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GLASS-, BORON-, AND GRAPHITE-FILAMENT-WOUND - RESIN COMPOSITES AND LINERS FOR CRYOGENIC PRESSURE VESSELS

TECHNICAL PAPER presented at Cryogenic Polymers Conference sponsored by NASA and Case Institute of Technology
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ABSTRACT

Tensile and interlaminar shear strengths are reported of NOL rings at 297° , 77° and 20° K. Filament translation efficiencies are compared. Cryogenic cyclic life of aluminum liners in glass filament-cylinders is reported.

INTRODUCTION

The utilization of filamentary materials has been pursued in applications where high strength to weight ratios are a design criteria. Glass filaments in a resin matrix, for example, have been used extensively for pressure vessels, rocket motor cases, and in some aircraft structures. In these applications, the materials are subjected to ambient or moderately elevated temperatures. An urgent need exists for these materials in the cryogenic temperature range for the containment of liquid oxygen and liquid hydrogen. Recently, other filamentary materials with unique properties have become available. Two of these materials - boron and graphite - were chosen for cryogenic evaluation. In tensile strength, these materials can be regarded as being eventually competitive with glass since they have a strength potential in the range from 500,000 to 1,000,000 psi. In addition to their high strengths the filaments also have tensile moduli which are several times that of glass.

The filaments of glass, boron, and graphite in composities are of particular interest in cryogenic applications. At low temperature, the loss of fracture toughness that plagues most isotropic materials is minimized in composites due to inherent discontinuities inhibiting crack propagation between filaments. Also, their strength properties may be enhanced at low temperatures.

Utilization of these composities in pressure systems presents a unique problem characteristic of these materials. Under stress, the composite becomes porous because of the cracking in the resin matrix. The problem exists at normal temperature and is probably more severe at cryogenic temperatures. A "barrier" or liner must be provided on the inner surface of the vessel to contain the pressurizing medium. A preliminary investigation (ref. 1) of the liner problem revealed that polymeric films and metallic foils were limited in performance. However, from subsequent investigations at the Lewis Research Center and in reference 2, results have indicated that plain metallic foil liners bonded to the composite with selected adhesives are promising as a cryogenic liner.

The purpose of this report is to present preliminary results on the evaluation of boron and graphite filaments as possible reinforcements for cryogenic propellant tanks. Also included are data on glass reinforcements that were used in fabrication of test cylinders for the evaluation of cryogenic liners. Composite tensile strength characteristics were determined of glass, boron, and graphite at temperatures of 297°, 77°, and 20° K. Composite interlaminar shear strength of these materials and single filament strengths of boron were determined at 297° and 77° K. Cyclic tests were performed on cylinders having aluminum foil liners at temperatures of 77° and 20° K to determine the cyclic life and mode of liner failure.

MATERIALS

The filament-resin materials and specimens evaluated are listed in table I. The glass and graphite filaments in the as-received condition were wound under 0.5 pound tension into single NOL rings (ref. 3). The boron was cleaned by passing it through a solution of boiling methanol just prior to the resin impregnation. All rings were 0.06 inch thick with the outer surface machined.

Table II lists the typical properties of the filamentary materials investigated as published in reference 4.

APPARATUS AND PROCEDURE

Tensile Tests

NOL rings. - Filamentary-resin composites in the form of NOL rings were tested at ambient and cryogenic temperatures using split disk fixtures as described in reference 3. The cryogenic temperatures were established by submersion of specimens in liquid nitrogen (77° K) or liquid hydrogen (20° K) in special cryostats mounted in a tensile machine. The load was applied at a crosshead rate of 0.1 inch per minute.

Interlaminar shear tests. - Interlaminar shear strengths of glass, boron, and graphite composites were determined by the method outlined in reference 3. The specimens were 0.06 inch thick by 0.25 inch wide and 1 inch long. The specimens were loaded in flexure at the midspan of supports with 0.5 inch centers.

Cast resin. - 0.125 inch thick castings of the ERL2256/ZZL0820 (25 phr) resin system cured for 2 hrs at 356 plus 3 hrs at 422° K were machined into specimens in accordance with ASTM D638-64T-Type I. The tensile specimens were tested at ambient temperature and 77° K at crosshead speeds of 0.2 inch per minute. Strain was measured by a clamp-on extensometer with a gage length of 1 inch at both temperature levels.

Single filaments. - The tensile strength of single filaments of boron were determined at 297° and 77° K. Filaments of 1-inch gage length were cemented with room-temperature curing epoxy resin to metal tabs to facilitate loading. The load was applied at 0.1 inch per minute.

Lined filament-wound cylinder tests. - The cylinders used in investigating bonded foil liners were right circular cylinders, 7.5 inches in diameter by 20 inches long. The cylinders were fabricated on mandrels of thick-wall aluminum tubing. A slight diametral taper was provided to facilitate removal of the finished cylinder from the mandrel. The details of liner assembly and cylinder construction are presented in the appendix.

The method used for capping the ends of the cylinders is shown in figure 1 and was also used in reference 1. A low-melting point alloy filled the groove effectively locking and sealing the end caps to allow pressurization. In cryogenic testing, the cylinders were placed in a cryostat with both inner and outer cylinder surfaces exposed to the cryogen. For the 77° K tests, nitrogen gas was used for pressurization. For the 20° K tests, the cylinder was pressurized with a liquid hydrogen pump.

Hoop and longitudinal strains were measured by utilizing deflection transducers that were instrumented with strain gages. Calibrations were made at ambinent and cryogenic temperatures using a screw micrometer as a standard. The hoop strain was determined by circumscribing a 10-mil wire about the cylinder at the midpoint of the test section to actuate the transducer. The longitudinal strain was measured similarly between clips secured in the cylinder wall. An installation is shown in figure 2. The strain rate was about 0.02 inch per inch per minute. Nominally, a maximum strain of 2.0 to 2.5 percent was selected for the cyclic endurance (liner failure) tests of the liners.

RESULTS AND DISCUSSION

Strength Characteristics of Filament-Resin Composites

Figure 3 shows the average tensile strength of filament-resin NOL ring composites as a function of temperature. The number of specimens tested for a given material and temperature are indicated. Also shown is the range of test data. Tensile strength is seen to vary with temperature for the materials investigated. The S/901 glass composite increased from 290,000 psi at 279° K to about 29 percent higher at crogenic temperatures whereas boron and graphite composites have essentially flat strength characteristics within the temperature range investigated.

With the high tensile strengths, it is apparent that the glass composites have an advantage over boron and graphite composites for pressure vessel application. This was also concluded in reference 5 where an analysis showed that glass reinforced cylinders have a significant weight advantage over that of boron for internal pressure vessels.

The boron and graphite filaments are of interest where high modulus is a desirable property. The tensile modulus may be a determining factor in pressure vessel design to provide rigidity for large booster applications or where strain is a limiting factor in liners for cryogenic propellant tanks. On a comparative basis, the materials possess unique properties that would have to be considered for a particular application.

In comparing the tensile strengths of single filaments from table II with the tensile strengths of the composites at normal temperature in figure 3, it is seen that the composite strengths are less than half of the filament strengths. At this low ratio, it is apparent that the composite strength behavior does not follow the law of mixtures since composites of filaments and resin generally contain a 65 to 70 percent filament content by volume. Beyond the correction of strength due to resin content, the reduction in filament strength in the composite may be attributed to (a) inability of the resin to transfer load from filament to filament (interlaminar shear), (b) the strain limitation of the resin inducing cracking and crazing, (c) fabrication and mechanical flaws in filaments, and (d) composite voids. An understanding of the effects of some of these parameters on the composite strength characteristics can be deduced from specific tests. The interlaminar shear strengths are influenced by both temperature and material. In figure 4, it is noted that the interlaminar shear strength of glass increased from about 11,000 psi at 297° K to about 18,000 psi at 77° K. The interlaminar shear strength of boron and graphite composites (10,000 and 3,000 psi, respectively), remained essentially constant at the two temperatures. The behavior of interlaminar shear reflects that of the tensile strength with temperature in figure 3. Both the tensile and interlaminar shear strengths of glass composites increased with lower temperature while boron and graphite composites remained essentially constant.

In figure 5, it is seen that the ERL2256/ZZL0820 epoxy resin system stress-strain behavior changed significantly with temperature. It is noted that both the modulus and the tensile strength increased about 100 percent as the temperature was changed from ambient to cryogenic temperatures, with an associated strain to fracture reduction from 5 percent to about 2 percent at 77° K. This loss of ductility points out a possible limitation of the resin matrix in composites where reinforcements are a low modulus, high strength material such as glass. Glass composites may strain as high as 5 percent to fracture at cryogenic temperatures (ref. 1). From these results it would appear that at cryogenic temperatures the glass composite would be degraded above the 2 percent strain level. It is apparent that the composite is not degraded significantly at cryogenic temperatures because of the noted 29 percent strength increase (fig. 3). Also the structural integrity of the composite is not destroyed under strain. Either the low fracture strain of 2 percent is not a true value or the cracking and crazing on a macrostructure level can be tolerated by the composite. In reference 6 it is shown that the resin matrix is subjected to local strain magnifications of more than 20. This points out a limitation of the resin even at ambient temperatures and possibly obscures the embrittlement problem of the resin at cryogenic temperatures.

No determinations of strength were made of single filaments of glass and graphite in this investigation; however, data at ambient temperature are avialable in reference 4 and 7. With these data and results of single filaments of boron at 297° and 77° K (fig. 6) it is significant to note that the composites do not realize the high strength that would be expected in translation from filament to composite. Table III lists the filament and composite strengths of the materials presently considered. Also shown is the composite filament strength which is based on only the total filament area. The assumption was made that the resin carried no load and that the volume of filaments was 65 percent of the composite exclusive of void content. The filament translation efficiency is defined as the ratio of the average composite filament strength to the average mono-filament strength (determined from single fibers). On this basis, the filament translation efficiency is seen to range from 58 for boron to 69 percent for glass S/901 at 297° and 77° K. Data from reference 7 of E-glass are included because of the cryogenic data. These data are also shown in figure 6. It is seen that the efficiencies for the E-glass were 61 and 63 percent at 297° and 77° K, respectively, which is within the range of the materials presently investigated. These results substantiate the argument that the composites are not degraded by low temperature when comparing strength of the filament with the composite.

Cyclic Characteristics of Liners for Glass-Filament Wound Cylinders

The impervious liner requirements for filament wound cylinders were presented in reference 1. In the present investigation, metallic liners of aluminum foil were adhesively bonded to the inner surface of glass-filament wound cylinders. Although no metals have elastic strain behavior comparable to glass, it appeared feasible that 1100-0 aluminum could be strained plastically in tension and compression, provided an adequate adhesive bond could be maintained. Reference 8 shows that 1100-0 aluminum can withstand high uniaxial plastic strain (3 percent for 1000 cycles) before a fatigue failure results. Figure 7 shows the probable stress-strain relation experienced by the glass-resin composite cylinder and the aluminum liner under a single 2.5 percent strain cycle. It is seen that the cylinder behaves essentially elastically within the strain range, whereas, the aluminum liner undergoes most of its strain cycle plastically in both tension and compression. At the end of the cycle the cylinder and liner retain some residual strain because of the compressive restraint of the aluminum. Upon subsequent cycling, the stress-strain relationship of the cylinder and liner may change due to the progressive cyclic damage of the composite and to cyclic effects on the aluminum properties. The high degree of elastic strain incompatibility between the aluminum liner and the low modulus glass-filament-resin composite points out a distinct advantage of the use of high modulus filaments such as boron and graphite in pressure vessel applications.

During the present investigation, a number of cylinders were fabricated with plain liners of 1100-0 aluminum to establish the feasibility of the system as a permeation barrier. The optimization of variables such as liner materials, thickness, surface preparation, adhesives, and fabrication techniques were limited to the extent of establishing the capability of strain cycling lined composite cylinders at cryogenic temperatures.

From reference 1 it was disclosed that plain liners would have to be bonded to the cylinder to prevent buckling under strain cycling. The G207 adhesive was chosen because of its high strength at cryogenic temperatures and convenience in handling. The adhesive is a thermoplastic polyester that is fusible at the curing temperature of the epoxy. This allowed the liner to be adequately coated with adhesive before the glass-filament winding is applied. The initial winding was applied dry with the composite resin added on the second layer whereby the blending of the polyester adhesive and the epoxy resin was accomplished within a layer of glass. The fabrication as outlined in appendix A resulted in an approximate 1 to 1 hoop to longitudinal strain ratio at 2.5 percent strain and an internal pressure of about 400 psi.

Table IV is a tabulation of test results of cylinders lined with 3-mil aluminum foil showing the variables of surface preparation, adhesive selection, test temperature, and strain level. It is noted that some of the liners were capable of over 100 cycles at cryogenic temperatures before failure occurred. From the table it is significant to note that the chemical surface preparation (Oakite 33) resulted in higher average cyclic life than did the sand blasting. Although the liquid hydrogen tests were limited, it appears that the adhesively bonded aluminum liner performance was comparable at both cryogenic temperatures. From table IV it should be noted that the one cylinder with a liner attached with the Cybond 4000 adhesive gave good performance indicating that there may be other adhesives to select.

All liner failures based on leaks were located at the lap seam. Generally, the seam contained numerous areas where buckling had occurred. A typical seam area buckling is seen in figure 8. As noted in table IV, some cylinders had small areas of buckling other than in the seam, however, none of these areas produced leaks.

SUMMARY OF RESULTS

The results obtained from an investigation of filament-resin composites of glass, boron, and graphite from 297° K to cryogenic temperatures were as follows:

1. The average composite tensile strength of NOL rings of S/901 glass was 290,000 psi at 297° K with an increase of 29 percent at cryogenic temperatures.

2. The composite tensile strength of NOL rings of boron and graphite was 174,000 and 87,000 psi, respectively, at 297° K. Both materials showed no significant increase at cryogenic temperatures.

3. A filament winding resin (ERL 2256/ZZL0820) had a fracture strain of about 5 percent at 297° K. At 77° K the fracture strain was reduced to about 2 percent.

4. The interlaminar shear strength of S/901 glass and boron composites at 297° K were both approximately 10,000 psi. At 77° K, glass shear strength increased to about 18,000 psi while the boron shear strength increased only to about 11,000 psi. The interlaminar shear strength of graphite was about 3000 psi at both 297° and 77° K.

5. Filaments of glass, boron, and graphite in composites showed filament efficiencies in a range from 53 to 70 percent at both 297° and 77° K with no apparent degradation at 77° K.

6. Pressure vessels with adhesive bonded aluminum foil liners with longitudinal lap seams were pressure cycled to about 2.5 percent strain for over 100 cycles at 77° and 20° K before failure occurred. The lap seam was found to be the source of all liner failures.

APPENDIX - LINER-CYLINDER FABRICATION

1. Aluminum mandrel coated with Teflon parting agent.

2. Liner surface preparation, either of following (see table IV):

   (a) Degrease with toluene and dry, abrade with 50 micron grit (after placing on mandrel)

   (b) Degrease with toluene and dry, clean in chromic acid solution and rinse with tap water (before placing on mandrel)

   (c) Clean surface in Oakite 33 (one part per 10 parts tap water), rinse with tap water

3. Aluminum foil liner placed on mandrel and lap seam formed that had been coated with G207 adhesive (G207B, toluene, methylethyl ketone, G207C) (100, 63, 27, 4 parts by weight).

4. Liner surface brush coated with G207 and allowed to dry at ambient temperature for 12 hours.

5. S/901 single end glass roving applied dry at 48 ends per inch with 0.5 pound tension in hoop direction. The dry roving was then brush coated with the epoxy resin system ERL 2256/ZZL0820 (27 phr). Four layers of No. 112-Volan A glass cloth in a 20-inch width was applied under 10 pound tension and wet with the 2256 resin. A final hoop wrap of single end roving at 48 ends per inch completed the basic cylinder.

6. Both ends were built up with No. 1542 Volan A glass cloth from ends of cylinder in the following sequence: Five layers, 1 inch wide; one layer, 2 inches wide; one layer, 3 inches wide; and one layer, 4 inches wide. Final end overwrap of single end roving, 5 inches from end.

7. Partial curing was achieved in the winding machine for 2 hours at 356° K. Final cure in oven at 422° K for 3 hours.

8. Cylinder removed from liquid nitrogen cooled mandrel over tapered end.

REFERENCES

1. Hanson, Morgan P.; Richards, Hadley T.; and Hickel, Robert O.: Preliminary Investigation of Filament-Wound Glass-Reinforced Plastics and Liners for Cryogenic Pressure Vessels. NASA TN D-2741, 1965.
2. Toth, J. M., Jr.; and Soltysiak, D. J.: Investigation of Smooth-Bonded Metal Liners for Glass Fiber Filament-Wound Pressure Vessels. Rep. No. DAC-60640 (NASA CR-72165), Douglas Aircraft Corp., May 1967.
3. Kinna, Marlin A.: NOL Ring Test Method, NOLTR 64-156, U. S. Naval Ordnance Lab., Nov. 1964.
4. Bacon, R.; Pollazzi, A. A.; Slosarik, S. E.: Carbon Filament Reinforced Composites. Proceedings of the 21st Annual Technical Conference, Reinforced Plastics Division Society of the Plastics Industry, Chicago, Feb. 1966, Section 8-E.
5. Herring, Harvey W.; Baucom, Robert M.; and Pride, Richard A.: Research on Boron Filaments and Boron Reinforced Composites. Advanced Fibrous Reinforced Composites. Vol. 10 of SAMPE Symposium Series. SAMPE, 1966, pp. B-21 to B-34.
6. Kies, J. A.: Maximum Strains in the Resin of Fiberglass Composites. Rep. No. 5752, Naval Research Lab., Mar. 26, 1962.

7. Hollinger, D. L.; and Plout, H. T.: The Role of Stress Corrosion in Glass Fibers. Proceedings of the 19th Annual Technical and Management Conference, Reinforced Plastics Division, Society of the Plastics Industry, Chicago, Feb. 1964, Section 11-A.

8. Coffin, L. F., Jr.; and Tavernelli, J.: The Cyclic Straining and Fatigue of Metals. Rep. No. 58-RL-2100, General Electric Co., Oct. 1958.

TABLE I. - COMPOSITE MATERIALS INVESTIGATED

Material	Designation	Epoxy resin system	Specimen	Cure cyle, hr	Cure cyle, °K
Strength tests					
Glass	S/901 roving[a] (single end)	ERL2256/ZZL0820[b]	NOL rings	2 3	356 422
Boron	Boron halide tungsten substrate	58-68R[c]	Single filament NOL rings	2 2 12	356 450 478
Graphite	Thornel-25[d]	ERL2256/ZZL0820	NOL rings	2 3	356 422
Liner tests					
Glass	S/901 roving, 112 fiber-glass cloth	ERL2256/ZZL0820	Cylinder	2 3	356 422
Aluminum (3 mil)	1100-0				

[a]Owens-Corning Fiberglass Co.

[b]Union Carbide Epoxy Resin, Union Carbide Corp.

[c]Shell Chemical Epoxy Resin, Shell Chemical Co.

[d]Carbon Products Division, Union Carbide Corp.

TABLE II. - TYPICAL AMBIENT PROPERTIES

OF FILAMENTARY MATERIALS[a]

Material	Density, lb/cu in.	Tensile strength, psi	Tensile modulus, psi
Glass-S/901	0.090	650 000	12 500 000
Boron	.090	500 000	60 000 000
Graphite (Thornel-25)	.054	200 000	25 000 000

[a]Published data from ref. 4.

TABLE III. - FILAMENT TRANSLATION EFFICIENCY

IN NOL RING COMPOSITES

Filament	Filament strength, psi	Composite[a] strength, psi	Composite[b] filament strength, psi	Filament translation efficiency, percent
297° K				
S/901 glass	650 000	290 000	447 000	69
E-glass	507 000	------	310 000	61 (ref. 7)
Boron	460 000	174 000	268 000	58
Graphite	200 000	87 000	134 000	67
77° K				
E-glass	814 000	------	510 000	63 (ref. 7)
Boron	483 000	186 000	286 000	59

[a]Based on total area.
[b]Based on filament area.

TABLE IV. - TABULATION OF CYCLIC TESTS OF CYLINDERS

WITH 3 MIL ALUMINUM FOIL

Cylinder number	Surface preparation and adhesive	Test temperature, °K	Strain, percent	Cycles to liner failure	
1	a, b	77	1.9	-------------	46
2	a, b	77	2.5	-------------	16
3	a, b	77	2.1	-------------	[g]40
4	a, b	77	2.5	-------------	14
5	a, b	20	2.5	-------------	65
6	a, b	77	2.4	-------------	[g]24
7	a, b	77	2.3	-------------	15
8	a, b	77	2.3	-------------	23
9	c, b	77	2.3	-------------	26
10	d, e	77	2.3	-------------	78
11	d, b	77	2.3	-------------	107
12	d, b	77	2.1	22 (no failure)	---
		20	2.1	100 (no failure)	---
		20	2.3	10 (no failure)	---
		77	2.3	[g]33	165
13	d, b	77	2.3	-------------	[f]40
14	d, b	77	2.2	-------------	[g]41
15	d, b	77	2.4	-------------	103

[a]Surface sand blasted.

[b]G207 adhesive used on all liners except where noted. (G207, Goodyear Aerospace Corporation).

[c]Sodium dichromate (10 pbw), 95 percent sulfuric acid (30 pbw), distilled water (100 pbw).

[d]Oakite 33, Oakite Corporation.

[e]Cybond 4000, American Cyanamid Company.

[f]Cylinder burst on pressure cycling.

[g]Small areas outside of seam buckled.

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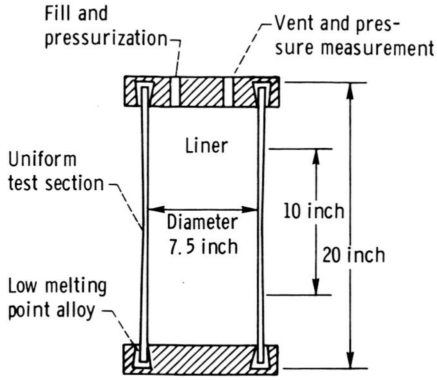

Figure 1. - Schematic diagram of biaxial cylinder with removable end caps for cyclic tests.

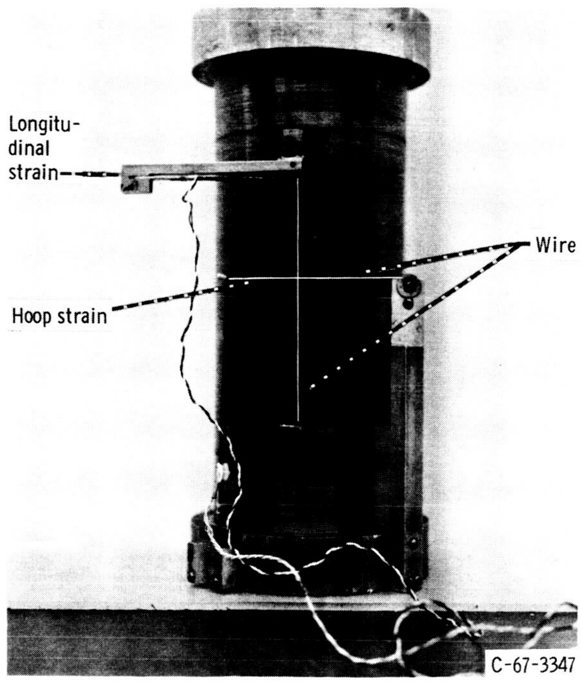

Figure 2. - Photograph of test cylinder with longitudinal and hoop strain measuring instrumentation.

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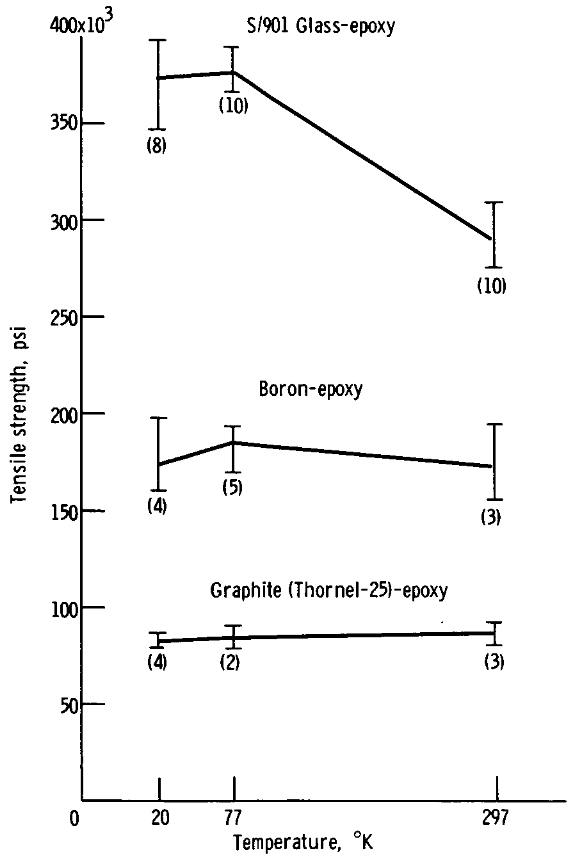

Figure 3. - Composite tensile strength of filament wound NOL rings as a function of temperature. Numbers in parentheses indicate the number of tests for each material and temperature.

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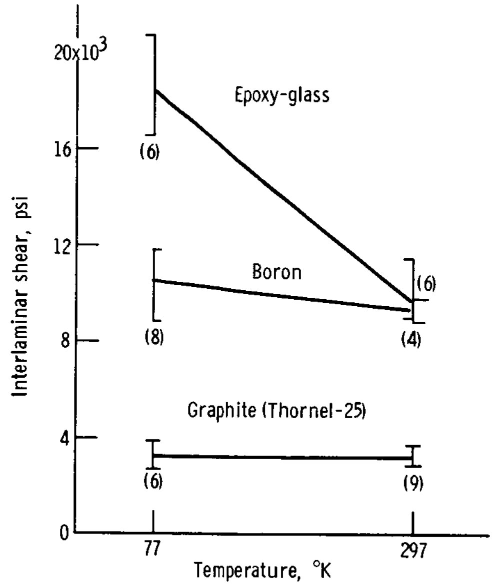

Figure 4. - Interlaminar shear strength of composites, as a function of temperature. Numbers in parentheses indicate the number of tests for each material and temperature.

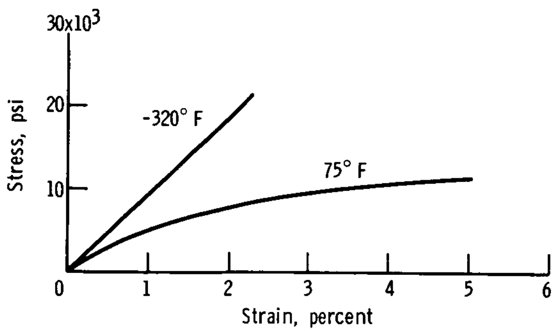

Figure 5. - Stress-strain diagram of ERL2256/ZZL0820 resin at 75° and -320° F (curves represent average of 3 specimens at each temperature).

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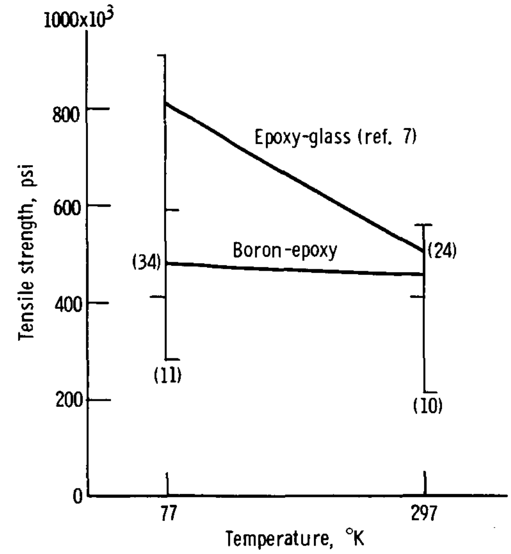

Figure 6. - Single filament tensile strength as a function of temperature. Numbers in parentheses indicate the number of tests for each material and temperature.

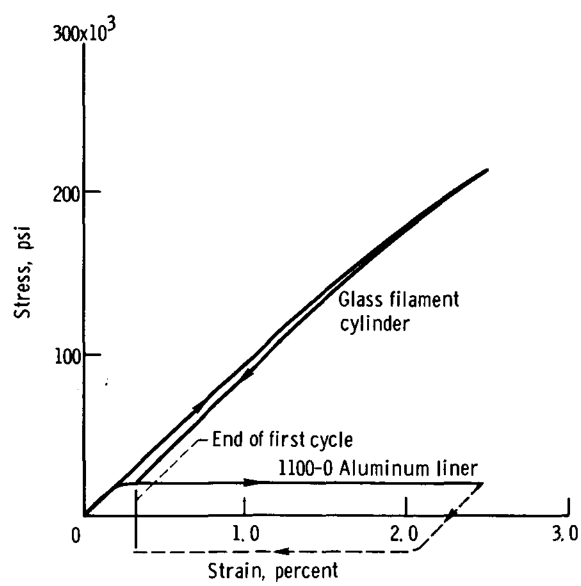

Figure 7. - Stress-strain relationship of cylinder and liner.

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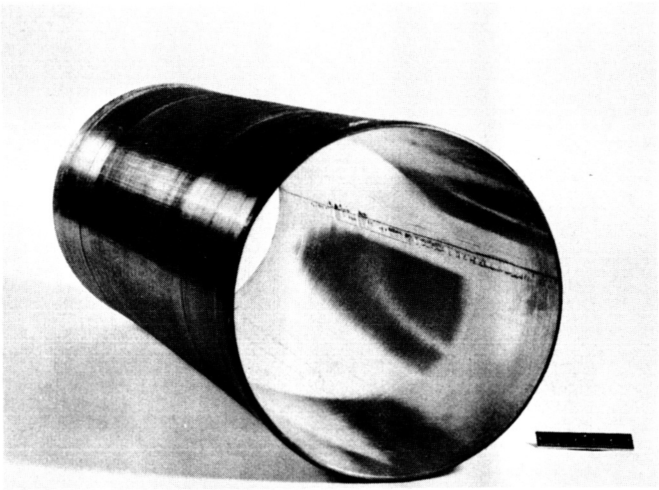

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Figure 8. - Seam failure of aluminum liner after 103 cycles to 2.4 percent strain in liquid nitrogen.