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HIGH STRENGTH GLASS FIBERS DEVELOPMENT PROGRAM
Task 2

May 20, 1963

Department of the Navy
Director, Special Projects (SPN)

Contract NOw 61-0641-c (FBM)

Final Report

Project Engineers	D.L. Hollinger H.T. Plant R.F. Mulvey
Project Manager	T.J. Jordan
	Manufacturing Engineering Service General Electric Company Schenectady, New York
Report Submitted by:	Flight Propulsion Laboratory Department General Electric Company Evendale, Ohio

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TABLE OF CONTENTS

TABLE OF CONTENTS - (Cont'd.)

Figures

Tables

I. ABSTRACT

The influence of moisture on the effective strength of E-glass fibers, both as single monofilaments and when incorporated with epoxy resin into filament-wound ring structures, has been investigated. Humidity in the atmosphere surrounding the fiber was controlled during various periods in its history. Split ring tensile tests on the composites showed a definite advantage for the maintenance of dry surroundings throughout all processing steps. Furthermore, these indicated that the presence of moisture at the time of application of high stress is of much greater significance in determining strength than mere exposure to moisture during other periods. Thus, a stress-activated corrosion reaction was suspected to be causing large strength losses during the actual testing.

Work with single bare fibers of E-glass has served to verify the importance of this stress corrosive reaction. By conducting tensile tests at liquid nitrogen temperature (-196 °C), the reaction rate was reduced essentially to zero with a resulting change in average fiber strength from 507,000 psi at room temperature to 814,000 psi at -196 °C. At the low temperature, 25% of the fibers exceeded 900,000 psi and values as high as 974,000 psi were recorded.

In order to separate the effect of moisture from any possible effect of temperature alone, bare fibers were tested submerged in a very powerful desiccant solution, lithium aluminum hydride in ether,

at room temperature. Strength values were obtained significantly above the normal room temperature range, although not equal to the results at low temperature. The hydride test at present entails considerable difficulty with grips and possible damage to the fiber from suspended solid material in the solution. Refinements are suggested.

II. INTRODUCTION

Task 2 of this program was a continuation of experimental work aiming to discover the reasons for the less than satisfactory strength efficiency obtained from fiberglass in commercial filament wound structures. The results of the initial phase of this work (herein referred to as Task 1) are to be found in the final report dated May 16, 1962, on High Strength Glass Fibers Development Program, Contract NOw61-0641-c (FBM).

The approach in Task 2, as in Task 1, was to consider possible ways to minimize strength losses from corrosion by water vapor and from mechanical damage due to fiber-on-fiber abrasion. In order to provide continuity with prior work, all tests were made with E-glass, even though higher strength glasses were becoming available for filament winding as a result of recent developments by the major fiberglass producers.

III. SCOPE OF CONTRACT

The original work statement followed the lines of endeavor started in Task 1, wherein the effects of experimental variables on glass fiber strength were to be judged from the performance of composite rings in tensile tests. Thus, it was required that E-glass monofilament be produced in a single orifice melting crucible, drawn and coated with various protective resin combinations in controlled humidity atmospheres, and finally wound into rings with epoxy resin binder. Included in this schedule of work was an investigation of the protection afforded to the glass fiber by a thin resin coating, which was cured to the solid state before the fiber became subjected to bearing pressures and/or abrasion during winding, curing, and testing of ring structures. The capability of the protective resin to reduce stress concentration on the surface of fibers in ring structures, under load, was to be studied by comparing the benefits of coatings with low modulus of elasticity and those from coatings which are more rigid. In each comparison, the bonding resin used in winding the test rings, was to remain constant. Also, the effects of coupling agents and type of bonding resin were to be checked, again from results of composite ring tests.

As soon as a fair amount of data on ring tests began to accumulate, we became aware that there were at least as many variables involved in the construction of rings, even from monofilament glass, which could influence the measured strength of the glass, as there were in the fiber drawing process. Furthermore, we soon became convinced that it was important to consider the total exposure history of the glass to moisture and other influences rather than simply the exposure which occurred immediately after formation of the fiber.

At the Polaris R & D Conference in Wilmington, Delaware, in July 1962, the program sponsors' representative suggested that we devote at least a part of our effort to measuring tensile strength of single filaments, as affected by moisture or other processing conditions. In subsequent conversations, it was decided that our major work should be centered on single fiber measurements, in lieu of pursuing all aspects of the previously outlined ring test program to completion.

Accordingly, our Task 2 program has consisted of two principle categories of work:

1. Investigation of the effects of controlled humidity at various stages in the history of glass fiber upon the final glass stress level in composite rings.
2. Determination of the role of moisture in the strength of single bare fibers of E-glass.

Work on Task 2 of this contract was authorized in May 1962 and has continued through April 1963.

IV. EXPERIMENTAL

A. Composite Rings

1. Fiber Production

The glass melting furnace, which has been used in the production of all test rings and fiber made on this program, is shown in Fig. 1 as a cross-section, schematic drawing. The crucible in which the glass marbles are melted is a cylindrical vessel with a conical bottom and a short straight-sided nozzle - all made of 87% platinum, 13% rhodium. Dimensions of this crucible are 1-3/4" diameter x approximately 4" in over-all height. It is suspended from the top in the tubular furnace section. A cover of the same platinum-rhodium alloy fits into the top of the crucible to prevent contamination from ceramic particles from the furnace insulation, dust, etc. Heating in the furnace is entirely by means of resistance coils of platinum-rhodium alloys. There are three separately controlled heating zones, the lowest of which is approximately level with the orifice from which the molten glass issues. Insulation in the furnace consists of various kinds of alumina - some of which were preformed, others cast in place. Temperature of the molten glass, near the orifice, is measured by a slender, well-type thermocouple of platinum and platinum-rhodium alloy, positioned as shown in Fig. 1. Temperatures at the bottom of the crucible and orifice were also monitored by an optical pyrometer.

2. Coating with Resins

A single resin-hardener combination was used for all rings tested on Task 2. This was Union-Carbide epoxy resin ERL-2256 with hardener ZZL-0820. Proportions were 27 parts by weight of hardener per 100 parts resin. Rings were cured overnight at 50-60°C, followed by 2 hours at 90°C, and 4 hours at 150°C. The bonding resin was applied to the newly formed fiber about 18" below the crucible outlet. At drawing speeds of 1250 ft. per min., the fiber was exposed to the atmosphere without resin protection for about .07 seconds. The coating applicator, with resin already flowing through it, was brought up to the moving fiber as soon as attachment to a winding mandrel had been accomplished.

3. Mandrels

Fig. 2 shows the type of split ring mandrel used for all monofilament composite rings in this program. In the background is the assembled ring as it appears when actually winding filament, while the separate parts are shown in the foreground. The two narrow rings, made of aluminum, are used as guides to help locate the ring edges when positioning the traverse mechanism. The two disk-shaped end pieces, also made of aluminum, are used to clamp the two halves of the split steel mandrel tightly together during ring winding and to mount the assembly to a motor shaft. These two center aluminum pieces must be removed before curing the rings at temperatures above 60°C in order to avoid stress in the ring generated by the larger thermal expansion of aluminum, compared to steel or the fiberglass ring itself.

4. Humidity Control

a. Room Temperature Tests

During drawing of the fibers, the atmosphere surrounding the newly formed monofilament between the crucible orifice and the resin applicator is either the normal unconditioned laboratory atmosphere, or else a low humidity air atmosphere provided artificially. In the latter case, the fiber is enclosed within a Pyrex tube, into which the dry air is fed continuously. Dew-point measurements on the atmosphere within the tube are taken by sampling at a point midway of its length. This setup is illustrated in Fig. 3.

Following the cure, the rings, on the mandrels, are placed in whatever atmospheric condition is specified for storage. In the case of "dry storage" this means they are kept in a desiccator, over silica gel. In "normal" storage, they are merely exposed to the laboratory atmosphere. Storage at 100% relative humidity is carried out in a desiccator, which contains a supply of liquid water, which is not in direct contact with the rings.

The atmosphere surrounding the rings during testing in the Instron machine has been designated either normal or dry. The "normal" is, again, the unconditioned laboratory atmosphere. For the "dry" tests, an enclosure of polyethylene was constructed around the grips of the Instron so that a mandrel could be mounted and tested within this enclosure. A supply of silica gel with extensive exposed surface was also contained within the enclosure at all times. Each ring mandrel was allowed to remain within the sealed enclosure for 1 hour prior to testing.

b. Composite Rings in Liquid Nitrogen

A set of four rings was made by our established procedure with E-glass monofilament and epoxy resin. The resin used was again Union Carbide ERL-2256 with hardener ZZL-0820. Immediately after completion of winding each of the first three rings, a fork of uncoated fibers was collected. This was done without altering drawing speed or changing other process conditions, except to remove the resin coater the moment before the fiber was taken. These fibers, then, were representative of the material in the rings with which they were associated. For purposes of identification, they were designated (and appear in Table 1) as follows:

9R1 = Fork No. 9 associated with Ring No. 1
10R2 = Fork No. 10 associated with Ring No. 2
11R3 = Fork No. 11 associated with Ring No. 3

No provision was made to reduce humidity during drawing and ring winding operations for this series. After curing, the four rings were stored in a desiccator over silica gel. The actual testing of these rings was conducted with the entire ring and split steel mandrel submerged in liquid nitrogen. A soaking period of about five minutes was allowed after complete submergence before cross-head motion was begun.

B. Single Fibers

1. Fiber Production

All E-glass fibers tested in this program were produced from our single hole platinum crucible. The glass batch was heated to 2400°F and held at or slightly above this temperature for at least two hours before fibers for test were collected. The actual drawing temperature, that is, the temperature at the orifice tip, was lower than the temperature in the body of the liquid, but was not determined with great accuracy. Optical pyrometer readings on the tip during drawing of fiber ranged from 2220°F to 2270°F.

Drawing speed was in the range of 1100-1300 ft. per min., which resulted in fiber diameters around .00040". This is approximately the size of filaments in commercially produced E-glass for reinforced plastics.

A Pyrex glass tube, two inches in diameter and six inches long, enclosed the fiber as it issued from the bottom of the furnace. This acted primarily to prevent drafts from moving the fiber out of alignment and was useful mainly during the start of winding.

When no composite rings were being made concurrently with the gathering of single fibers, the fiber was wound on a 12" diameter drum. When rings were also being made from the fiber, the winding apparatus was the 4" diameter split ring mandrel. In the latter case, fibers for test were always gathered immediately after the composite ring was completed. No process conditions were changed with the exception of the removal of the resin coater.

2. Fiber Gathering and Storage

A sample of fiber approximately three ft. long was obtained by first clamping the filament just above the winding drum to break it free, then severing it at a point about 10" below the crucible orifice. The upper end was weighted with a piece of cellophane tape, then the two ends were cautiously inverted so that the weighted end hung free and the fiber was straight and vertical. It was then a relatively simple matter to wind the fiber onto a fork, such as that shown in Fig. 4, with any desired spacing between the segments of the continuous fiber. Double-sided adhesive tape on the arms of the fork helped prevent slipping of the fiber segments.

Once wound, the forks were stored in closed containers in such a way that the fibers did not contact any object.

3. Method of Mounting Fibers for Tensile Test

For tensile tests at either room or low temperature, the fiber must be held in some sort of grips. It has become customary in this work to use sealing wax to fasten the fiber ends to the pulling mechanism. We were afraid that adhesion of the wax to the fixture and to the glass fiber might be poor at liquid nitrogen temperature. Therefore, we designed small stainless steel blocks to contain the wax and to provide gripping by wedge action in the event of adhesion failure.

Fig. 5 is a drawing of these blocks. The method of potting the fibers in wax by using the blocks, is indicated in the photograph of Fig. 6.

As the wax congealed in a set of blocks with a fiber in place, the fiber was severed from the gathering fork, and the assembly of two blocks with their suspended fiber was slid onto the arms of a transfer rack. As many as ten fibers can be accommodated on one rack. Fig. 7 shows five fibers in place on a transfer rack after potting with sealing wax.

4. Test Environments

Three distinctly different environments were used for single fiber tensile tests. The first was the normal laboratory atmosphere with uncontrolled humidity and temperature in the neighborhood of 75°F. The second environment was nitrogen vapor at -196°C. The third environment was a solution of lithium aluminum hydride in diethyl ether in which the fiber samples were completely immersed. In all cases, the fibers used were drawn in the normal laboratory atmosphere, were stored in closed containers, over silica gel, for varying periods of time, and were exposed to the normal laboratory atmosphere during mounting in the gripping blocks and to the fixtures of the Instron machine.

For each test, regardless of environment, the potted fibers were transferred, one at a time, from the rack to special fixtures called stirrups, in the Instron test machine. Two prongs on each stirrup fit into holes in the blocks containing the fiber. Fig. 8 illustrates the method of performing the transfer. This step required considerable care to avoid over-stressing the fiber when the upper block became free to swing at the end of the long wire hook.

a. Room Temperature Tests

In the case of a room temperature test, the next, and last step was simply to start the cross-head motion of the machine and observe the breaking load on the fiber. The nominal strain rate employed was 0.05 inch per inch-minute.

b. Testing at Liquid Nitrogen Temperature

For tests of single fibers at liquid nitrogen temperature (-196 °C) the procedure was identical to that described above for room temperature tests, with one added feature: an insulated tank to contain liquid nitrogen was lowered over the fiber sample after it was suspended in the Instron machine. This tank was gasketed and bolted to the bottom cross-head member - as pictured in Figs. 9 and 10. Liquid nitrogen was pumped into the container to a level just below the fiber sample. Temperature was monitored in the vapor phase somewhat above the upper block of the test specimen. Once the vapor temperature had reached -196°C, a soak period of about 5 minutes was allowed to insure equilibrium and then the cross-head motion was begun.

c. Tests in Lithium Aluminum Hydride Solution

An attempt was made to test single fibers in an anhydrous condition at room temperature. It was reasoned that if this were possible, the effect on fiber strength of moisture during testing might be assessed without introducing temperature as a variable. Lithium aluminum hydride, either alone or in solution in ether, is an extremely active desiccant. It reacts violently with water, with the formation of lithium aluminate and hydrogen gas. Since it is almost impossible to prevent the occurrence of this reaction with adsorbed moisture in the apparatus and atmosphere during handling of the solution, there is always a small amount of the precipitated aluminate in the solution.

The tests of single fibers in the hydride solution were conducted by surrounding the mounted fiber by an aluminum tube into which could be run the solution of hydride. This tube is shown in Fig. 11, and the equipment for transferring hydride solution in and out of the test chamber is shown in Fig. 12. Transfer was accomplished by pressurizing with dry nitrogen gas. Two of the tubes shown at the top of the sample chamber are to conduct cooling water into and out of a hollow cover which served to discourage loss of ether from the solution. The third tube at the top of the chamber bleeds nitrogen gas during periods when the chamber is empty to avoid excessive moisture pick-up.

5. Measurement of Fiber Diameter

In order to calculate the breaking stress in the fiber, one must have an accurate measure of the cross-section area. Ideally, this measurement should be made in the same portion of fiber which is tested in order to eliminate inaccuracies due to possible variations in diameter along the length of the fiber sample. To achieve the same accuracy without subjecting the test samples to the handling required when making diameter measurements, we measured the fibers on one side of a gathering fork and tested those from the other side. By averaging the measurements obtained on several segments from a given fork, we obtained a good value for the diameter of the test samples from that fork.

Diameter measurements were made by optical microscope using a magnification of about 500 X. Immersion oil surrounded the fiber sample to reduce refractive effects at the edges of the image. A calibrated filar micrometer eyepiece was used, and at least two measurements, approaching the fiber from each side, were made on each segment from a fork. Generally, four segments from each fork were measured.

V. TEST RESULTS

A. Composite Rings - Effects of Moisture

1. Room Temperature Tests

Fig. 13 summarizes the results of all room temperature tests on composite rings made to study the effects of moisture. Complete data on all sets in this series are shown in Table 2. These data have been subjected to statistical analysis which indicates that the results for Set No. 1 are significantly higher at the 5% level than all the other sets. Although there may be real differences among some of the other sets of data, the significance is believed to be of a lower order.

2. Low Temperature Tests

The four rings tested in liquid nitrogen showed glass stresses from 495,000 psi to 535,000 psi! (Table 3) These are in sharp contrast to prior results with rings made and stored under similar conditions, but tested in the normal room atmosphere, which yielded glass stress values from 300,000 to 320,000 psi.

B. Single Fibers

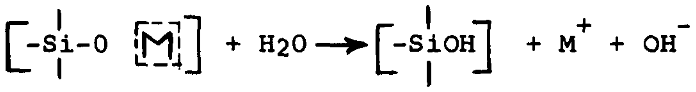
Fig. 14 summarizes the data obtained on single fiber strength at both room temperature and liquid nitrogen temperature. This particular comparison shows several interesting things about the test results. Obviously, a large difference in strength under the two conditions is indicated. The median strength is 60% higher at -196°C than at room temperature. It is also notable that at least one-fourth of the fibers show strengths in excess of 900,000 psi at low temperature. The difference in slopes of the two lines indicate a somewhat lower dispersion of strengths when measurements are made at room temperature, even though the fibers are weaker in this environment.

Those fibers tested in the lithium aluminum hydride desiccant solution showed a considerable scatter in breaking stress. However, the frequency distribution of strength values was quite different from that for room temperature tests in normal humidity. This comparison is illustrated in Fig. 15, and the significance is discussed in a later section of this report, page 24 . The individual strength values are tabulated in Table 4.

VI. DISCUSSION

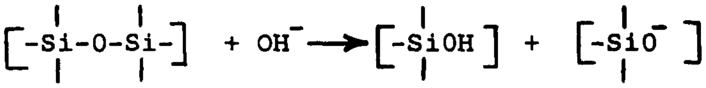
A. Single Fiber Tensile Strength

The role of moisture in the failure process with various glasses and fused silica has been broadly reviewed by R.J. Charles(1) of the General Electric Company Research Laboratory. In particular, for glasses such as soda-lime glass which contains a silica network structure plus alkali ions which are associated to the silica network as terminal structures, the corrosion reaction mechanism is described as follows:



$$\left[-\overset{|}{\underset{|}{\text{Si}}}-\text{O}\ \boxed{\text{M}}\right] + H_2O \rightarrow \left[-\overset{|}{\underset{|}{\text{Si}}}\text{OH}\right] + M^{+} + OH^{-} \qquad (1)$$

This first step is a typical hydrolysis reaction of the salt of a weak acid, where $\boxed{\text{M}}$ represents an alkali metal ion, e.g. sodium in soda-lime glass. This reaction in itself would not significantly degrade the strength since the backbone network of covalent bonded silicon and oxygen atoms is not involved. However, free hydroxyl ion is formed in the process and the second important step may proceed:



$$\left[-\overset{|}{\underset{|}{\text{Si}}}-\text{O}-\overset{|}{\underset{|}{\text{Si}}}-\right] + OH^{-} \rightarrow \left[-\overset{|}{\underset{|}{\text{Si}}}\text{OH}\right] + \left[-\overset{|}{\underset{|}{\text{Si}}}\text{O}^{-}\right] \qquad (2)$$

In this step, which can proceed only if the first step has already been taken, the very strong Si-O-Si bond is broken.

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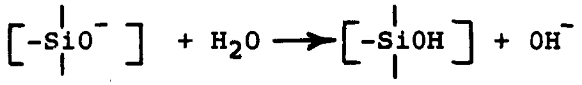
(1) Charles, R.J., Journal of Applied Physics, Vol. 29, No. 11, p., 1554-1560 (1958).

Furthermore, one product of this second reaction is an end structure capable of dissociating another water molecule, viz.,



$$\left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}^-\right] + \mathrm{H_2O} \longrightarrow \left[-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH}\right] + \mathrm{OH}^- \qquad (3)$$

Thus, excess hydroxyl ion is formed in equivalent amount to each alkali metal ion that is no longer associated with silica. This increase in pH within the corrosion layer tends to make the glass dissolution process autocatalytic and acceleration occurs. Reaction 1 is a triggering reaction for alkali-silica glass dissolution in water vapor and should be dependent on the ease of migration or diffusion of the alkali metal ion through the glass.

One can imagine a situation in which the rate of the corrosion reaction is sensitive to the state of stress in the glass structure in such a way that the fastest corrosion occurs in the region of highest tensile stress. In such a case, stress concentrating cracks in the glass surface would grow and perhaps even sharpen in the presence of applied stress and a corrosive environment.

That the corrosion reaction is indeed faster when the glass structure is expanded than when compacted was also shown by Charles in experiments in which fibers of the same glass were exposed to steam in the "as drawn" or expanded condition and after annealing to compact the structure. The depth of the corrosion layer was nearly three times as great after a two hour exposure period in the "as drawn" fibers as in the annealed samples. Charles states, "It seems entirely feasible that expansion of the glass structure by large triaxial tensile stresses of mechanical origin would result in a condition, as far as the migration and diffusion of Na+ ions are concerned, very similar to the expansion of the structure by a high fictive temperature."

Evidence for this sort of behavior in alkali silicate glasses was found by Charles in measurements of delayed failure times versus applied stress at various temperatures. The temperature dependence of the delayed failure process at a particular stress level is shown in Fig. 16. The linear relationship over the temperature range from -50°C to +50°C allows calculation of an apparent activation energy for the failure process which equals 18.8 kcal/mole. This value agrees closely with the activation energy for Na+ ion diffusion in the same glass calculated from electrical conductivity measurements (19.4 kcal/mole).

With this background of information pointing to stress corrosion by water as the principal cause of low strength in many glasses, our own experiments were designed to investigate this phenomenon in E-glass fibers.

The strength of E-glass fibers which have not been mechanically damaged is generally reported in the 500,000 - 550,000 psi range when tested at room temperatures. Recognizing that this is at least a 50% reduction from theoretical strength, most investigators have acknowledged the existence of flaws, generally considered to be surface cracks, as being responsible for the lowered strength. According to the well-known Inglis and Griffith theories, there is a critical flaw size associated with a given failure stress in a brittle material such as glass. The familiar Griffith equation expresses this relationship:

$$\sigma_{cr} = \sqrt{\frac{4ES}{\pi c}}$$

where σ_{cr} = applied failure stress
E = Young's Modulus
S = surface energy
c = crack depth

Any existing flaw larger than this critical size would be expected to propagate spontaneously and cause failure when the applied stress level reached the corresponding critical value. This picture, then, in the absence of further interpretative information, would lead one to the supposition that the measured strength of E-glass fibers was limited by the size of cracks already in place in the sample when the test began.

This naive viewpoint becomes quickly confounded by data which have been reported from many sources indicating strong dependence of the strength of glass upon its environment and also upon the duration of the load application. Variously referred to as static fatigue or delayed failure, these effects have generally been ascribed to a destructive reaction at the tip of surface flaws, involving water vapor and components of the glass.

The dependence of strength upon time under load implies a rate controlled failure process of some kind. If this rate is sharply reduced, as by lowering the temperature, then the measured strength, under the same load duration, should be increased significantly. This is precisely the effect shown by our data on fibers at liquid nitrogen temperature and room temperature.

Both the large percentage increase in strength and the approach to theoretical strength achieved by a significant proportion of the fibers at liquid nitrogen temperature supports the view that at room temperature, stress corrosion is responsible for the relatively low fiber strength.

It might be argued that one expects the strength of materials to increase as temperature is lowered, even in the absence of chemical reactions. It is true that most theories of mechanical strength, including the Griffith relationship for the effect of cracks, do indicate a dependence of strength upon the elastic modulus which, in turn, is often temperature dependent. However, actual measurements on silica-based glasses show only a minor change in modulus, in the neighborhood of 5%, in going from room temperature down to liquid nitrogen temperature. In contrast to this, the 60% improvement in measured strength of E-glass fiber at low temperature can best be explained by the great reduction in rate of stress corrosion reactions involving water vapor.

1. <u>Tests on Fibers Desiccated at Room Temperature</u>

Certainly, the results of tensile tests on single fibers immersed in lithium aluminum hydride at room temperature were not as spectacular as those at liquid nitrogen temperature. They do indicate, nevertheless, that by removing moisture from the surface at room temperature, strength values can be obtained well above the range which is found for the same fibers tested under normal atmospheric conditions. The plot of failure stress versus percent frequency of occurrence, shown in Fig. 15, illustrates this point. Included in this figure, in addition to our own data, is a curve for E-glass fibers adapted from Owens-Corning data which was presented at a recent Polaris R & D Conference.(1) The figure shows a

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(1) "Textile Strength of Glass Filaments" by Dr. G.R. Machlan et al, Owens-Corning Fiberglas Corp.; presented at Polaris R & D Conference, Wilmington, Delaware, July 17, 1962.

considerable proportion of strength values from the desiccated tests which lie above the customary envelope of room temperature data.

We feel that this test suffers, not from lack of sound theoretical basis, but mainly from the need for refinement of technique. The reaction of $Li\ Al\ H_4$ with water on the glass surface may be too violent, particularly if it occurs right in the root of an existing crack. Also, we were not able to prevent a considerable amount of solid sediment from being carried into the test chamber with the solution. This solid material is probably lithium aluminate, formed from the reaction of the hydride with adsorbed moisture in the equipment. It may have actually damaged some fibers to the point where their strength was low, even in the absence of moisture.

B. Composite Rings

From all of the work done with composite rings at room temperature, there appears to be a general pattern in the dependence of strength upon exposure to moisture. We can say that there is a statistically significant advantage for the maintenance of relatively dry conditions throughout the entire processing history of the glass monofilament. Because of the appreciable scatter in strength values for rings within a given set, as shown in Table 2, it is probably not possible to decide from these data at which points in the fiber's history the presence of moisture is most degrading. It does seem clearly demonstrated, however, that provision of a dry atmosphere around the fiber between the crucible orifice and the resin coater is not all that is required to insure maximum glass stress in the composite ring.

It was as a result of these ring tests that we began to think that the more important consideration was the presence or absence of moisture on the fiber surface at the time of application of high stress, regardless of the prior history of the fiber with respect to exposure to moisture. The results of testing rings at liquid nitrogen temperature support this viewpoint.

It is well known that the large difference in coefficients of thermal expansion for glass and epoxy resin could cause problems when composites of these two materials are subjected to large changes in temperature. One might expect, therefore, that filament-wound rings cured at 150°C and then tested at -196°C might suffer some loss in strength as a result of resin cracking, glass fiber surface spalling, de-bonding, etc. On the other hand, having found that the glass fiber alone showed so much improved tensile strength at liquid nitrogen temperature, we were anxious to see how much carry-over of this improvement could be obtained in a composite ring.

It is especially interesting to note that the improvement in glass stress in the composite rings at low temperature was the same percentage as the improvement in tensile strength of the fiber from which they were made: approximately 60%. In view of this fact, it is hard to imagine that any significant damage to the glass occurred because of shrinkage stresses in the bonding resin, despite the drop in temperature from curing to test of some 350 °C. Neither is there any apparent loss of efficiency in load distribution among the many fibers, which depends upon the maintenance of some sort of bond, either chemical or mechanical, between the resin and glass.

VII. CONCLUSIONS

1. It has been demonstrated that the instantaneous strength of E-glass fibers, produced in a normal atmosphere, can be nearly 1,000,000 psi. This strength level is obtained by conducting tests at liquid nitrogen temperature, thereby greatly suppressing chemical reaction rates. The commonly measured strength of 500,000 psi for E-glass fibers at room temperature is considered to be not limited solely by the crack structure existing before test, but by a stress-activated corrosion reaction during the test itself which increases the stress concentration at the tips of the cracks and leads to failure at lower applied loads.

2. An equivalent percentage increase in glass stress within composite ring structures is obtained by testing the rings at liquid nitrogen temperature, the comparable values being 500,000 psi at -196°C and 310,000 psi at room temperature. The apparent glass stress in rings, however, calculated simply from the applied load and the supporting cross-sectional area of glass, remains lower than the tensile strength of the fiber at the same temperature. This must reflect either inefficient load distribution among all fibers in rings or the presence of stress concentrating effects and stress modes other than pure tension.

3. By performing tensile tests on single bare fibers of E-glass submerged in a powerful desiccant solution at room temperature, strength values were obtained as high as 653,000 psi. This is considerably higher than any found in room temperature tests at normal humidity and lends support to the theory that strength losses at room temperature can be prevented by keeping moisture away from the glass surface.

VIII. RECOMMENDATIONS

The full story on moisture effects in glasses is not yet elucidated. It would be well to consider ways of eliminating all sources of water, during formation of the glass from its chemical components as well as during all later phases in fiber production and handling.

A test similar to the lithium aluminum hydride desiccation should be refined so that a clearer picture of surface moisture effects may be obtained. It has been suggested (1) that aluminum hydride, without the presence of the lithium ion, might be a more suitable desiccant, since we are not certain what interactions may occur between the small, mobile lithium ions and alkali ions within the glass structure.

Practical protection from external moisture will probably require a continuous coating of some dense material, such as a metal, which is applied at a time when the glass surface is free of moisture.

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(1) Dr. W.B. Hillig, General Electric Company Research Laboratory

Fig. 1
Glass Melting Furnace Design

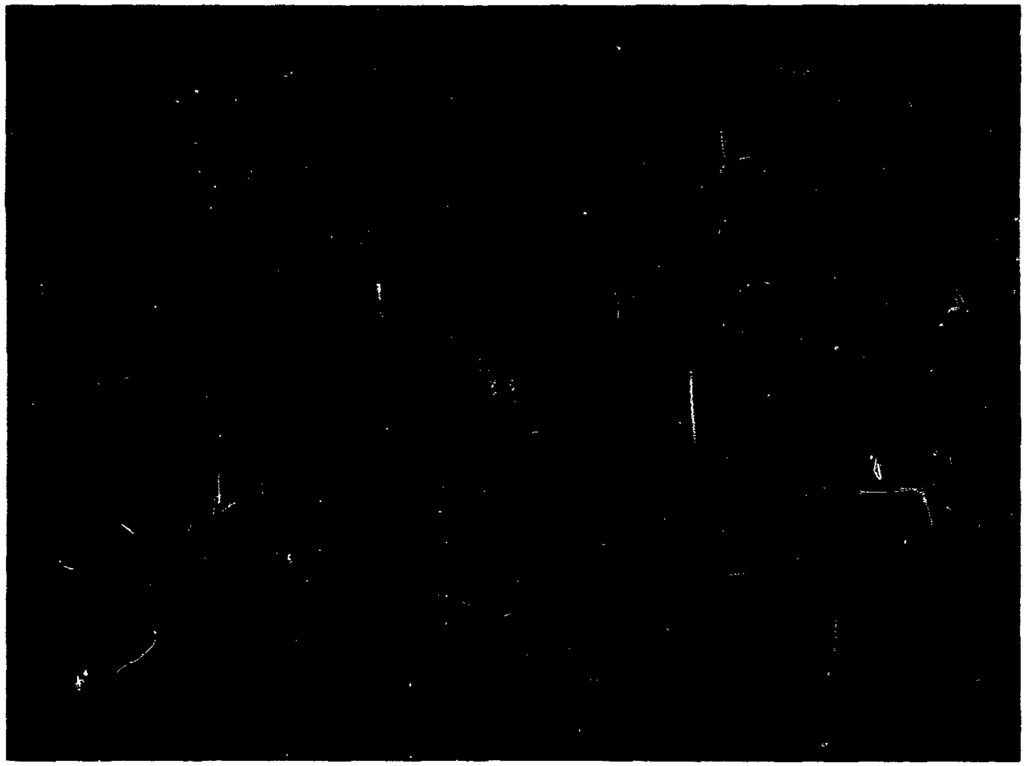


Figure 2

Split D-Ring Winding Mandrel

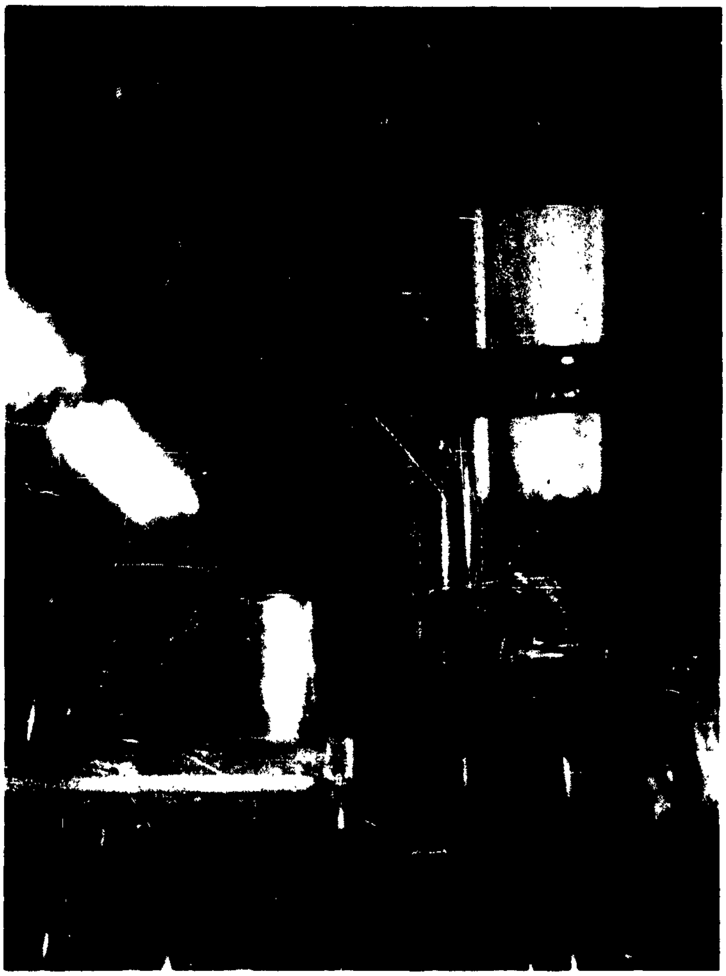


Figure 3
Secondary Dry Ambient Enclosure

Figure 4

Fork for gathering fiber during drawing operations

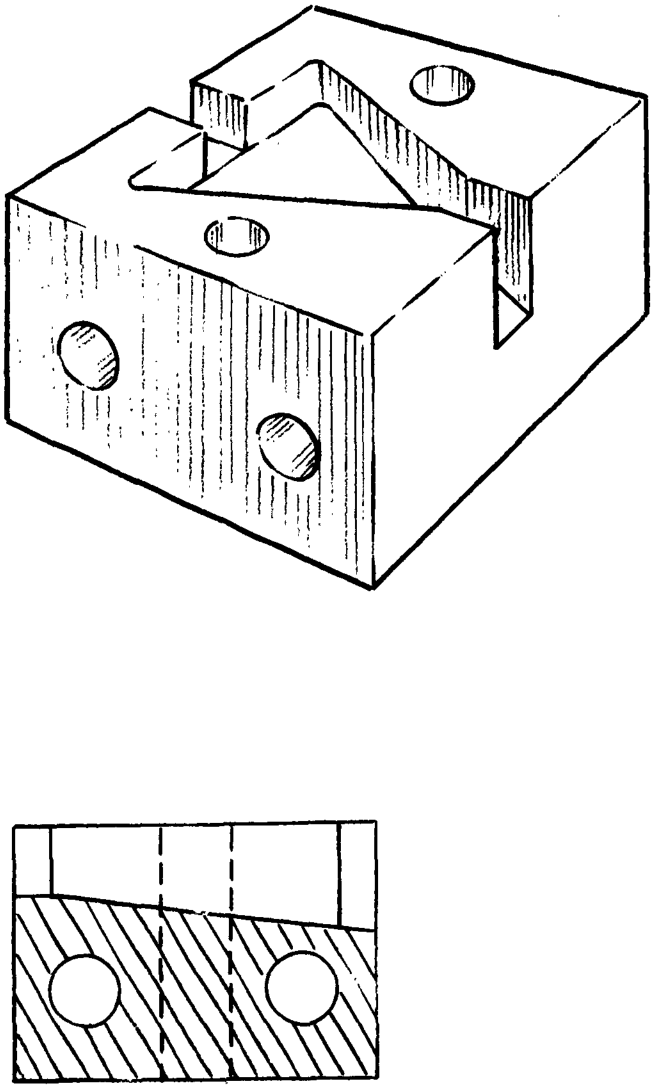


Figure 5

Stainless steel blocks for potting ends of glass fibers

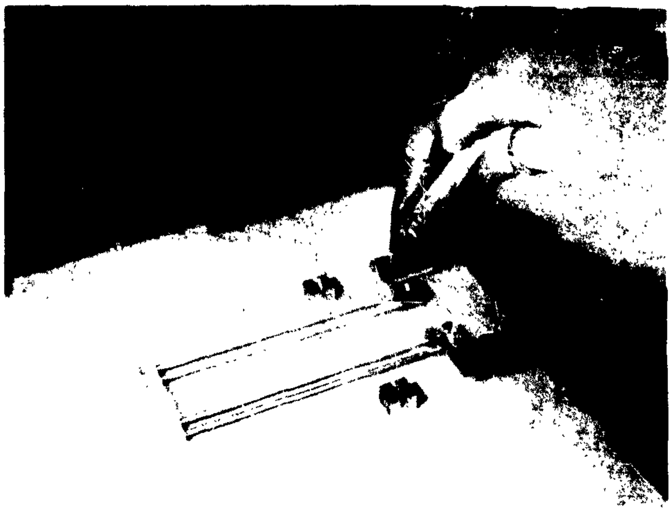


Figure 6

Mounting fiber in sealing wax grips for tensile test

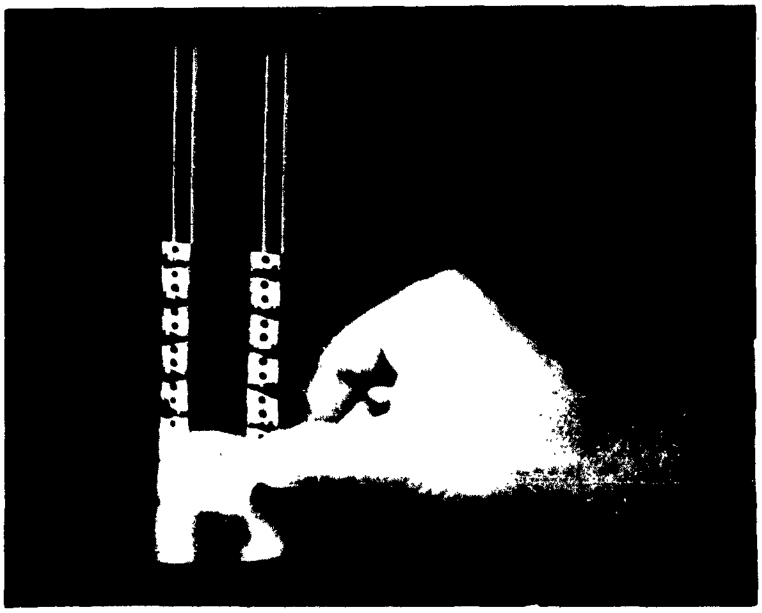


Figure 7

Fiber tensile test specimens on transfer rack

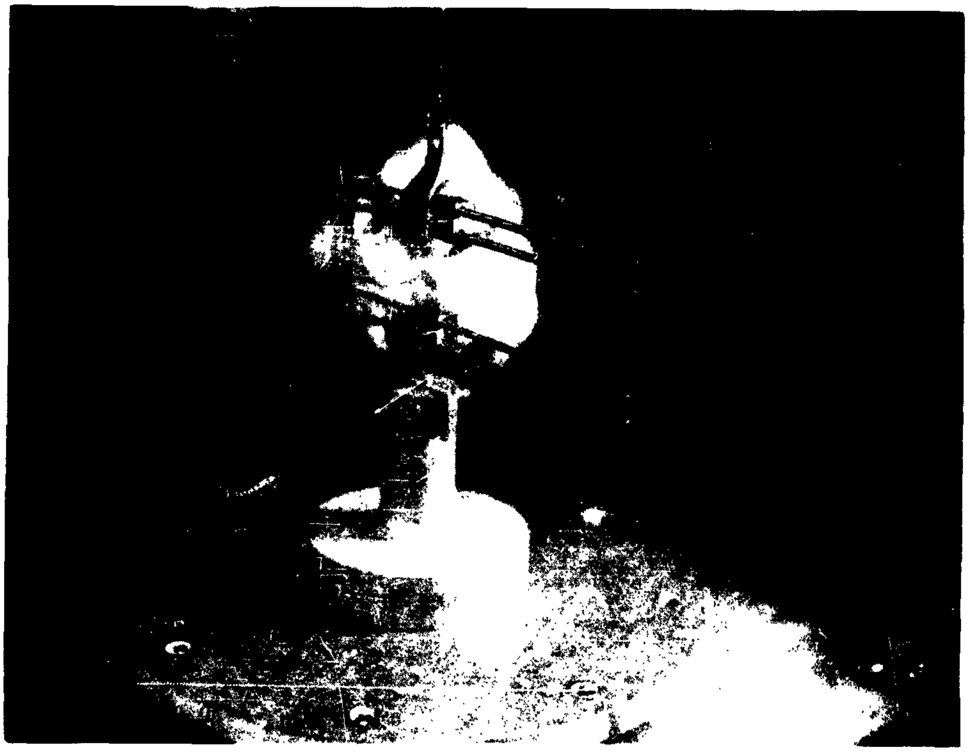


Figure 8

Transfer of test specimen to stirrups in Instron machine

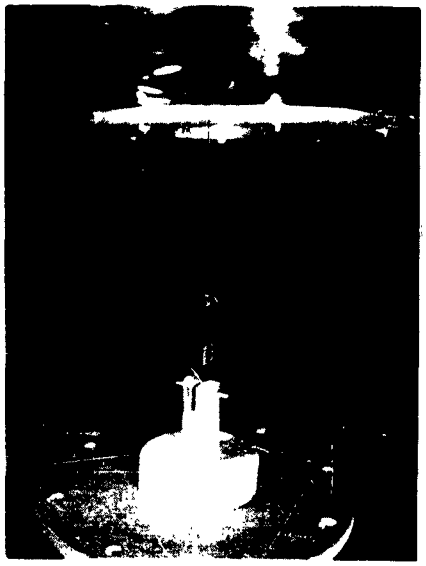


Figure 9

Fiber in position for test before adding liquid nitrogen

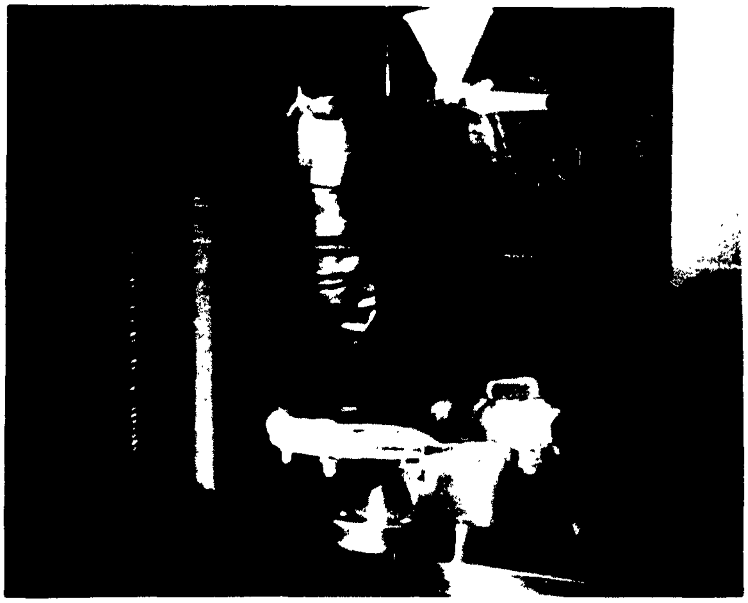


Figure 10

Fiber enclosed in liquid nitrogen container

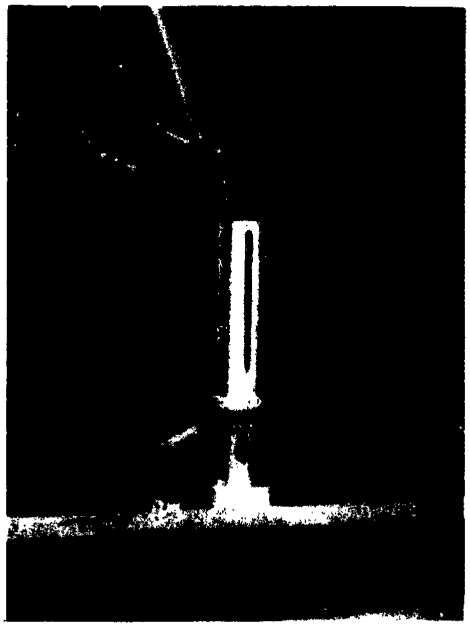


Figure 11

Chamber for Testing Fibers in Li Al H_4

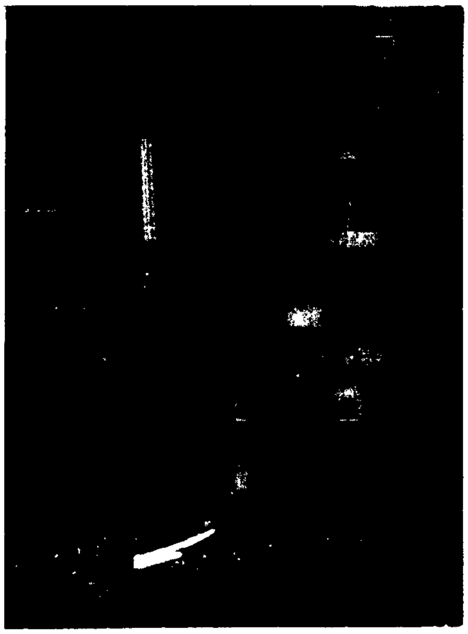
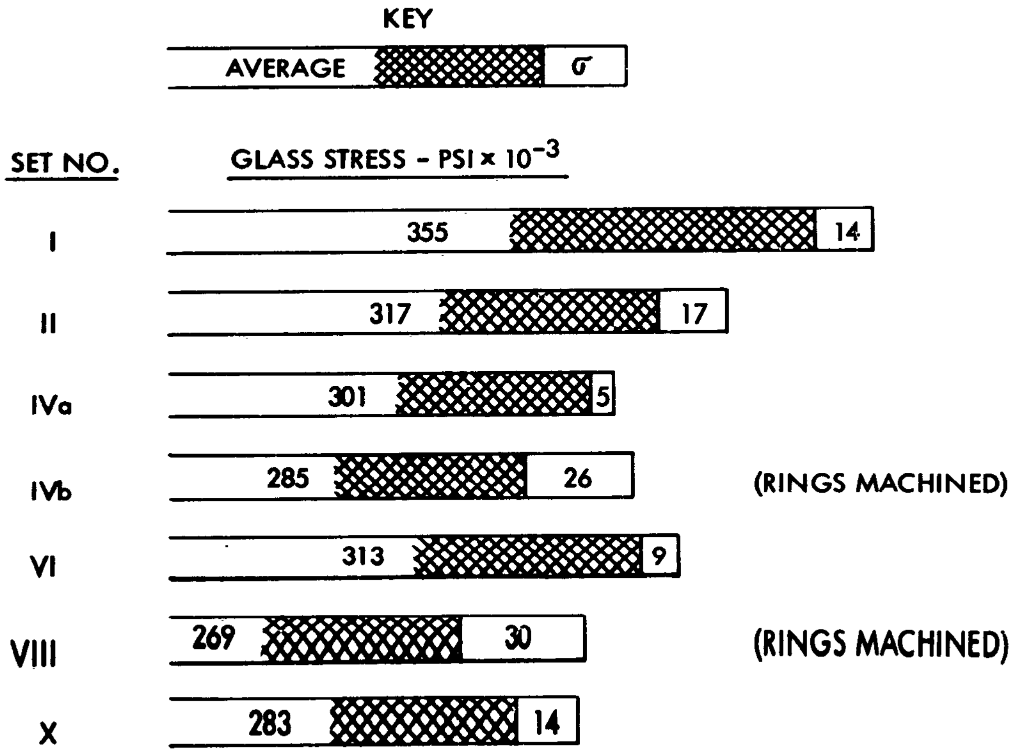


Figure 12

Equipment for Transfer of Li Al H_4 into Test Chamber

Figure 13

EFFECT OF HUMIDITY ON GLASS STRESS IN MONOFILAMENT RINGS



SET NO.	GLASS STRESS - PSI × 10^{-3} AVERAGE	σ		HUMIDITY DRAWING	CONDITIONS STORAGE	DURING TESTING
I	355	14		DRY	DRY	DRY
II	317	17		DRY	DRY	NORMAL
IVa	301	5		DRY	NORMAL	NORMAL
IVb	285	26	(RINGS MACHINED)	DRY	NORMAL	NORMAL
VI	313	9		NORMAL	DRY	NORMAL
VIII	269	30	(RINGS MACHINED)	NORMAL	NORMAL	NORMAL
X	283	14		NORMAL	100% R.H.	NORMAL

Figure 14

E-Glass Fiber Tensile Strength at Room Temperature and Liquid Nitrogen Temperature

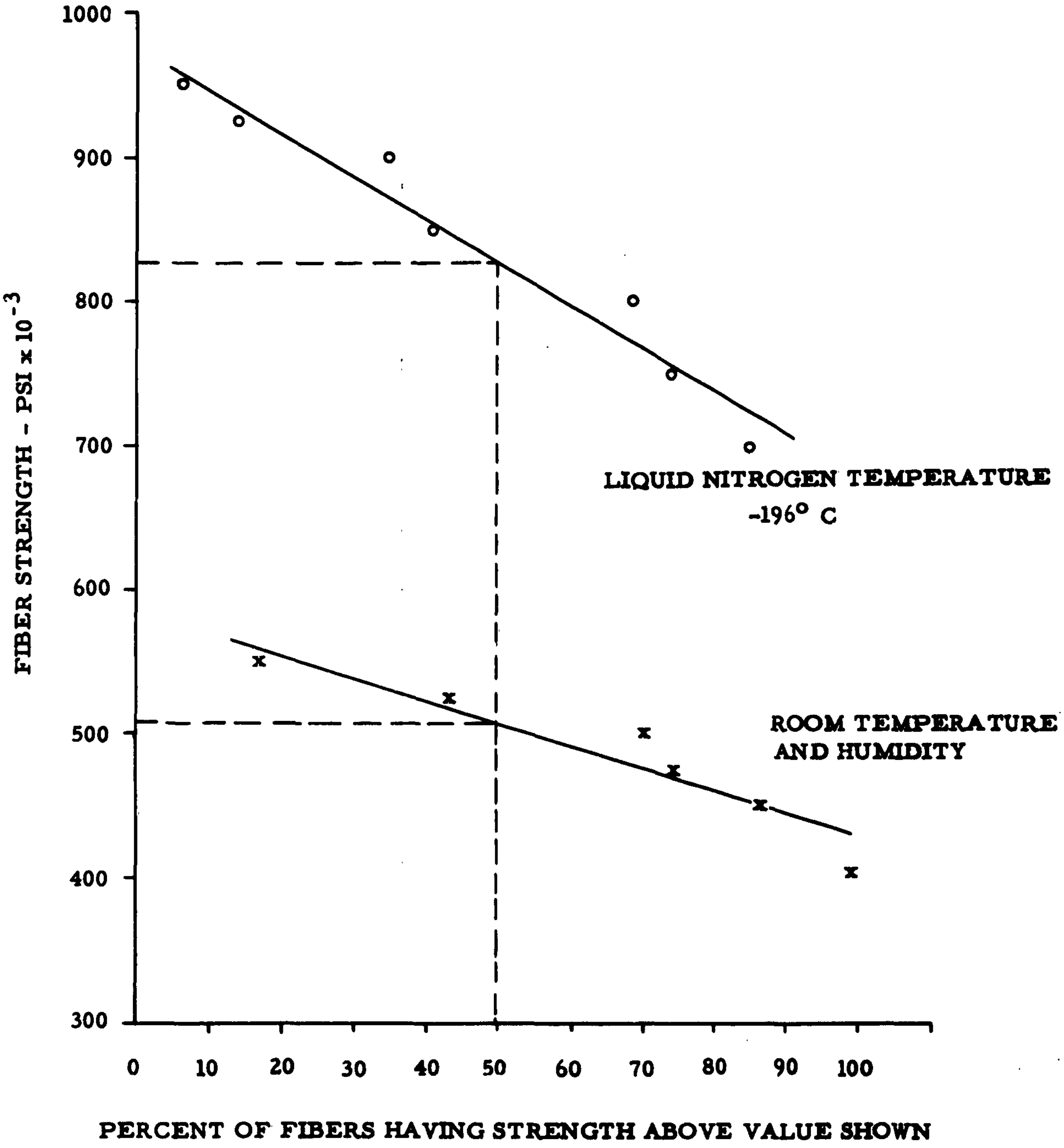
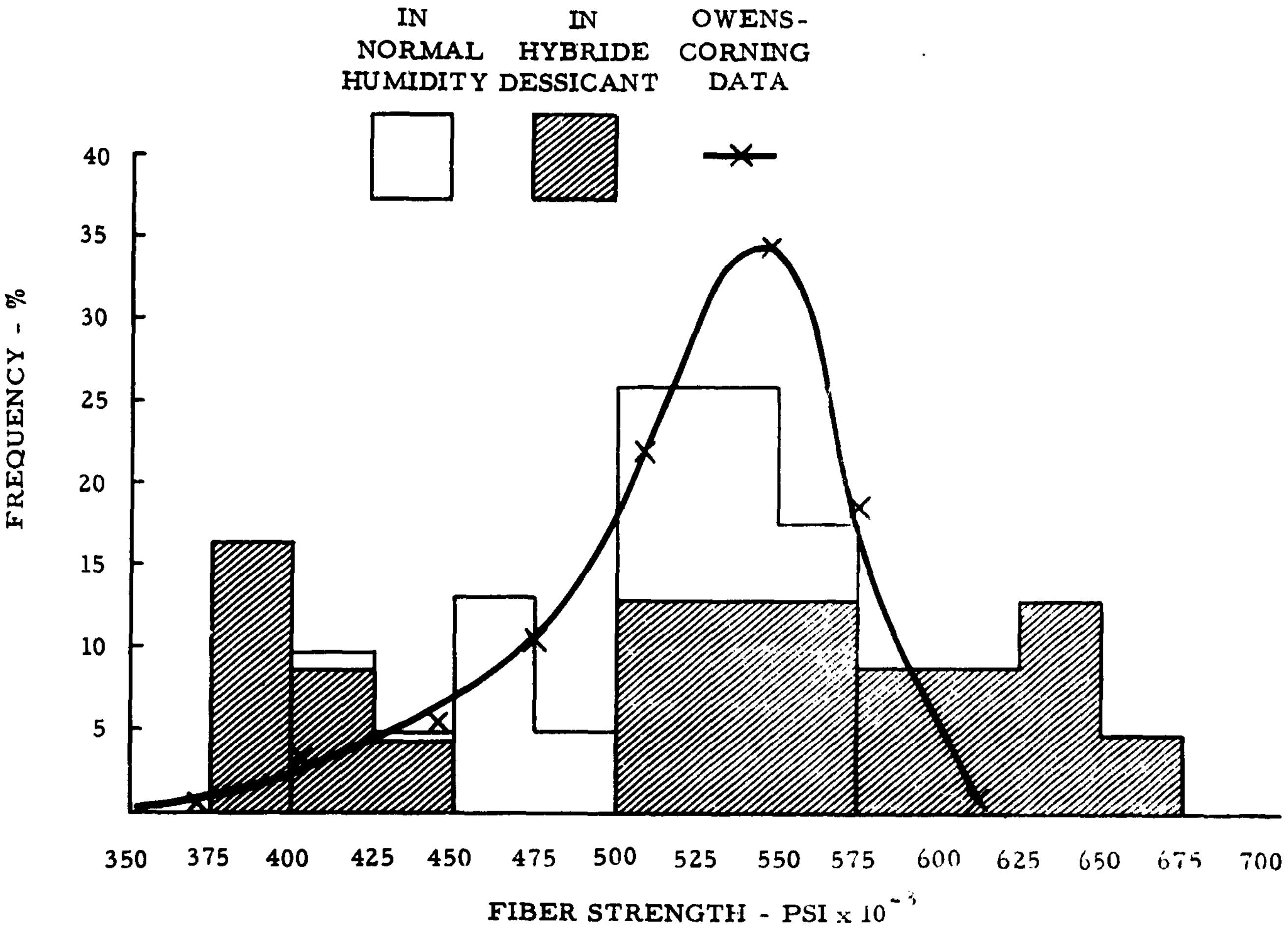


Figure 15

Single Fiber Strength Distribution in Li Al H_4 and Normal Atmosphere



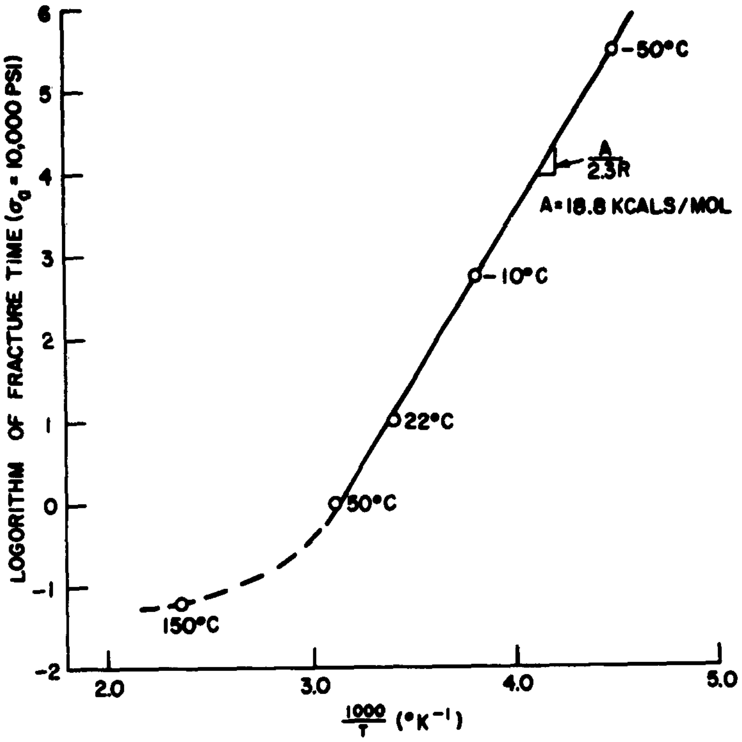


Figure 16 Temperature dependence of the delayed failure process.

Table 1

SINGLE FIBER TEST DATA - E GLASS

Fork No.	Segment No.	Fiber Diam.- Mils	Tensile Strength-PSI Room Temp.	Tensile Strength-PSI -196°C	Remarks
1	1	.47	464,000		
1	2		502,000		
1	3		417,000		
1	4		520,000		
1	5		-		Slipped out of wax.
1	6		416,000		
2	1	.43	519,000		
2	2		520,000		
2	3		-		Broken in handling.
2	4		-		" " "
2	5		475,000		
3	1	.41	-		Slipped out of wax.
3	2			588,000	
3	3			411,000	
3	4			743,000	
3	5			815,000	
3	6			724,000	
4	1	.46	>438,000	833,000	Not broken at R.T. Retested at -196°C.
4	2			847,000	
4	3			795,000	
5	1	.42		-	Damaged in liquid N_2 bath.
5	2			749,000	
5	3			916,000	
5	4			671,000	
5	5			800,000	
5	6			835,000	
5	7		465,000		
5	8		450,000		
5	9		445,000		
6	1	.40	525,000		
6	2		525,000		
6	3			895,000	
6	4			578,000	(Fibers cooled down under compression-
6	5			578,000	(sharply bent.
6	6			847,000	
6	7			842,000	
6	8			827,000	
6	9			900,000	
6	10			754,000	
7	1	.39	524,000		
7	2		535,000		
7	3			701,000	
7	4			974,000	
7	5			912,000	
9R1	1	.42	554,000		
9R1	2		560,000		
9R1	3		548,000		
9R1	4			930,000	
9R1	5			960,000	
9R1	6			913,000	
11R3	1	.45		936,000	
11R3	2			905,000	
11R3	3			>876,000	
11R3	4		551,000		
11R3	5		548,000		
10R2	1	.44	512,000		
10R2	3		540,000		
10R2	4		557,000		
10R2	5			920,000	
10R2	6			915,000	
10R2	7			828,000	
10R2	8			944,000	
AVERAGE			507,000	814,000	

TABLE 2

EFFECT OF HUMIDITY ON GLASS STRESS IN MONOFILAMENT RINGS
E-GLASS AND EPOXY RESIN (UNION CARBIDE ERL 2256/ZZL 0820)

Set No.	I	II	IVa	IVb	VI	VIII	X
Fiber Drawing Conditions							
Nominal	Dry	Dry	Dry	Dry	Normal	Normal	Normal
Dew Point	-11°F	-40°F	-26°F	-45°F	-	-	-
Ring Storage Conditions							
Nominal	Dry	Dry	Normal	Normal(2)	Dry	Normal(2)	100% R.H.
Storage Time	14-24 Days	5 Days	5 Days	4 Days	1 Day	7 Days	6 Days
Ring Testing Conditions	Dry	Normal	Normal	Normal	Normal	Normal	Normal
Glass Stress - PSI	354,000	309,000	292,000	313,000	300,000	302,000	308,000
	329,000	293,000	307,000	288,000	304,000	292,000	(146,000)
	366,000	321,000	299,000	297,000	321,000	255,000	284,000
	358,000	320,000	299,000	242,000	320,000	228,000	279,000
	368,000	344,000	306,000		319,000		278,000
							265,000
Average	355,000	317,000	301,000	285,000	313,000	269,000	283,000(1)
Std. Deviation	14,000	17,000	5,000	26,000	9,000	30,000	14,000(1)

Notes

(1) Calculated with the 146,000 PSI Value Omitted.
(2) Rings in Sets IVb and VIII were Machined on O.D. Prior to Storage.

TABLE 3

E-GLASS AND EPOXY COMPOSITE RINGS TESTED IN LIQUID NITROGEN

Ring No.	Load to Break - Lbs.	Wt. of Glass in Ring - Gms.	Glass Stress PSI
1	2525	1.3716	495,000
2	2525	1.3565	502,000
3	2970	1.4937	535,000
4	2360	1.2830	495,000

NOTES:

1. Rings are 4 inch diameter x .070 inch wide x .030 inch thick.
2. Cross-head speed is 0.10 inch/min.

TABLE 4
SINGLE FIBER STRENGTH IN LITHIUM ALUMINUM HYDRIDE

Fork No.		Segment No.	Fiber Diam.- Mils	Tensile Strength PSI	Remarks
13	-	1	.50	503,000	
13	-	2		625,000	
13	-	3		638,000	
13	-	4		597,000	
13	-	5		653,000	
14	-	1	.50	618,000	
14	-	2		595,000	
14	-	3		602,000	
14	-	4		640,000	
14	-	5		389,000	
15	-	1	.51	522,000	
15	-	2		192,000	Fiber damaged in mounting.
15	-	3		410,000	
15	-	4		573,000	
15	-	5		557,000	
15	-	6		383,000	Broke in grip.
16	-	1	.52	547,000	
16	-	2		511,000	
16	-	3		392,000	
16	-	4		426,000	
17	-	1	.51	533,000	
17	-	2		409,000	
17	-	3		541,000	
17	-	4		395,000	
17	-	5		522,000	
17	-	6		556,000	