finish material had deposited as a relatively thick coating. The photomicrograph in Fig. 7 shows a typical region so thick with finish that a groove had been left in it by another filament after they had been pulled apart. A more quantitative estimate of the amount of finish carried by the glass was obtained by determining the weight loss after the yarn had been cleaned by heating to a red heat or by solvent extraction using acetone in a soxhlet extractor. Both methods gave a finish content of 0.8% to 1.0% by weight. During observation of wetting as filaments were pulled through a hanging drop it appeared that most of the finish material dissolved rapidly into the epoxy resin. However, solution was not always instantaneous; when the wetting liquid was allowed to recede it was evident that some of the larger sizing patches had not dissolved completely even after many minutes. There was no observable difference between the advancing angle on regions from which the coating had been dissolved and regions where there had been no coating evident. It was also observed that as the fiber was being pulled through the drop the dynamic advancing angle was greater than the equilibrium advancing angle. For the bisphenol A monomer, for instance, the dynamic contact angle was greater than 90 degrees as compared to 70 to 80 degrees for the static angle.

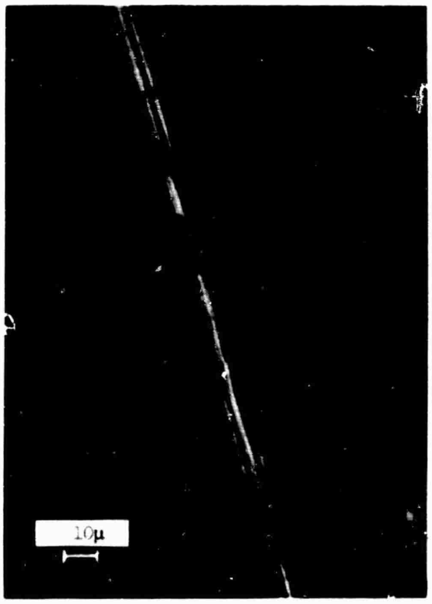


Fig. 7 - A dark field photomicrograph of a single filament of HTS-finished E-glass showing a region of thick coating

The most interesting characteristics of the silane coatings were the marked decrease in the wettability and solubility of the coating materials as they dried and the fact that capillary holdup even on single fibers left a macro coating of material on the glass surface. All of the hydrolysate solutions wet the clean fibers with contact angles of 8 to 10 degrees so that when withdrawn from the solution the fibers carried a thin film of liquid which pulled up into a series of droplets. These droplets rapidly evaporated to leave a water insoluble coating, and inspection of the coating with an interference microscope revealed large patches of material showing a thickness of about one micron.

The wettability of the silane coatings was very dependent on the extent to which the fibers had been dried. Typical results for water and for the bisphenol A monomer on the aminosilane hydrolysate are given in Table 6. Comparable results were obtained on the vinyl and epoxysilane coatings. Air drying produced a substantial increase in the contact angle for the bisphenol A epoxy and for water. The poor solubility of these coating materials in the bisphenol A epoxy and in water was determined qualitatively both on the fibers and with hydrolysate prepared in bulk.

The wettability of the epoxy liquids on polyethylene was studied not only for comparison with the results on the glass surfaces but also to look for any anomalies in the wetting behavior of the liquids themselves. Polyethylene was used as the reference surface because its wettability by organic liquids has been thoroughly characterized by Zisman and coworkers (12). They have found for this solid that liquids having a surface tension (γ_{LV}) less than 32 dynes/cm have a zero contact angle and spread spontaneously (see Discussion section). In Table 5 it can be seen that epoxydodecane (γ_{LV} = 27.9 dynes/cm) shows the anticipated spreading behavior on polyethylene but that the trifluoromethyl bisphenol A monomer (γ_{LV} = 25.2 dynes/cm) is anomalous in that it has a 43 degree contact angle on this solid.

Various fluorochemicals were added to bisphenol A diglycidyl ether monomer to depress the surface tension of the epoxy in an effort to determine if, by using such surfactants, its wetting could be improved. The results on polyethylene are given in Table 6.

Table 6
The Effect of Fluoroorganic Additives on the Wetting of Polyethylene by Bisphenol A, Diglycidyl Ether

Additive	Conc (wt-%)	γ_{LV} (dyne/cm)	θ (degree)	Source
Alcohols				
1H,1H pentadecafluorooctanol	satd	32.5	40-45	*
1H,1H undecafluorohexanol	5	23.7	35	*
1H,1H heptafluorobutanol	5	42.4	50	*
1H,1H,11H eicosafluoroundecanol	5	24.8	43	†
1H,1H,7H dodecafluoroheptanol	5	30.7	43	†
Esters				
Ethyltrifluoroacetate	5	41.2	55	‡
Ethyl 1H,1H heptafluorobutyrate	5	38.0	55	*
Bis(1H,1H pentadecafluorooctyl)n-octylsuccinate	1	23.2	42	§
Bis(1H,1H heptafluorobutyl)adipate	satd	25.5	25-35	§
Bis(1H,1H heptafluorobutyl)3-methylglutarate	2	21.7	<20	§
Miscellaneous				
1,1,2,2,3,3,4,4,-tetrafluoro 5,5-dimethylhexane	2	41.1	54	†
Perfluorobutylether	satd	42.5	56	¶
Perfluorotributylamine	satd	38.2	53	¶
Fluoroorganic ionic surfactant	satd	22.5	>50	¶

*Columbia Organic Chemicals Co., Inc., Columbia, S.C.
†E.I. duPont deNemours and Co., Wilmington, Del.
‡The Dow Chemical Co., Midland, Mich.
§Naval Research Laboratory (see Ref. 6).
¶Minnesota Mining and Mfg. Co., St. Paul, Minn.

The effort was only partially successful since only a few of the additives gave a substantial improvement in wettability. Many of the solutions which had surface tensions less than 32 dynes/cm were nonspreading, thus duplicating the anomaly already observed for the fluoroepoxy. The solution containing 2% of perfluorobutyl-3-methylgluturate was tested on the HTS-fiber. The result is given in Table 3 where it can be seen that the improved wetting obtained for this solution on polyethylene was not obtained on the commercial fiber.

WEAKENING OF GLASS-RESIN COMPOSITES BY AIR INCLUSIONS

Air bubbles lodged in filament-wound composites or in composites of any type represent flaws and regions of weakness which seriously impair the strength of the material. The thin interfiber voids observed here have very short radii of curvature at their ends and because of this sharp curvature they act as regions of stress concentration from which cracks can initiate as load is applied to the material. The large cross-filament voids have less curvature but there will still be stress concentration in the region around each fiber where it enters the void. Stress concentration occurs in this case because of the angle of contact the resin makes against the filament. It has been shown that for contact angles between 60 and 90 degrees the stress concentration factor is approximately 2-3 (13). The presence of these flaws throughout the composite would explain why water can be forced through the material at pressures less than the bursting pressure of the structure. The bubbles observed here in the yarn were not interconnecting so that water passage could only occur if internal cracking took place from one void to the next, thereby creating paths through the material. McGarry (14) has commented that during cyclic-loading, glass-resin laminates frequently lose their initial stiffness after the first test, presumably as a result of internal cracking resulting in part from the presence of voids. In a recent study (15) a direct correlation has been found between the void content of glass-resin laminates and the interlaminate shear strength. For instance, a void content of 5% reduced the laminate strength by one-third.

FACTORS RESPONSIBLE FOR AIR INCLUSIONS

A complete analysis of the impregnation process would be a formidable problem, but by making various assumptions it is possible to obtain some indication of how air is entrapped in the yarn and what steps might be taken to minimize entrapment. The resin can enter the yarn either by axial flow along the narrow capillary spaces between filaments or by lateral flow across the fibers from the periphery of the yarn. The problem is simplified by assuming that the individual filaments are arranged in a square array as indicated in Fig. 8A and that a steady state has been reached between the rate at which resin flows into the yarn and the rate the yarn enters the trough. If the steady state were such that the liquid in the capillary space is exactly at the resin level it is possible to assign an "equivalent" capillary length in which the capillary pressure ΔP provides the necessary driving force for lateral flow between fibers into the capillary space as well as the axial flow through the capillary. The Poiseuille equation for the rate of liquid flow through fine tubes is:

$$v = \frac{r^2 \Delta P}{8 \eta l} \qquad (1)$$

where v is the rate of axial flow, r is the capillary radius (Fig. 8A), η is the viscosity of the liquid and l is the "equivalent" capillary length. The capillary pressure ΔP is given by $(2\gamma/r) \cos \theta$. By assigning an arbitrary, "equivalent" capillary length of 0.5 inch, Eq. (1) gives a maximum possible rate of flow of 0.3 inch/min which is more than three orders of magnitude too slow for the resin to penetrate the yarn axially as it enters

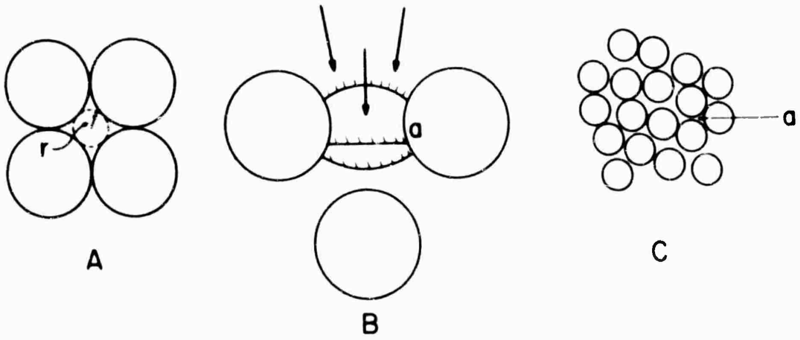


Fig. 8 - Various geometric representations showing: (A) the capillary cross section between parallel filaments in a square array; (B) the change in liquid meniscus as the resin passes between filaments; (C) possible differences in spacing between filaments due to a nonuniform distribution

the trough at 500 inches/min. It is not possible to find resins of sufficiently low viscosity or high surface tension to offset this viscous resistance.

Evidently, most impregnation occurs via lateral penetration although penetration in this direction may also be resisted or interdicted by a capillary effect if the contact angle is high. The reason for this can be seen in Fig. 8B, where the meniscus shape is drawn for a liquid which wets the fiber surface at 70 degrees as it progresses between two parallel filaments. In order to maintain the contact angle the meniscus must change from convex to concave toward the resin and in the latter configuration the capillary pressure opposes liquid flow. The maximum capillary pressure resisting penetration has been evaluated by Cassie and Baxter (16) in an equation which in an approximate form is,

$$\Delta P_{max} = \frac{\gamma}{r \cos \theta} + \sqrt{\frac{d^2}{4} - r^2 \sin^2\theta}, \qquad (2)$$

where d is the distance between fibers measured from center to center and the other symbols have been previously defined. When the fibers are very small and close together, Eq. (2) reduces to $\gamma/r \cos \theta$ so that in the case of glass fiber impregnation, high resistance to liquid penetration results not only because of poor wetting but also because of the small filament diameter. However, if the fibers are so closely packed that one layer intersects the common tangent to the fibers in the next layer, the resisting pressure will be that required to make the advancing interface reach the next filament which will be less than ΔP_{max} in Eq. (2). Resin penetration is further complicated by the nonuniform spacing and the twisting of the filaments in the glass yarn. In any cross section of a bundle of filaments such as in Fig. 8C there will be relatively narrow regions such as "a" which will be bypassed as the resin enters adjacent spaces which have a wider clearance between fibers. This bypassing favors air entrapment. This analysis has ignored the fact that the yarn is drawn through an eyelet at the bottom of the trough and that passage through the eyelet probably expels some of the entrapped air bubbles. However, the events taking place at the eyelet are very complex and their analysis will require further experiment and observation.

The impregnation apparatus of most commercial winding machines is more sophisticated than the simple trough employed here but the basic problems in capillarity and wetting would be the same. In general, penetration of resin into the yarn will be aided by capillarity if the contact angle is zero. However, the small spacing between filaments imposes a serious viscous resistance to resin flow. It is inevitable that some air will be trapped. Therefore, any successful winding process must allow for some mechanical means of releasing air bubbles by relieving tension on the yarn while it is still submerged in the liquid or by working the yarn over rollers. Another approach to the problem that has not been considered explicitly here would be to force the resin into the yarn under pressure. This procedure would overcome any viscous or capillary resistance but the operational difficulties might be prohibitive.

SIGNIFICANCE OF WETTING DATA AND OBSERVATIONS

The wetting and spreading behavior of liquids on solid surfaces has been very thoroughly studied by Zisman and Shafrin (17) and from their research it is possible to draw useful conclusions from the wetting data obtained here. However, before discussing the results it will be helpful to review some of the major surface chemical concepts of wetting phenomena which they have developed. It has been shown that for solids having relatively low surface free energies such as organic polymers there exists a critical surface tension of wetting, γ_c. This is an experimentally determined quantity obtained for any given surface from measurements of the contact angles of a series of reference liquids. The value of γ_c represents the surface tension of a liquid which will just spread on the solid; liquids having surface tensions greater than γ_c will show finite contact angles on the solid whereas liquids that have surface tensions less than γ_c will show a zero contact angle and spread. The critical surface tension is determined by the chemical constitution of the molecular grouping existing in the surface. Surfaces containing fluorocarbon groups have low critical surface tensions of about 20 dynes/cm or less, whereas hydrocarbon solids have γ_c values ranging from 25 to 35 dynes/cm. Thus, hexadecane, which has a surface tension of 28 dynes/cm, spreads spontaneously on polyethylene (γ_c = 32 dynes/cm) but has a contact angle of 46 degrees on Teflon (γ_c = 19 dynes/cm). Polar materials such as glass have relatively high surface energies and as a consequence their critical surface tensions would be greater than the surface tension of any existing liquid. This fact means of course, that all liquids should spread on clean glass. However, the high surface energy of polar solids causes them to adsorb any available organic substance, thereby reducing the critical surface tension. The resulting value of γ_c will depend upon the chemical constitution of the adsorbate. Perfluoroorganic compounds or certain silicone compounds reduce the value of γ_c considerably more than do hydrocarbon derivatives.

The poor wettability of the HTS-glass by the epoxy resins, when compared with the low contact angles these same liquids showed against the clean glass fibers, demonstrates that the applied coating determines the wetting characteristics of the filament. In fact, the results on the HTS-glass were more closely comparable with the results on polyethylene than with the results on clean glass; this suggests that, although the resins dissolved the bulk of the finish, enough material was left adsorbed on the surface to reduce the critical surface tension of the glass to that of an organic solid. On the clean glass fibers the zero contact angle for water demonstrates that the surface was free of organic contamination (18). The small, finite contact angles which the epoxy liquids had on the freshly drawn fibers indicates that the surface energy of the glass had in this case been reduced either by adsorbed water, by the vapor of the liquid itself adsorbing ahead of the advancing edge or by a combination of these effects. The phenomena of a liquid exhibiting a contact angle on a self-deposited monolayer is called autophobicity and has been studied by Zisman and coworkers (19, 20).

The contact angle hysteresis that was observed for some of the systems studied may have an important significance for the study of glass-resin adhesion. The advancing angle, of course, is pertinent to the wetting and impregnation of the fabric. The receding angle on the other hand gives information about the events that have occurred at the glass/resin interface once the fiber has been wet. For instance, the fact that the receding angle for the bisphenol A epoxy and the aminosilane coating was smaller in the presence of the amine curing agent implies that the amine has promoted either a chemical reaction between the finish and resin or the solution of the finish into the resin. Full use will be made of receding angle measurements and the information they can provide in the anticipated study of the adhesive bond between glass and resin.

The inability of the trifluoro-substituted epoxy liquid and the solutions of fluoroorganic additives in an epoxy liquid to wet the HTS-glass or the polyethylene was an unexpected result. It probably resulted from an autophobic behavior of the fluorinated compounds. These liquids had lower surface tensions and therefore should have had lower contact angles than the parent epoxy. In fact, many of the liquids had surface tensions less than the critical surface tension of polyethylene, and should have spread on this solid. Evidently, these fluoroorganic compounds are adsorbed on the HTS-finish and on the polyethylene ahead of the advancing liquid to form monolayers having much lower critical surface tensions than the underlying substrate. Evidence for the adsorption of the fluorocompounds was obtained when drops of the solution of perfluorooctyl succinate (1% of bis[1H,1H pentadecafluorooctyl]n-octylsuccinate) in the bisphenol A epoxy were placed on a polyethylene surface and then caused to recede from the point of application. Using methylene iodide and water as test liquids, contact angle measurements were made on the areas from which the fluoroadditive solution had been removed. The test liquids had higher contact angles than they normally do on polyethylene, thus implying the presence of an adsorbed film of the fluorodiester. Bernett and Zisman (21) encountered unusually high contact angles for aqueous solutions of fluoroorganic surfactants on polyethylene and were able to demonstrate in a similar manner that the fluorocompounds were being adsorbed onto the substrate.

In general the surface chemical behavior of the fluoroorganic additives was consistent with the known behavior of fluorocompounds in organic solution (22). Perfluoro derivatives are usually more surface active than the structurally similar ω-monohydro compounds and accordingly the surface tension of the perfluorohexanol (1H,1H,undecafluorohexanol) solution was lower than the solution of the ω-monohydrofluoroheptanol (1H,1H,7H, dodecafluoroheptanol). Also, an effective lowering of the surface tension usually requires the additive to be an assymetric polar-nonpolar compound. Evidently, the perfluorobutyl ether and amine were not sufficiently assymetric and did not have a distinct enough polar-nonpolar character to be as effective in reducing the surface tension of the epoxy liquids as were the fluoroesters and alcohols. Other factors which undoubtedly played a part in the relative surface activity of the fluoro additives were differences in their solubility and differences in the fluorocarbon chain length.

A disappointing feature of the results using the fluoro additives was the failure of the epoxy solution containing the 3-methylglutarate diester to show a low contact angle on the HTS-finished filament even though this same solution exhibited the smallest contact angle on polyethylene of any of the additive solutions. The low angle on polyethylene was probably due to the fact that the 3-methylglutarate fluoroester has a substantially higher volatility than any of the other fluoroorganics that were surface active in the epoxy. As a result of this volatility, evaporation of the additive from the solid surface prevented the establishment of a monolayer of the fluoroadditive ahead of the drop edge. However, in the wetting of the filament evaporative dissipation of the additive monolayer from the filament surface is prevented by the high ratio of liquid to solid surface which tends to maintain a large vapor concentration of the additive around the fiber near the advancing liquid edge.

THE FUNCTION OF THE FINISH COATING

The observations made here of the silane-finished glass permit some comment on current theories of how these materials improve glass-epoxy composites. Laminates prepared using glass fabric that has been finished by treatment with hydrolyzed silane solutions have been found to have improved mechanical properties especially when tested in water (23). Some of the explanations offered for the effect of these coatings are: (a) that the silane improves the wettability of the filaments by the resin (14), (b) the silane acts as a coupling agent between resin and glass so as to improve the glass-to-resin bond (23), or (c) that the improved wet strength is due to the well known hydrophobic character of silicone coatings (24).

It was found here that the silanes did not significantly improve resin wettability nor did they impart an unusually hydrophobic character to the fiber. The contact angle for the bisphenol A diglycidyl ether monomer was above 50 degrees on dried silane coatings whereas the resin would need to wet the glass at a zero angle to obtain any significant improvement in impregnation. Water had a contact angle of about 70 degrees against the silane coatings, making them less hydrophobic than the cured bisphenol A resin itself, against which water had an 80 degree contact angle. However, it is possible that the silane treatment is effective against molecular water penetration by diffusion along the glass/resin interface. The theory that the silanes act as coupling agents between the glass and the resin proposes that the hydrolyzed silane molecule adsorbs by condensation of the hydroxyl groups with the silanol groups on the glass surface while the other end of the molecule couples with the epoxy group of the resin. Actually, there is no obvious reason why the silane hydroxyl group should be adsorbed to the glass in preference to other polar functions in the molecule such as the amino group in the aminopropyl silane. It should be further noted that the silane triols have a strong tendency to polymerize in aqueous solution to a three dimensional siloxane polymers (25) and it is a macrocoating of this polymer that is left on the fiber and not some idealized monolayer of the triol. For most of the silanes the siloxane polymer is formed when the alcohol and water are driven off, although one vinylsilane ester, vinyltriethoxysilane, precipitated the siloxane from solution immediately upon hydrolysis. The silanes used to form the coatings give clear hydrolysate solutions which by viscosity measurements showed no evidence of polymeric species. However, as the solutions were allowed to evaporate they became increasingly viscous, finally yielding a clear, water-insoluble resin. This viscous material was observed on the test fibers within a few minutes after emergence from the treating solution and it became progressively more hydrophobic as the film dried. An alternate method for applying silane finishes is to treat the fabric with the ester dissolved in toluene or xylene, allow the solvent to evaporate and then to hydrolyze the silane residue in situ by immersion in water. This procedure leaves a coating that is 1% to 2% of the glass weight (2). More recently silane compounds have been used as additives in the resin in amounts up to 5%. Preliminary experiments here indicate that these additives do not improve resin wettability of the glass.

The quantity of coating that was found on the glass filaments is sufficiently large that the possible effect of this material on the composite cannot be ignored. The HTS-finish, for example, amounted to 1% of the weight of glass so that in a typical composite where the glass/resin ratio is about 4 to 1 the coating would represent more than 5% of the resin content. The presence of this amount of additive must have some affect on the mechanical properties of the resin but the possible consequences of this fact appear to have been ignored. The silane coatings are also present in sufficient amount to affect resin properties. However, due to the poor solubility of the siloxane polymers in epoxy resins, these finishes would remain near the glass/resin interfacial region. In this connection it has been proposed that an importaht function of the finishes on the glass fibers is to provide a deformable layer for stress relief in the interfacial region (26). Internal stress of considerable magnitude can arise near the glass/resin interface as a result of differences in the thermal coefficient of expansion of the glass and the resin. Proponents of the deformable layer theory suggest that in order to achieve sufficient stress relief the finish must reduce the tensile modulus of the resin in a layer about 400A thick around the glass fiber. It has been suggested (27) that finishing agents capable of relieving this internal stress do so by promoting adsorption of the amine curing agent at the glass/resin interface. The excess amine would of course reduce the modulus of the resin.

However, it is not necessary to assume an adsorption phenomena. A 1% coating evenly distributed over a fiber of 0.0036-inch diameter represents a layer 400A thick and the loading of most commercial finishing agents is usually in excess of 1%. Therefore, the required deformable layer will be established by the coating material itself provided that it has the necessary elastic properties to relieve internal stress or that it can act as a plasticiser in the resin and provided further that it is not completely dissipated into the resin before the latter hardens.

FUTURE WORK

This research has served to emphasize that an important source of weakness in filament-wound composites is the presence of voids due to air entrapment during the winding operation. It was therefore decided to construct a pilot plant winding apparatus that would fabricate nearly void-free composites and to base the design of this apparatus on the observation made here of the impregnation process. Although this engineering study will not be undertaken as part of this surface chemical investigation, it will require that work continue on the surface chemical characterization of specific commercial glass-epoxy systems and that an experimental study of the variables affecting the impregnation process be started.

The fundamental surface chemical investigation will continue work on improving the wetting of glass yarn by epoxy liquids and will explore experimental approaches to the study of glass-resin adhesion. In connection with the problem of improving wetting, it is worth noting that the failure of the fluoroepoxy resin and the fluorochemical-epoxy additive systems to spread on the glass does not exclude the possibility that zero contact angles can be achieved by such means. It is entirely possible that by a judicious selection of chemical structure the anomalous spreading behavior can be avoided. Therefore, a study will be made of the wetting behavior of fluorochemicals on various polymer substrates as a function of the chemical constitution of both the wetting liquid and the solid surface. In connection with the study of glass-resin adhesion, an experimental procedure will be sought which will give fundamental information on the glass-resin bond and quantitative data helpful in understanding the mechanical properties of the composite material.

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