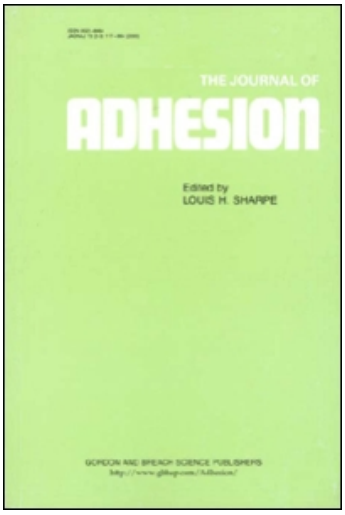


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Mechanical Requirements of the Fiber-Matrix Interface

Lawrence J. Broutman

To cite this Article Broutman, Lawrence J.(1970) 'Mechanical Requirements of the Fiber-Matrix Interface', The Journal of Adhesion, 2: 3, 147 — 160
To link to this Article: DOI: 10.1080/0021846708544590
URL: http://dx.doi.org/10.1080/0021846708544590

Mechanical Requirements of the Fiber-Matrix Interface

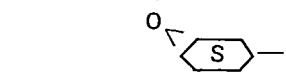
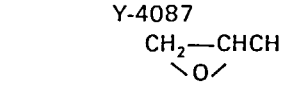
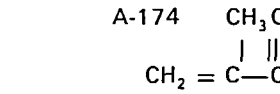
LAWRENCE J. BROUTMAN
Illinois Institute of Technology, Chicago, Illinois

INTRODUCTION

THE GREAT STRENGTH enhancement and resistance to fracture which occurs when one combines high strength fibers with a low strength, low modulus polymer matrix is well known. The high strength and toughness of the resulting composite material, to a great extent, is dependent upon the many polymer glass interfaces which exist and their ability to deflect cracks propagating normal to them. The presence of these large number of interfaces, however, results in problems which may partially overcome the advantage of their existence. Sufficient adhesive strength must be developed at every point along the polymer-fiber interface so that the maximum stress can be transferred from the polymer matrix to the fiber reinforcement. The critical fiber length or length of fiber required to achieve this maximum stress is thus dependent upon the interfacial strength. A void or an air pocket existing at the interface will cause a stress concentration regardless of the stress state; in addition, this unsupported length of fiber (i.e. the length of the void parallel to the fiber axis) will be subjected to buckling when compressive stresses exist in the fiber. A poorly bonded area at the interface will cause rupture of the interface at very low stresses and the resulting discontinuity will act as a stress concentration.

The importance of the coupling agents which serve as an intermediate layer between the matrix and the reinforcement and can be applied directly to the reinforcement surface or as an integral blend with the matrix has been amply demonstrated by many investigators.[1-7] Some of the strength increases which have been observed in glass fiber reinforced plastics are summarized in Table 1. This represents only a small portion of the data which has been accumulated but is sufficient to demonstrate the effectiveness of a coupling agent and the specific nature of its enhancement with a given polymer matrix. Significant improvements have been made in the permanence properties (wet strength) of glass reinforced plastics (Table 1) with over 200 percent enhancement occurring in some cases. This great enhancement causes most attention to be focused on the permanence properties. However, the dry flexural strength also appears to be increased by as much as 43 percent in one case (Table 1). This illustrates the important influence of the glass-polymer interface on the failure strength of the composite material under certain loading conditions, in this case flexural loading. Tensile strength and compressive strength can also be increased by nearly 100 percent for

Table 1.[2] Effectiveness of a Coupling Agent in Glass Reinforced Plastics

Material	Flexural Strength (10^3 psi) Dry	Flexural Strength (10^3 psi) Wet (8 hr. Boil)	Per Cent Improvement Dry	Per Cent Improvement Wet (8 hr. Boil)
Glass Cloth (181) Reinforced Polyester Resins (Paraplex—P43)				
Control	61	23	—	—
Y-4086* 	71	58	16	152
Y-4087 	76	58	24	152
A-172 $CH_2 = CHSi(OCH_2CH_2OCH_3)_3$	69	61	13	165
A-174 	87	79	43	243
Glass Cloth (181) Reinforced Epoxy (Epon 828) Resins				
Control	78	29**	—	—
A-1100 $NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$	92	67	18	130
Y-4086	81	51	4	76
Y-4087	97	60	24	107
Y-2967 $(HOCH_2CH_2)_2NCH_2(CH_2)_2Si(OC_2H_5)_3$	87	55	12	90

*Union Carbide Identification Numbers

**72-hour Boil Used for Epoxy Resins

polyester laminates with silane finishes.[4] In order to account for this enhancement in physical properties the following coupling agent mechanisms have been proposed: (1) coupling agents increase adhesive strength of the glass-polymer interface, (2) coupling agent provides a flexible, low modulus layer at the interface and (3) coupling agent promotes better wetting between the polymer matrix and reinforcement surface or reduces voids at interface by displacing the air by itself especially between close packed fibers.[8]

The data obtained from actual composites to demonstrate the effect of interfacial changes must be carefully interpreted. In the preparation of a glass fiber reinforced plastic composite, in order to evaluate only interfacial changes, all other material and process variables should remain constant. This includes, resin content, void content and distribution, fiber spacing and alignment, glass strength, etc. Thus, measuring the flexural strength for

composites prepared with various coupling agents will only lead to proper conclusions when the other variables remain constant, particularly the fiber strength which can easily be changed by the application of various coupling agents and surface treatments.

The interfacial regions in the composite are very critical because of large stress concentrations which exist when the composite is subjected to external loads or temperature changes. Cracks can be initiated from the interface, as shown in Fig. 1, particularly when the filaments are close together or in contact. The interfacial strength or fracture toughness will not only determine if cracks will be initiated but also whether they will continue to propagate along the interface or branch into the matrix.

Figure 1. Crack initiation where filaments come into contact. (500x) Specimen was loaded to 80 percent of compressive strength for 16 hours.

MEASUREMENT OF GLASS-POLYMER JOINT STRENGTHS

The test speciments which have been thus far employed to determine glass-resin joint strengths can be separated into two kinds: (1) flat plate specimens and (2) rod or fiber bond strength specimens. The flat plate specimens typically consist of either two glass plates as adherends with a polymer as the adhesive or a polymer bonded directly to only one plate (the polymer then acts as an adherend).[9-11] They are thought to possess the following advantages: (1) easy to prepare, (2) easy to characterize and prepare glass surfaces, (3) easy to observe bond failure and characterize failure mode. The fiber or rod bond strength specimens usually consist of a single embedded fiber or partially embedded rod in a polymer matrix which is failed by loading the resin matrix in the first case and loading the rod in the latter case. The proponents of this method propose the following advantages: (1) geometrically this is more similar to actual glass fiber reinforced composite, (2) residual stresses produced in specimen due to resin curing are similar to those in actual composite, and (3) failure initiation is more realistic.

SINGLE FILAMENT PULL-OUT TESTS

Shear and tensile joint strengths have been measured with both the flat plate specimens and the rod or fiber specimens. Glass rod specimens have been used to measure the shear strength of a joint by pulling or pushing a rod through a resin disc cast around a portion of the rod[2]. The glass rods varied from 1 to 4mm in diameter. The load-displacement curve resulting from such a test on these rod-disc specimens is shown in Fig. 2. The bond strength is

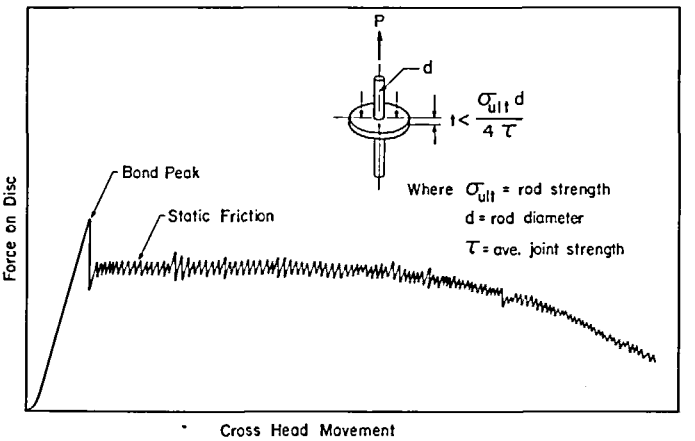


Figure 2. Typical load-displacement curve for rod-disc joint strength specimen (Ref. 12).

determined from the bond peak and the bond surface area between the glass rod and polymer disc. The relationship is as follows:

$$\tau = \frac{P_m}{2\pi r l} = \frac{\sigma_m r}{2l} \tag{1}$$

where:
- τ = average shear strength of joint
- P_m = maximum load applied to fiber or rod
- r = radius of rod
- l = embedded rod length
- σ_m = maximum stress applied to rod

The embedded rod length is influenced by the rod strength so that the maximum embedded length which can be used is determined by

$$y = \frac{\sigma_{ult} r}{2\tau} \tag{2}$$

where σ_{ult} = rod ultimate strength. If the embedded length is greater than that predicted by eq. 2 the rod will fail in tension before pull-out occurs. Thus for a 4 mil boron filament whose strength is 300,000 psi, an embedded length of only .030 inch can be used assuming the interfacial shear strength is 10,000 psi. A common experimental technique is to measure the failure load as a function of embedded rod length and to then determine the joint shear

strength from eq. 1 by plotting P_m vs. l and calculating the slope of this straight line relationship. The joint shear strength determined from eq. 1 is only an average value since stress concentrations exist at the rod ends or exit points from the surrounding matrix disc and the equation assumes a uniform distribution of shear stress. Average shear strength values for glass rods in a polyester matrix are shown in Table 2.

Table 2. Typical Values of Polymer-Glass Joint Strengths

Test Method	*Material Types*	*Glass Treatment*	*Failure Mode*	*Bond Strength (psi)*
Rod-Disc (Push Test)	Polyester (Paraplex P43)	Acetone cleaned	shear	605
Rod-Disc (Push Test)	Polyester (Paraplex P43)	Vinyltrichloro-silane	shear	680
Trapezoidal Fiber	Polyester (Paraplex P43)	Acetone cleaned	shear	1000
Trapezoidal Fiber	Epoxy (Epon 828)	Acetone cleaned	shear	3000-3500
Curved Neck Fiber	Polyester (Selectron 5026) and E glass	Heat cleaned	tension	750
Curved Neck Fiber	Polyester (Selectron 5026) and E glass	2% A172 in polymer	tension	1220
Curved Neck Fiber	Epoxy (Epon 828)	Toluene cleaned	tension	>1540

In addition to the bond peak shown in Fig. 2, a considerable friction force exists after initial bond breakage which allows the bond to carry considerable loads for large displacements. The friction force is due to the large residual curing pressures resulting from the polymer shinkage. The shrinkage causes a radial compressive stress to act normal to the glass surface which serves to increase the bond strength of the interface. There has always been considerable debate concerning the contribution this friction bond makes to the total bond strength of the joint and whether this mechanical bond would be sufficient to form an interface capable of transmitting full load into the fiber in the composite.

Joint Shear Strengths for Metal and Boron Fibers Using Filament Pull Out Test

The joint shear strength between 10 mil diameter steel filaments and epoxy, polyethylene and polypropylene resins was investigated by McGarry and Marshall[14]. A 1 inch diameter resin disc was cast around the filament and shear failure was obtained by directly loading the filament. The thickness of

Table 3. Interfacial Shear Strength by Fiber Pull Out Test

Fiber	*Resin*	*Fiber Diameter (inches)*	*Average Shear Strength (psi)*
Brass Plated Steel	Epoxy	.011	3196
Phoscoat Stel	Epoxy	.010	3169
Phoscoat Steel	Polyethylene	.010	125
Stainless Steel	Purified Polyethylene	.0099	814
Boron (Untreated)	Epoxy	.004	4150
Boron (Trichloroethylene wash)	Epoxy	.004	5221

the disc depended on the strength of the wire and the type of resin used but was approximately ¼" for the epoxy resins and 1" for the polyolefins. The shear strength was investigated for various wire cleaning methods and this was shown to be an important variable. Some of the joint strengths obtained are shown in Table 3.

Investigators at Avco[15] have used this technique to study joint strengths between 4 mil boron filaments and epoxy resins in order to determine the influence of cleaning methods in search for a good surface treatment. A resin block was cast around one end of the fiber and it was noted that the filament immersion depth must not be greater than 30 mils to insure pullout rather than filament rupture. A few of the results are also included in Table 3. However, it was concluded that this technique was unreliable due to the inaccuracy of measuring embedded fiber depths, alignment of the fiber and end effects.

Measurement of Tensile Debonding and Shear Debonding Using Single Filament Test Specimens

In order to simulate the glass reinforced plastic composite, completely embedded single filament or fiber bond strength specimens were developed.[8, 13] Two types of specimens were initially investigated: (1) a trapezoidal specimen, and (2) a curved neck specimen. The trapezoidal specimen was designed to fail the interface in shear when axially loaded in compression since a sharply changing axial stress was produced in the specimen by the sloping sides. This continuous change of axial stress results in a shear stress at the interface which can be easily calculated.[13] The curved neck specimen was designed so that a tensile debonding failure would result rather than a shear failure. A compressive axial load on this specimen causes a radial expansion governed by Poisson's ratio of the polymer. Since Poisson's ratio of the polymer is greater than that of the glass, it expands transversely more than the glass and an interfacial tensile

stress is created to preserve continuity. The resulting interfacial tension can be calculated from the following:

$$S = \text{Debonding Stress} = -\frac{\sigma_m(\mu_m - \mu_f)E_f}{(1+\mu_m)E_f + (1-\mu_f-2\mu_f^2)E_m} \quad (3)$$

where σ_m = axial stress on minimum section, μ = Poission's ratio, E = elastic modulus, and subscripts f, m refer to fiber and matrix. Bond failures produced by this specimen are then similar to those produced by cross-lap tensile tests on flat plates while shear bond failures produced in the trapezoidal fiber specimen are analogous to failures produced by flat plate lap joint specimens. Bond failure in the fiber test specimens can be observed visually as a definite separation at the fiber polymer interface beginning at the neck or minimum cross section area where the stress is highest. The curved neck test specimen is shown in Fig. 3. Representative values of tensile debonding strengths for 10 mil glass filaments have been included in Table 2 and also shear debonding strengths obtained from the trapezoidal specimen have been included.

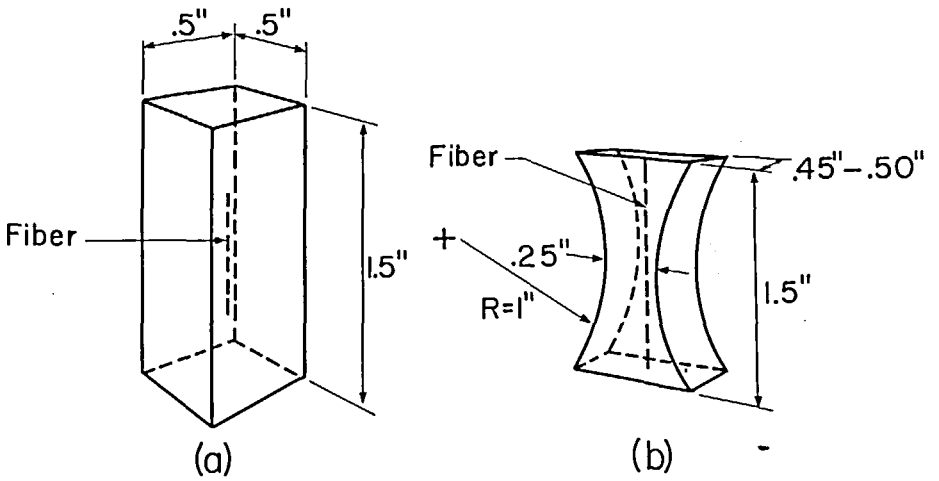


Figure 3. Single fiber specimens for interface shear and tensile strengths.

Investigators at Arthur D. Little, Inc.[16] have used the curved neck specimen to evaluate the effect of several different surface finishes on interfacial strength using 10 mil "E" glass filaments and an epoxy resin matrix. The results are indicated in Table 4. The first finish shown is actually used as a release agent and the poor bond obtained is evident.

An alternative method of data analysis for this curved neck specimen was suggested by Mozzo and Chabord.[17] Rather than using the maximum load or axial stress in the specimen at the initiation of bond failure, they have used the work done or area under the force-deflection curve obtained for the specimen up till bond failure. Thus, if resin matrices are used which display much non-linear elastic behavior the data can be more properly interpreted. They have used this technique with polyester resin matrices and glass

Table 4. Interfacial Strength Data for Curved Neck Specimen

Finish	Axial Specimen Stress at Debonding (psi)	Remarks
1. Silicone (Dow Corning R-671)	7,400	Partially debonded prior to test.
2. Epoxy (Ciba Araldite 6005 Resin + 10% Triethylene tetramine)	No Debonding	Finish was not cured prior to embedding in specimen.
3. Same as No. 2	18,000	Finish oven-cured for one hour at 100°C prior to embedding.
4. Dow Corning Buton-Silane	No Debonding	
5. Urethane (ADL Prepn)	18,000	Partially debonded.
6. Dow Corning Z-6020 (n-Trimethoxysilyl-propyl ethylenediamine)	15,700	Some debonded areas prior to testing.
7. Ciba Araldite 6005 with 20% organic ammonium silicate II 6 (Philadelphia Quartz Co.) 20 pts.	18,000	
8. Dow Corning Oxiron Silane	10,000	

Note: All specimens were embedded in a matrix consisting of 100 parts ARALDITE 6005 and 10 parts TRIETHYLENE TETRAMINE and cured at room temperature. Ultimate compressive failure of the specimens occurred at about 18,000 psi. Where no debonding stress is noted, bond was unaffected at specimen failure. The debonding stress data is based on an average of 10 individual determinations.

filaments treated to change the surface energy of the filament. They have found that for a given surface energy the adhesion will depend on the conditions in which the bond was made. For example if an untouched "E" glass filament was allowed to stand for 4 hours at 25°C in a water vapor saturated atmosphere, the adhesion was reduced by approximately 20 per cent.

The curved neck specimen has recently been used to measure the tensile debonding strength between 4 mil boron filaments and epoxy resins. The failures initiated at the center of the specimen where the stress is a maximum and only propagated a short distance. Therefore it was certain that failure did not initiate from the specimen ends. The maximum load was recorded and used to calculate the debonding stress from eq. 3. Some of the data obtained for debonding stress are represented as a cumulative probability curve and shown in Figure 4. The epoxy resin used in these experiments was Epon 828 cured with metaphenylenediamine. The cure schedule was 150° F for 2 hours

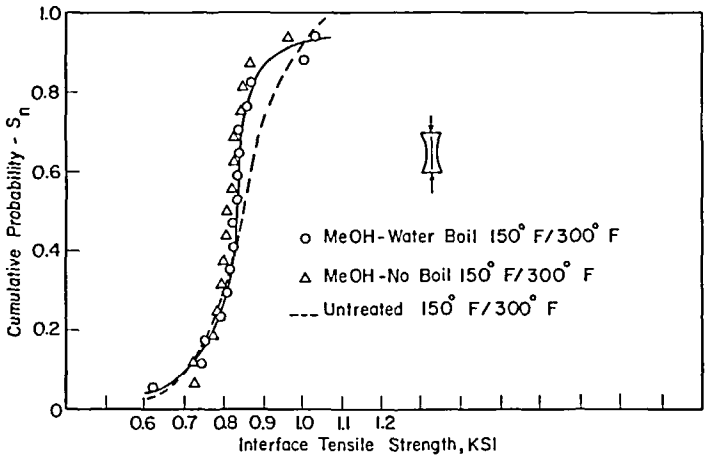


Figure 4. Statistical distribution of interface tensile strength methanol treated filament—effect of exposure.

with the casting in the mold, followed by a post cure of 4 hours at 300° F with the casting out of the mold. The data in Fig. 4 compares the interfacial tensile strength of untreated filaments to filaments washed in methanol at 65°C for 1 hour prior to their embedment. There is virtually no difference in interfacial strengths. Also are the results for specimens which had been boiled in water and there appears to be no loss in interfacial strength. However, it is doubtful that the water could have penetrated to interfacial regions at the center of the sample.

A new specimen for measuring shear debonding strengths was developed in the studies concerning interfacial strengths of boron filaments.[18] Because of the difficulties of performing a pull-out test with the brittle 4 mil boron filaments it was decided to use the specimen shown in Fig. 3, a rectangular column of resin with a single embedded filament, $1/2$ inch in length. The specimen is loaded in compression and stress is thus transferred into the embedded fiber by interfacial shear stresses at the fiber ends. The load is increased until interfacial failures are observed at the fiber ends.

Specimens are prepared in brass molds measuring 0.5x0.5x12 inches in length. The fibers are placed in the resin by first filling the mold half full and partially curing the resin until the surface can easily support the fiber. The individual fibers are then placed in the molds and carefully aligned with the mold surfaces. The remainder of the mold is filled with resin and the entire casting is then cured and post cured. The casting is cut into individual specimens and, of course, the fibers are parallel to the long axis and suspended in the center of the casting.

The specimens were compression loaded in an Instron and a deflection rate of 0.01 in/min was used. The specimen was illuminated with a microscope lamp so that the fractured interface appeared as a highly reflective region. Interface fracture in these specimens does not occur at one discrete load value. Furthermore the interfaces at both ends of the fiber do not fail

simultaneously. The bond failure, after initiating, grows in a stick-slip fashion from the fiber end towards the center of the fiber. At some critical length and axial load value there is an instability and it makes a large jump which has been taken as the failure load of the interface. Two failure loads are recorded, one for each end of the fiber. The difference in shape of the fiber ends is most likely responsible for the differing failure loads since the stress concentrations at the fiber ends are influenced by the shape of the fiber end.

Many studies, both theoretical and experimental have been conducted to predict the stresses surrounding a single fiber embedded in a matrix[20-26]. Some of the results for the shear stress concentration at the interface are presented in Fig. 5 taken from Ref. 21. Since there is not good agreement between the various results and since the stress distribution will be dependent on the exact geometry of the filament end and matrix properties the following relation was used in the shear debonding studies.

$$\tau_{max} = 2.5\,\sigma_{ave} \tag{4}$$

where τ_{max} = maximum shear stress at fiber ends and σ_{ave} = average axial stress in specimen. This was a good compromise particularly when the end geometry of the fibers used for the debonding test was not precisely known.

The data for shear debonding strengths for surface treated boron filaments in an epoxy resin matrix are shown in Fig. 6. Each point shown is the average fracture load for each specimen (i.e., the average of the fracture loads for each end). It can be seen that post curing the resin does not appear to alter the shear debonding strength and that the hot methanol wash of the filament before embedment appears to lower the debonding strength.

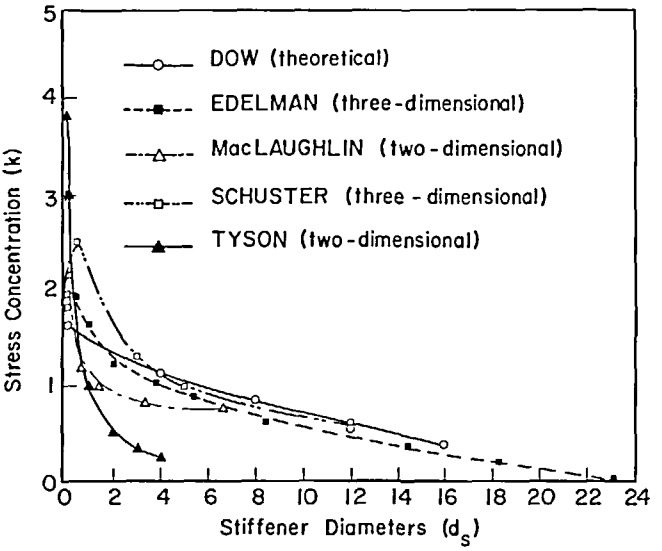


Figure 5. Shear stress along the matrix-stiffener interface as determined by five different investigators. Square ended stiffener under tensile loading.

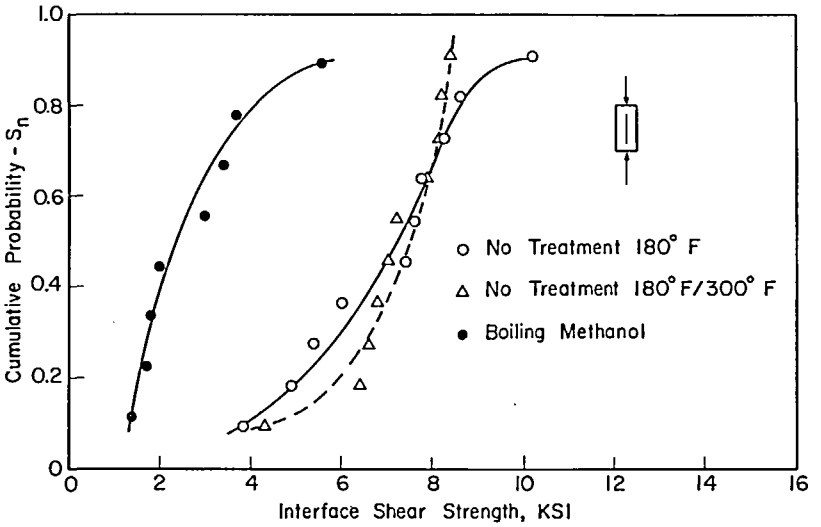


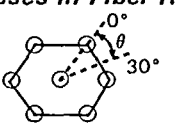
Figure 6. Statistical distribution of interface shear strength. Effect of filament treatment and resin cure.

INTERFACIAL STRESSES

In order to determine the mechanical requirements of the fiber-resin interface, the stresses of the interface must be calculated and compared to the interfacial strengths. The total stresses at the interface which are a combination of the thermal residual stresses, curing shrinkage stresses and stresses created by external loading of the composite must be considered. The residual stresses are dependent upon the fiber packing, fiber volume percent, the modulus ratio between fiber and matrix and, of course, the resin cure shrinkage, curing temperature and differential expansion coefficients between fiber and matrix. The interfacial stresses due to external loading can be altered by varying the fiber array or packing, fiber volume percent, elastic constants of constituents and direction of stress with respect to the fiber direction.

Approximate calculations can be made in order to obtain the relation between interfacial stresses and strengths. For example, consider a composite with the fibers aligned in one direction. Two loading cases will be considered; namely, loading in the fiber direction and loading normal to the fibers or in the transverse direction since this places the most demands on the interface. In order to simplify this comparision it will be assumed that the fiber volume percent is 65 to 70 percent and that E_f/E_m is equal to approximately 25 or 150 representing glass reinforced polymers and boron reinforced polymers. Haener[27] has calculated the shrinkage stresses at the interface assuming an hexagonal array of fibers and a resin shrinkage of 1 percent. He has also calculated the stress due to external loading for the hexagonally packed filaments and the results are summarized in Table 5. It has been assumed that a stress of 100,000 psi is applied to the composite so the fiber stress is

Table 5. Interfacial Stresses in Fiber Reinforced Polymers



Shrinkage Stresses (Resin Shrinkage = 1%)

V_f	E_f/E_m	σ_r (psi) $\theta = 0°$	$\theta = 30°$	(σ_θ) max (psi) $\theta = 30°$	$(\tau_{r\theta})$ max (psi)
.64	150	−2000	+ 500	5000	1000
	26	−2500	+ 500	5000	1000
.70	150	−2000	+1000	6000	1000
	26	−3000	+1000	6000	1000

Stresses Due to External Tensile Stress ($\bar{\sigma}$ = 100,000 psi)

V_f	E_f/E_m	σ_r (psi) 0°	30°	(σ_θ) max (psi) $\theta = 30°$	$(\tau_{r\theta})_{max}$ (psi)
.64	150	− 700	400	7500	1500
	26	−1000	1000	7500	2000
.70	150	−1200	1000	9000	2500
	26	−1300	1300	9000	2200

Total Stresses

V_f	E_f/E_m	σ_r (psi) $\theta = 0°$	$\theta = 30°$	(σ_θ) max (psi) $\theta = 30°$	$(\tau_{r\theta})$ max (psi)
.64	150	−2700	900	12,500	2500
	26	−3500	1500	12,500	3000
.70	150	−3200	2000	15,000	3500
	26	−4300	2300	15,000	3200

157,000 psi and 143,000 for the cases shown of V_f = .64 and .70, respectively. This assumes the fiber carries all of the load. This will be less than the strength of the composite but it is interesting to consider the interfacial stresses at this stress level which is less than the strength.

The radial stress at the interface due to resin shrinkage is dependent upon the angle θ as shown in Table 5. For the fiber volume fractions considered a radial tensile stress always exists at the interface. The hoop stress is a maximum at θ=30° and is quite large. The internal stresses created by the external load in the fiber direction must be added to the residual stresses. A radial tensile stress component exists which is a maximum at θ = 30° so that the total radial tensile stress can become large. This radial tensile stress increases as V_f increases and as E_f/E_m decreases so that radial bond failure is more likely with glass fiber reinforcement than for boron fiber reinforcement unless the interfacial strength is greater. If the external stress is compressive, the internal radial stresses created will change sign and tend to cancel the stresses due to resin shrinkage as will the hoop stresses. For the conditions shown in Table 5, a composite with a polyester resin as matrix should be subject to bond failure since the interfacial radial tensile strengths are less

than 2000 psi. An epoxy resin composite would not be subject to radial bond failure but the large values of the hoop stress might create matrix failure at the interface.

Interfacial fracture is most critical when the composite is loaded normal to the fiber direction or in the transverse direction. Adams *et al*[28] have calculated residual stresses and internal stress concentrations due to external loading for a square array of fibers. They have calculated that a maximum radial compressive stress at the interface of approximately 5000psi would exist for a composite with $V_f = 60$ percent, $E_f/E_m = 25$ and representative thermal expansion coefficients. The maximum stress concentration factor for the above parameters is approximately 1.8, thus an applied stress of 4000 psi would produce a maximum tensile stress at the interface of 7200 psi. The net stress is therefore 2200 psi. The interfacial strength is thus quite instrumental in determining the transverse strength of the composite. It should also be noted that the residual stresses at the interface greatly aid in increasing the composite strength.

For discontinuous fiber composites such as glass reinforced thermoplastics the interface must be able to transfer the stress from matrix to fiber as indicated by eqs. 1 and 2. When the fibers are short the matrix will either yield at the interface if it is a ductile thermoplastic or fail in a brittle fashion if it is a more brittle thermosetting resin. Obviously, the stress transfer capability of the matrix and interface are key to the properties of a composite material. A chemical bond is not required for stress transfer since the residual compressive stresses acting normal to the interface will allow stress transfer to occur by the frictional force created at the interface.

In addition to considering the stresses created at the interface and the interfacial strength, the fracture toughness of the interface should be considered. The interface can deflect or stop propagating cracks or an approaching crack can debond the interface. An understanding of the phenomenom is lacking and this is an area where further research is needed.

SUMMARY

The various methods for measuring shear and tensile joint strengths between fibers or rods and a polymer matrix have been discussed. The pull-out test is useful with fibers at least 10 mils in diameter providing the strength is high so that long embedment lengths can be used. For smaller diameter fibers the tensile debonding or shear debonding methods should be utilized depending on which mode of failure is of most interest. The tensile debonding test is more reproducible than the shear debonding test and bond failures are easier to observe.

It has been shown that the interface is subjected to large stresses as a result of the composite fabrication and external loading. Even when the composite is loaded parallel to the fibers, the stresses created can exceed the interfacial strength.

REFERENCES

1. H. A. Clark, and E. P. Plueddemann, *Modern Plastics,* 133 (June 1963).
2. S. Sterman, and J. G. Marsden, "The Newer Silane Coupling Agents," Regional Technical Conference of the Society of Plastic Engineers, Inc., Cleveland, Oct. 1, 1963, p. 67.
3. N. M. Trivisionno, and L. H. Lee, "The Effect of Glass Finishing Agents on the Strength of Polyester-Fiberglass Laminates," *Proc. 12th SPI Reinforced Plastics Division,* Feb., 1957, Section 16-B.
4. K. Ito, "Evaluation of Surface Treatment of Glass Fiber in Fabric-Reinforced Plastics," *J. Poly. Sci.* **45,** 155 (1960).
5. B. M. Vanderbilt, "Effectiveness of Coupling Agents in Glass-Reinforced Plastics," *Modern Plastics* 125 (Sept. 1959).
6. S. Sterman, and H. B. Bradley, "A New Interpretation of the Glass Coupling Agent Surface Through Use of Electron Microscopy," *Proc. 16th SPI Reinforced Plastics Division,* Feb., 1961, Section 8-D.
7. E. P. Plueddemann, *et al,* "Evaluation of New Silane Coupling Agents for Glass Fiber Reinforced Plastics," *Proc. 17th SPI Reinforced Plastics Division,* Feb., 1962, Section 14-A.
8. L. J. Broutman, "Glass-Resin Joint Strengths and Their Effect on Failure Mechanisms in Reinforced Plastics," *Polymer Engineering and Science* (in press), presented at SPE Retec *Reinforced Plastics '65* Seattle, Washington, July 14, 1965.
9. J. A. Laird, and F. W. Nelson, "Glass Surface Chemistry Relating to the Glass-Finish-Resin Interface," *Proc. 19th SPI Reinforced Plastics Division,* Feb., 1964, Section 11-C.
10. N. M. Trivissonno, L. H. Lee, and S. M. Skinner, *Ind. Eng. Chem.* **50,** 912 (1958).
11. T. D. Schlabach, and S. Klosowski, "Compression Shear Evaluation of Glass-Resin Joints," *Proc. 20th SPI Reinforced Plastics Division,* Feb., 1965, Section 19-C.
12. "Bond Studies in Glass Reinforced Plastics," Progress Report MCA-MIT Plastics Research Project, Plastics Research Laboratory, Mass. Inst. of Tech., Oct. 1, 1957.
13. R. D. Mooney, and F. J. McGarry, "Resin-Glass Bond Study," *Proc. 14th SPI Reinforced Plastics Division,* Feb., 1959, Section 12-E.
14. F. J. McGarry and D. W. Marshall, *Research on Wire Wound Composite Materials,* ASTM Special Technical Publication No. 327, 1963.
15. B. V. Coplan, R. S. Timmons, *et al,* "Research on Boron Filaments and Composites" Technical Report AFML-TR-65-312, Sept. 1965. (Avco Corporation)
16. J. Shulman, S. L. Kaplan and H. P. Buetner, "Development of Protective Finishes for Glass Monofilaments," NASA CR-54774, March 1966 (Arthur D. Little, Inc.)
17. G. Mozzo and R. Chabord, "Contribution to the Study of Glass-Resin Adhesion" Proceedings of 23rd Annual Technical Conference, Reinforced Plastics/Composites Division, SPI, Feb., 1968.
18. L. J. Broutman, K. Gutfreund and E. H. Jaffe, "Interfacial Investigations of Boron Fiber-Reinforced Plastics," SAMPE Proceedings, Vol. 10, 1966.
19. K. Gutfreund and D. Kutscha, "Interfacial Investigations in Advanced Fiber Reinforced Plastics" AFML-TR-67-275, Sept. 1967 (IIT Research Institute).
20. A. S. Carrara and F. J. McGarry, "The Effect of Fiber End Geometry on the Stresses in a Resin-Glass Composite," Dept. of Civil Engineering, MIT, Research Report R67-43, Sept. 1967.
21. W. E. Edelman, Jr., and J. H. Dahlke, "Photomechanics of Stress Transfer Mechanisms in Composite Materials," SESA Annual Meeting, Nov. 1967.
22. T. F. MacLaughlin, *Experimental Mechanics* **6,** 49 (1966).
23. D. M. Schuster and E. Scala, *Transactions of AIME* **230,** 1635 (1964).
24. W. R. Tyson and G. J. Davies, *Brit. J. App. Phys.* **16,** 199 (1965).
25. N. F. Dow, "Study of Stresses Near a Discontinuity in a Filament Reinforced Composite Metal," General Electric Co., Report R63SD61, 1963.
26. J. M. Allison and L. C. Holloway, *Brit. J. App. Phys.* **18** (1967).
27. J. Haener *et al,* "Investigation of Micromechanical Behavior of Fiber Reinforced Plastics", USAAVLABS Technical Report 67-66, Feb. 1968.
28. D. Adams, D. Doner, and R. Thomas, "Mechanical Behavior of Fiber Reinforced Composite Materials", Technical Report AFML-TR-67-96, May, 1967.