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CARBON FIBER COMPOSITES FOR CRYOGENIC FILAMENT-WOUND VESSELS

By
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ABSTRACT: Compared to metallic vessels, filament-wound vessels for containment of cryogens offer high potential weight savings for NASA spacecraft applications. Since carbon fiber/epoxy resin composites exhibit high strength-to-density ratios, high fatigue life, and excellent strain compatibility with internal metallic liners, advanced unidirectional and bidirectional carbon fiber/epoxy resin composites were evaluated for physical and mechanical properties over a cryogenic to room temperature range for potential application to cryogenic vessels. The results showed that Courtaulds HTS carbon fiber was the superior fiber in terms of cryogenic strength properties in epoxy composites. Of the resin systems tested in NOL Ring composites, CTBN/ERLB 4617 exhibited the highest composite strengths at cryogenic temperatures but very low interlaminar shear strengths at room temperature. Tests of unidirectional and bidirectional composite bars showed that the Epon 828/Empol 1040 resin was better at all test temperatures, with the CTBN/ERLB 4617 composites giving somewhat unpredictable results. Neither fatigue cycling nor thermal shock had a significant effect on composite strengths or moduli. Thermal expansion measurements gave negative values in the fiber direction and positive values in the transverse direction of the composites.

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CARBON FIBER COMPOSITES FOR CRYOGENIC FILAMENT-WOUND VESSELS

This report describes the test results on unidirectional and bi-directional carbon fiber composites fabricated using various fibers and resin systems. The tests were conducted to provide data leading toward the potential use of carbon fiber composites in the construction of cryogenic tankage for spacecraft.

This report covers Task VI under NASA Defense Purchase Request (DPR) C-10360-B, and is the third report in a series on Tasks I-VI. The work on Task I began in May 1967 and consisted of preliminary materials screening and testing. In Task II, the best resin and fibers were used to filament-wind internal pressure vessels, and these were burst tested at room and cryogenic temperatures. The results of tasks I and II were reported in reference (a). Task III, begun in April 1969, was an evaluation of elastomer/epoxy resins and composites, and was reported in reference (b). Tasks IV and V were more extensive evaluations of elastomer/epoxy resins and composites, and Task VI is the report on Tasks IV and V.

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INTRODUCTION

High modulus carbon (or graphite) fiber/epoxy resin composites are being evaluated as candidate materials for potential use in the construction of high strength-to-density, filament-wound internal pressure vessels for Space Shuttle applications.

The first effort under DPR C-10360-B began in May, 1967, as Task I, and results indicated filament-wound carbon fiber composites have ultimate strain values of less than 0.5% at cryogenic temperatures. Such strains are low enough to be elastically compatible with thin internal high strength metallic liners required for leak-free filament-wound internal pressure vessels (ref. (c) and (d)). The brittle failure of vessels reported in Task II indicated that composites exhibiting more ductile failure modes would be desirable. Task III was a study to evaluate the preliminary properties of carbon fiber composites using elastomer (CTBN)-modified epoxy resin systems. Results of this work indicated that such additions significantly increased the tensile strength and toughness of ERLB 4617/Courtaulds HTS composite NOL Rings. Tasks IV and V were continuations of the study of the effects of elastomer additions to epoxy resins on the physical and mechanical properties of carbon fiber/epoxy resin composites.

EXPERIMENTAL WORK

The experimental work on Tasks IV and V is described below.

A. TASK IV

Task IV was a preliminary investigation to determine the physical and mechanical properties of unidirectional composites made from four fibers and four resin systems. The resins and fibers were chosen from the Task III effort (ref. (b)).

1. Resins

The resin systems used in Task IV are presented in Table 1.

Table 1

RESIN SYSTEMS

Assigned Nomenclature	Epoxy Resin	Curing Agent	Additives
828/Empol	Epon 828	DSA 115.9 phr BDMA 1 phr	Empol 1040, 20 phr
4617	ERLB 4617	MDA 46 phr	None
828 polyblend	Epon 828	D 5 phr	Hycar CTBN, 7.5 phr
4617 polyblend	ERLB 4617	MDA 46 phr	Hycar CTBN, 10 phr

DSA = dodecenyl succinic anhydride, Monsanto Chemical Co., St. Louis, Mo.

BDMA = benzyl dimethyl amine, Matheson, Coleman and Bell Co., Norwood, Ohio.

MDA = methylene dianiline, Dow Chemical Co., Midland, Mich.

D = polyamine salt, Shell Chemical Co., New York, N. Y.

Empol 1040 = trimer acid, Emery Industries Inc., Cincinnati, Ohio.

Hycar CTBN = carboxyl terminated butadiene/acrylonitrile copolymer, B. F. Goodrich Co., Cleveland, Ohio.

The systems with a CTNB additive are called "polyblend" systems because on curing the rubber separates as a separate phase (in particles nominally one micron in diameter). Reference (b) details Task III test results of these resins.

2. Fibers

The fibers used in Task IV are listed in Table 2 along with their advertised properties.

Table 2

FIBERS AND THEIR PROPERTIES

Fiber	Density	Mfr's Advertised Mean Tensile Strength		Mfr's Advertised Mean Tensile Modulus	
	gm/cm^3	$10^8 n/m^2$	(psi)	$10^{10} n/m^2$	(psi)
Thornel 50	1.62	18	(260,000)	34	(49×10^6)
HITCO HMG 50	1.72	21	(310,000)	35	(50×10^6)
Courtaulds HTS	1.77	28	(400,000)	26	(38×10^6)
Courtaulds HMS	1.88	20	(290,000)	38	(55×10^6)

3. Composites

The NOL Ring was the only composite specimen used in Task IV. These were filament wound in a vacuum, with wet resin dip impregnation at 22° C and strand tensions up to three kilograms to control resin content. Fiber contents in completed rings ranged from 42 to 48 volume percent. Reference (f) gives additional information on the fabrication of NOL rings.

4. Specimens and Tests

Tests were conducted on resin as well as NOL Ring composite specimens, as shown in Table 3.

Table 3

SPECIMENS AND TESTS

Specimen	Specimen Size	Test	Test Method
Cast resin bar	0.32 cm thick	tensile modulus	ASTM D638-67T
		tensile strength	ASTM D638-67T
NOL Ring	full ring	tensile modulus	Split pin (ref. (f))
		tensile strength	Split-D (ref. (f))*
			Case (ref. (g))**
NOL Ring segment	5/1 span/depth	interlaminar shear strength	Short beam (ref. (f))

* Used for cryogenic temperature testing
** Used for room temperature testing

Five replicates were used for each data point. Tests were run at 22° C, -195° C, and -253° C. Testing at -253° C was contracted to the Research and Development Division of the Whittaker Corporation, San Diego, California.

B. TASK V

The Task V effort was an intensive study of selected materials from Task IV, in the form of unidirectional and bidirectional laminates, NOL Rings and tow specimens.

1. Resins

The 828/Empol and 4617 polyblend resins were the most promising, and were chosen for the Task V work.

2. Fibers

Based on Task IV data, Courtaulds HTS fiber was selected for fabrication of the majority of the specimens in Task V. (A limited study was conducted in Task V to determine if Modmor II fiber was equivalent to Courtaulds HTS fiber.)

3. Composites

Composites fabricated included unidirectional and bidirectional flat plates, NOL Rings, and impregnated tows. The fiber used in the flat plates was preimpregnated with the resins by Hercules, Inc., Cumberland, Maryland (now Bacchus, Utah), and was supplied to NOL in the form of unidirectional broadgoods. To make the flat plates, pieces were cut from the broadgoods, laid in a mold in the proper orientation, then heat and pressure were applied to effect cure. The plates were 28 x 28 cm, and of various thicknesses from 0.15 to 0.32 cm. Fiber orientations were unidirectional and 2:1 bidirectional with plies at angles of 0°, 90°, 0°, 0°, 90°, 0°, 0°, 90° and 0° to each other. Fiber contents ranged from 49 to 56 volume percent. A few NOL Rings were made with Modmor II fiber by wet winding as described in the Task IV work.

4. Specimens and Tests

Table 4 lists the specimens and the tests performed.

The allocation of flat plate test samples to the various tests, the test temperatures, and the number of replicates are listed in Table 5.

Testing of NOL Rings (5 replicates) was conducted at -235°C. A minimum of 5 tow specimens, each, were tested at 22°, 195°, and -253°C. Testing at -253°C was conducted by the Whittaker Corporation.

RESULTS AND DISCUSSION

A. TASK IV

Test results indicated that unidirectional composites made from Courtaulds HTS fiber yielded the highest values of tensile and interlaminar shear strengths at all three test temperatures. Composites made from 4617 polyblend resin yielded the highest tensile strength values at cryogenic and the lowest values at room temperature. Composites made from 828/Empol resin performed consistently well over the range of test conditions. Details of the Task IV results are as follows:

1. Resins

a. Tensile Strengths. The resin tensile strengths at

Table 4

SPECIMENS AND TESTS

Specimen	Preparation or gripping method	Test	Remarks
Tensile bar	Carbon fiber composite tabs bonded on. Bars cut to 28 cm long with 1 cm wide by 5 cm long gage section. Whole bar 0.15 cm thick.	Tensile modulus Tensile strength	Mount extensometer on specimen. Pull at 0.1 cm/min.
		100 cycle fatigue	Stress to 75% ultimate tensile strength 1000 times, then test for modulus and strength as noted above.
		Thermal shock	Immerse in cryogenic liquid, remove, warm to room temperature. Repeat 50 times. Test for transverse modulus, strength.
Bar	Cut to 1.27 x 0.635 cm (4/1 span/depth)	Interlaminar shear strength	ASTM D2344, with modified fixture for holding strength specimen.
		Thermal shock	Immerse in cryogenic liquid, remove, warm to room temperature. Repeat 50 times. Test for shear strength.
Plate	Cut to 2.5 x 2.5 x 0.25 cm	Thermal expansion/contraction	ASTM D696, with specimen holder modified to take plate specimen.
NOL Ring		Tensile strength	Split-D, ref. (f).
Tow	Cardboard tabs bonded to ends. Gage length 6.35 cm	Tensile strength	Pull at 0.1 cm/minute.

TABLE 5 TASK V TEST MATRIX

TESTS	FLAT PLATE MOLDED TEST SPECIMENS All specimens with Courtaulds HTS fiber			NUMBER OF SPECIMENS TESTED					
				TESTED AT 70°F.		TESTED AT -320°F.		TESTED AT -423°F.	
	COMPOSITE FIBER ORIENTATION	SPECIMEN PRE-CONDITIONING	TEST DIRECTION RELATIVE TO FIBER DIRECTION	Composite with 828/Empol Resin	Composite with 4617 Poly Resin	Composite with 828/Empol Resin	Composite with 4617 Poly Resin	Composite with 828/Empol Resin	Composite with 4617 Poly Resin
Tensile Strength and Tensile Modulus	Unidirectional	None	Axial	5	5	5	5	5	5
			Transverse	5	5	5	5	5	5
	2:1 Bidirectional	None	0°	5	5	5	5	5	5
			90°	5	5	5	5	5	5
	Unidirectional	Tensile Fatigue (1000 cycles at 75% ultimate stress)	Axial	5	5	5	5	5	5
			Transverse	5	5	5	5	5	5
	2:1 Bidirectional	Tensile Fatigue (1000 cycles at 75% ultimate stress)	0°	5	5	5	5	5	5
			90°	5	5	5	5	5	5
	Unidirectional	Thermal Shock 50 Cycles	Transverse	0	0	5	5	5	5
Interlaminar Shear Strength	Unidirectional	None	Axial	5	5	5	5	5	5
	2:1 Bidirectional	None	0°	5	5	5	5	5	5
			90°	5	5	5	5	5	5
	Unidirectional	Thermal Shock 50 Cycles	Axial	5	5	5	5	5	5
	Unidirectional	Fiber Content Effect (45 to 70%, Vol.)	Axial	5	5	5	5	5	5
Thermal Contraction	Unidirectional	None	Axial	5	5	5	5	5	5
			Transverse	5	5	5	5	5	5
	2:1 Bidirectional	None	0°	5	5	5	5	5	5
			90°	5	5	5	5	5	5
Total Number of Specimens to Be Tested At 70°F.				85	85				
Total Number of Specimens to Be Tested At -320°F.						90	90		
Total Number of Specimens to Be Tested At -423°F.								90	90

the three test temperatures are shown in Figure 1. At -253° C, the strengths of all four resin systems were approximately the same, 92 x 10^6 n/m^2 (12000 psi). The coefficients of variation were higher with the cryogenic measurements, the highest being 0.24 in the liquid hydrogen tests and probably caused by increased brittleness at cryogenic temperatures.

b. Moduli. All four resin systems showed increased moduli at lower test temperatures. Moduli at room temperature were in the 21-45 x 10^8 n/m^2 (0.3-0.6 x 10^6 psi) range, and increased 70 to 150 percent to 50-80 x 10^8 n/m^2 (0.65-1.1 x 10^6 psi) at cryogenic temperatures (Fig. 1). Moduli increases at lower temperatures are typical of polymeric materials.

2. Composites

a. Tensile Strengths. Composite NOL Ring tensile testing was conducted to select the most promising fiber/resin combination. Test results indicated that no single fiber/resin combination indicated a clear superiority. The highest cryogenic fiber tensile strength, 24 x 10^8 n/m^2 (350,000 psi), was exhibited by the HTS/4617 polyblend composite. This was the only resin/fiber combination that exhibited higher strengths at cryogenic than room temperature (Fig. 2b). Composites made from 828/Empol resin performed reasonably well over a broad range of fiber types and test temperature conditions, as shown in Figures 2a and 2b. In data not shown in the figures, a decrease in the CTBN content from 10 to 7.5 phr did not significantly affect cryogenic composite tensile strength values. Increasing the CTBN content to 15 phr, however, led to a decrease in the effective fiber strengths at cryogenic temperatures to 17 x 10^8 n/m^2 (250,000 psi), a 30% reduction over values obtained with 10 phr CTBN content.

b. Interlaminar Shear Strengths. The best fiber was Courtaulds HTS with composite interlaminar shear strengths as much as 100% higher than those for the other fibers. The margin was greatest at cryogenic temperatures where HTS composites exhibited large strength increases (to 130 x 10^6 n/m^2 or 20,000 psi) over room temperature strengths, while composites of other fibers exhibited only small increases. The 828/Empol resin with the HTS fiber gave highest strengths at cryogenic temperature followed by 828 polyblend and 4617 polyblend resins (Fig. 3a, 3b). The 4617 polyblend resin exhibited very low room temperature interlaminar shear strengths, these being in the 12-25 x 10^6 n/m^2 (2-4 x 10^3 psi) range. Variations in the CTBN content of the ERLB 4617 to 7.5 and 15 phr did not improve low shear strength values at room temperature. Additional postcuring of the composite slightly improved the shear strength values but not nearly to the level exhibited by composites incorporating the unmodified resin. Apparently the CTBN additive inhibits good bonding of the matrix to the fibers, at least at room temperature.

B. Task V

Task V was the further, more extensive testing of the 828/Empol and 4617 polyblend resin systems and Courtaulds HTS fiber in both unidirectional and bidirectional composites. The fiber strengths obtained in these tests were the same as or slightly lower than the strengths obtained in the Task IV ring testing effort. Composites with the 828/Empol resin generally gave the higher values. Task V included some tensile fatigue testing to 1000 cycles. Results showed that such testing had no effect on axial (0°) tensile properties. Transverse (90°) fatigue testing broke some of the specimens, but those specimens that survived were as strong as the uncycled specimens. Details of Task V results follow:

1. Tensile Strengths

a. Unidirectional Composites.

(1) Axial direction. Fiber tensile strength values of NOL Rings were lower at room temperature but the same at liquid hydrogen temperature as the Task IV NOL Ring results. Composites made with the two resin systems were generally equivalent in strength properties except that composites with the 4617 polyblend system showed slightly superior tensile fatigue performance at -253°C (Figure 4).

(2) Transverse direction. Figure 5 shows that the transverse tensile strengths of 4617 polyblend composites are very low (less than 10 x 10^6 n/m^2, or 1000 psi). The 828/Empol system in composites performed reasonably well in both the single cycle and the 1000 cycle fatigue tests. Reasons for the poor performance of the 4617 polyblend are not evident since the interlaminar shear strengths in both Tasks IV and V were high at cryogenic temperatures. Postcures of these composites produced only slight improvements in transverse tensile strengths.

Composites with the 828/Empol resin showed some strength increases after cyclic fatigue but these improvements may not be significant due to the high coefficients of variation of both the uncycled and cycled test specimens. The 4617 polyblend composites were so weak that cyclic tests were not meaningful. Only one of the room temperature specimens made it through the 1000 cycles. Specimens subjected to thermal shock (50 immersions in the cryogenic liquid) showed no apparent changes in tensile strengths.

b. Bidirectional Composites (2:1)

Bidirectional composites with the 828/Empol system had approximately 2/3 the strength in the 0° direction and 1/3 the strength in the 90° direction of the axial strength of unidirectional composites. The bidirectional layup, therefore, did not result in reduction of fiber strengths when the 828/Empol resin was used. The strengths of the 4617 polyblend composites were,

however, somewhat reduced in the bidirectional layup, particularly in the 0° direction and after tensile fatigue. The high modulus and low extensibility of the 4617 polyblend system probably resulted in high internal stresses in the crossply configuration, resulting in resin microcracking and reduced composite tensile strength (Fig. 6).

2. Tensile Moduli

a. Unidirectional Composites

(1) Axial direction. Moduli of unidirectional composites, measured in the axial direction at the three temperatures showed very little difference between composites employing the two resin systems. Moduli increased an average of 20% with decreasing temperatures, which is consistent with results in previous tasks. Cycling had very little effect on the moduli. Composite moduli were in the range of 10-15 x 10^{10} n/m^2 (15-20 million psi), as shown in Figure 7.

(2) Transverse direction. Moduli in the transverse direction of unidirectional composites increased with decreasing temperatures, in some cases over 200% (Fig. 8), with the 828/Empol resin showing the higher moduli of the two. The 4617 polyblend neat resin had the higher moduli at all temperatures (Fig. 1), but in composites there evidently was enough resin microcracking and debonding from the fibers to result in low composite moduli values. The coefficients of variation of the measurements of the 4617 polyblend resin composites averaged 0.23. This high variation is another indication of the probable presence of cracks or flaws which could have a significant effect on the moduli values. The effects of tensile cycling on moduli values were negligible with the 828/Empol composites, and indeterminate with the 4617 polyblend composites because of the number of specimens that fractured during the test. This is indicated in the extremely low transverse tensile strength and high coefficients of variation values for this resin system shown in Figure 6.

b. Bidirectional Composites (2:1)

Moduli of bidirectional composites generally increased with decreasing temperature (Fig. 9). For composites with the 828/Empol resin the 0° moduli values were twice the 90° values, as expected for these 2:1 layups. However, with the 4617 polyblend composites the moduli values were lower, and the 0° values were only approximately 70% higher than the 90° values, which indicates poor bonding of the crossplied layers.

3. Interlaminar Shear Strengths

a. Unidirectional Composites

Unidirectional composites with the 828/Empol System gave room temperature shear strengths more than twice as high as

the 4617 polyblend composites (Fig. 10). At cryogenic temperatures the same difference existed with strength generally increasing. Thermal shock had no noticeable effect on shear strengths. All of these results are consistent with the Task IV results on tests of rings.

b. Bidirectional Composites

Bidirectional shear strengths at room temperature were the same as the unidirectional strength values (Fig. 10). At cryogenic temperatures, however, the bidirectional values were considerably lower than the unidirectional values. This is assumed to be the result of increased thermal stresses which occur in the composites when they are cooled to cryogenic temperatures. The 0° shear strengths at cryogenic temperatures were essentially the same as the 90° strengths. The 4617 polyblend composites gave lower shear strengths than the 828/Empol composites throughout the Task V testing and was consistent with the Task IV shear strength results.

c. Fiber Content Effect

Fiber content effects on shear strengths were measured on specimens with fiber contents ranging from 42 to 58 volume percent. There was no difference in shear strength attributable to fiber content over the range of 42 to 52 percent. At 58 volume percent fiber, shear strengths decreased generally by 10 to 15 per cent. At cryogenic temperatures the coefficients of variation were greater than 10%; therefore, firm conclusions cannot be drawn. It appears that over the small range tested the fiber content effect may be negligible.

4. Thermal Contraction

a. Unidirectional Composites

Average thermal contraction coefficients for unidirectional specimens in the transverse direction were large, resulting in specimen contraction of 0.006 cm/cm or more when cooled from 22°C to -253°C (Fig. 11). In the axial direction the response was different. On cooling from room temperature, expansion occurred until some temperature above -195°C when a reversal occurred and the specimens began contracting. The contraction continued through the range -195°C to -253°C, but at -253°C the contraction did not equal the prior expansion that had occurred and the net result was an expansion. The coefficients of thermal expansion presented are averages over the entire range and are not valid for calculating other points within the range.

b. Bidirectional Composites

Bidirectional composite specimens exhibited low

coefficients of thermal expansion in both the 0° and 90° directions. In the 0° direction, the thermal expansion values were negative and small in magnitude at both -195°C and -253°C. In the 90° direction, the expansion was positive and similar in magnitude. These differences in the axial and transverse expansions result in large thermal stresses within bidirectional specimens and contribute to their reduced composite strengths.

5. Tow Tests

Tow test results using Courtaulds HTS and three resin systems are shown in Table 6.

Table 6

TENSILE STRENGTH OF SINGLE IMPREGNATED TOW

Temp	Tow with 828/Empol resin		Tow with 4617 polyblend resin		Tow with ERLB 4617 resin	
°C	10^8 n/m^2	Cv	10^8 n/m^2	Cv	10^8 n/m^2	Cv
22	21.7	0.10	16.6	0.10	19.1	0.05
-195	18.7	0.16	21.4	0.08	14.6	0.12
-253	22.2	0.27	19.2	0.20	16.1	0.04
Average	20.9	0.18	19.1	0.13	16.6	0.07

The same table is shown below in English units.

°F	psi	psi	psi
72	315,000	241,000	277,000
-320	271,000	310,000	211,000
-423	322,000	278,000	234,000
Average	303,000	276,000	241,000

Five replicates were tested for each value. These results show that the 828/Empol system generally yielded higher results than the ERLB 4617 systems. This was in contrast to results obtained in Tasks IV and V in tests of NOL Rings, in which the 4617 polyblend system yielded the highest values. This conflict in results is believed to result from the different specimen configurations that were utilized. The NOL Ring, as tensile tested in Tasks IV and V by the "Split D" method, undergoes bending. This combination loading of tension and bending evidently is better accommodated by composites incorporating the polyblend resins than the nonpolyblend types. The tow test is "pure" tension, with no bending and the nonpolyblend resin yielded higher fiber strength values than the polyblend resin.

6. Tests of Modmor II Fiber

Tensile strengths of NOL Rings fabricated using Modmor II, instead of Courtaulds HTS, and 4617 polyblend resin averaged 10.2 x 10^8 n/m^2 (148,000 psi) at -253°C (-423°F). This value compares with 10.3 x 10^8 n/m^2 (150,000 psi) for the Courtaulds HTS fibers in NOL Rings of equivalent fiber content. Shear strengths of Modmor II composites using the 828/Empol and 4617 polyblend resin systems were approximately the same as the values obtained in Task IV tests. Based on limited test data, Modmor II fiber appeared to be equivalent to Courtaulds HTS fiber.

CONCLUSIONS

1. Conclusions from the Task IV effort are as follows:

a. Courtaulds HTS fiber composites yielded fiber tensile strengths in NOL Rings of up to 24 x 10^8 n/m^2 (350,000 psi) at cryogenic temperatures. HITCO HMG 50, Thornel 50, or Courtaulds HMS fibers in composites, while sometimes stronger at room temperature, yielded strength values at cryogenic temperatures only 50 to 80% as high. The Courtaulds fiber composites showed composite interlaminar shear strength values ranging from 10 to 125 x 10^6 n/m^2 (1500 to 20,000 psi), depending on resin and temperature. Coldest temperatures gave highest values. Other fibers in composites gave shear strengths averaging about two thirds as high.

b. The ERLB 4617 polyblend resin system generally yielded the strongest composites, followed by the Epon 828/Empol 1040 resin system. These two resins and the Courtaulds HTS fiber were chosen for the Task V work.

2. Conclusions from the Task V effort are as follows:

a. Fiber tensile strength values in both unidirectional and bidirectional bars were similar to values developed in the Task IV ring studies when the 828 Empol resin system was used. The 4617 polyblend resin in composites resulted in lower strengths, typically 80% of the Task IV values but with wide variations depending on the test and temperature.

b. Composite and fiber tensile moduli increased with decreasing temperature. The 828/Empol resin system in composites gave composite moduli as predicted by the law of mixtures. The 4617 polyblend resin system in crossply laminates gave composite moduli nominally 70% of that predicted by the law of mixtures, indicating that the composite probably contained microcracks and unbonded areas possibly caused by thermal stresses on cooling.

c. Interlaminar shear strengths for both resins in unidirectional composites were about as measured in Task IV. But strengths in bidirectional composites were lowered, no value exceeding 105 x 10^6 n/m^2 (15,000 psi). Internal stresses in the

crossply laminates probably were responsible for this.

d. Generally, neither tensile cycling nor thermal shock had a significant effect on strengths or moduli.

e. Coefficients of thermal expansion of composites were negative in the fiber direction and positive transverse to the fiber direction. For 2:1 crossply layups, the coefficient was essentially zero in the "2" direction and positive in the "1" direction.

f. A small amount of tensile testing of impregnated tows showed that tows impregnated with 828/Empol resin gave higher strengths than tows impregnated with 4617 polyblend resin, a result in conflict with ring test results in Task IV. The measured strength apparently depends on specimen configuration and the types of nontensile loads introduced into the specimens during tensile testing of NOL Rings.

g. Modmor II tow was found to be equivalent to Courtaulds HTS for cryogenic applications.

3. From both the Task IV and Task V results, it is concluded that Courtaulds HTS fiber and the Epon 828/Empol 1040 resin systems are the best materials tested for general cryogenic use in both unidirectional and crossplied laminates.

RECOMMENDATIONS

Based on the work performed in this program, the following recommendations are presented:

1. Perform single filament tests at cryogenic temperatures to determine if strength and modulus changes are intrinsic to the fiber.

2. Fabricate internal pressure vessels with the best materials, and determine the mechanical properties over a cryogenic to room temperature range.

FOLLOW-ON WORK

Recommended work described above (2) is continuing as Tasks VII and VIII, and will consist of the design, fabrication and testing of up to 20 internal pressure vessels. The work will be contracted, as was the Task II vessel work, and is expected to be completed in September 1972.

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General Notes for Figures 1 thru 10

1. 4617, 4617 Poly, 828/Empol, and 828 Poly are resin system designations. (applies to figures 1 - 3
2. Each number in parenthesis is average coefficient of variation for all measurements at that temperature.

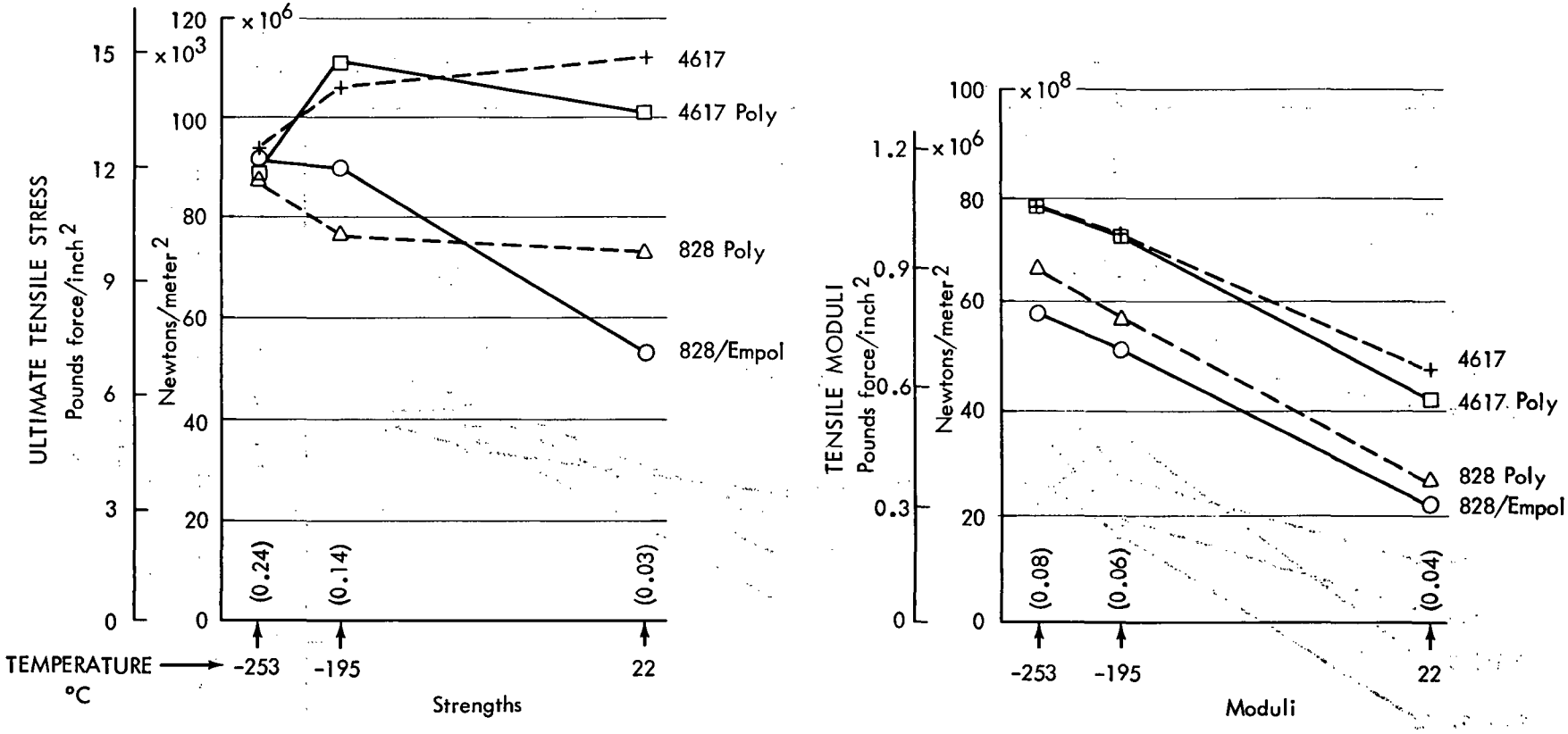

FIG. 1 RESIN TENSILE STRENGTHS AND MODULI
Average values from cast resin bars.

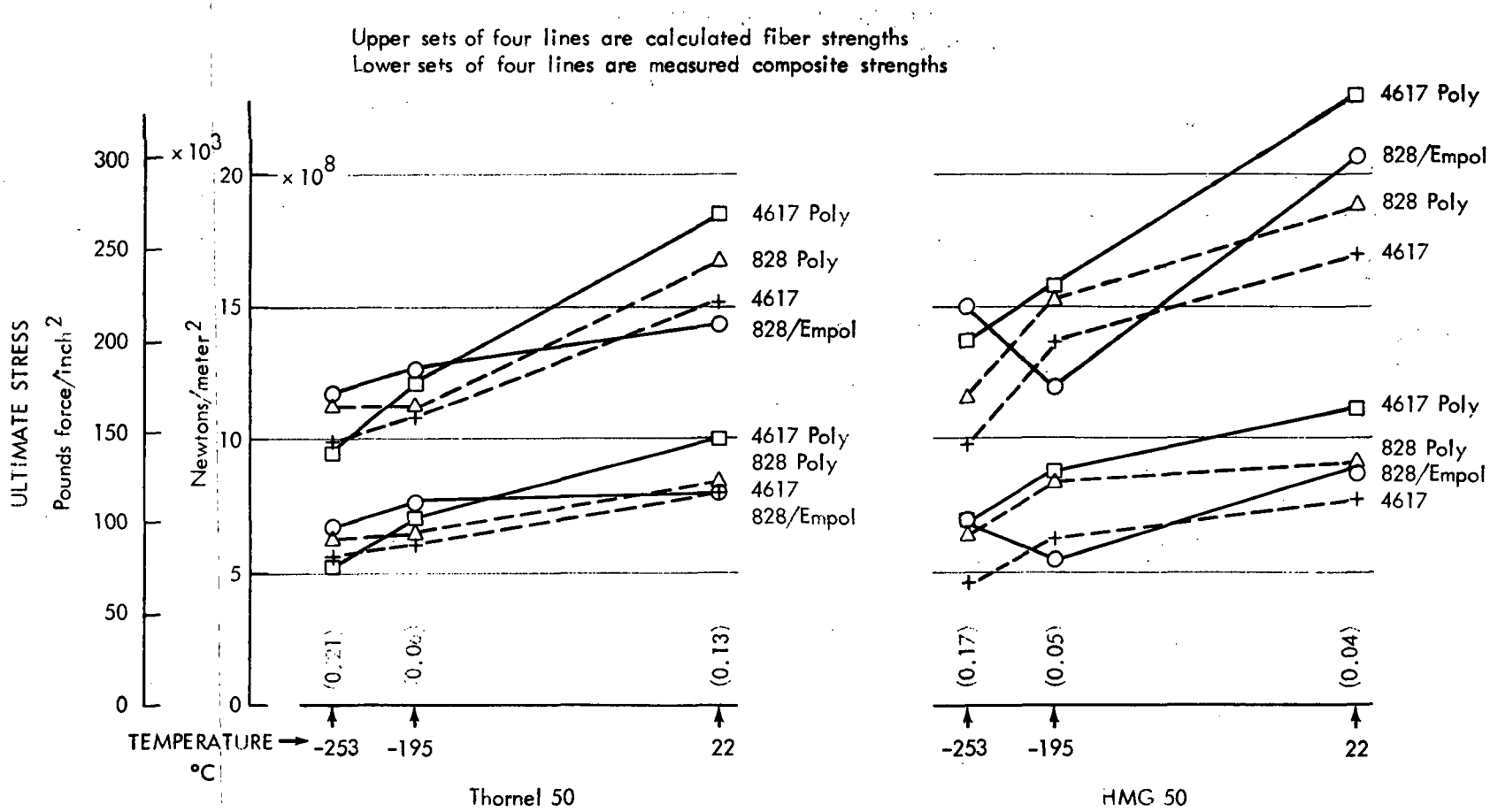

FIG. 2a COMPOSITE AND FIBER TENSILE STRENGTHS
Average values from NOL Rings.

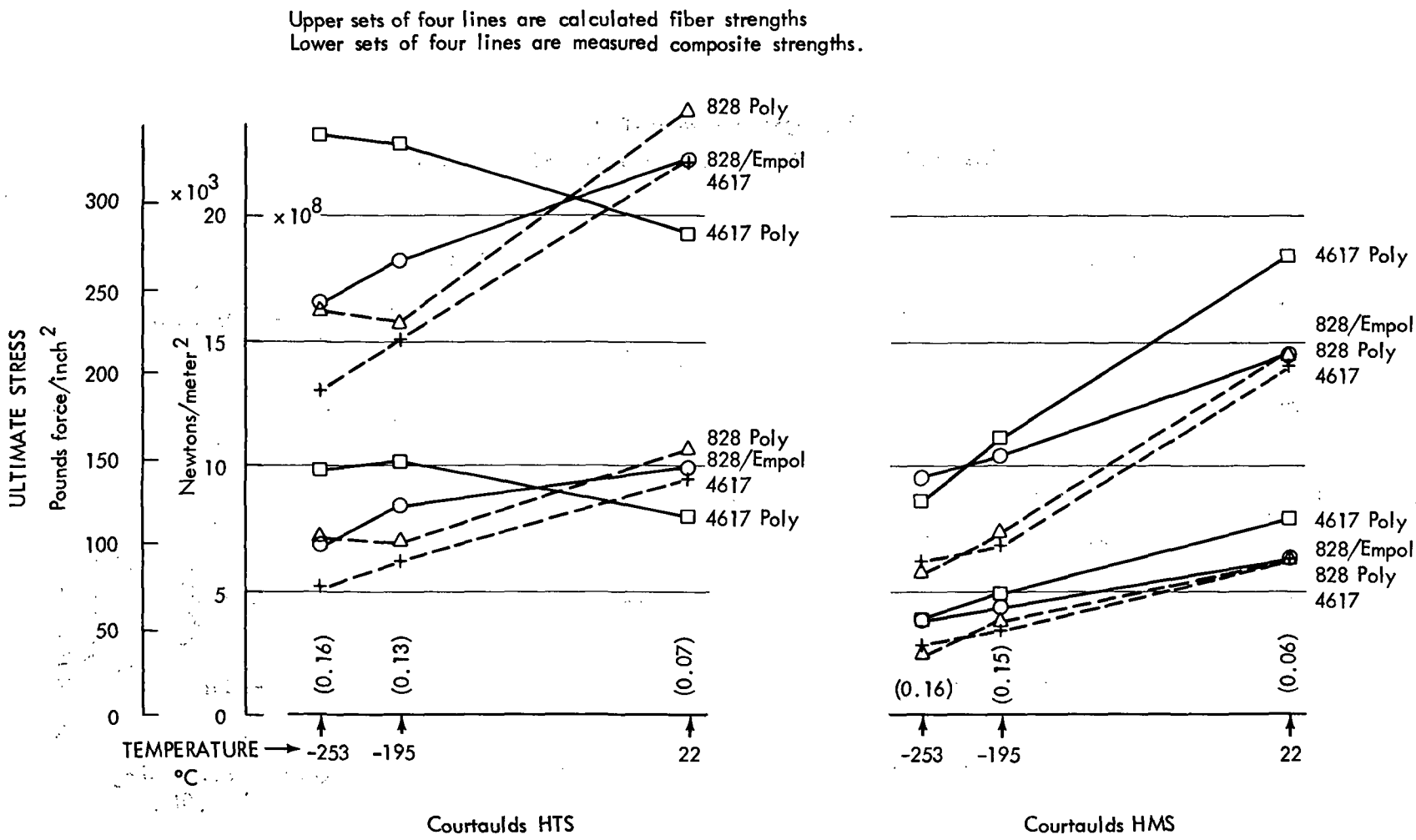

FIG. 2b COMPOSITE AND FIBER TENSILE STRENGTHS

Average values from NOL Rings.

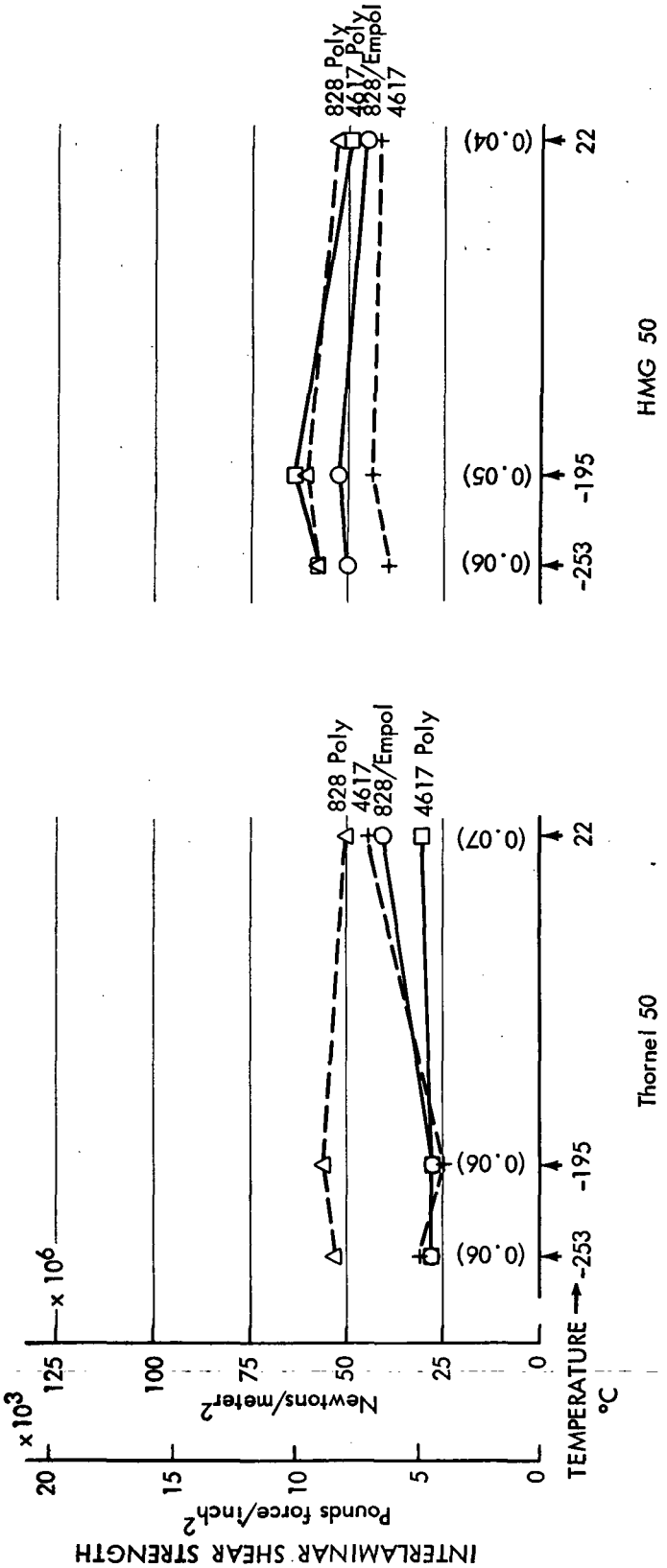

FIG. 3a COMPOSITE INTERLAMINAR SHEAR STRENGTHS
Average values from NOL Rings.

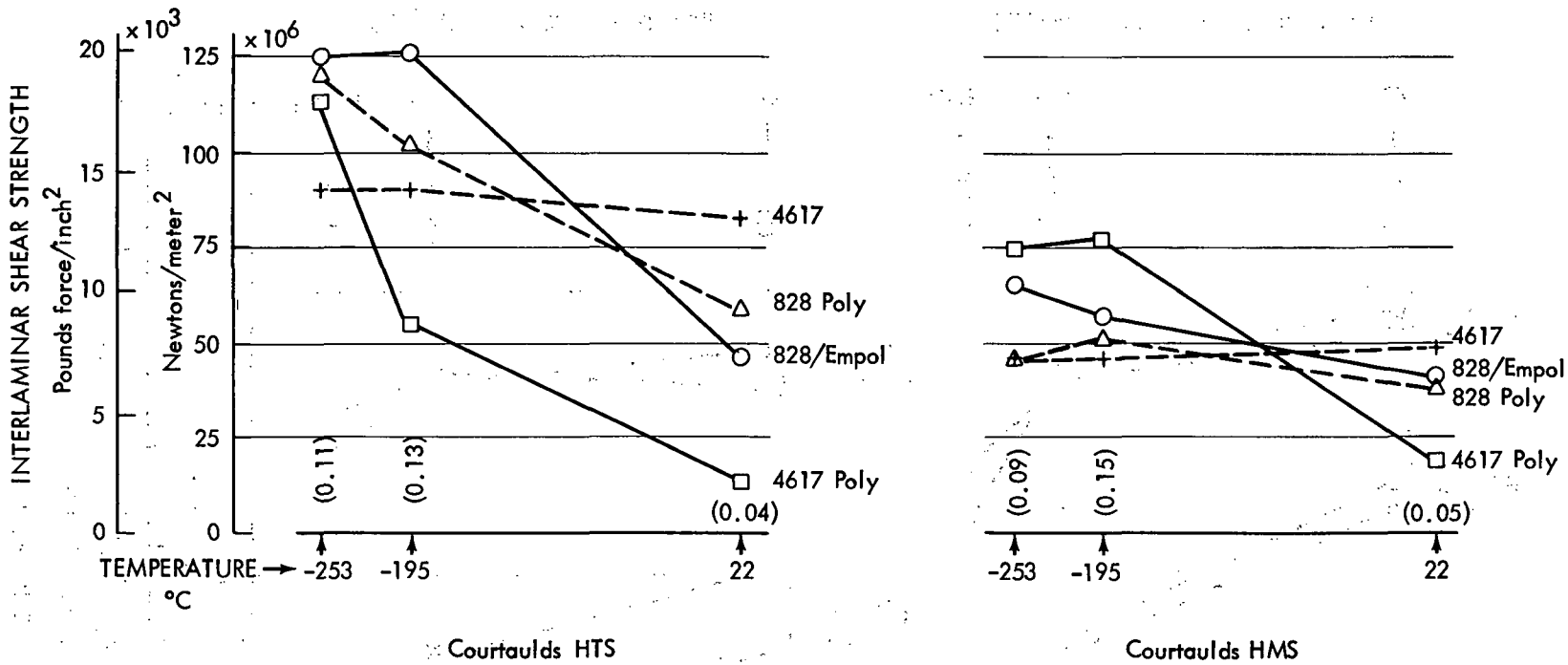

FIG. 3b COMPOSITE INTERLAMINAR SHEAR STRENGTHS
Average values from NOL Rings.

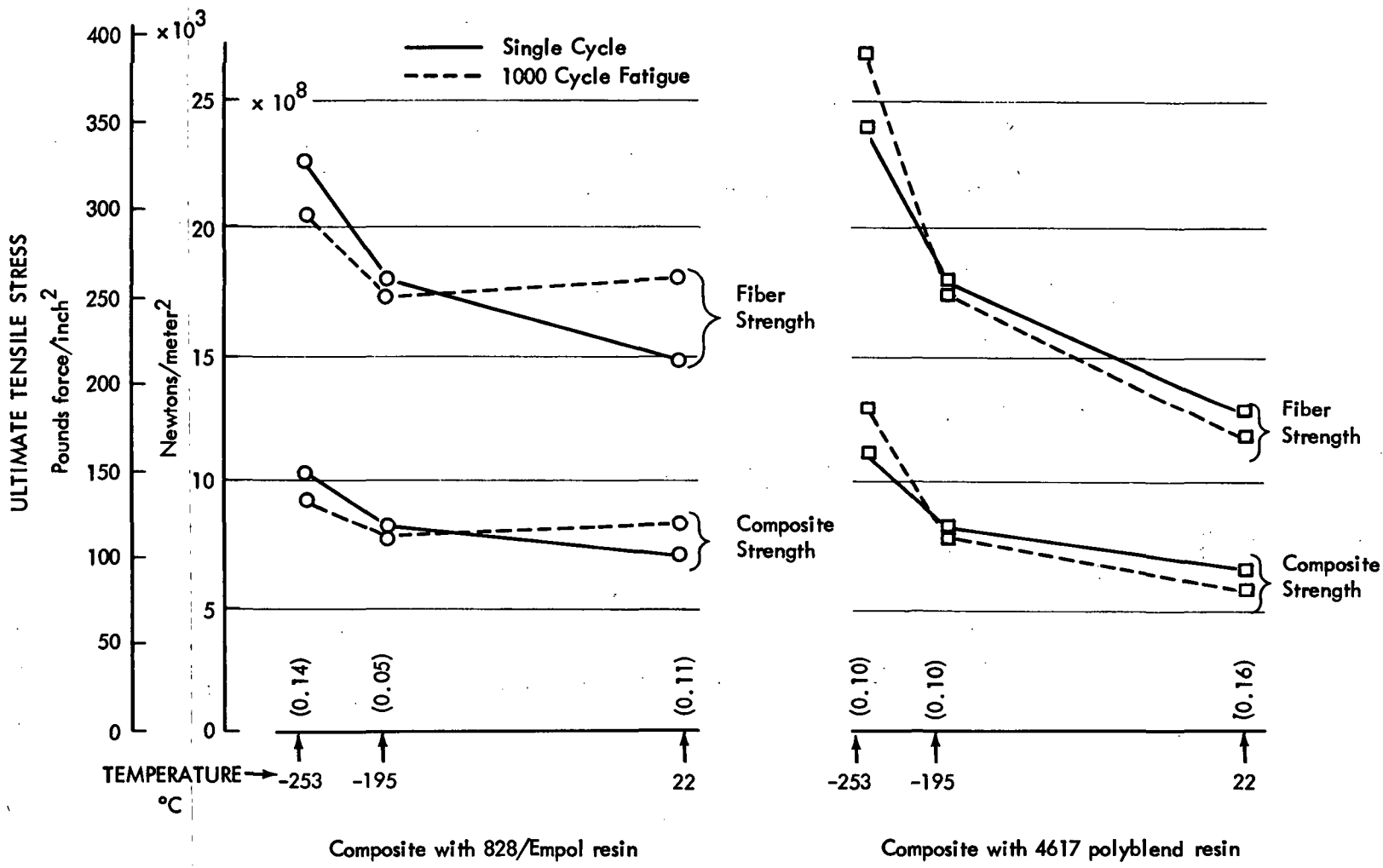

FIG. 4 AXIAL TENSILE STRENGTHS
Average values from unidirectional molded flat plates using Courtaulds HTS fiber.

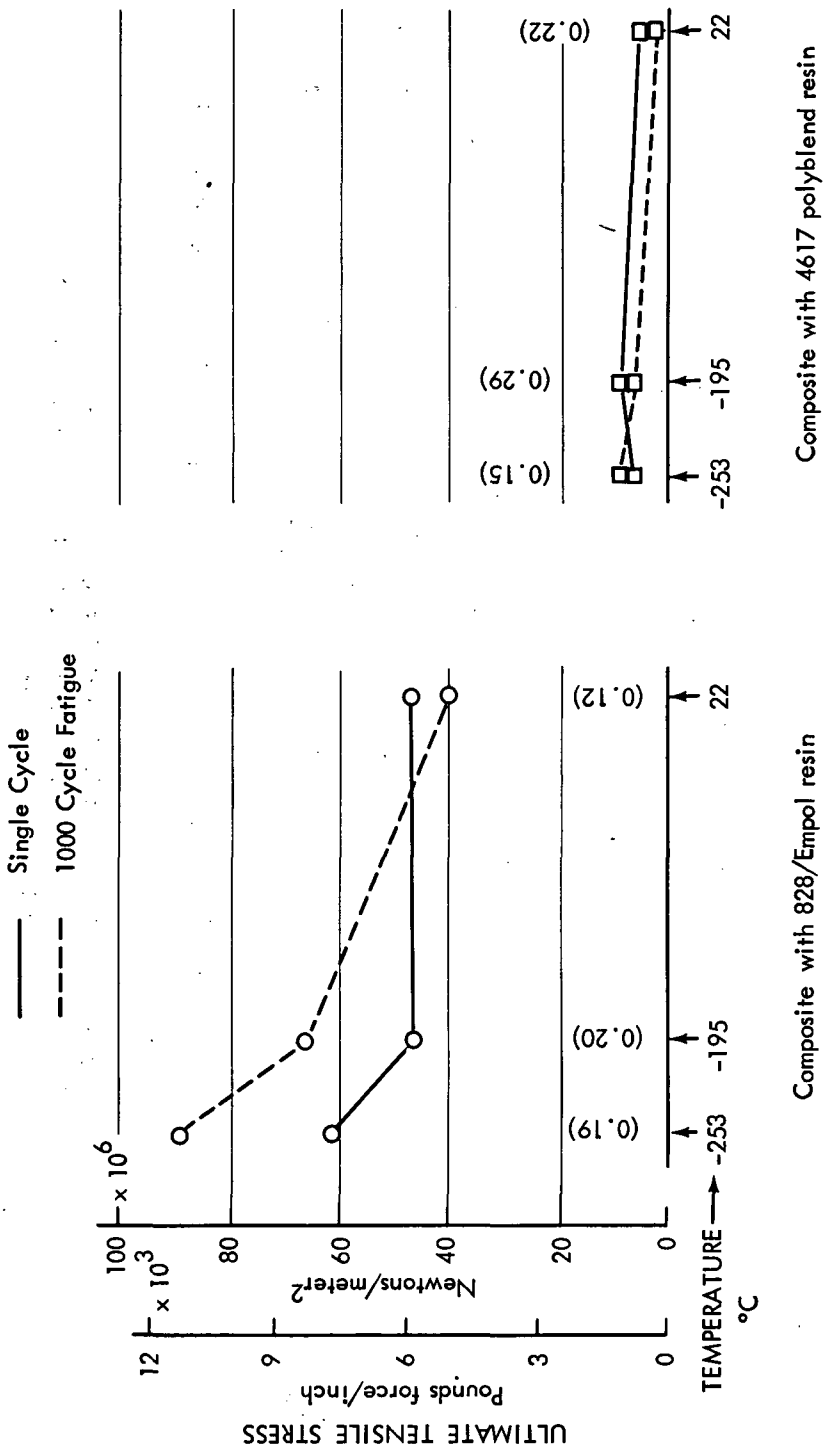

FIG. 5 TRANSVERSE TENSILE STRENGTHS
Average values from unidirectional molded flat plates using Courtaulds HTS fiber.

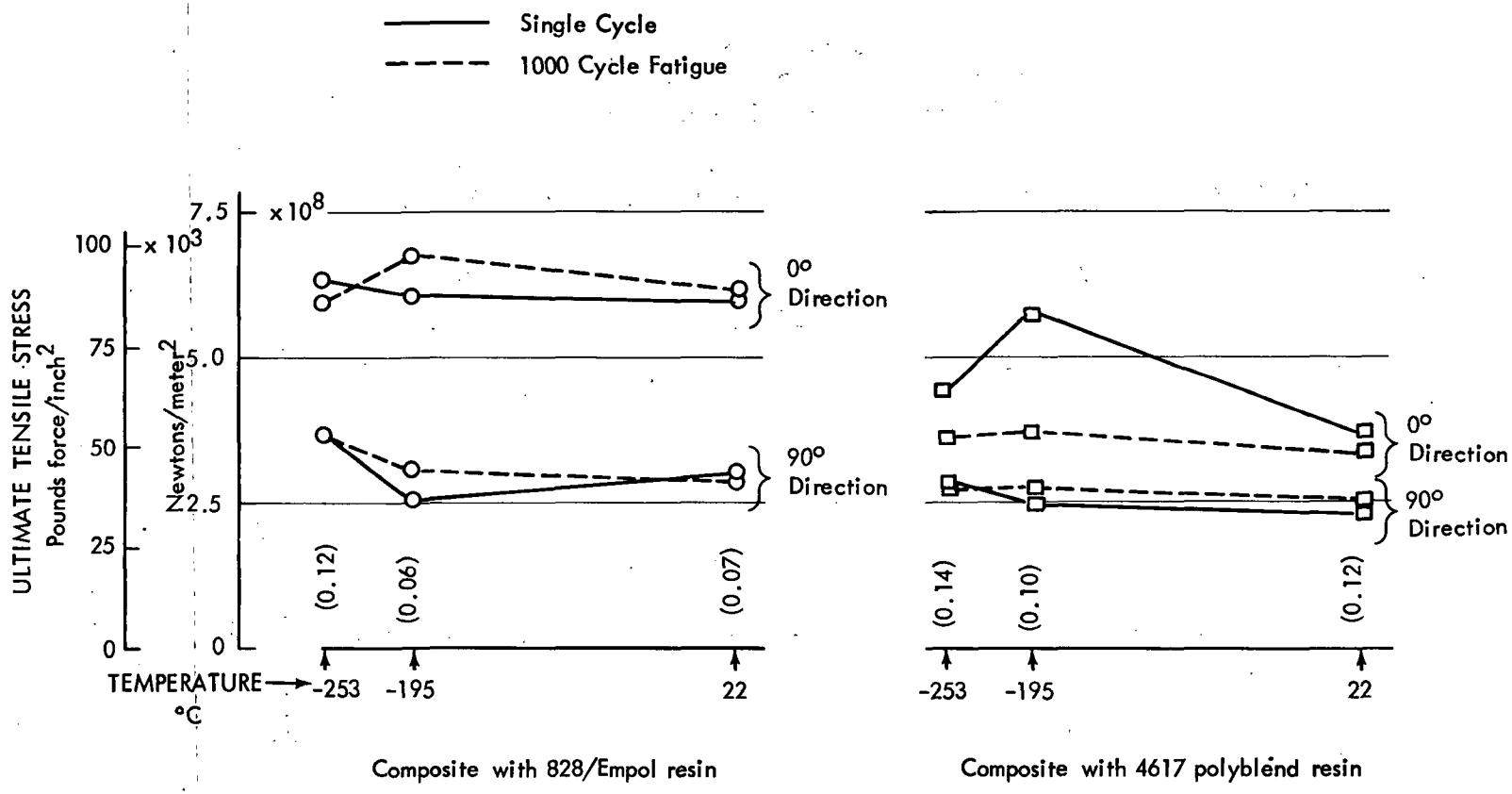

FIG. 6 0° AND 90° COMPOSITE TENSILE STRENGTHS
Average Values from 2:1 bidirectional molded flat plates
using Courtaulds HTS fiber.

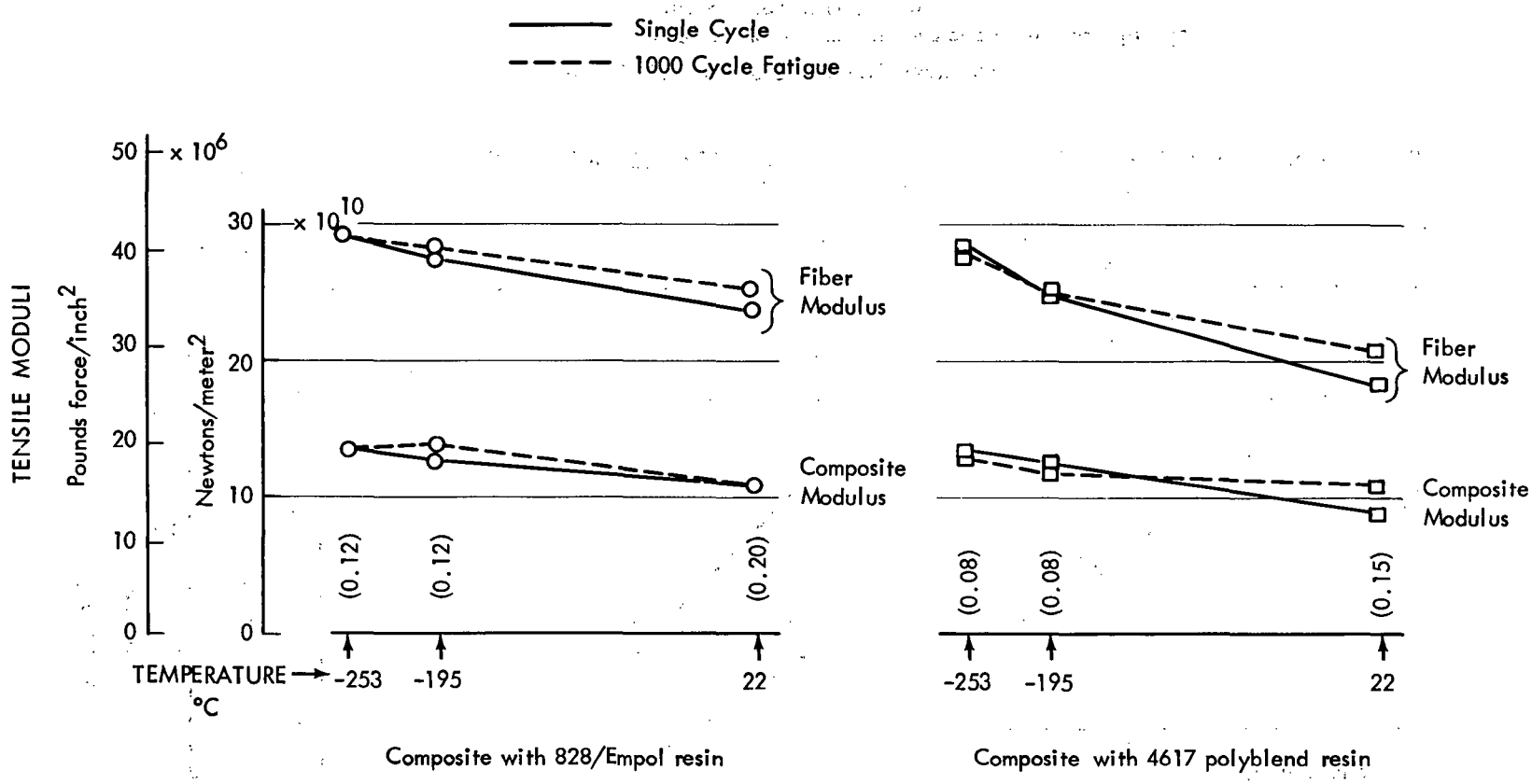

FIG. 7 AXIAL TENSILE MODULI
Average values from unidirectional molded flat plates using Courtaulds HTS fiber.

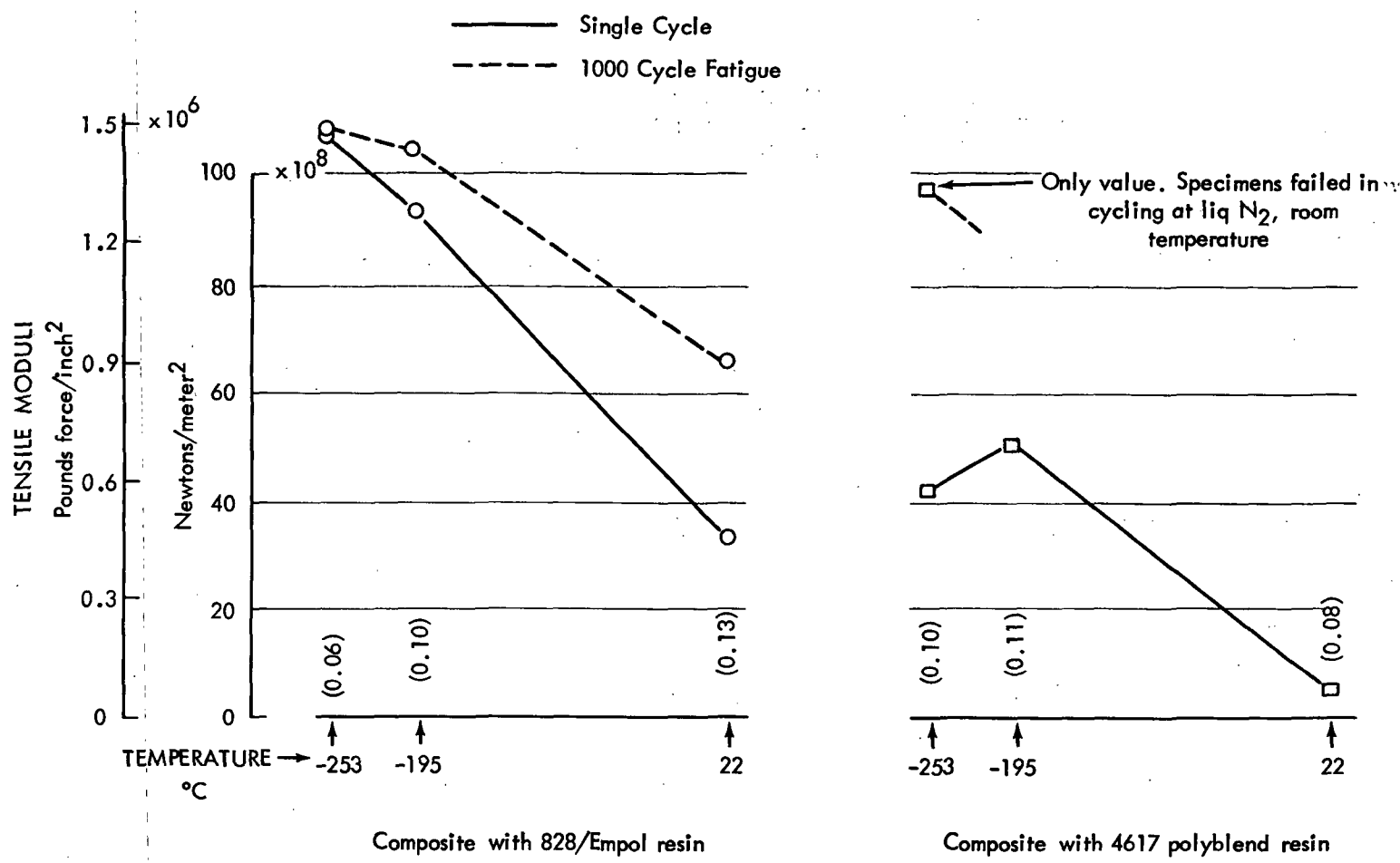

FIG. 8 TRANSVERSE TENSILE MODULI
Average values from unidirectional molded flat plates using Courtaulds HTS fiber.

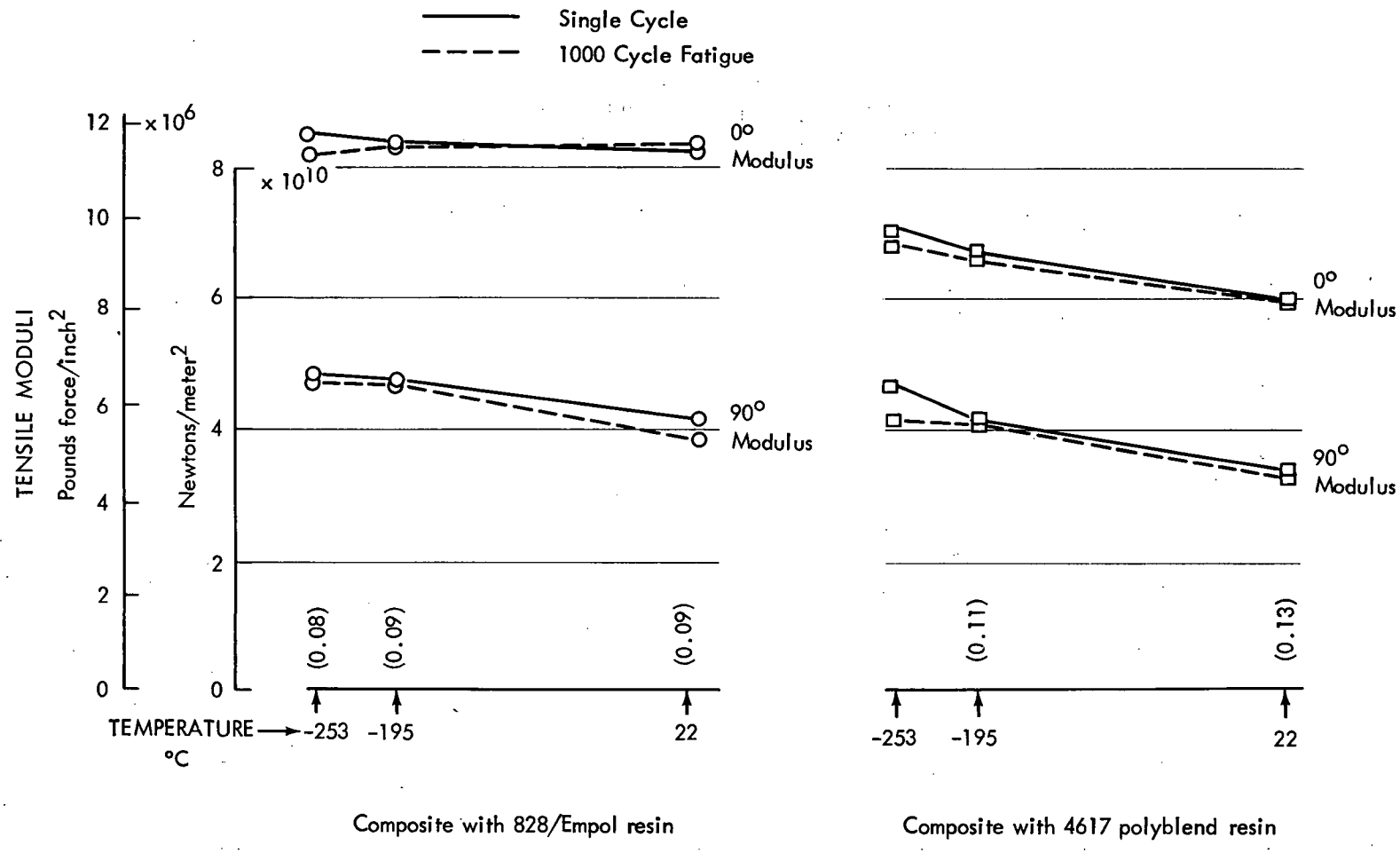

FIG. 9 0° AND 90° COMPOSITE TENSILE MODULI
Average values from 2:1 bidirectional molded flat plates using Courtaulds HTS fiber.

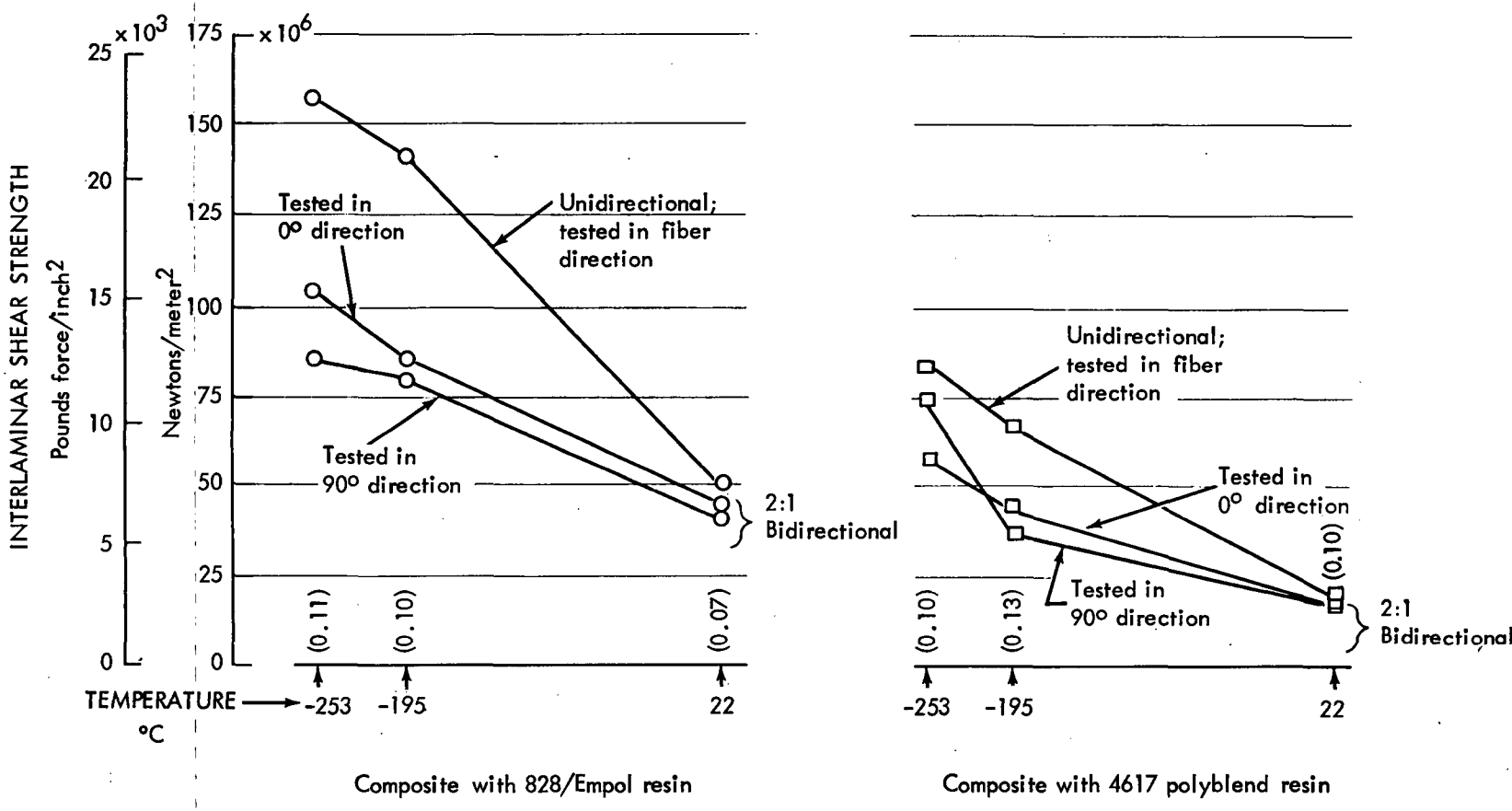

FIG. 10 COMPOSITE INTERLAMINAR SHEAR STRENGTHS
Average values from molded flat plates using Courtaulds HTS fiber.

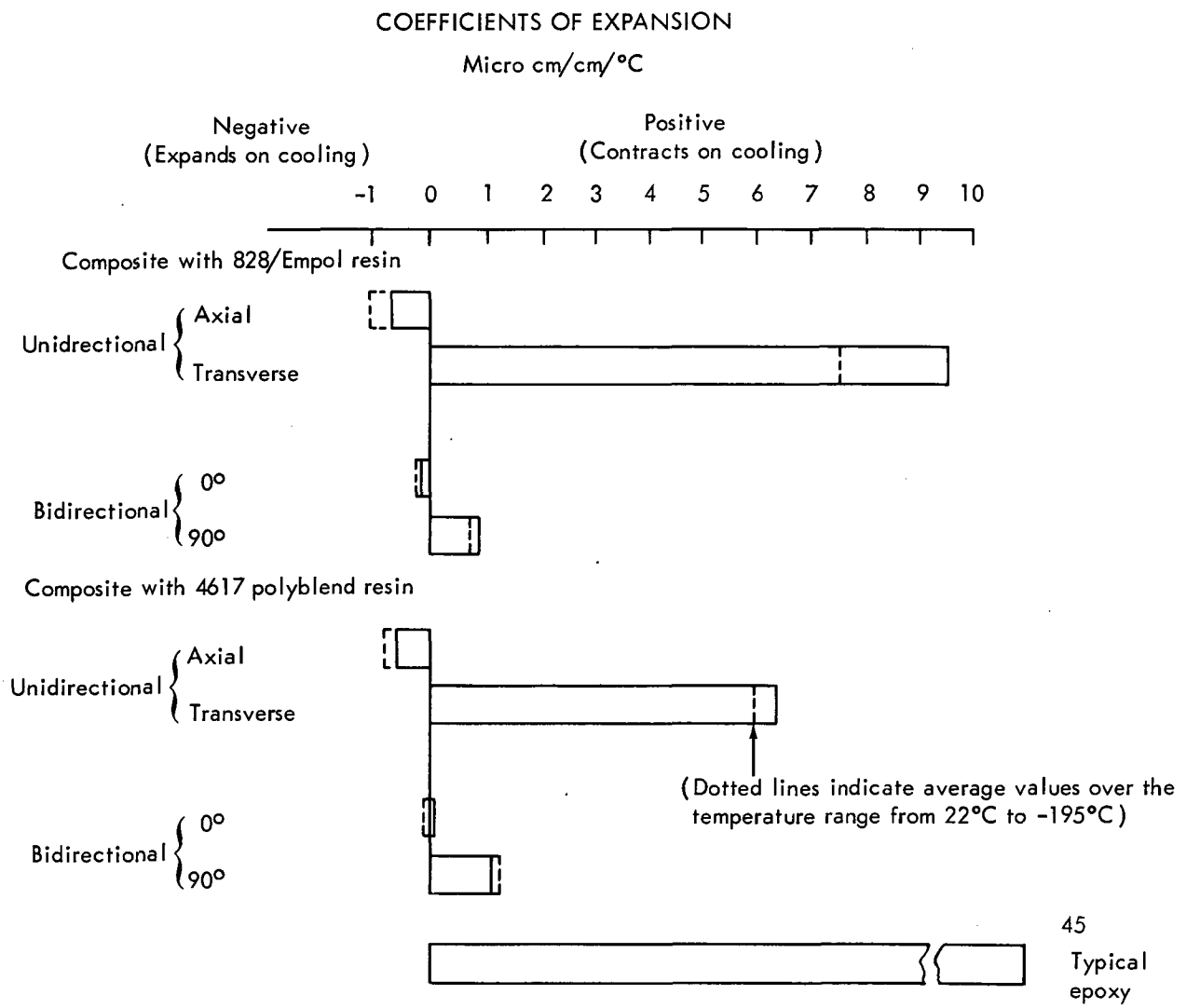

FIG. 11 THERMAL COEFFICIENTS OF EXPANSION
Average values for composite bars over the temperature range from 22°C to -253°C.
All composites with Courtaulds HTS fiber.

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13. ABSTRACT

Compared to metallic vessels, filament-wound vessels for containment of cryogens offer high potential weight savings for NASA spacecraft applications. Since carbon fiber/epoxy resin composites exhibit high strength-to-density ratios, high fatigue life, and excellent strain compatibility with internal metallic liners, advanced unidirectional and bidirectional carbon fiber/epoxy resin composites were evaluated for physical and mechanical properties over a cryogenic to room temperature range for potential application to cryogenic vessels. The results showed that Courtaulds HTS carbon fiber was the superior fiber in terms of cryogenic strength properties in epoxy composites. Of the resin systems tested in NOL Ring composites, CTBN/ERLB 4617 exhibited the highest composite strengths at cryogenic temperatures but very low interlaminar shear strengths at room temperature. Tests of unidirectional and bidirectional composite bars showed that the Epon 828/Empol 1040 resin was better at all test temperatures, with the CTBN/ERLB 4717 composites giving somewhat unpredictable results. Neither fatigue cycling nor thermal shock had a significant effect on composite strengths or moduli. Thermal expansion measurements gave negative values in the fiber direction and positive values in the transverse direction of the composites.

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