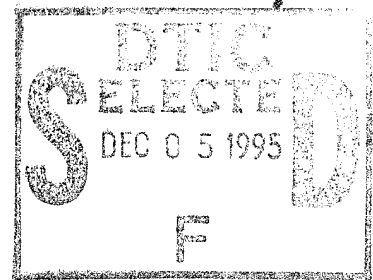
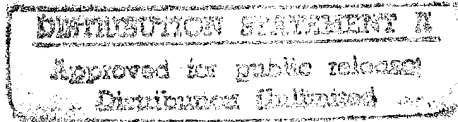


NASA Contract Report 158946



# Research on Graphite Reinforced Glass Matrix Composites



J. F. Bacon, K. M. Prewo,  
E. R. Thompson

UNITED TECHNOLOGIES RESEARCH CENTER  
East Hartford, Ct. 06108

Contract NAS1 - 14346  
June 1978



19951128 094

National Aeronautics and  
Space Administration

Langley Research Center  
Hampton, Virginia 23665

DTIC QUALITY INSPECTED B

DEPARTMENT OF DEFENSE  
PLASTICS TECHNICAL EVALUATION CENTER  
ARRARCOM, DOVER, N. J. 07801

78-10-025

PLASTER 30558

1. Report No. NASA CR-158946		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle RESEARCH ON GRAPHITE REINFORCED GLASS MATRIX COMPOSITES				5. Report Date June 1978	
				6. Performing Organization Code	
7. Author(s) J. F. Bacon, K. M. Prewo, E. R. Thompson				8. Performing Organization Report No. R78-912545-28	
9. Performing Organization Name and Address United Technologies Research Center East Hartford, CT 06108				10. Work Unit No.	
				11. Contract or Grant No. NAS1-14346	
12. Sponsoring Agency Name and Address National Aeronautics & Space Administration Washington, DC 20546				13. Type of Report and Period Covered Annual Report June 1977 - May 1978	
				14. Sponsoring Agency Code	
15. Supplementary Notes Project Manager, Dennis Dicus, NASA Langley Research Center, Hampton, VA 23665					
16. Abstract <p>The consideration of glass as a high temperature thermoplastic has resulted in a new composite that can be used at temperatures up to 875 K with mechanical properties equal or superior to graphite fiber reinforced epoxy composites whose upper use temperature is between 420 and 470 K or graphite fiber reinforced aluminum composites with an upper use temperature of 600 K. Furthermore, this new composite has superior thermal and environmental stability in comparison to these other composites. This composite system consists of graphite fiber, uniaxially or biaxially, reinforced borosilicate glass. The mechanical and thermal properties of such a graphite fiber reinforced glass composite are described, and the system is shown to offer promise as a high performance structural material.</p> <p>Specific properties which have been measured for the composite system are as follows: a modified borosilicate glass uniaxially reinforced by Hercules HMS graphite fiber has a three-point flexural strength of 1030 MPa, a four-point flexural strength of 964 MPa, an elastic modulus of 199 GPa and a failure strain of 0.0052. The flexural strength markedly increases with temperature to 875 K; above this temperature the strength falls rapidly as the softening point of the glass is exceeded. The fracture toughness of these composites compares favorably to aluminum alloys and graphite fiber reinforced epoxy composites. The graphite reinforced glass composite also displays excellent strength retention after exposure to 100 fatigue and thermal cycles, when heated in air for 100 hrs at 723 K, and when thermally cycled in a salt-coated condition. The glass matrix composites exhibit a much lower coefficient of thermal expansion than graphite fiber reinforced epoxy composites which indicates their higher degree of dimensional stability.</p> <p>In addition to the work on Hercules HMS graphite fiber reinforced glass, the preparation and properties of similar composites with Hercules HTS, Celanese DG-102, Thornel 300 and Thornel Pitch graphite fibers are described.</p>					
17. Key Words (Suggested by Author(s)) composites                      flexural strength glass                                reinforced glass graphite fibers                  reinforced ceramic graphite glass                    ceramic matrix composite fiber reinforced                  glass matrix composite high temperature			18. Distribution Statement  Unclassified - unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 113	22. Price*

# UNITED TECHNOLOGIES RESEARCH CENTER



East Hartford, Connecticut 06108

Report R78-912545-28

Research on Graphite Reinforced  
Glass Matrix Composites

ANNUAL REPORT  
Contract NAS1-14346

Accession For		
NTIS	CRA&I	<input checked="" type="checkbox"/>
DTIC	TAB	<input type="checkbox"/>
Unannounced		<input type="checkbox"/>
Justification		.....
By .....		
Distribution / .....		
Availability Codes		
Dist	Avail and/or Special	
A-1		

REPORTED BY J. F. Bacon / ERT  
J. F. Bacon

Karl M. Prewo  
K. M. Prewo

E. R. Thompson  
E. R. Thompson

APPROVED BY [Signature]  
F. L. VerSnyder, Manager  
Materials Technology

DATE June 1978

NO. OF PAGES \_\_\_\_\_

COPY NO. \_\_\_\_\_

Research on Graphite Reinforced Glass Matrix Composites

TABLE OF CONTENTS

SUMMARY . . . . .	1
INTRODUCTION AND BACKGROUND . . . . .	3
EXPERIMENTAL PROCEDURE . . . . .	4
Materials . . . . .	4
Glass . . . . .	4
Graphite Fiber . . . . .	4
Composite Fabrication . . . . .	11
Slurry Technique . . . . .	11
Slurry Variation . . . . .	11
Hot Pressing Procedures . . . . .	14
Composite Characterization . . . . .	17
Sample Preparation . . . . .	17
Flexural Testing and the Effect of Span-to-Depth Ratio . . . . .	17
Oxidation Studies . . . . .	19
Thermal Expansion . . . . .	19
Exposure to Sea Salt . . . . .	22
Cycling Under Flexural Load . . . . .	22
Instrumented Impact . . . . .	22
Thermal Cycling . . . . .	22
RESULTS AND DISCUSSION . . . . .	23
Digest of First Year's Research . . . . .	23
Strength, Distribution of Strength, High Temperature Strength . . . . .	23
Comparison of Graphite Fiber Reinforced Glass Matrices with Other Composites . . . . .	26
Comparison of 3 Point and 4 Point Flexural Data for Graphite Fiber Glass Matrix Systems . . . . .	31

Fracture Toughness Characteristics of HMS Fiber Reinforced 7740 Glass Matrix . . . . .	31
Cyclic Testing of HMS Fiber Reinforced 7740 Glass Matrices . .	31
Discussion of Recent Advances . . . . .	41
Processing Effects . . . . .	41
Shear, Transverse and Cross Ply Strengths . . . . .	54
Shear Strength . . . . .	54
Transverse Strength . . . . .	56
Cross-Ply Composites . . . . .	56
Woven Cloth . . . . .	61
Thermal Expansion . . . . .	61
Oxidation Properties . . . . .	72
 CONCLUSIONS . . . . .	 76
 REFERENCES . . . . .	 77
 APPENDIX A - Summary of Graphite Fiber Reinforced Glass Matrix Composites Made . . . . .	 79
 APPENDIX B - Properties of Selected Graphite Fiber Reinforced Glass Matrix Composites . . . . .	 87

## LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
I	Characteristic Properties of Glasses Used	5
II	Carbon Fibers and Their Characteristic Properties	8
III	Carbon Fiber Obtained for this Study	10
IV	Effect of Amount of Glass in Slurry A on Achieved Flexural Strength of Graphite Fiber Reinforced Glass Composite	13
V	Comparative Weight of 7.62 cm Squares of Graphite Fiber-Powder Glass Cut from One Large Tape, GT 234, Slurry B	15
VI	Room Temperature Elastic Modulus Comparison	34
VII	Comparison of 3-Point Bend and 4-Point Bend Test Data for Several Graphite Fiber-Glass Composites, Slurry A	35
VIII	Fracture Toughness Specimen Dimensions, Slurry A	37
IX	Fracture Toughness Comparison at 295 K	38
X	Three Point Flexural Strengths for Several Samples of HMS Graphite Fiber Reinforced 7740 Glass Matrix (no silica), Hot Pressed at 1473 K, 13.8 MPa, Slurry B	46
XI	Verification of Consistency of Results Obtained with New Type Slurry, HMS Graphite Reinforced 7740 Glass (Silica Addition) Made at 1723 K, 6.9 MPa, 1 hr dwell time, argon atmosphere, Slurry C	47
XII	Effect of Change in Slurry and Hot Pressing Temperature on Three-Point Flexural Strength of HTS Fiber Reinforced 7740 Composites	53
XIII	Effect of Hot Pressing Temperature on Three Point Flexural Strength of Composites Formed from Celanese DG-102 Fiber Reinforced C.G.W. 7740 + 2% SiO <sub>2</sub> Glass Matrix Hot Pressed Using Newest Slurry, 6.9 MPa, 1 Hr Dwell Time, Slurry C	55
XIV	Three Point Bend Data for Cross Ply Specimens, Slurry B	60
XV	Comparison of Composite Coefficients of Thermal Expansion	71

## LIST OF ILLUSTRATIONS

<u>Fig. No.</u>		<u>Page</u>
1	Viscosity - Temperature Curves	6
2	Scanning Electron Micrographs of Glass Powders	7
3	Typical Fibers as Seen in Specimen Electron Micrographs	9
4	Slurry Method of Coating Graphite Fiber	12
5	Centorr Hot Press at UTRC	16
6	Relative Motion of Die Plunger After Application of Full Pressure During Hot Pressing, Slurry B	18
7	Calculated Values of Maximum Applied Shear Stress at Failure for Three Point Bend Testing as a Function of Specimen Span (L) to Depth (h) Ratio	20
8	Calculated Values of Maximum Applied Flexural Stress at Failure for Three Point Bend Testing as a Function of Specimen Span (L) to Depth (h) Ratio	21
9	Three Point Bend Strength of Specimen Tested at 295 K, Slurry A	24
10	Flexural Strength of Hercules HMS - 10 K Fiber Reinforced 7740 Glass as a Function of Test Temperature, Slurry A	25
11	Load-Deflection Traces for the 4-Pt. Bend Tests on Hercules HMS - 10 K Reinforced 7740, Slurry A	27
12	Flexural Strength of Hercules HMS - 10 K Fiber Reinforced Thermoplastics as a Function of Test Temperature	28
13	Flexural Strength Comparison	29
14	Specific Flexural Strength Comparison	30
15	Flexural Strength Comparison	32
16	Specific Flexural Strength Comparison	33

LIST OF ILLUSTRATIONS (Cont'd)

<u>Fig. No.</u>		<u>Page</u>
17	Fracture Toughness Specimen	36
18	Temperature Cycle	39
19	Flexural Strength of HMS-7740 Glass Composite After Thermal Cycling, Slurry A	40
20	Microstructure of HMS Graphite Fiber Reinforced 7740 Glass Matrix (G.C. 281) Hot Pressed at 1473 K, Slurry B	42
21	Microstructure of HMS Graphite Reinforced 7740 + 2% SiO <sub>2</sub> (GC 326) Hot Pressed at 1723 K, Slurry C	43
22	Tape Map of Cross Section of HMS Graphite Fiber Reinforced 7740 Glass Matrix (GC 281) Hot Pressed at 1473 K, Slurry B	44
23	Tape Map of Cross Section of HMS Graphite Reinforced 7740 + 2% SiO <sub>2</sub> Glass Matrix (GC 326) Hot Pressed at 1723 K, Slurry A	45
24	Failure Probability of HMS Graphite Fiber Reinforced CGW 7740 Glass with and without Silica	48
25	Stress Strain Curve of HMS Graphite Fiber Reinforced 7740 + 2% SiO <sub>2</sub> , Slurry C, Determined by Four Point Bend Test	49
26	Relation of Hot Pressing Pressure to Three-Point Flexural Strength of Composite	51
27	Relationship of Three-Point Flexural Strength of HMS-7740 + 2% SiO <sub>2</sub> Composite to Temperature at which Composite is Hot Pressed, Slurry C	52
28	Microstructure of Specimen GC 30 203 Celanese DG-102 Reinforced 7740, [(90 <sub>2</sub> 0 <sub>2</sub> ) <sub>2</sub> ] <sub>S</sub> , Slurry B	58
29	Microstructure of Specimen GC 215-5 HMS Reinforced 7740, [(0/90) <sub>4</sub> ] <sub>S</sub> Samples Surface Ground and Polished, Slurry B	59
30	Microstructure of Specimen GC 218-5 Thornel 300 Cloth Reinforced 7740, Slurry B	62

LIST OF ILLUSTRATIONS (Cont'd)

<u>Fig. No.</u>		<u>Page</u>
31	Transparent Glass Surface of Specimen GC 220 0°/90° Thornel 300 Reinforced 7740 Fabricated Using Woven Cloth, Slurry B	63
32	Thermal Expansion of 0° Celanese DG-102 Fiber Reinforced 7740, Slurry B	65
33	Thermal Expansion of 90° Celanese DG-102 Fiber Reinforced 7740, Slurry B	66
34	Thermal Expansion of 0° Thornel 300 Reinforced 7740, Slurry B	67
35	Thermal Expansion of 90° Thornel 300 Fiber Reinforced 7740, Slurry B	68
36	Thermal Expansion of 0° HMS Reinforced 7740, Slurry B	69
37	Thermal Expansion of 90° HMS Reinforced 7740 Spec. GC 216, Slurry B	70
38	Thermal Expansion of 0°/90° HMS Reinforced 7740, Bars Represent Confidence in these Data Points for this Cycle	73
39	Effect of Oxidation on Three-Point Flexural Strength of Graphite Fiber-7740 Glass Matrix Composites With Added Silica, Slurry C	74

## SUMMARY

Graphite fiber reinforced glass matrix composites which offer excellent structural performance at temperatures up to 875 K, low density, excellent environmental stability, and low cost have been synthesized. Further, these composites can be made so that consistent properties are obtained together with 93% retention in flexural strength after exposure to air at 813 K for 100 hrs or complete strength retention after 100 hrs in air at 723 K. The oxidation resistance of a Hercules HMS graphite fiber reinforced C.G.W. 7740\* +2% SiO<sub>2</sub> glass matrix composite is in contrast with the result found at the end of the first year's research for similar Hercules HMS graphite fiber glass matrices where only 72% of their original strength was retained after 4 hrs exposure to air at 833 K. The increased oxidation resistance of the Hercules HMS graphite fiber reinforced glass matrix composite is believed to be due both to the introduction of a new slurry and the fact that the composite is formed at a higher temperature, 1723 vs 1473 K. These changes also yielded a Hercules HMS graphite fiber reinforced glass matrix with higher flexural strength; its three-point bend strength is 1030 MPa (150 000 psi) and the four-point flexural strength is 964 MPa (140 000 psi), and a higher percent strain to failure (up to 0.52%) as well as a composite modulus of 200 GPa or 29 million psi. Results obtained with Hercules HTS, Thornel 300 and Thornel Pitch, and Celanese Type DG-102 graphite fibers reinforced C.G.W. 7740 and 7740 +2% SiO<sub>2</sub> glass matrix composites are also included but are not yet as impressive as are the results with the Hercules HMS graphite fiber reinforced C.G.W. 7740 +2% SiO<sub>2</sub> glass matrix composites.

The work of characterizing the Hercules HMS graphite fiber reinforced C.G.W. 7740 + 2% SiO<sub>2</sub> and of developing the process for making it has started. At the current stage of development, graphite fiber reinforced borosilicate glass matrix composites have exhibited a strength which increases with temperature up to 875 K (the softening point of the glass), excellent fracture toughness, no influence of 100 thermal cycles from 383 to 833 K in argon or 100 flexural fatigue cycles from low load to high load on the residual strength, and no strength degradation when painted with sea salt concentrates and thermally cycled in argon to 833 K. The Hercules HMS graphite fiber reinforced C.G.W. 7740 glass matrix composite made with one of the new slurries but without added silica has an average interlaminar shear strength of 39.8 MPa (5780 psi). Such graphite fiber reinforced glass matrix composites can be made as uniaxial, biaxial, or multiaxially reinforced

\*C.G.W. is Corning Glass Works; C.G.W. 7740 is their code for a borosilicate glass or one of their Pyrex compositions

Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

composites. They can also be made from tapes containing sufficient glass that no additional glass between layers need be added, and these tapes can be transferred from take-up spool to die without loss of glass. Further, three thin composites can be hot pressed at one time just as easily as one thicker composite, and using the presently available equipment at the Research Center, composites can be formed as large as squares 10 cm x 10 cm. Again, tapes with 12 layers of slurry impregnated graphite fiber can be used as readily as the usual uni-layer tapes to form composites. When the coefficient of thermal expansion of uniaxial graphite fiber reinforced glass matrix composite is measured in the  $90^{\circ}$  direction, the value obtained for the coefficient of thermal expansion is only one-eighth that of a similar graphite fiber reinforced epoxy resin indicating the greater dimensional stability of the glass matrix composite. Despite these advances, much work remains to be done to more completely characterize the Hercules HMS graphite reinforced C.G.W. 7740 + 2%  $\text{SiO}_2$  glass matrix composite and similar composites and in further simplification of the process for forming the composite.

## INTRODUCTION AND BACKGROUND

Fiber reinforced composites are widely accepted as structural materials because of their desirable attributes of high strength, high modulus and low density. At the inception of this program the sales of high performance fiber reinforced composite materials exceeded a million pounds yearly. In general, most of these composites were organic polymer (epoxy resins, polyimides, polycarbonates, and similar materials) matrices reinforced with a great variety of fibers including Kevlar\*, carbon, graphite, fused silica, glass, and boron. In general, almost all of these composites were limited to use temperatures not exceeding 575 K and many of these to temperatures not exceeding 425 K.

At the start of this contract, there were no reinforced glass matrix composites commercially available except the age-old wire reinforced glass used for improving the burglar resistance of homes and stores and the AVCO developed tungsten mesh reinforced fused silica intercontinental ballistic missile nose cones. Yet if one conceives of glass as just a high-temperature thermoplastic, the substitution of a glassy matrix for the low temperature polymers in composite materials seems a natural way to proceed. This concept, however, had attracted sparse attention in the past. Upon examining the technical literature, only 12 references by British and American scientists (Refs. 1-12) could be found. Since these references were discussed in detail in the first annual report on this subject (Ref. 13), it is sufficient to indicate that the fabrication approach has followed along the directions suggested by Sambell, et al (Ref. 4) and Levitt (Ref. 7) and has emphasized the use of a slurry in forming the graphite fiber reinforced glass matrix composite to the virtual exclusion of the other possible procedures. The materials and process are considered in more detail in the next sections.

\*Aramid Fiber, trademark of DuPont

## EXPERIMENTAL PROCEDURE

## Materials

Glass

The types of glasses which were considered for use on this program are shown in Table I. Just as the graphite fibers show individual characteristics, the glasses also vary widely in their nature possessing different coefficients of linear expansion, different chemical compositions, varied environmental stability, and, of course, different temperature working ranges. Although all the glasses in the table have relatively low thermal expansion coefficients, only the titanium silicate glass has an expansion coefficient as low as that of the graphite fibers.

Just how different the working characteristics of these glasses are is shown in Fig. 1. It is apparent, therefore, that any resultant graphite fiber-glass matrix composites will have their own fabrication conditions. The glasses as they actually arrive at UTRC are shown in the scanning electron micrograph of Fig. 2. Although each glass is purchased solely on the basis that 90% must pass through a 360 mesh screen; actually all glasses contain numerous fine particles under one micron in size, and it is believed that these fine particles contribute greatly to the fabrication process to be described in the next section.

Graphite Fiber

The types of fibers readily available in this country for a research program on the generation of new types of graphite fiber reinforced glass matrix composites are shown in Table II. It will be noted that they vary widely in several important characteristics such as the number of fibers in each, the strength and modulus of the fiber, the precursor used to make the fiber, and the price. It is perhaps not so obvious that the use of each fiber presents a distinct surface chemistry problem, but if one considers the finish on the fiber surface and the chemical elements found on the fiber surface as shown in Table II the problem is evident. This is particularly true if one examines the distinctive shape of each carbon fiber as shown in Fig. 3. It is apparent, therefore, that any given glass matrix reinforced with a given graphite fiber will show its own characteristic behavior.

To broaden the investigation as much as practicable, UTRC purchased some of each carbon fiber shown in Table III.

Table I  
Characteristic Properties of Glasses Used

Type of Glass	Nature of Glass	Strain Point $\times 10^{13.5}$	Anneal Point $\times 10^{12.0}$	Softening Point $\times 10^{6.5-7}$	Liquidus	Working Point $\times 10^3$	Density $\text{kg/m}^3$	Index of Refract.	Dielectric Constant	Coef. Linear Expansion $\text{cm/cm K} \times 10^{-7}$	Modulus GPa
C.G.W. 7740	Boro-silicate	833 K	833 K	1094 K	1290 K	1525 K	2230	1.474	4.6	32.5	63
C.G.W. 1723	Alumino-silicate	938	983	1181	1343	1441	2640	1.574	6.3	46	88
Ferro S	Magnesium-alumino-silicate	1033	1083	1243	1323		2490	1.547	5.2	29	85
C.G.W. 7913	High silica	1163	1293	1803	1973		2180	1.458	3.8	5.5	68
C.G.W. 7940	Pure silica	1229	1357	1853	1973		2200	1.459	3.8	3.5	72
C.G.W. 7971	Titanium silicate		1273	1773	1873		2210	1.484	4.0	-2	68

\*viscosity, N·S/m<sup>2</sup>

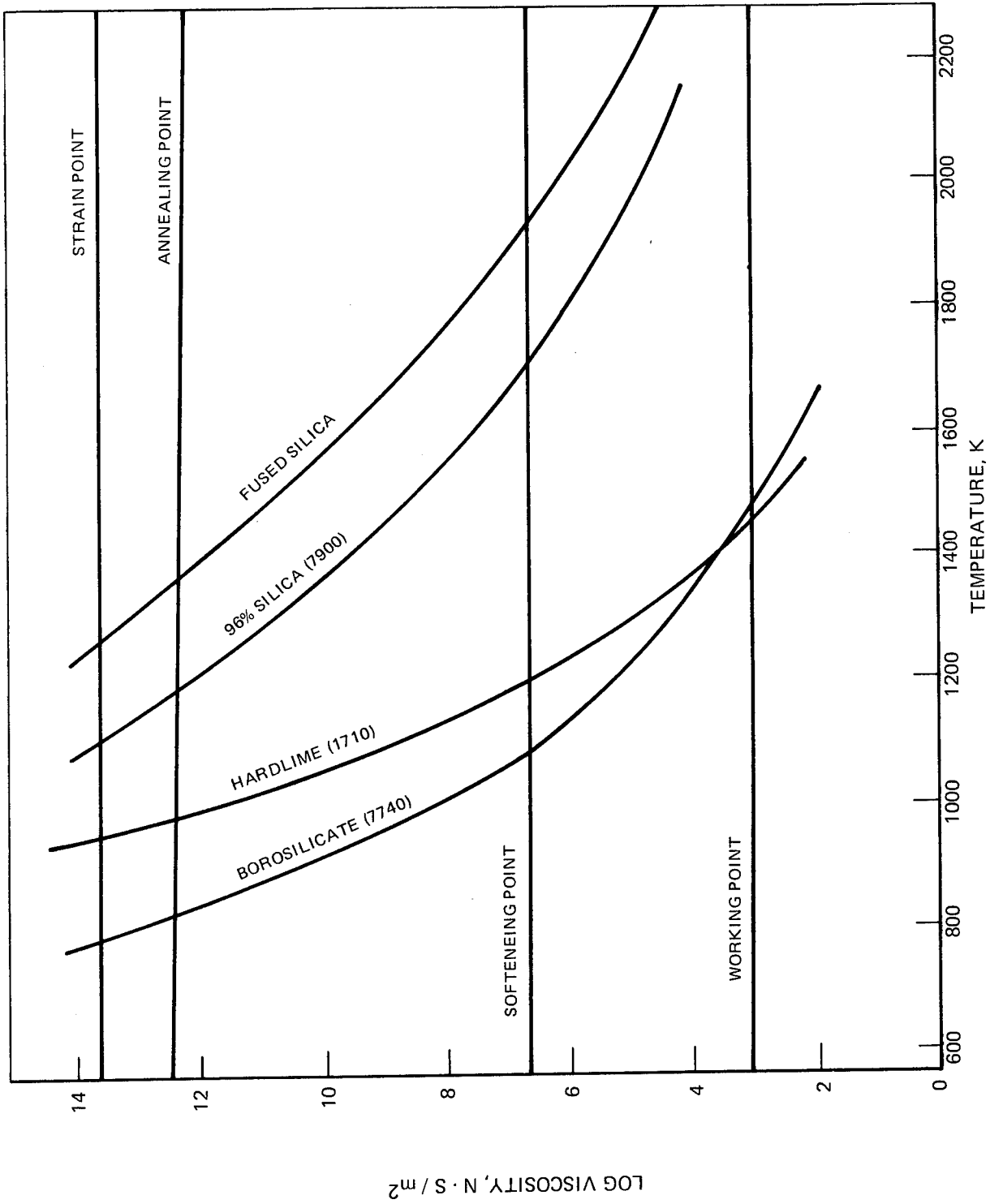


Figure 1. Viscosity — Temperature Curves



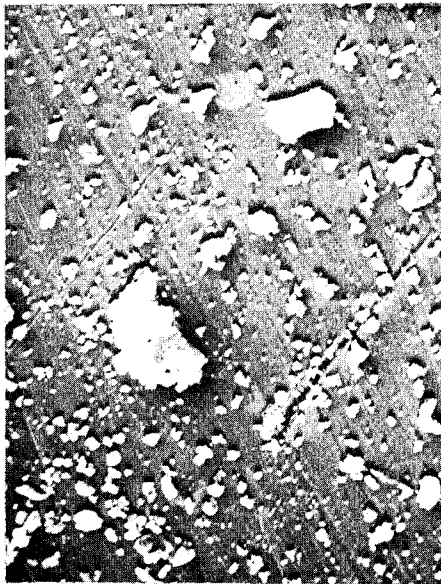
C.G.W. 1740

5  $\mu$ m



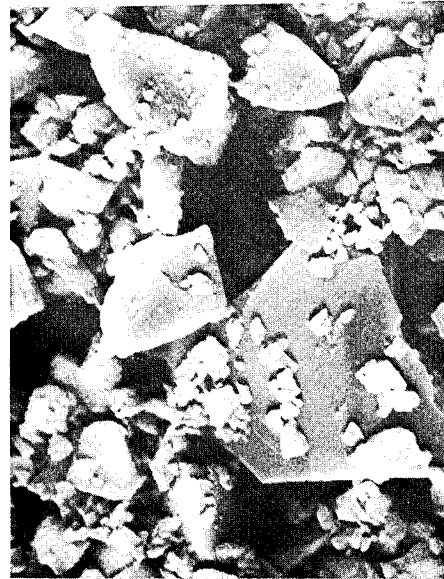
FERRO "S"

50  $\mu$ m



C.G.W. 7913

10  $\mu$ m



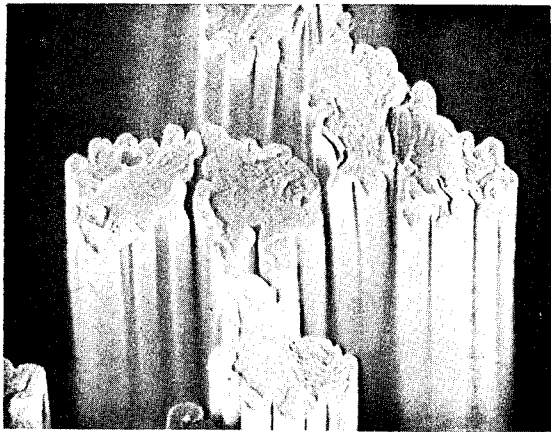
C.G.W. 1723

5  $\mu$ m

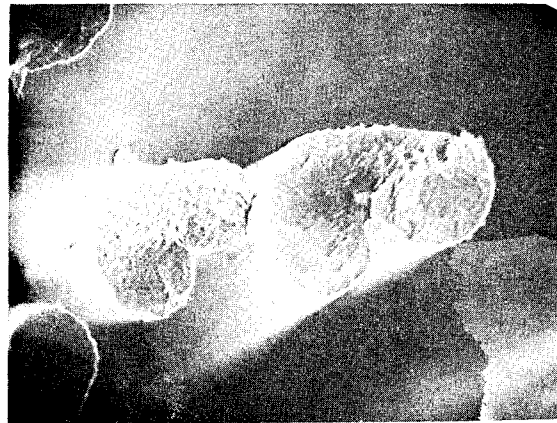
Figure 2. Scanning Electron Micrographs of Glass Powders

Table II  
Carbon Fibers and Their Characteristic Properties

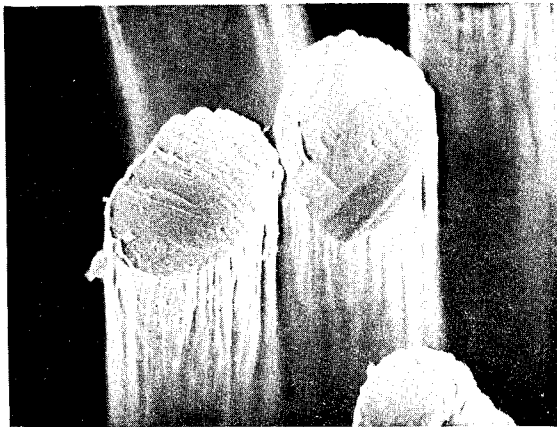
Type of Fiber	No. of Fibers in Tow	Finish Used	Precursor and Diameter of Fiber (microns)	Modulus GPa	Strength MPa	Density kg/m <sup>3</sup>	Coeff. Linear Expansion cm/cm K (axial)	Cost per Pound \$	Result of Spectroscopic Examination
Hercules HM/PVA	1 000	PVA 0.86	PAN	385	2427	1850		300	
Hercules HMS	10 000	Oxidized	PAN 7.3	351	2703	1808	-5.7 x 10 <sup>-7</sup>	90	High Na, high Si, Cr
Hercules HTS	10 000	Oxidized	PAN 7.6	256	2830	1658	-3.8 x 10 <sup>-7</sup>	75	High Na, very high K
Celanese DG-102	384	Oxidized	PAN 8	531	1724	1960		250	Very low Na highest Fe, Si, Ti, Zr
Thornel 300 Grade WYP30 1/0	3 000	UC 309	PAN 6.9	234	2482	1760		40	Very high Na, high Cu high Sn, Zn
Thornel 300 Grade WYP90 1/0	1 000	UC 309	PAN 8.4	228	2655	1750		32	Moderate Na high Mg, Sn, P
Thornel 75 Grade WYL160 1/2	720	PVA	Rayon 6.0	538	2620	1800		385	Intermediate Na very high P high Ca, Ta, Zn
Thornel 50 Grade WYG130 1/2	720	PVA	Rayon 6.6	393	2172	1660		320	



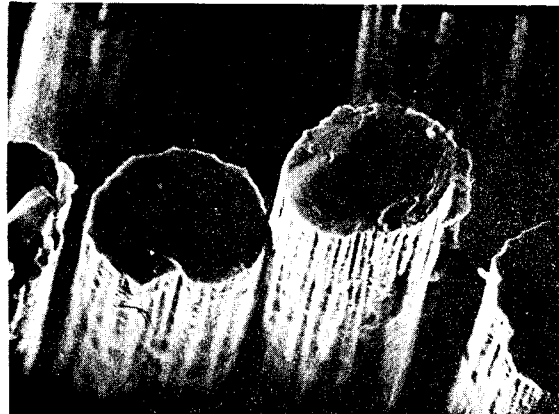
THORNEL 75 GRADE WYL 160 2 μm



CELANESE DG 102 2 μm



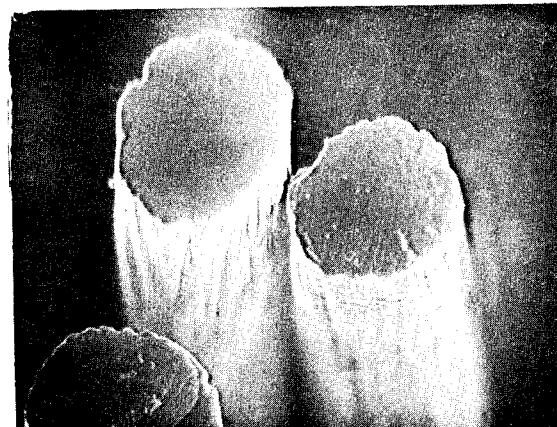
THORNEL 300 GRADE WYP 30 2 μm



THORNEL 300 GRADE WYP 90 2 μm



HERCULES HMS 2 μm



HERCULES HTS 2 μm

Figure 3. Typical Fibers as Seen in Scanning Electron Micrograph

Table III

## Carbon Fiber Obtained for this Study

	Number of Fibers in Tow	Tensile Strength		Young's Modulus		Cost (\$/lb)
		MPa	(ksi)	GPa	(10 <sup>6</sup> psi)	
Hercules HTS	10 000	2979	432	234	34	75
Hercules HTS Special	1 000	2875	417	234	34	300
Hercules HM ( $\mu$ ) - PVA	1 000	2427	352	385	55.9	300
Hercules HMS - 10 K	10 000	2344	340	296-331	43-48	90
Hercules HMS - 3 K	3 000	2330	338	370	53.7	175
Thornel 50 WYG 130 1/2	1 540	2172	315	393	57	320
Thornel 75 WYL 160 1/2	1 540	2620	380	538	78	385
Thornel 300 WYP 30 1/2	3 000	2482	360	234	34	40
Thornel 300 WYP 90 1/0	1 000	2655	385	227	33	32
Thornel Pitch VS 0022-1	2 160	1145	166	469	68	55
Thornel Pitch VS 0022-2	2 160	945	137	345	50	55
Thornel Pitch VS 0022-3	2 160	993	144	414	60	55
Thornel Pitch VS 0032-1	720	1282	186	386	56	270
Thornel Pitch VS 0032-2	720	1083	157	400	58	270
Celanese DG-102	384	1724	250	531	77	250

## Composite Fabrication

### Slurry Technique

While several methods exist for coating the fiber as required in the construction of a fiber reinforced glass composite, much the simplest and lowest cost method, if it can be made to work, consists of pulling the graphite fiber tow through a slurry containing a suspension of the finely ground glass particles.

In the slurry process for coating the graphite fiber with glass, the graphite fiber is unwound from the spool and pulled through an agitated organic solution containing a suspension of fine glass particles. The process is shown schematically in Fig. 4. The slip may be composed of 40 grams of powdered glass and 3 grams of polyvinyl alcohol dissolved in 100 grams of water to which 2 grams of ethylene glycol is added as a plasticizer. Alternately, the slip may comprise 85 grams of glass in 225 ml of toluene to which 5 grams of polystyrene and 5 drops of tergitol have been added. Excess glass and solvent are removed by pressing a squeegee against the drum as it winds. The ground glass used is sized, so that 90% passes through a 325 mesh sieve. After the tape is dry (sometimes heating with a radiant heat source is required to remove excess solvent) it is cut and removed from the drum and then cut into strips or squares which are layed up to give unidirectional or cross-plyed fiber alignment and then hot pressed.

The effect of the amount of glass in the slurry used to form the graphite fiber-glass tape is shown in Table IV where it is shown that doubling the glass added to the slurry results in a decrease of strength. Similar tests run with 45 grams of glass and with 135 grams of glass in the slurry confirm that the best choice seems to be 85 grams of glass in 200 grams of isopropyl alcohol, 10 grams of polyvinyl alcohol and 5 drops of a wetting agent such as tergitol H.D. 527.

### Slurry Variation

The procedure just described was used in all of the earlier work, i.e. up to and including (cf Appendix A) sample LB 174. As mentioned, the isopropyl alcohol furnished the solvent or suspension vehicle and the polyvinyl alcohol formed the plasticizer part of the suspension and is Slurry A. This process worked well until a specific supply of polyvinyl alcohol was exhausted. Then, although polyvinyl alcohol, reagent grade, under the same formula number from Baker Chemicals was reordered, the new supply of polyvinyl alcohol would not either dissolve or stay in suspension in the isopropyl alcohol with a consequence that all the new graphite fiber-glass powder tapes made lacked green strength and lost copious

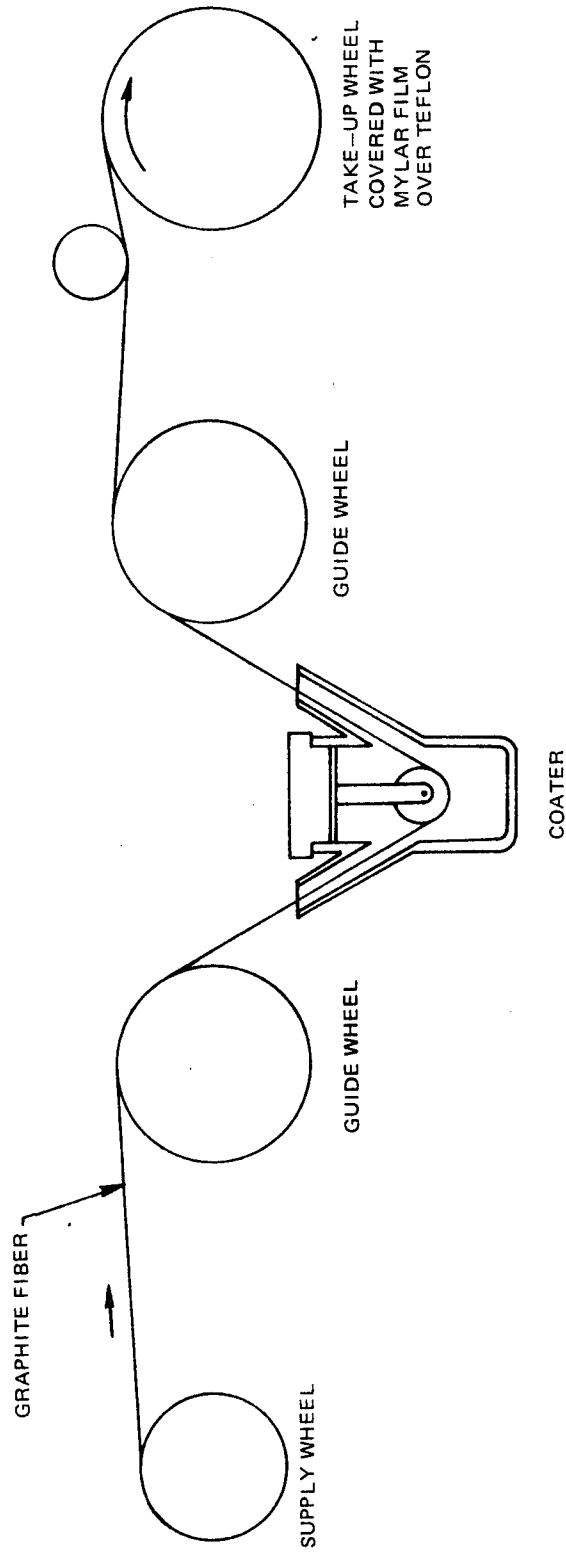


Figure 4 Slurry Method of Coating Graphite Fiber

Table IV

Effect of Amount of Glass in Slurry A on Achieved Flexural Strength of Graphite Fiber Reinforced Glass Composite

Specimen	Glass	Fiber	Temp. of Hot Press K	Pressure MPa	3-Point Flexural Strength		Glass in Slurry gms	Glass Added Between Layers gms
					MPa	psi		
LB 75-2	7740	Thornel 300	1323 argon	13.8	287	41 700	170	0.11
-3					277	40 200		
-5					242	35 000		
-6					261	37 800		
-7					271	39 300		
-9					306	44 400		
Average					274	39 700		
LB 78-1	7740	Thornel 300	1323 argon	13.8	418	60 600	85	0.063
-2					326	47 300		
-4					504	73 100		
-5					355	51 500		
-7					456	66 200		
-8					505	73 400		
Average					427.5	63 000		

amounts of glass powder on handling. Since then a number of organic solvents and plasticizers have been tried without finding anything as useful as the old polyvinyl alcohol-isopropyl alcohol combination. As a result of these efforts, however, a superior slurry consisting of isopropyl alcohol, polyethylene glycol and a small amount of polystyrene was discovered. This combination of ingredients yields a tape with considerable "green" strength which can be handled without shedding much of its glass powder. Further, the amount of glass picked up by the graphite fiber with these organic materials present in the slurry is so great that no glass powder need be added between the layers of material as they are charged in the die for hot pressing. Elimination of this step of adding carefully weighed amounts of glass powder between the tape layers both greatly speeds up the process of filling the die and eliminates a significant factor in the variability due to nonuniform distribution of the glass powder between layers. This newer slurry was used for samples GC 256 through GC 291 (cf Appendix A). The remarkable success achieved with this slurry, hereafter called slurry B, in achieving a uniform distribution of glass powder on the tape is shown in Table V where the weight of 12, 7.62 cm squares of tape cut from a larger tape are compared. It will be noted that these squares vary in weight by less than 1%. Slurry B specifically consisted of 85 grams of glass in 260 ml of isopropyl alcohol, 24 grams of polyethylene glycol and 2 grams of polystyrene with 5 drops of a wetting agent added.

Further investigation of slurry modification has resulted in a third slurry which is similar to that used previously except that it contains 6 grams of DuPont Company's Ludox\* H.S. 30 in place of the 2 grams of polystyrene. The results obtained with this slurry to which only 6 grams of Ludox H.S. 30, containing approximately 2 grams of silica, have led to remarkable improvements in graphite fiber reinforced glass composites. This slurry hereafter called slurry C has been used in preparing all composites from GC 292 to GC 360 inclusive.

#### Hot Pressing Procedures

All of the specimens prepared in the second year of this contract were fabricated using a Centorr Hot Press shown in Fig. 5. The equipment can be used for the fabrication of specimens as large as 15 x 10 x 2.5 cm (7.6 cm thick before hot pressing). The press can provide a load of 530 kN, temperatures up to 3373 K, and a vacuum of 21  $\mu\text{N}/\text{m}^2$  ( $10^{-6}$  Torr) or alternately it can operate in argon. The press is double acting in contrast to the single acting presses used during the first year of this program.

\*Registered trademark, E. I. DuPont de Nemours Corporation, Wilmington, Delaware

Table V

Comparative Weight of 7.62 cm Squares of Graphite  
Fiber-Powdered Glass Cut from One Large Tape, GT 234  
(Slurry B)

<u>Square</u>	<u>Weight grams</u>	<u>Difference from Average grams</u>	<u>% Variation from Average</u>
1	4.727	+0.027	0.57
2	4.728	+0.028	0.60
3	4.683	-0.017	0.36
4	4.676	-0.024	0.51
5	4.737	+0.037	0.79
6	4.713	+0.013	0.28
7	4.706	+0.006	0.13
8	4.642	-0.058	1.23
9	4.771	+0.071	1.51
10	4.729	+0.029	0.62
11	4.644	-0.056	1.19
12	4.642	-0.058	1.23
Average	4.700		<u>±0.75</u>

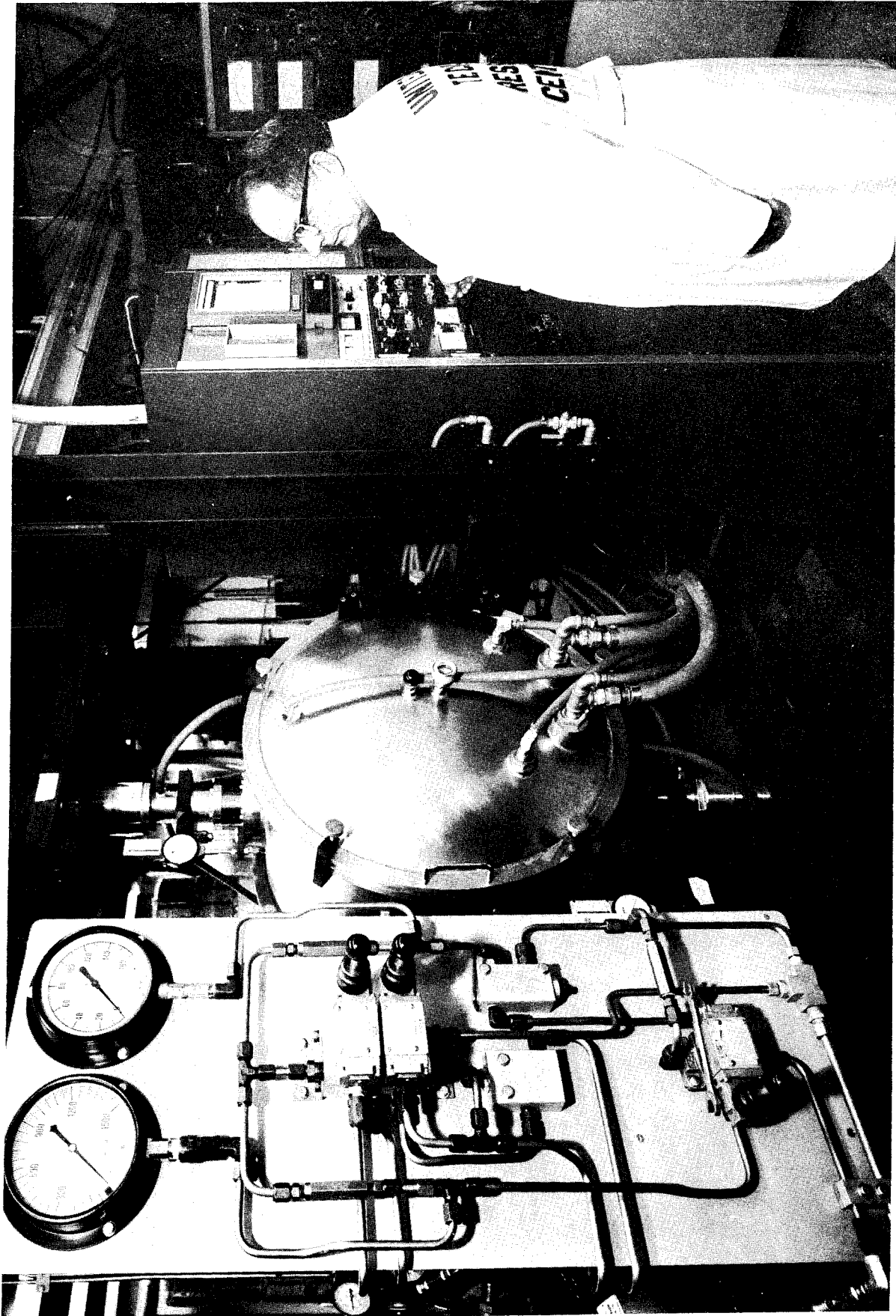


Figure 5. Centorr Hot Press at UTRC

In actual operation the HMS graphite fiber C.G.W. 7740 glass matrix composites made from slurry B tapes were usually hot pressed at temperatures of 1473 K, 13.8 MPa, 1 hr dwell time, argon atmosphere, and the pressure was not released until the sample had cooled to 773 K. Composites reinforced with Hercules HTS or Celanese DG-102 were prepared similarly. On the other hand, the HMS graphite fiber reinforced C.G.W. 7740 + 2% SiO<sub>2</sub> glass matrix composites, slurry C, were most generally prepared by hot pressing at 1723 K, 6.9 MPa, argon atmosphere, 1 hr dwell time and no release of pressure until the sample was cooled to 773 K. The Hercules HTS, Thornel Pitch, and Celanese DG-102 graphite fiber reinforced C.G.W. 7740 + 2% SiO<sub>2</sub> (slurry C tapes) were prepared in the same manner. As may be seen from Fig. 6, where the relative motion of the die plunger after application of full hot pressing pressure is shown, since most of the plunger motion takes place earlier than the usual 60 min dwell time, it may be possible to appreciably speed up the hot pressing operation. It is not known, however, whether the last relatively small motion of the plunger removes the last traces of porosity or whether it is caused by the extrusion of glass out of the die cavity. These questions would need to be studied before any drastic change in dwell time could be justified. All composites shown on this figure were formulated with slurry A and hot pressed at 1473 K, GC 221 and 223 at 13.8 MPa and GC 221 at 6.9 MPa.

## Composite Characterization

### Sample Preparation

The majority of the experimental composites prepared in the second year were of two sizes, either 7.6 cm x 7.6 cm x 0.25 cm or 6.67 cm x 2.22 cm x 1 cm. These composite plates were then cut into individual samples using diamond grit cutting and grinding wheels. In every case, except where specifically noted in this report, the surfaces of all specimens were ground flat and parallel thus exposing graphite fibers on all sides.

### Flexural Testing and the Effect of Span-to-Depth Ratio

Flexural tests have been used for determining the strength properties of these composites. This technique has been chosen because of simple shapes (bars) required and because it avoids all the difficulties associated with gripping the specimen.

The fracture of a composite specimen during three-point flexural strength testing can be controlled by the applied flexural stresses or the applied shear stresses. The relative levels of these stresses, and the relative levels of inherent composite tensile and shear strength determine material performance. This complex type of behavior can be expressed using an interaction diagram

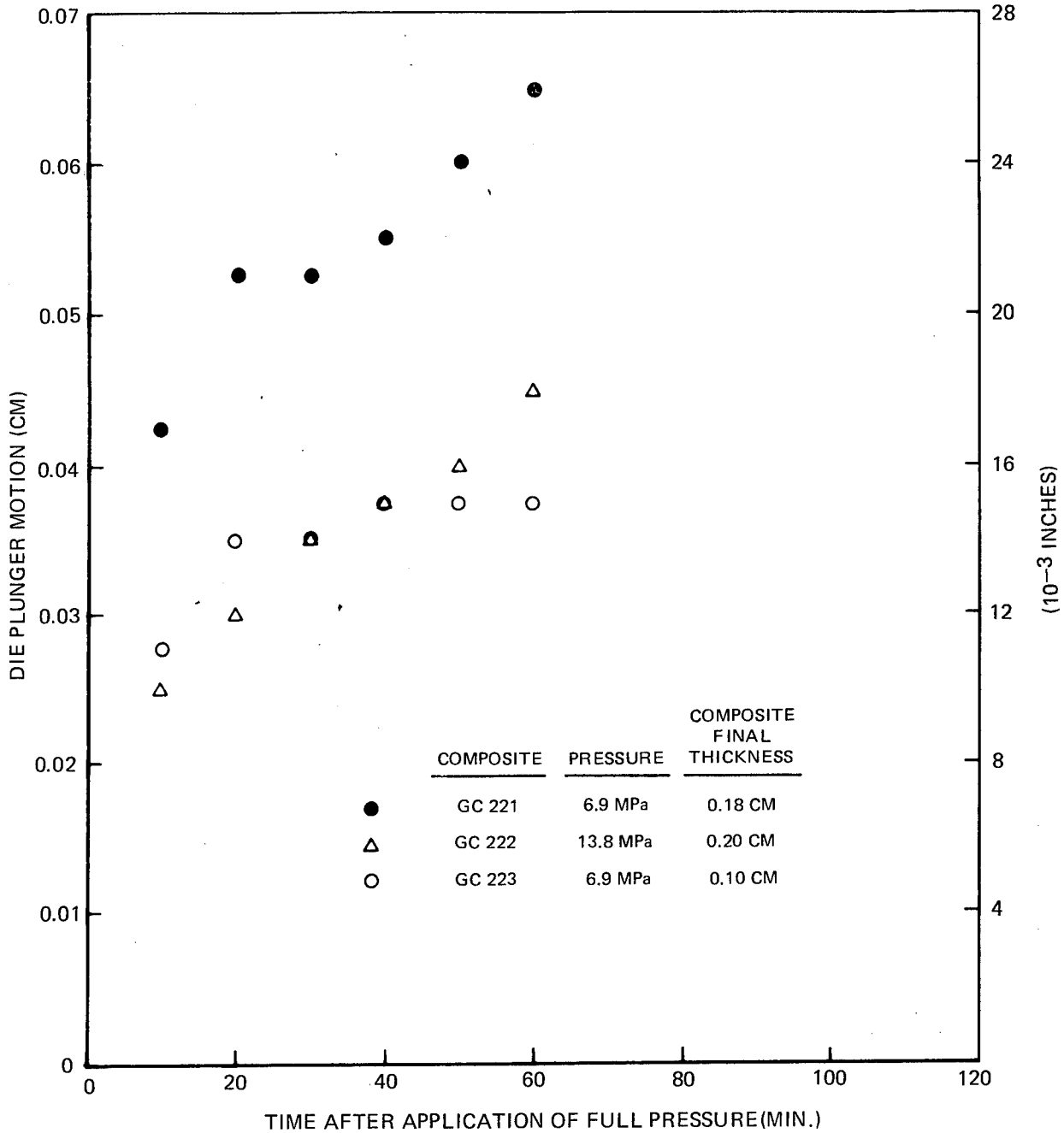


Figure 6. Relative Motion of Die Plunger After Application of Full Pressure During Hot Pressing, Slurry B

approach. By this method both the flexural strength and shear strength of each composite specimen are calculated and plotted as a function of test specimen span-to-depth ratio (L/h). At low values of L/h specimen failure should be controlled by shear deformation, while at high values of L/h the flexural strength of the specimen should control. This type of representation has been successfully used in the past for a wide range of composites (Refs. 14,15).

A uniaxially reinforced specimen containing 50 vol % HMS fiber in 7740 glass was fabricated and tested over an L/h range of 10 to 40. All specimen surfaces were machined prior to testing and the resultant data are presented in Figs. 7 and 8. The shear interaction diagram, Fig. 7, was obtained by calculating the maximum shear stress applied to each specimen based on the maximum applied load at fracture. Also included in the figure are two calculated curves that would represent the maximum applied shear stress of specimens that failed in flexure with actual material flexural strengths ( $\sigma_0$ ) of 689 MPa and 550 MPa.

The same specimen data used in Fig. 7 are replotted in Fig. 8; however, in this case flexural strengths were calculated and plotted vs (L/h). Again, calculated lines are included for specimens failing by flexure at 689 MPa and 550 MPa. In addition, the line for a specimen failing by shear at a level of 16.2 MPa was plotted. This shear strength is equal to the average value of shear stress calculated for L/h = 10 from Fig. 7.

Although the data do exhibit the trends expected, it is also clear that the scatter in data is very significant. Additional testing during the later phases of this program will provide additional data; however, the practice in this program of testing specimens for flexural strengths at (L/h) values above 30 in general is amply justified.

#### Oxidation Studies

The investigation of the resistance to oxidation of various graphite fiber reinforced glass matrix composites was carried out by heating samples prepared for flexural testing to the test temperature in air. The temperature was controlled within  $\pm 5$  K at temperatures of 723, 813 and 833 K for times of 4 hrs, 24 hrs, and 100 hrs. At the end of these exposures the flexural strength of the sample was measured at room temperature.

#### Thermal Expansion

The thermal expansion of the composite specimen was measured using a Dilatronic III High Resolution dilatometer purchased from Theta Industries Inc. of Port Washington, New York. In this instrument the change in length of the specimen is measured in reference to an NBS fused silica standard (SRM #739).

50 v/o-O-HMS-7740  
SHEAR INTERACTION DIAGRAM

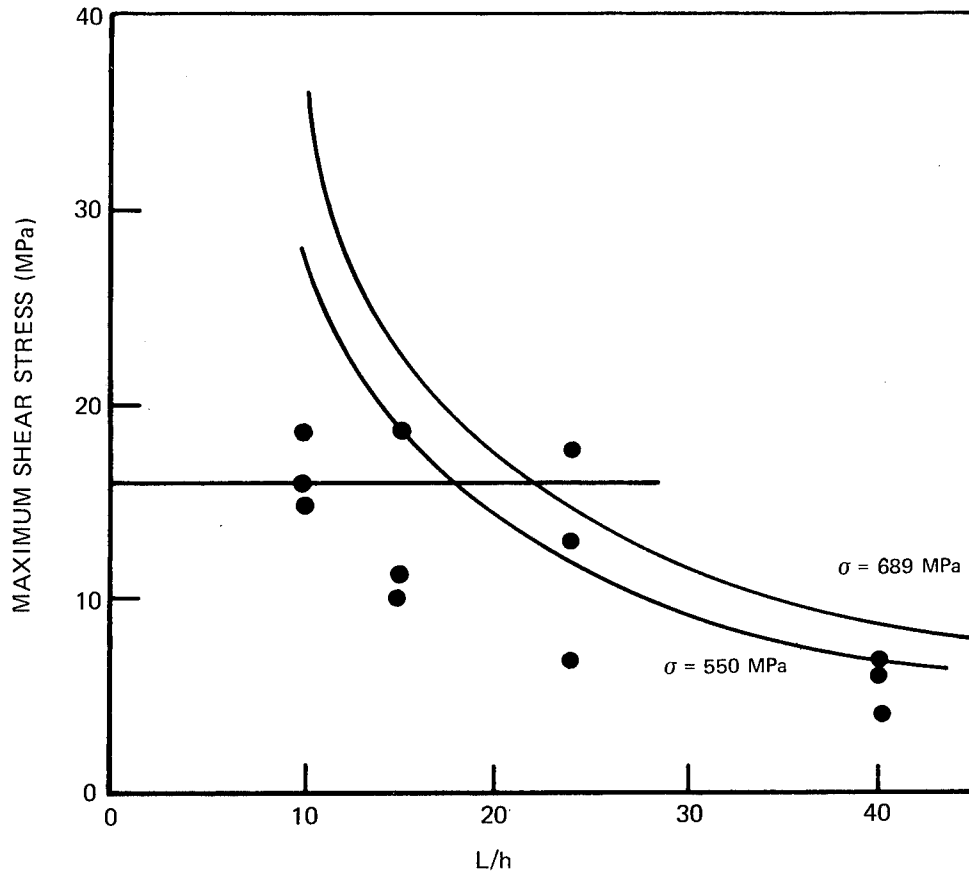


Figure 7. Calculated Values of Maximum Applied Shear Stress at Failure for Three Point Bend Testing as a Function of Specimen Span (L) to Depth (h) Ratio

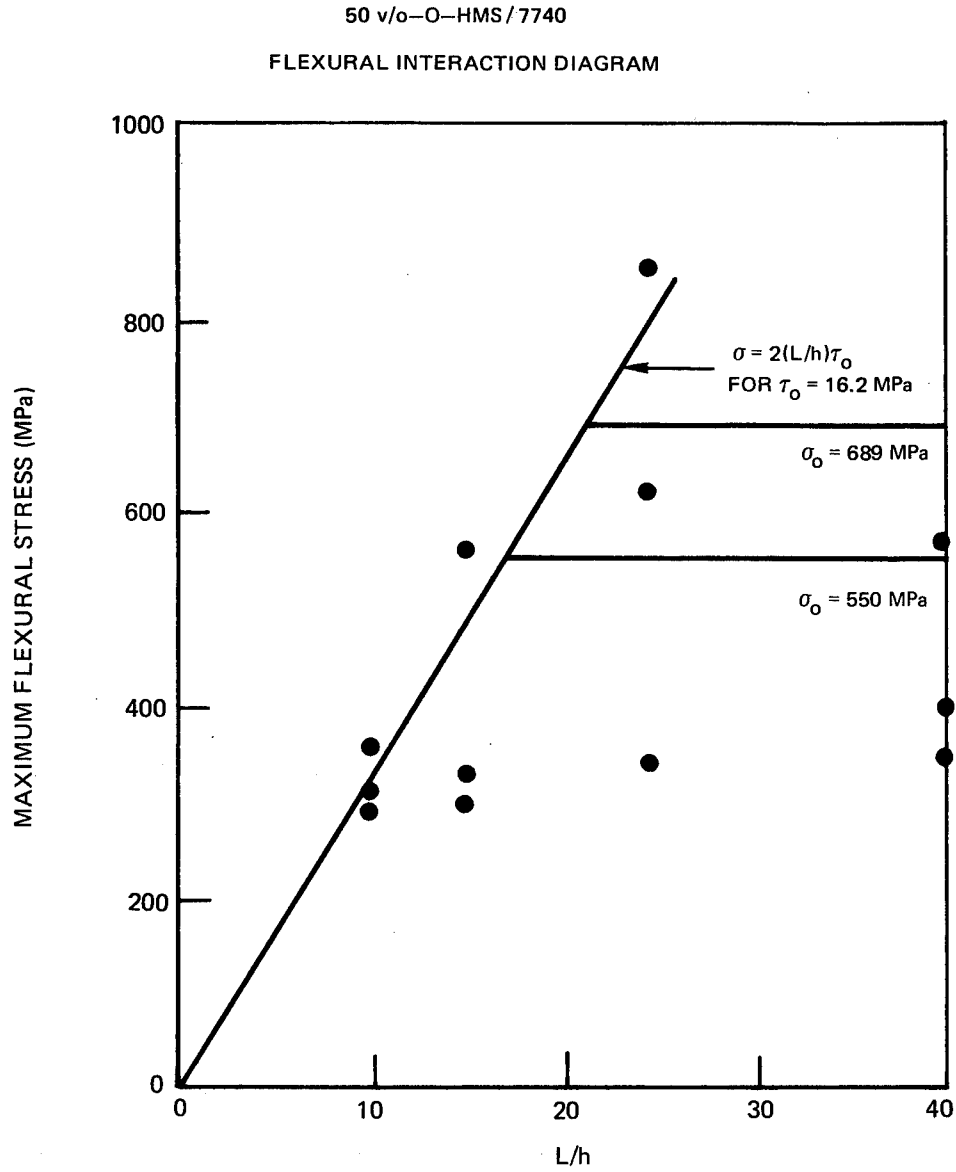


Figure 8. Calculated Values of Maximum Applied Flexural Stress at Failure for Three Point Bend Testing as a Function of Specimen Span (L) to Depth (h) Ratio

The absolute expansion is determined by correcting the measured curve for the expansion of the standard and for the expansion of the specimen holder if the sample and standard are not the same length. The change in length is referred to the initial length of the specimen at 293 K.

#### Exposure to Sea Salt

To simulate exposure to spray with sea water and sea air damage it was necessary to improvise since UTRC does not at this time possess a standard salt spray controlled humidity cabinet. This was done by painting standard flexural test specimens with a solution containing six times the normal concentration of sea salt, drying, repainting to give a total of eight coats of sea salt. The coated flexural specimen was then sealed in a silica tube in an argon atmosphere and thermally cycled from 383 to 833 K for 100 cycles at the rate of 1 cycle every eight minutes.

#### Cycling Under Flexural Load

Cycling under a flexural load which drops to 1/20th of the assessed strength of the sample and rises to 8/10ths of this load was carried out under a four-point bend mode.

#### Instrumented Impact

A Charpy test is an impact failure conducted in three-point bending. This test is a measure of the toughness of a material at moderate impact velocities (up to 3.6 meters/sec). While the value of the energy required for fracture is dependent on the size of the specimen, and therefore is not an intrinsic material value, the tests are useful for comparative purposes. The instrumented Charpy test in particular has been a valuable asset for the comparison of material toughness and for illustration of the fracture modes under dynamic conditions. The impact machine is instrumented with strain gages so a record can be made of the force as a function of time.

#### Thermal Cycling

Premachined flexural test specimens were cycled between 383 and 833 K while encapsulated in glass tubes containing argon. The use of an inert atmosphere permitted the exclusion of any effects due to specimen oxidation.

## RESULTS AND DISCUSSION

In the appendices are tabulated specific data that are not needed for an understanding of the results obtained in this study. In Appendix A, a summary listing of the graphite fiber reinforced glass matrix composites is given. In Appendix B, data which are mainly represented in the report by figures are tabulated. A paper based on this sponsored research entitled "Glass Matrix Composites I - Graphite Reinforced Glass" and authored by K. M. Prewo and J. F. Bacon was presented at the Second International Conference on Composite Materials (Ref. 14).

## Digest of First Year's Research

Since an annual report has been issued (Ref. 13) detailing the first year's research on graphite fiber reinforced glass matrix composites, this section of the report contains only those results which serve to characterize results of these composites which were not repeated in the second year's research.

Strength, Distribution of Strength, High Temperature Strength

Strengths as high as 977 MPa or 142 ksi (Appendix B - Table 1) had been achieved by the end of the first year with HMS graphite fiber reinforced 7740 glass matrix composites made with slurry A using the old press at 1273 K and 13.8 MPa. More usually, composites made with HMS graphite fiber and 7740 glass matrix under the same conditions would have an average strength of 689 MPa or 99.98 ksi (Appendix B, Table 1). Such composites showed a very narrow strength distribution as shown in the probability paper plot of Fig. 9 and tabulated in Appendix B, Table 1. These HMS graphite fiber reinforced 7740 glass matrix composites can be used to temperatures of 873 K. The slurry A data of Fig. 10 and Table 2, Appendix B, demonstrate that a typical HMS fiber-7740 glass composite has an average strength of 825 MPa (120 ksi) at room temperature and increases in strength to 1213 MPa (175 ksi) at 873 K when studied by means of three point bend tests, and only at 973 K does the specimen deform excessively. A similar increase in strength with temperature is shown for slurry A composites of Celanese DG-102 graphite fiber reinforced C.G.W. 7740 glass matrix composites (Table 3, Appendix B). These Celanese DG-102 graphite fiber 7740 composites start out lower in strength, however, and never approach the level of the HMS graphite fiber reinforced composites.

LB-135  
HERCULES HMS-10K REINFORCED 7740

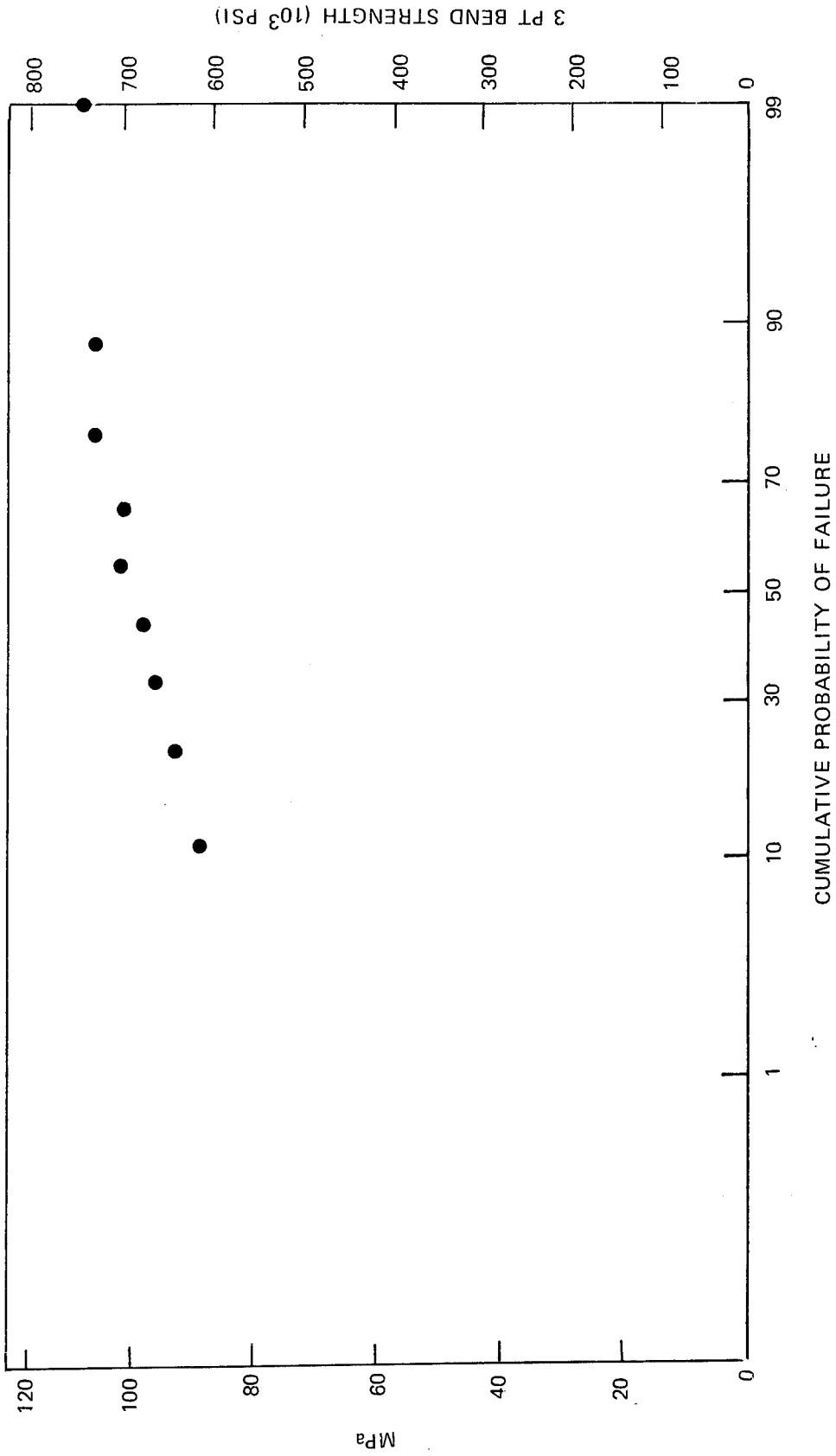


Figure 9. Three Point Bend Strength of Specimen Tested at 295 K, Slurry A

SPECIMEN SET LB-139

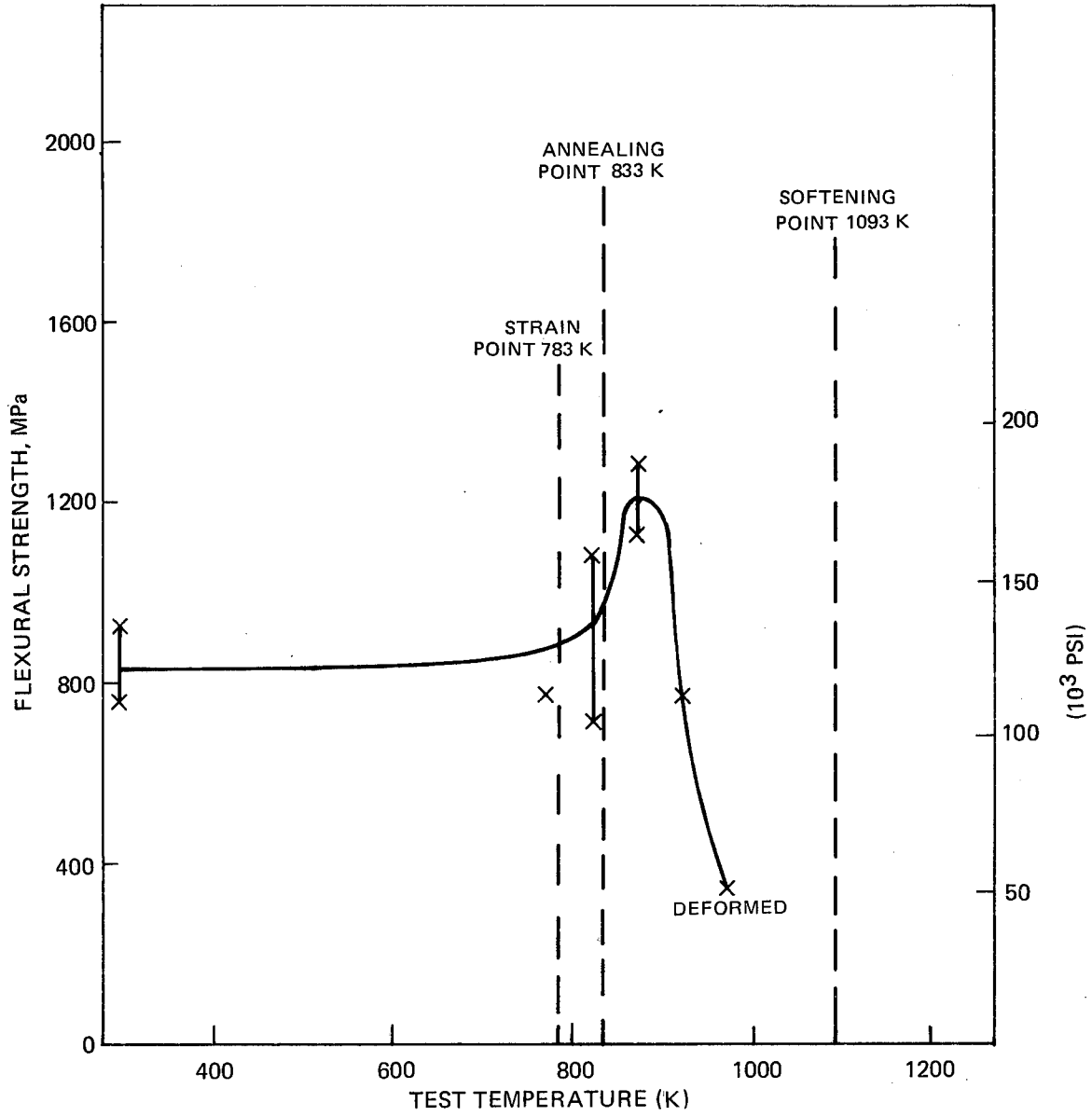


Figure 10. Flexural Strength of Hercules HMS - 10 K Fiber Reinforced 7740 Glass as a Function of Test Temperature, Slurry A

The manner in which these HMS graphite fiber reinforced C.G.W. 7740 glass matrix composites fail is shown by the four-point flexural test data of Fig. 11. Again these composites were made with slurry A, old press, temperature 1273 K and pressure of 13.8 MPa. Both totally linear and combined linear-nonlinear deflections are shown; however, in all cases specimens did not fracture completely but instead cracks were diverted in the interior of the specimen so that failed specimens remained visibly intact after test.

#### Comparison of Graphite Fiber Reinforced Glass Matrices with Other Composites

Three-point bend data for the Hercules HMS graphite fiber reinforced C.G.W. 7740 glass matrix composites have been compared with graphite fiber reinforced thermoplastics, graphite fiber reinforced aluminum, and BORSIC\* fiber reinforced titanium alloy.

The data used to compare graphite reinforced thermoplastics with HMS graphite fiber reinforced C.G.W. 7740 glass matrix composites (slurry A) are shown in Fig. 12 and were obtained from a NASA-sponsored program at UTRC\*\*. The fiber is the same Hercules HMS fiber used in this program and if one compares Figs. 12 and 10 it can be seen that the resin matrix composite maximum flexural strength at room temperature is approximately equal to the strength of the HMS-7740 composite at 873 K although greater at room temperature. The comparison also shows that the rate of strength decrease in the vicinity of the resin glass transition temperature is rapid and similar to that for the glass matrix composite above 923 K.

To compare the flexural strength of graphite reinforced glass matrix composites (slurry A) with that of graphite fiber reinforced aluminum, the recently published data of W. Harrigan of Aerospace Corporation shown in Fig. 13 was used. Again in comparing these data which are for wire and plates with the data of Fig. 10 for the HMS graphite fiber reinforced C.G.W. 7740 glass, it can be seen that the glass matrix composite is equal or superior to the aluminum matrix composite over the entire test temperature. As Fig. 13 also shows on a specific property basis, the glass matrix composite offers an additional advantage. The specific strength comparison of the graphite fiber reinforced aluminum with the HMS graphite fiber C.G.W. 7740 matrix specimen is shown in Fig. 14. The maximum use temperature of the glass matrix composite is significantly higher than that of the graphite aluminum.

\*Trademark, United Technologies Corporation

\*\*R. C. Novak, Graphite Fiber Reinforced Thermoplastic Resins, NAS3-20077, CR-135196, 1976.

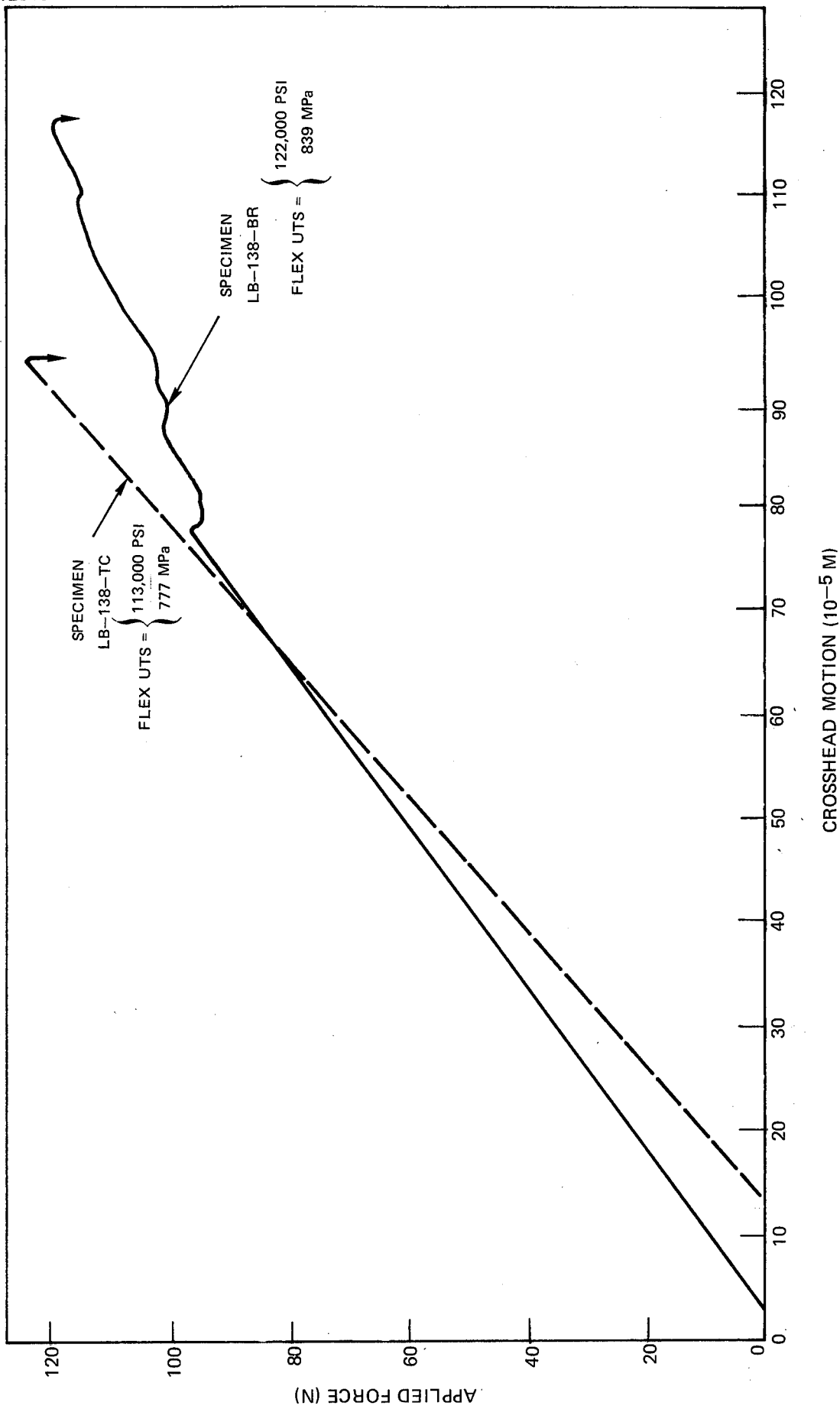
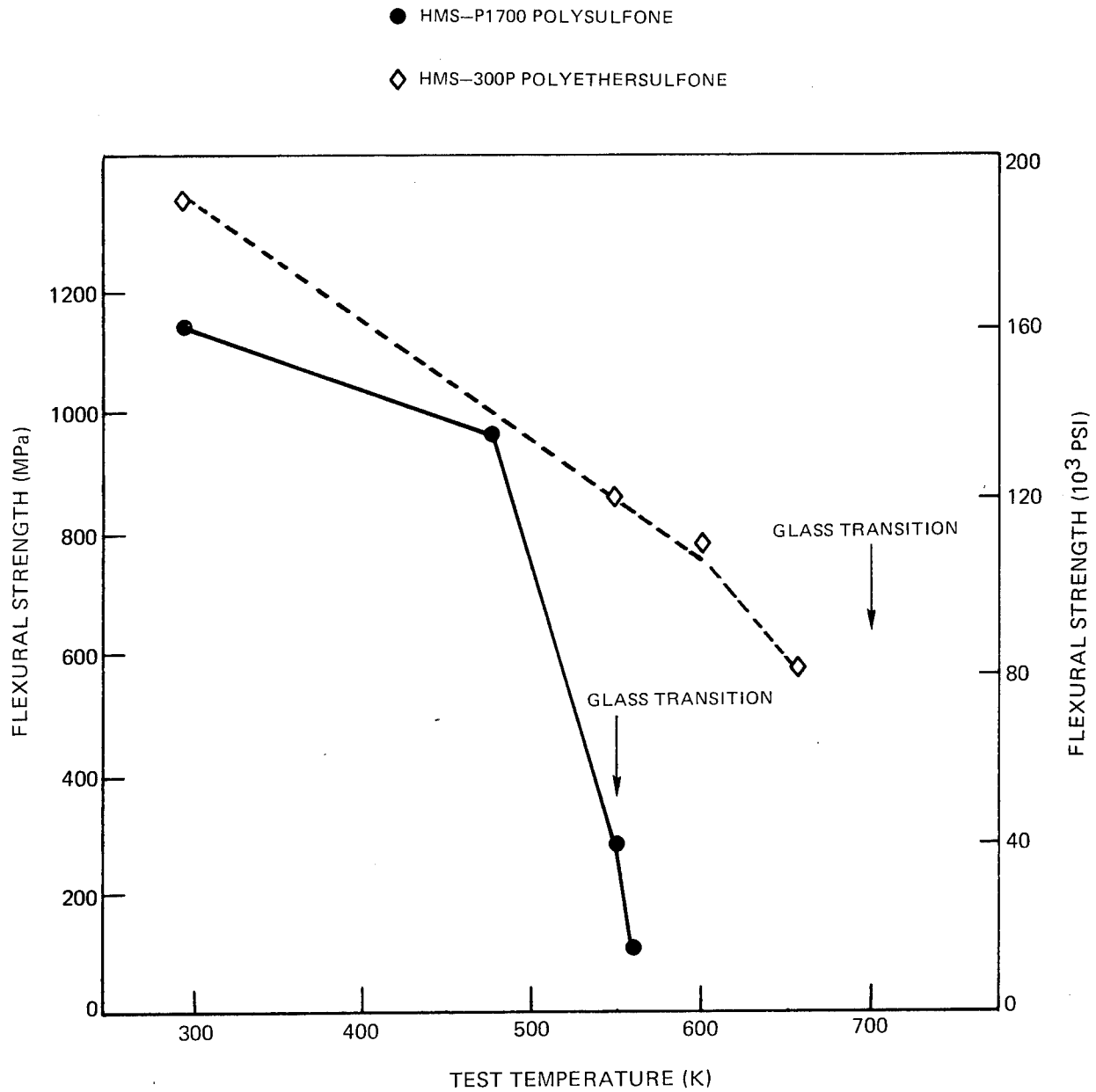


Figure 11. Load - Deflection Traces for the 4 - Pt. Bend Tests on Hercules HMS - 10 K Reinforced 7740 , Slurry A



\* UTRC CONTRACT NAS3-20077, 1976

Figure 12. Flexural Strength of Hercules HMS - 10 K Fiber Reinforced Thermoplastics as a Function of Test Temperature \*

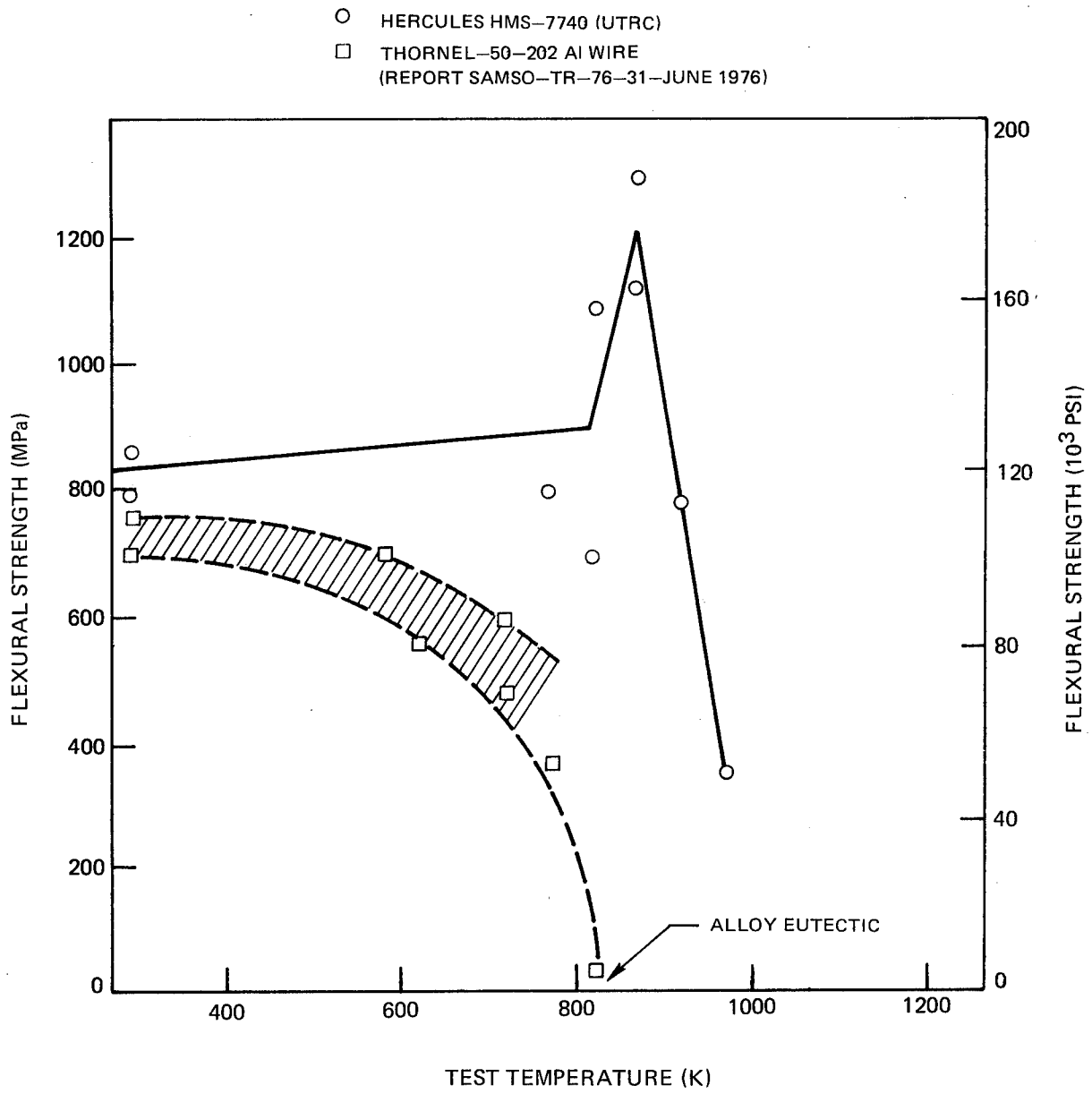


Figure 13. Flexural Strength Comparison

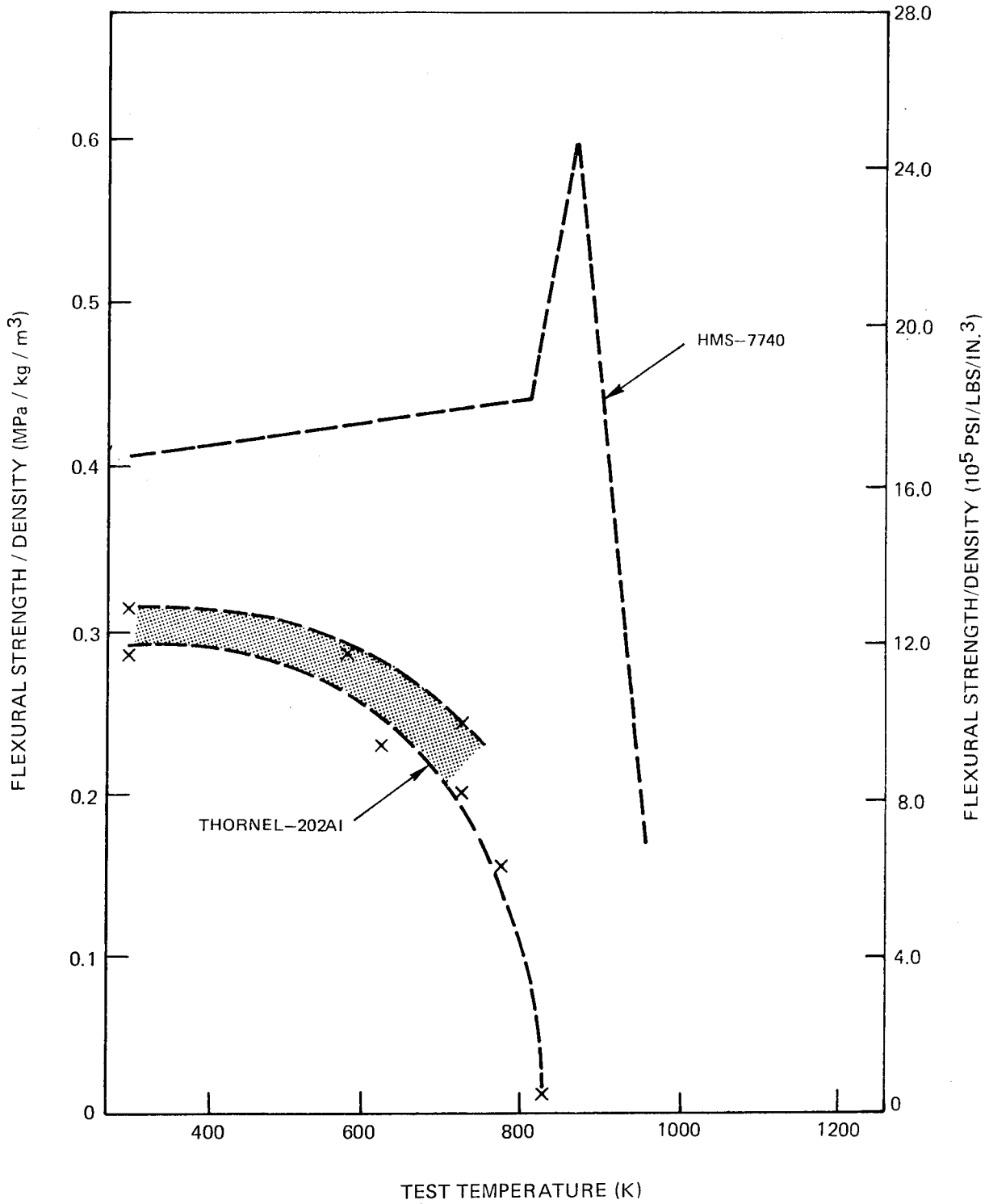


Figure 14. Specific Flexural Strength Comparison

The only metal matrix composite with a possible use temperature in the range of room temperature to 773 K (excluding the much higher density, reinforced super alloys) is Borsic fiber reinforced Ti-6Al-4V. It is important, therefore, to compare the HMS graphite fiber reinforced C.G.W. 7740 matrix, slurry A, with this titanium alloy system at temperatures above 573 K. The data are shown in Fig. 15. Unfortunately, the flexural data over the temperature range of interest are not available for the titanium alloy so that Borsic-Ti tensile data are used. To provide a more realistic comparison the Borsic-Ti tensile strengths were multiplied by a factor of 1.4, a factor experimentally determined at UTRC for the ratio of flexural strength to tensile strength at room temperature for the Borsic-Ti composite. In addition, the data were divided by composite density to obtain the specific flexural strength comparison shown in Fig. 16. At temperatures above 423 K the glass matrix composite is clearly superior to the titanium matrix composite.

The elastic modulus for HMS graphite fiber reinforced 7740 glass slurry A is compared with values of  $E_{11}$  characteristic of other composite systems in Table VI. The higher value for the glass matrix composite stands out.

#### Comparison of 3 Point and 4 Point Flexural Data for Graphite Fiber Glass Matrix Systems

The nature of the flexural strength test, i.e. whether it is a three-point or a four-point flexural strength test might be expected to affect the validity of a flexural-strength test for screening composite progress, but as Table VII shows, there is a definite relationship between the two tests.

#### Fracture Toughness Characteristics of HMS Fiber Reinforced 7740 Glass Matrix

Notched three-point bend systems were fabricated and tested in an attempt to characterize the fracture toughness of the HMS-7740 system. The specimen geometry is given in Fig. 17 and specimen dimensions with resultant data in Table VIII. As may be seen from the data of Table VIII, the fracture toughness does decrease with increasing temperature in a manner opposite to the variation in strength with temperature. It will be noted, however, that even the values obtained at the higher temperatures are favorable when compared to other composites and more conventional engineering alloys, Table IX.

#### Cyclic Testing of HMS Fiber Reinforced 7740 Glass Matrices

As in all the tests described to date, cyclic testing was carried out using uniaxial specimens of HMS fiber reinforced 7740 glass matrix composites. The thermal cycle interval was 8 min and 20 sec as shown in Fig. 18 and as may be seen from Fig. 19 and Table 4 of Appendix B the flexural strength of the HMS

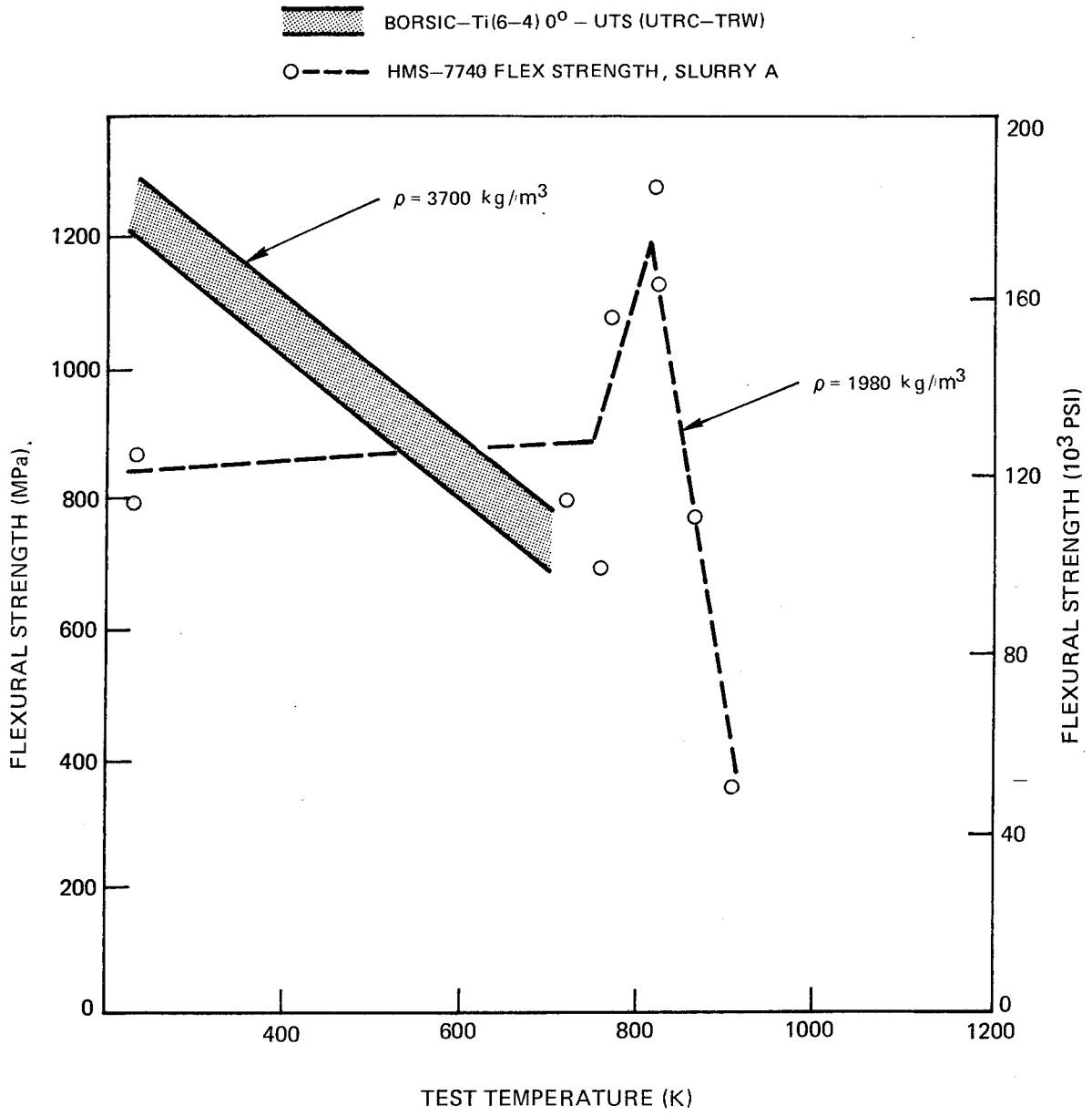


Figure 15. Flexural Strength Comparison

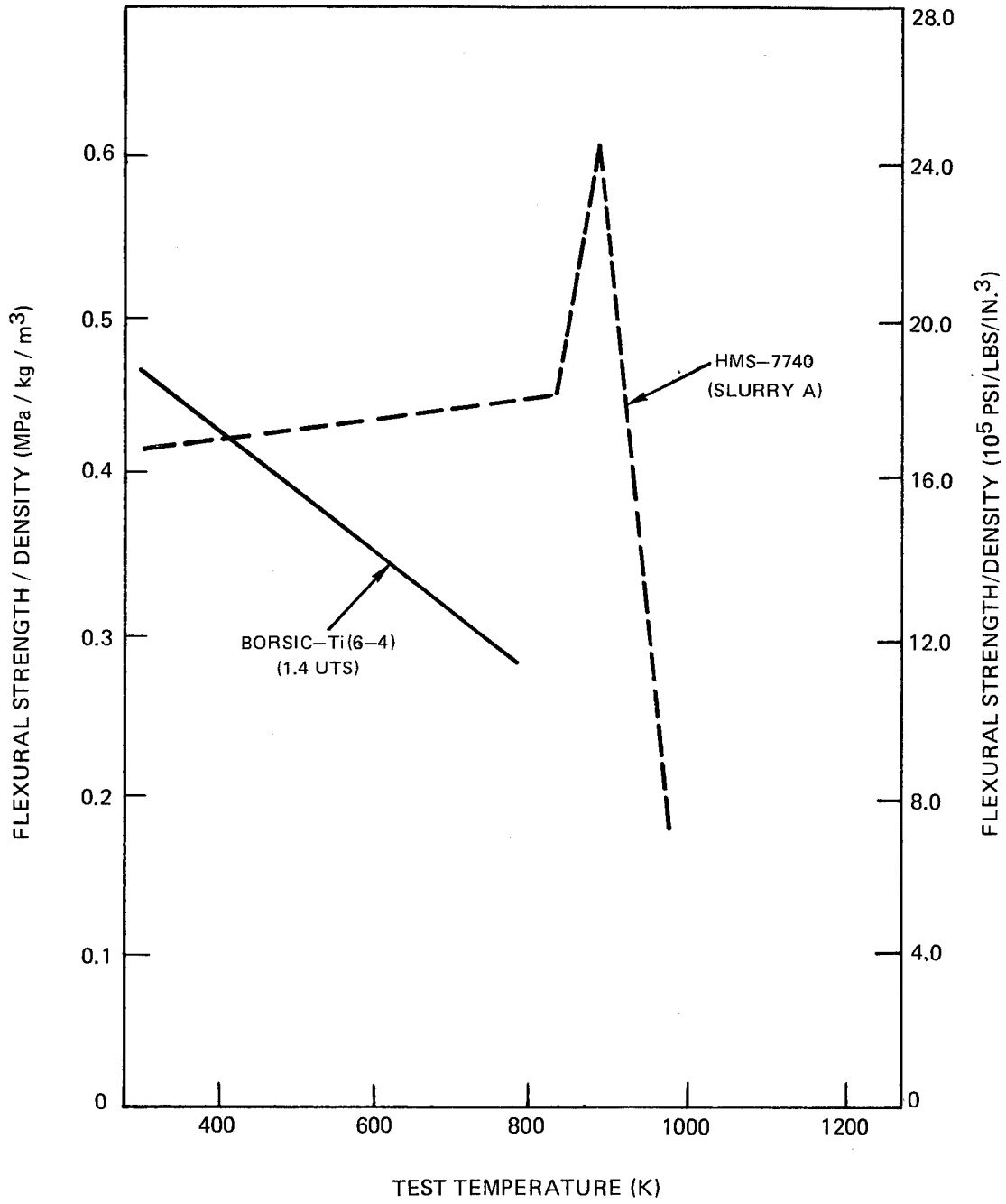


Figure 16. Specific Flexural Strength Comparison

Table VI

## Room Temperature Elastic Modulus Comparison

<u>System with Calculated Fiber Contents</u>	<u>Density</u>		<u>Elastic Modulus</u>		<u><math>E_{11}/\rho</math> (GPa/kg/m<sup>3</sup>)</u>
	<u><math>\rho</math> (kg/m<sup>3</sup>)</u>	<u>(lb/in<sup>3</sup>)</u>	<u>E GPa</u>	<u>10<sup>6</sup> psi</u>	
50 v/o Celanese DG-102-7740	2020	0.072	296	43	0.146
50 v/o HMS-7740	1980	0.071	193	28	0.097
42 v/o T50-A1	2300	0.083	207	30	0.090
50 v/o B-A1	2700	0.097	227	33	0.084
43 v/o B-Ti	3700	0.133	234	34	0.063

Table VII

Comparison of 3-Point Bend and 4-Point Bend Test  
Data for Several Graphite Fiber-Glass Composites  
Slurry A

<u>Sample</u>		3-Point Flexural Strength		Strain Gaged 4-Point Flexural Strength	
		<u>MPa</u>	<u>psi</u>	<u>MPa</u>	<u>psi</u>
LB 136 - 3 tests	HMS/	648	94 000		
- 6 tests	7740			517	75 000
LB 135F - 9 tests	HMS/	977	142 000		
LB 135G - 9 tests	7740			848	127 300
LB 97 - 9 tests	DG-102/	342	49 600		
LB 97D - 9 tests	7740			309	44 800

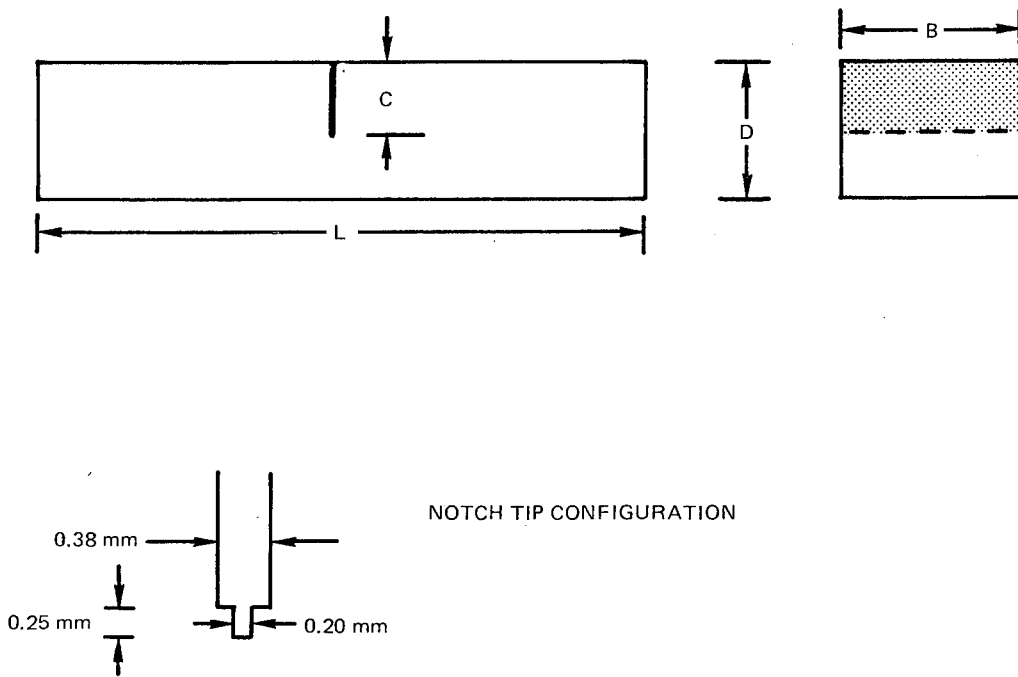


Figure 17. Fracture Toughness Specimen

Table VIII  
Fracture Toughness Specimen Dimensions  
Slurry A

Specimen	C (cm)	B (cm)	D (cm)	Test Span cm	L cm
LB-140-1 -2	0.330 0.305	0.990 0.990	0.691 0.691	3.98 3.80	5.0 5.0
LB-157-1 -2	0.330 0.330	0.954 0.954	0.852 0.852	3.98 3.98	5.0 5.0

Specimen	Test Speed (cm/min)	Test Temp K	$MN/m^{3/2}$	$K_C$ $10^3 \text{ psiv}^{1/2}$	Energy Per Unit Area $\frac{\text{Joules/m}^2}{\text{ft-lbs/in}^2}$
LB-140-1 -2	20 000 0.127	295 295	21.4 22.1	19.5 20.1	23 500 -
LB-157-1 -2	20 000 20 000	873 923	15.8 19.0	14.3 17.3	10 600 11 800

Table IX

## Fracture Toughness Comparison at 295 K

<u>Material</u>	<u>MN/m<sup>3/2</sup></u>	<sup>K<sub>IC</sub></sup> <u>10<sup>3</sup> psi <math>\sqrt{\text{in}}</math></u>
0°-HMS/7740, Slurry A	21.7	19.8
0/90-AS Graphite/AR 288*	14.25-1.973	13-18
Morganite II/Epoxy**		
0°	35	32
90°	1.75	1.6
45°	2.52	2.3
+45°	19.73	18
0/+45°/90	24.1	22
2014-T6 Aluminum Alloy***	21.92	20
6061-T651 Aluminum Alloy***	29.6	27

\*UTRC data using compact tension specimens

\*\*H. Konish and T. Cruse, J. Comp. Materials, Vol. 6, p 114, 1972

\*\*\*Damage Tolerant Design Handbook MCIC-HB-01

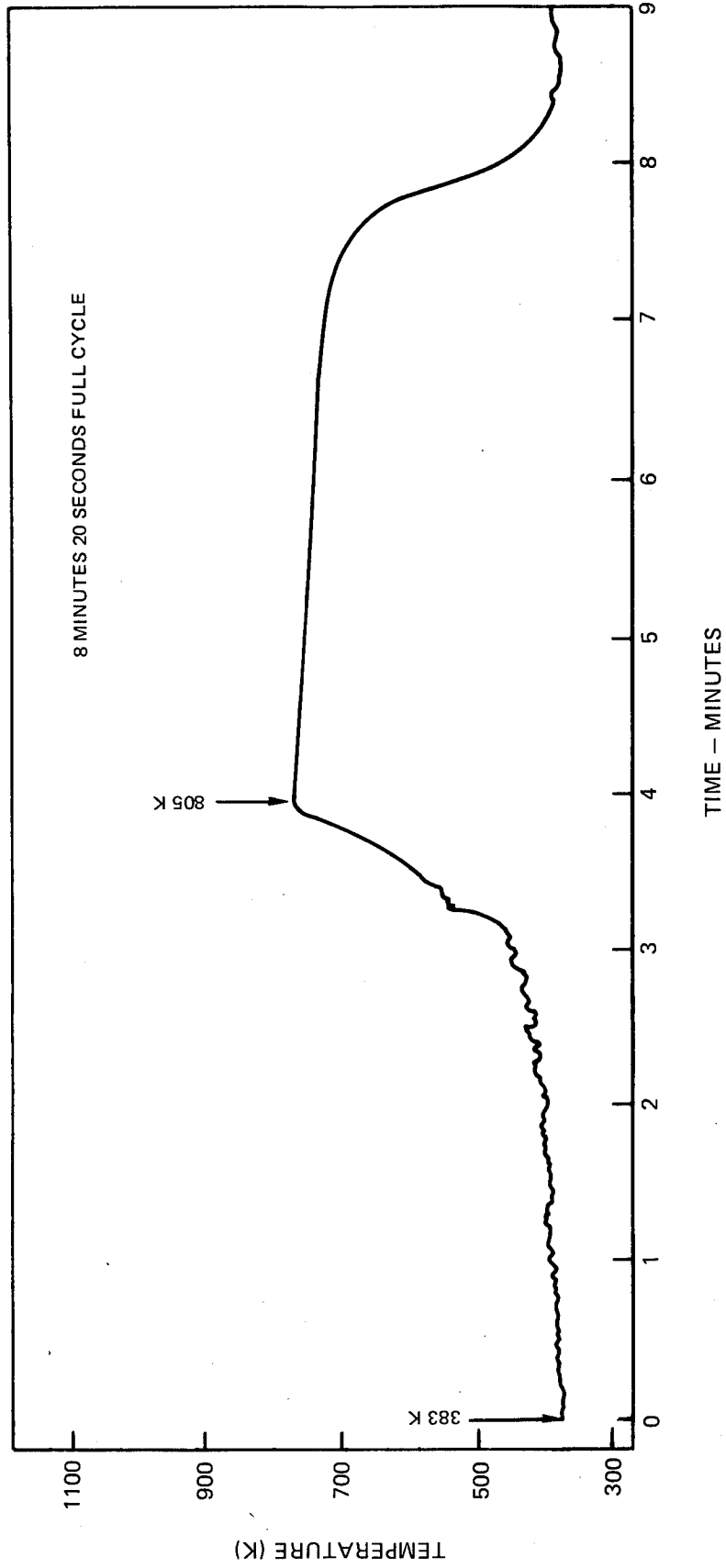


Figure 18. Temperature Cycle

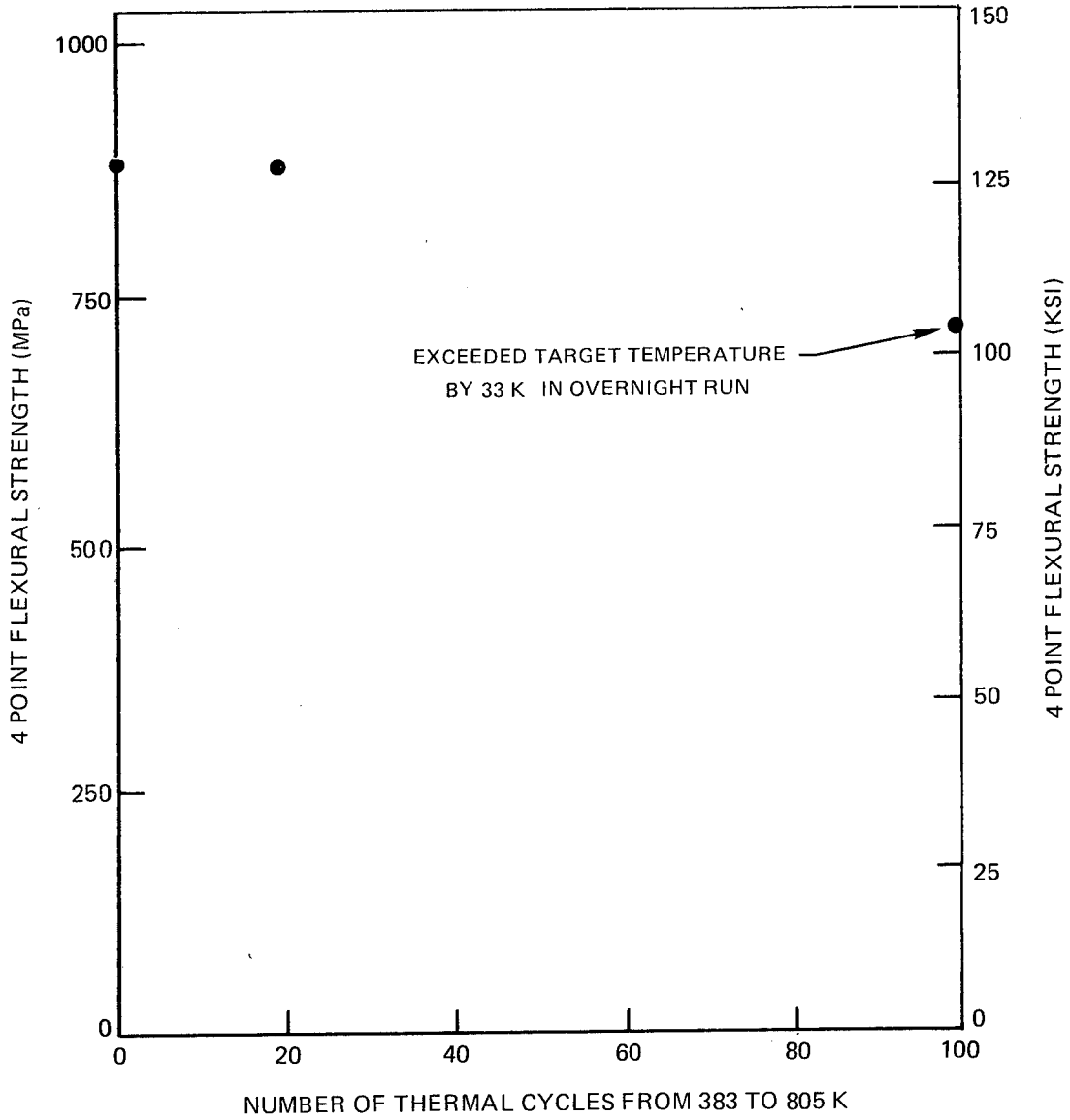


Figure 19. Flexural Strength of HMS – 7740 Glass Composite After Thermal Cycling , Slurry A

graphite reinforced 7740 glass matrix composite was unaffected by a hundred such cycles. Similarly, 100 cycles of flexural fatigue between 0.8 and 0.08 of the as-fabricated four-point bend strength left the graphite fiber glass matrix composite unaffected. Again, painting the composite specimens with six times normal sea salt concentration and thermally cycling the samples between temperatures of 383 and 833 K (encapsulated in silica tubes) left the composites unaffected.

### Discussion of Recent Advances

The progress made since the last annual report is summarized below. Processing effects on the microstructural characteristics and flexural strength properties, the shear, transverse, and cross-ply strengths, the thermal expansion response and the oxidation characteristics of these composites are topics that will be discussed in turn.

#### Processing Effects

A positive effect of very high temperature hot pressing on the flexural properties of graphite fiber reinforced 7740 containing Ludox (slurry C) has been discovered as will be described below. In order to make a qualitative assessment of the graphite-glass composites, a comparison of the microstructures of HMS graphite fiber reinforced 7740 pressed, slurry B, at 1473 K and the Ludox containing 7740 pressed at 1723 K, slurry C, can be made by considering Figs. 20-23. In both samples the glass is seen to surround each graphite fiber. The tape maps (Figs. 22,23) of the composites suggest that there is somewhat less memory of the tows in the slurry C composite pressed at 1723 K, more intimate contact of the adjacent tows and therefore fewer glass rich areas.

The three-point flexural properties of samples processed in a fashion similar to those represented in Figs. 20-23 are shown in Tables X and XI; these data are also represented in the cumulative failure probability plot of Fig. 24. Taking the data from the samples in each curve as belonging to a single population, the average strength and standard deviations are for the composites hot-pressed at 1473 K (no silica), slurry B,  $785 \pm 118$  MPa and at 1723 K with silica addition, slurry C,  $1023 \pm 104$  MPa.

Specimens of HMS graphite fiber reinforced 7740 + 2% SiO<sub>2</sub>, slurry C, hot pressed at 1723 K (GC 326), have also been flexurally tested in four-point bending. The data for these tests are listed in Appendix B, Table 8. The stress-strain behavior of one of these specimens is displayed in Fig. 25. Its ultimate strength is 1105 MPa, its modulus is 217 GPa and its failure strain is 0.53%. Although the average failure strain of HMS graphite (0.0077) is not achieved in this test, 70% of this value is achieved which is especially significant and impressive for a brittle matrix-brittle fiber composite combination.

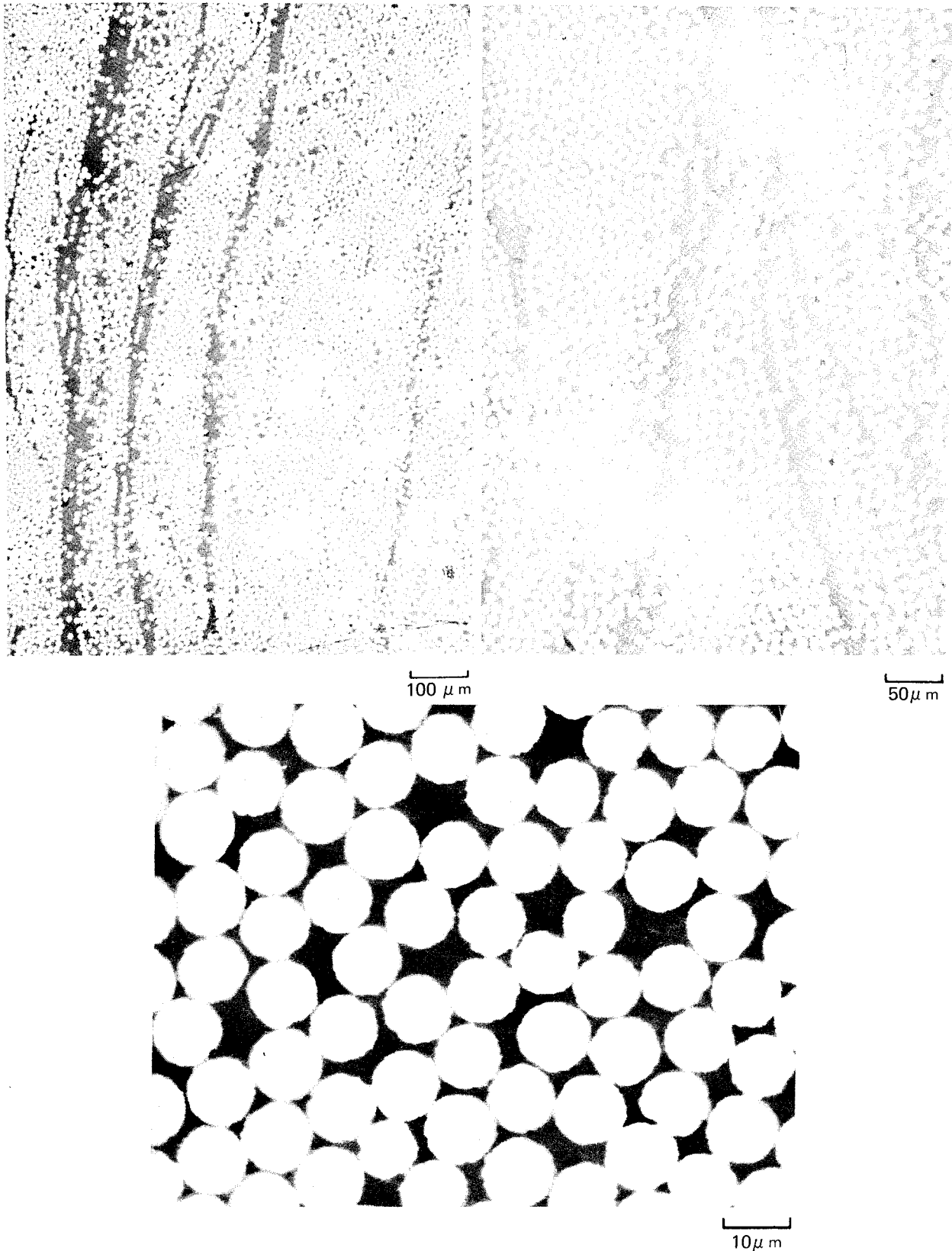
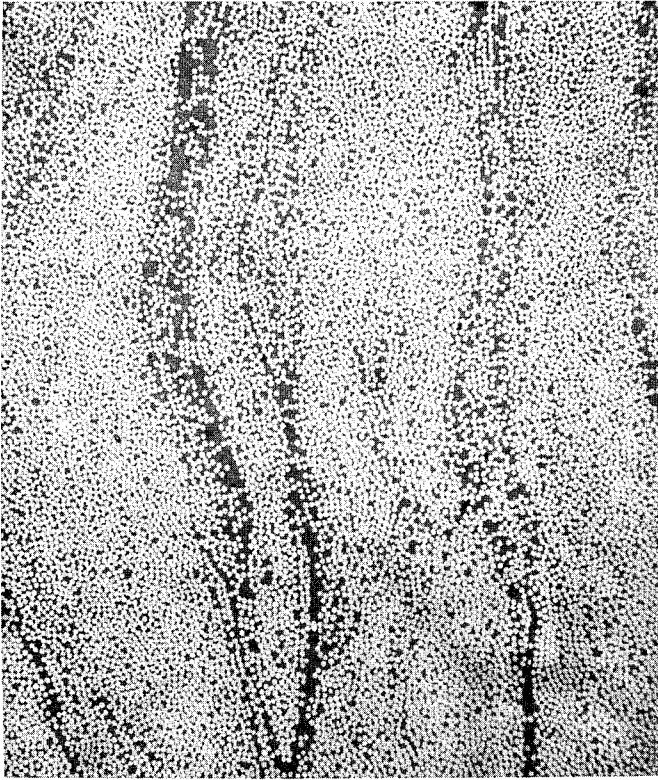


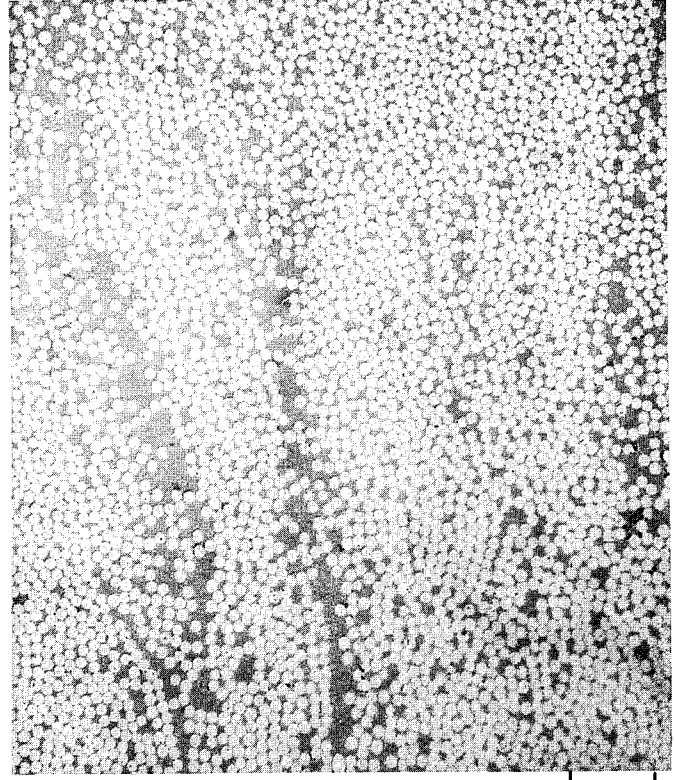
Figure 20. Microstructure of HMS Graphite Fiber Reinforced 7740 Glass Matrix (G.C. 281) Hot Pressed at 1473 K, Slurry B

100 X



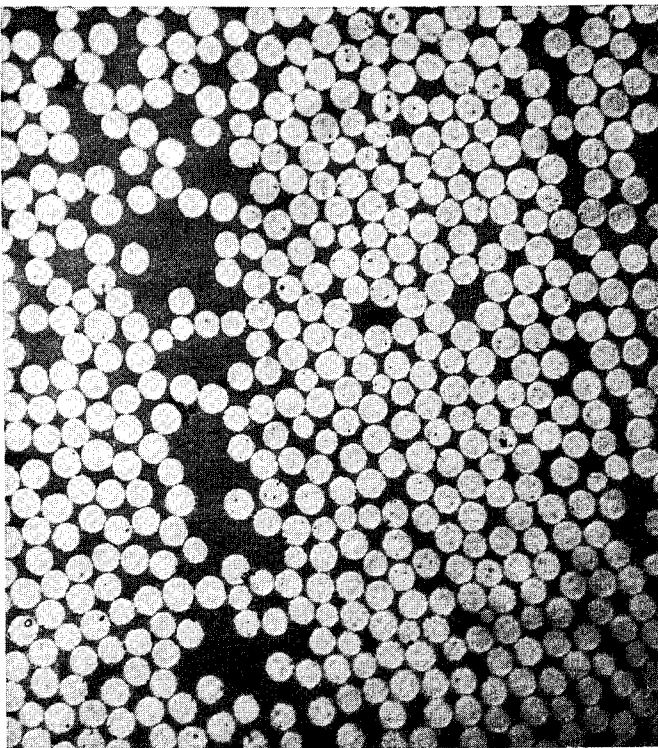
100  $\mu$  m

200 X



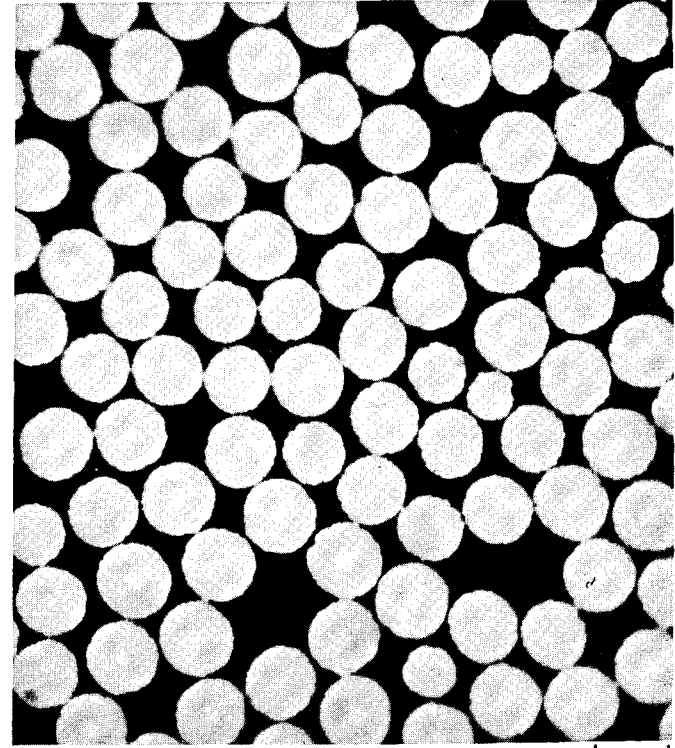
50  $\mu$  m

500 X



20  $\mu$  m

1250 X



10  $\mu$  m

Figure 21. Microstructure of HMS Graphite Reinforced 7740 + 2% SiO<sub>2</sub> (GC 326)

Hot Pressed at 1723 K, Slurry C

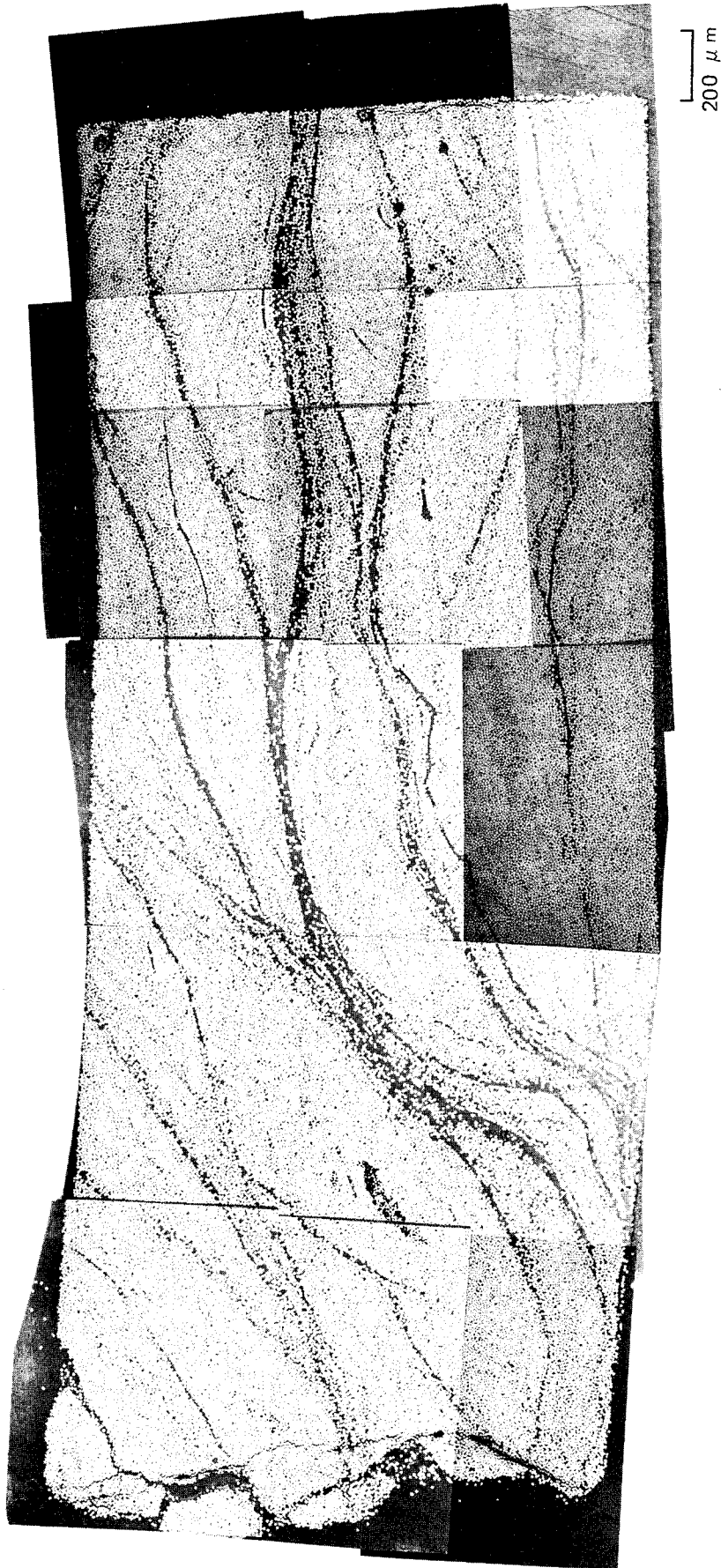
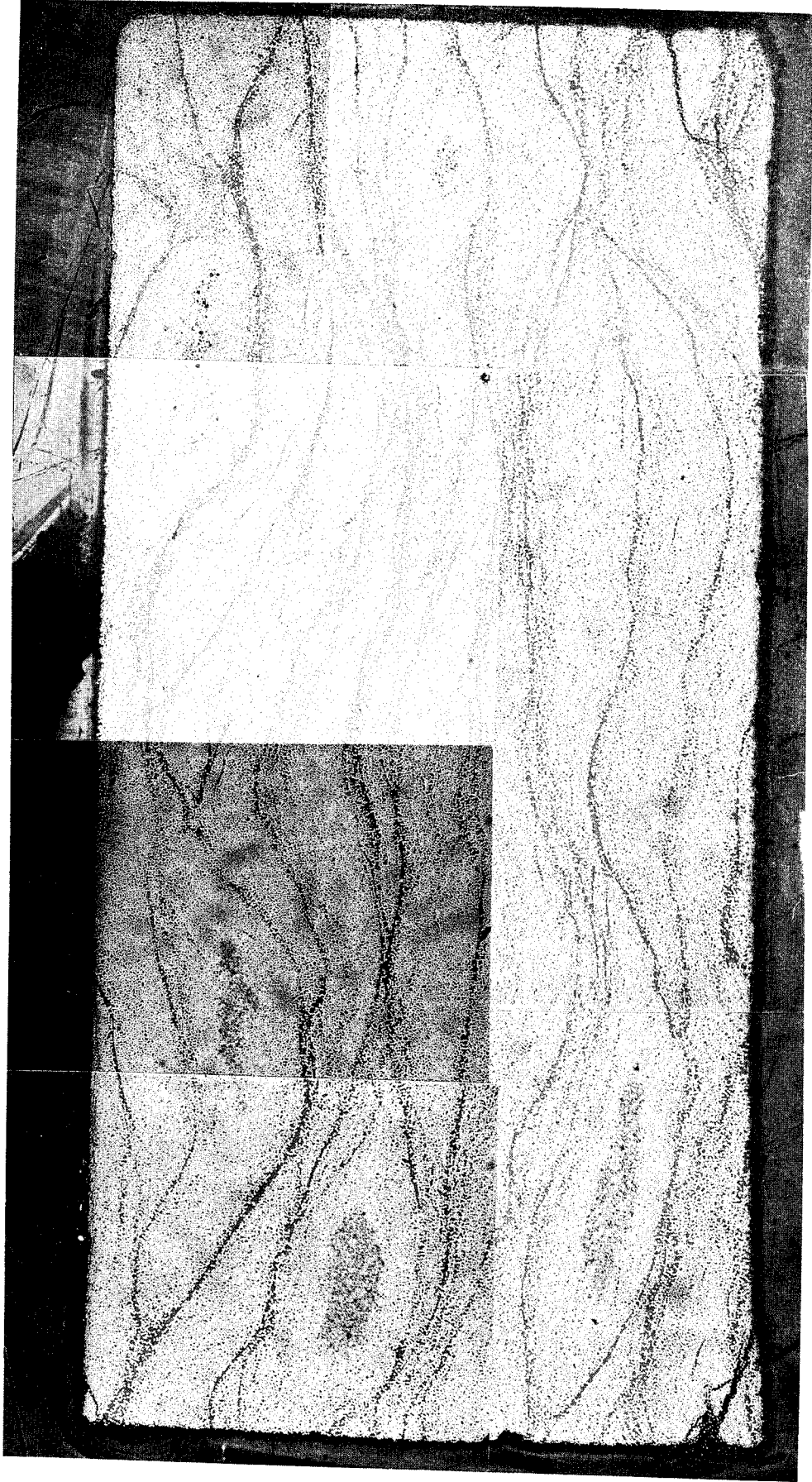


Figure 22. Tape Map of Cross Section of HMS Graphite Fiber Reinforced 7740  
Glass Matrix (GC 281) Hot Pressed at 1473 K, Slurry B



200  $\mu\text{m}$

Figure 23. Tape Map of Cross Section of HMS Graphite Reinforced 7740 + 2% SiO<sub>2</sub> Glass Matrix (GC326) Hot Pressed at 1723 K, Slurry A

Table X

Three Point Flexural Strengths for Several Samples of HMS Graphite  
Fiber Reinforced 7740 Glass Matrix (no silica),  
Hot Pressed at 1473 K, 13.8 MPa, Slurry B

	GC 281		GC 289 Top		GC 289 Middle		GC 289 Bottom	
	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi
1	965	140	660	95.8	852	124	746	108
2	674	97.7	895	130	839	122	491	71.2
3	688	99.8	928	135	939	136	799	116
4	752	109	759	110	908	132	799	116
5	786	114	652	94.6	572	83.0	710	103
6	745	108	692	100	913	132	968	140
7	793	115	747	108	642	93.1	908	132
8	800	116	658	95.4	905	131	778	113
9	660	95.7	1030	149	680	98.6	774	112
10			757	110	879	127	841	123
Mean	765	111	779	113	814	118	779	113
Std. Dev.	91.7	13.3	130	18.9	131	19.0	128	18.5
Std. Error	30.6	4.44	40	5.78	41	6.00	40	5.85

Table XI

Verification of Consistency of Results Obtained with New Type Slurry,  
 HMS Graphite Reinforced 7740 Glass (Silica Addition) Made at 1723 K  
 6.9 MPa, 1 hr dwell time, argon atmosphere, slurry C

Sample	Three-Point Flexural Strength		Sample	Three-Point Flexural Strength		Sample	Three-Point Flexural Strength	
	MPa	ksi		MPa	ksi		MPa	ksi
GC 326			GC 328			GC 339		
A1	1110	162	A2	866.9	125.7	A2	1102	160
A2	1150	166	A6	859.6	124.7	A5	1005	146
A3	1240	180	A8	1061.6	154.0	A7	954	138
A4	1170	170	A12	1046.1	151.7	A10	1107	161
A5	1060	153	B2	1109.9	161.0	B2	982	142
A6	931	135	B6	1199.7	174.0	B5	961	139
A7	835	121	B8	1149.8	166.8	B7	935	136
A8	942	137	B12	911.4	132.2	B10	1069	155
A9	1020	147	C2	935.0	135.6	C2	1015	147
A10	823	119	C6	999.5	144.2	C5	1020	148
A11	1040	150	C8	1140.0	165.3	C7	1015	147
A12	1070	155	C12	922.3	133.8	C10	1063	154
Avg	1034	150		1016.4	147.4		1019	148
Std Dev	130	18.9		117.7	17.1		56.7	8.34
Std Err	37.6	5.46						

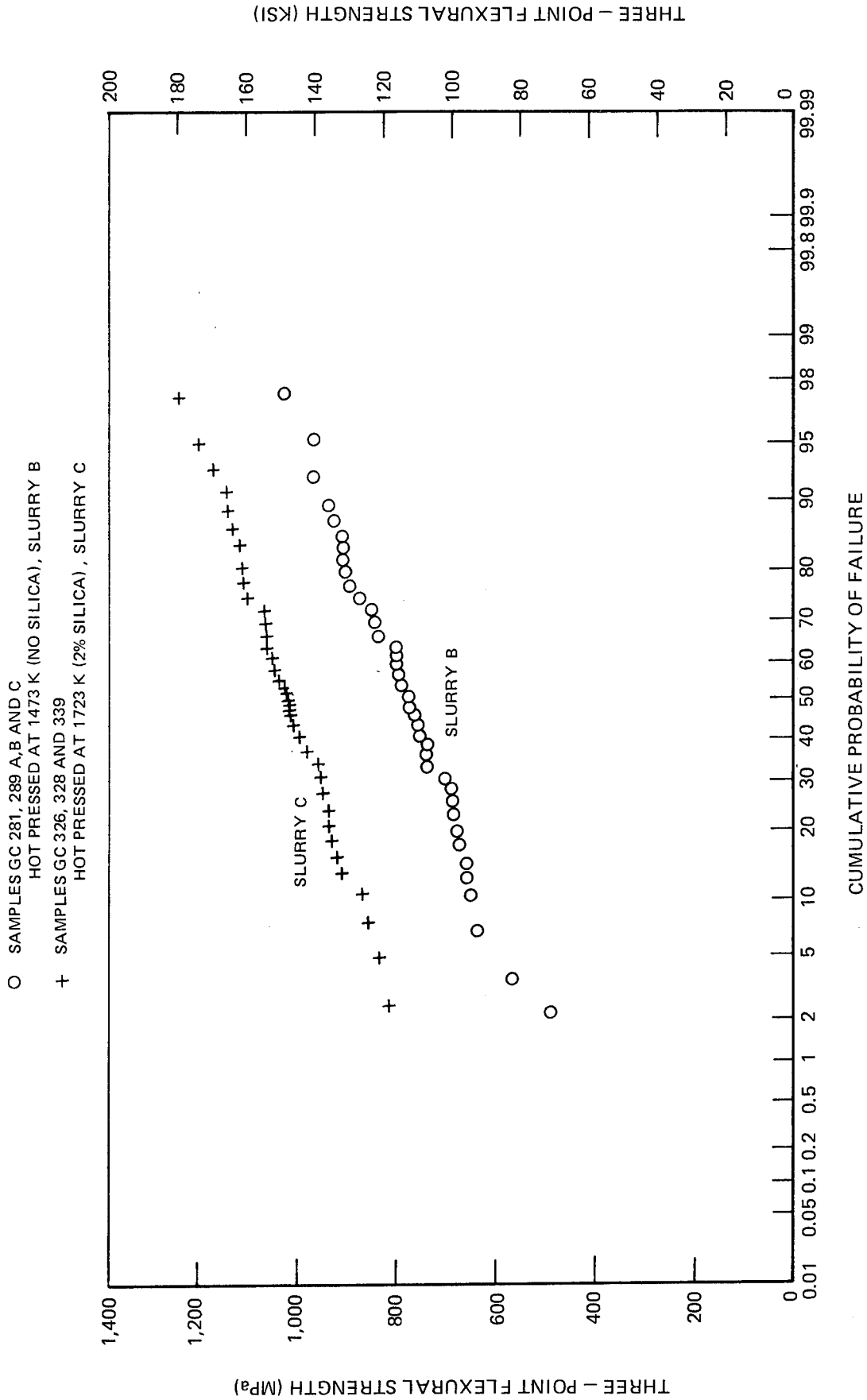


Figure 24. Failure Probability of HMS Graphite Fiber Reinforced CGW 7740 Glass with and without Silica

STRESS STRAIN CURVE  
4 POINT FLEXURE TEST WITH STRAIN GAGES

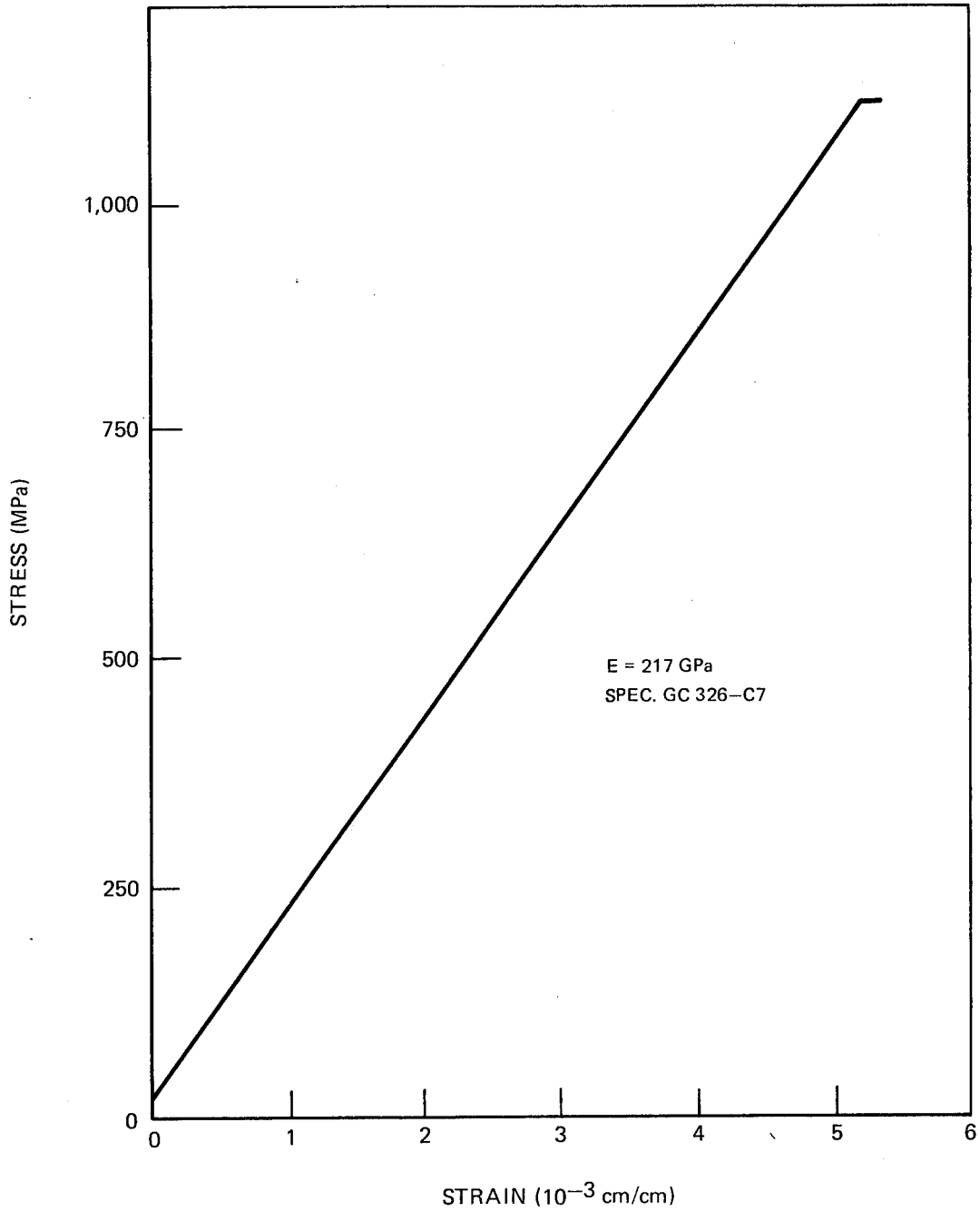


Figure 25. Stress Strain Curve of HMS Graphite Fiber Reinforced 7740 + 2% SiO<sub>2</sub>, Slurry C, Determined by Four Point Bend Test

Prior to the discovery of the advantages of very high temperature hot pressing, other variables which might influence composite behavior were explored. One such variable was the relationship between hot pressing pressure at a temperature of 1473 K and resultant strength in HMS graphite fiber reinforced 7740 matrix composites, slurry B. The strength data from the four pressures evaluated, i.e. 4.1, 6.1, 10.1 and 13.8 MPa, are listed in Appendix B, Table 7, the average flexural strengths are plotted as a function of pressure in Fig. 26. The strength increases in a linear fashion with pressure, reaching a value of 765 MPa at a 13.8 MPa pressure.

Another variable explored was the effect of hot pressing the samples (in series) simultaneously. At a hot pressing temperature of 1473 K (slurry B) and a pressure of 13.8 MPa, the average flexural strengths from the samples were 113, 118 and 113 MPa for the top, center and bottom, respectively (Appendix B, Table 8).

After the observation was made of the positive effect of increasing the hot pressing temperature to greater than 1473 K, a study was made to determine the optimum temperature for the HMS-7740 + 2% SiO<sub>2</sub> composite system, slurry C. The relationship between temperature and strength, which are listed in Appendix B, Table 9 and which are plotted in Fig. 27, show an optimum temperature of 1723 K with a corresponding strength of 1034 MPa. Furthermore, the strength of the system pressed at 1473 K is only 225 MPa; in comparison, the 7740 matrix without the silica additive, pressed at 1473 K, would be expected to exhibit a strength of ~550 MPa when pressed at 6.9 MPa (Fig. 26). Therefore, not only does the colloidal silica influence the green strength of the composite, but also has a definite influence on the composite consolidation.

The consistency of strength results obtained in HMS graphite fiber reinforced 7740 + 2% SiO<sub>2</sub> glass matrix composites (slurry C) hot pressed at 1623 and 1723 K at a pressure of 6.9 MPa are demonstrated by comparing the data listed in Table 12 of Appendix B and Table XI of the text and the averages mentioned below. At 1623 K, the average strengths from three separate samples were 616, 639 and 651 MPa; at 1723 K, the average strengths of three separate samples were 1016, 1019 and 1034 MPa. This corresponds to an approximately 5 and 2% difference between extremes in the two cases respectively.

Holding the pressure constant, the effect of fiber type on the flexural strength properties of graphite fiber reinforced glass matrix composites made with a matrix of C.G.W. 7740 plus added silica (slurry C) was evaluated. The HTS fiber reinforced matrices had a flexural strength of 455 MPa when hot pressed at 1473 K and 731 MPa when hot pressed at 1623 K, Table XII. In comparison the average flexural strength of a similar system hot pressed at 1373 K but without silica addition (slurry B) was 370 MPa. It is evident, therefore, that the silica addition which permits hot pressing at a higher temperature by reducing fluidity of the glass is beneficial. However, the optimum temperature of hot pressing this fiber has not been achieved.

COMPOSITE IS HMS GRAPHITE FIBER REINFORCED 7740 GLASS MATRIX PREPARED 1473 K, ONE HOUR DWELL TIME, SLURRY B

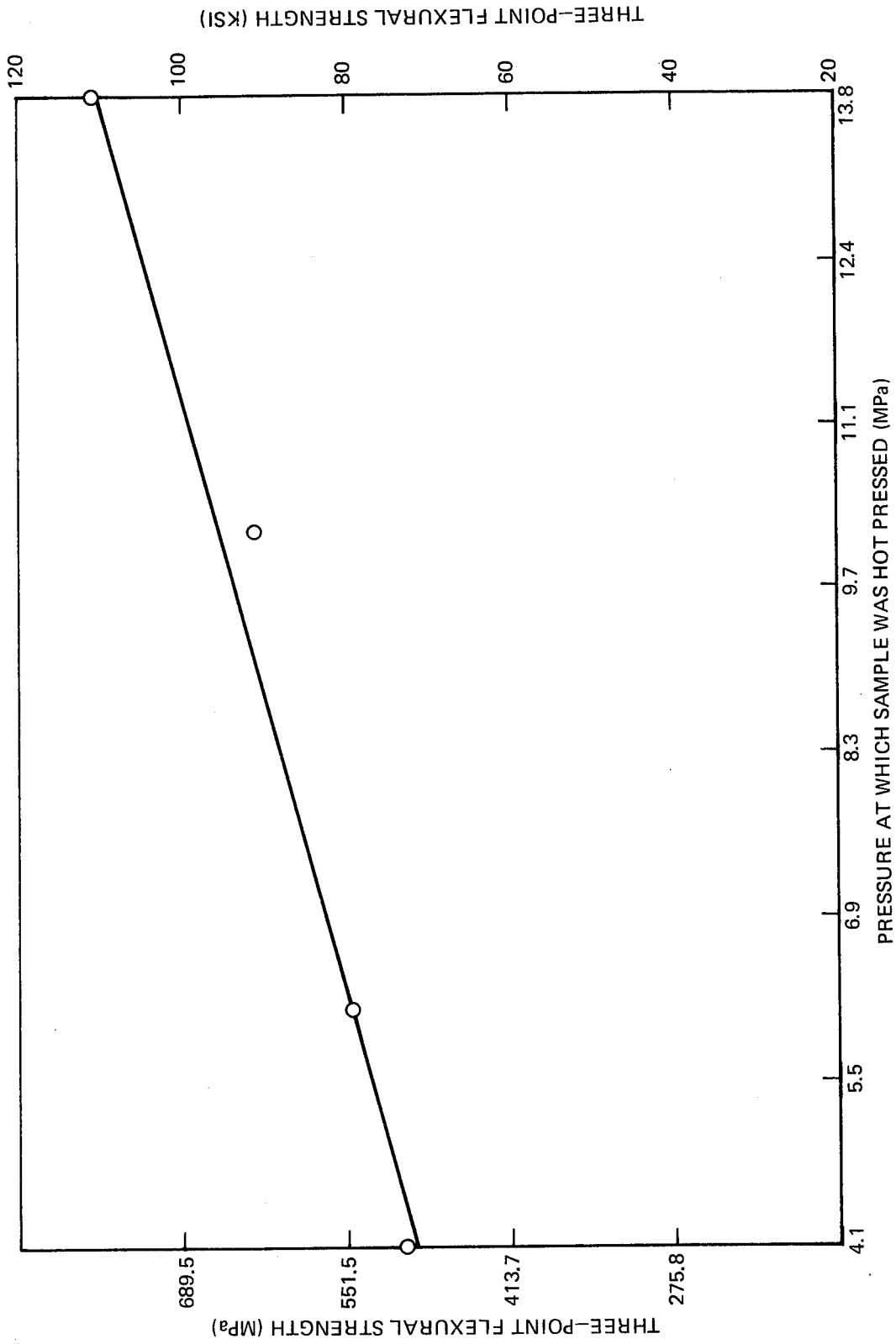


Figure 26. Relation of Hot Pressing Pressure to Three - Point Flexural Strength of Composite

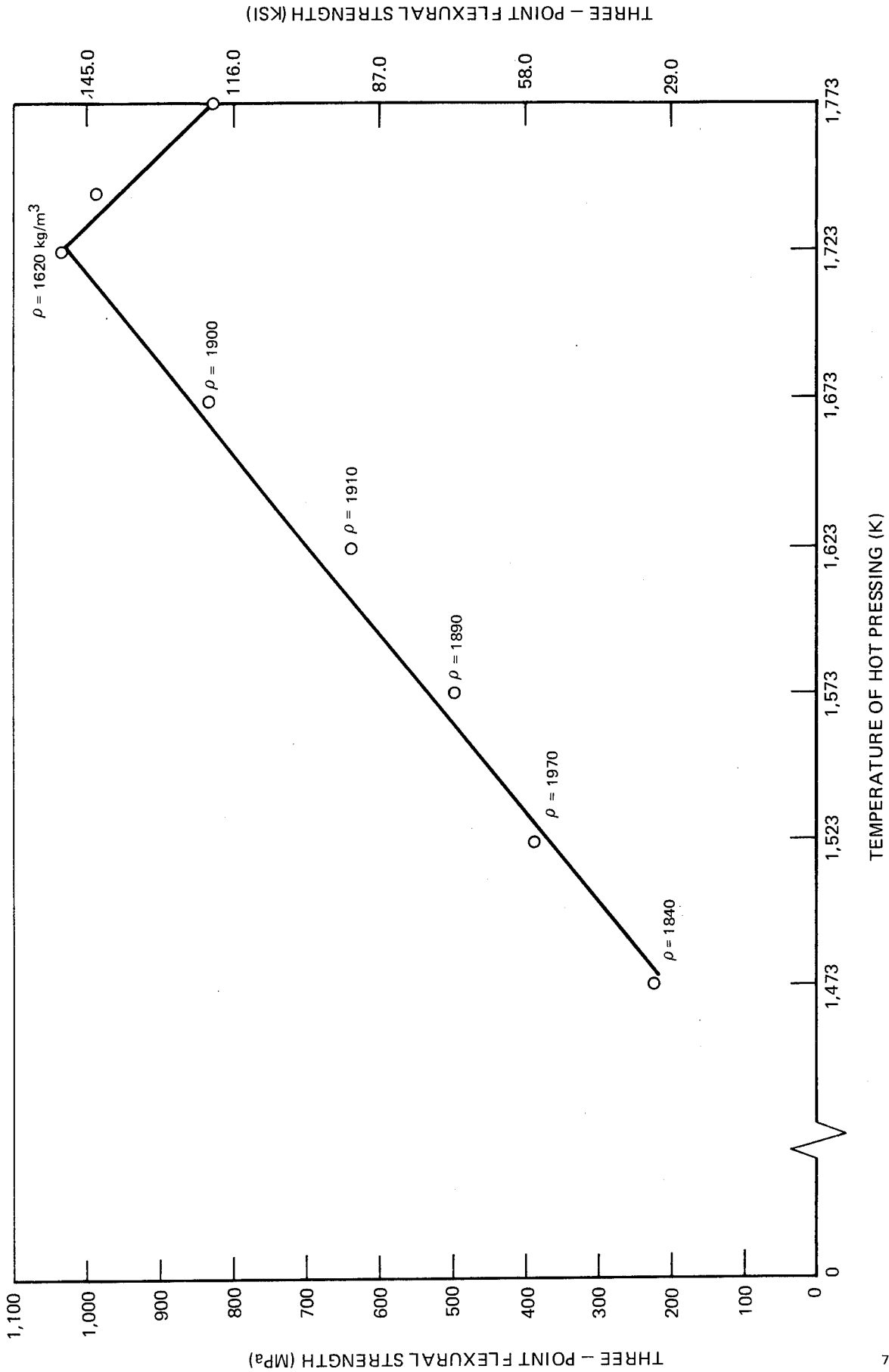


Figure 27. Relationship of Three-Point Flexural Strength of HMS-7740 + 2% SiO<sub>2</sub> Composite to Temperature at which Composite is not Pressed, Slurry C

Table XII

Effect of Change in Slurry and Hot Pressing  
Temperature on Three-Point Flexural Strength  
of HTS Fiber Reinforced 7740 Composites

<u>Sample</u>	3-Point Flexural Strength		<u>Sample</u>	3-Point Flexural Strength		<u>Sample</u>	3-Point Flexural Strength	
	<u>MPa</u>	<u>ksi</u>		<u>MPa</u>	<u>ksi</u>		<u>MPa</u>	<u>ksi</u>
LB 148			GC 292			GC 304		
Old Slurry A			7740+2% SiO <sub>2</sub> (slurry C)			7740+2% SiO <sub>2</sub> (slurry C)		
Old Press			New Press			New Press		
1373 K			1473 K			1623 K		
(13.8 MPa)			(13.8 MPa)			(6.9 MPa)		
1	338	49.0	TR	475	68.8	A2	766	111
2	408	59.2	CR	488	70.7	A7	651	94.4
3	341	49.5	BR	405	58.8	A12	681	98.7
4	357	51.7	TC	434	63.0	B2	695	101
5	410	59.4	CC	466	67.6	B7	698	101
6	389	56.4	CB	448	65.0	B12	844	122
7	408	59.2	TL	476	69.1	C2	789	114
8	379	54.9	LC	435	63.1	C7	708	103
9	456	66.1	LC	468	67.8	C12	749	109
10	354	51.4						
11	343	49.8						
12	407	59.1						
13	319	46.3						
14	297	43.0						
15	348	50.4						
Mean	370	63.7		455	66.0		731	106
Std Dev	42.4	6.15		26.5	3.80		59.8	8.67
Std Err	11.0	1.59		8.83	1.27		19.9	2.89

In the case of Celanese DG-102 fiber reinforced 7740 + 2% SiO<sub>2</sub> (slurry C), flexural strength data have been obtained from samples hot pressed at 1473, 1623 and 1723 K, Table XIII. The average respective strengths were 209, 417 and 460 MPa. The positive influence of higher hot pressing temperature is again apparent. The flexural strength of DG-102 reinforced 7740 prepared using the previous slurry B process method (7740 pressed at 1473 K) was 340 MPa.

An experiment was also conducted with Thornel pitch VS 0032 fiber in slurry C 7740 + 2% SiO<sub>2</sub>. After hot pressing at 1623 K, the average flexural strength of such specimens was 448 MPa. The data are given in Table 11 of Appendix B.

For composites utilizing a matrix of 7740 + 2% SiO<sub>2</sub> (slurry C) and hot pressed at the nonoptimum temperature of 1623 K, the following comments with respect to fiber type are appropriate. The HTS fiber reinforced system was strongest (731 MPa) as might be expected from the nominally higher strength of this fiber. The HMS reinforced system displayed the next highest strength (635 MPa) in keeping with HMS being the next strongest fiber. The pitch and DG-102 fiber reinforced systems were weakest (448 and 417 MPa, respectively). Although the strength of both fibers is relatively low with the pitch fibers being the weaker, the strength of the composites derived from these fibers is in reverse order.

Composites employing higher percentages of Ludox have also been prepared (GC 225 and 226). Tapes have demonstrated excellent green strength and were easily handled without the loss of glass powder. Specimens prepared from these samples which were hot pressed at 1473 K were weaker than comparison samples without Ludox. In retrospect, based on the most recent data, a much higher hot pressing temperature might provide composites from these type compositions with equivalent or superior flexural strengths to the comparison composites pressed at 1473 K.

### Shear, Transverse and Cross Ply Strengths

#### Shear Strength

The interlaminar shear strength was determined in three-point bending using a 3.5 to 1 span-to-depth ratio. The strength for an HMS graphite fiber reinforced 7740 glass matrix hot pressed at 1473 K, slurry B, was 39.8 MPa. This low value of shear strength illustrates the poor bonding that exists between matrix and fiber. Data for specimens hot pressed at 1723 K have not, as yet, been obtained and specimens made with 2% added silica, slurry C, have not yet been evaluated.

Table XIII

Effect of Hot Pressing Temperature on Three Point Flexural Strength of Composites  
 Formed from Celanese DG-102 Fiber Reinforced C.G.W. 7740 + 2% SiO<sub>2</sub> Glass  
 Matrix Hot Pressed Using Newest Slurry, 6.9 MPa, 1 Hr Dwell Time  
 Slurry C

Specimen	Three Point		Specimen	Three Point		Specimen	Three Point	
	Flexural Strength MPa	ksi		Flexural Strength MPa	ksi		Flexural Strength MPa	ksi
A1	120	17.4	A1	221	32.1	A1	413.5	59.98
A6	279	40.5	A4	457	66.4	A5	379.3	55.02
A12	113	16.4	A7	533	77.4	A8	320.3	46.40
B1	145	21.1	A10	416	60.3	A11	358.6	52.01
B6	233	33.8	B1	351	50.9	B1	480.5	69.68
B12	267	38.8	B4	489	70.9	B5	515.8	74.81
C1	175	25.4	B7	451	65.4	B8	511.7	74.22
C6	256	37.2	B10	424	61.6	B11	576.8	83.66
C12	293	42.6	C1	330	47.9	C1	501.3	72.70
			C4	469	68.0	C5	543.7	78.86
			C7	409	59.4	C8	555.9	80.62
			C10	450	65.2	C11	364.1	52.81
Avg	209.4	30.37	417	60.5	460.1	66.74		
Std Dev	72.4	10.5	82.7	12.0	88.12	12.78		
Std Err	41.8	6.1	73.9	3.47				

GC-306 - 1473 K

GC-331 - 1623 K

GC-336 - 1723 K

### Transverse Strength

Hercules HMS fiber unidirectionally reinforced 7740 glass matrix composites were fabricated from slurry B. Two composite thicknesses of 4 ply and 16 ply were used and the resultant panels were cut into 90° oriented specimens for three-point bend testing. The specimen surfaces were glass rich and this layer was not removed prior to testing since its presence simulates a surface protected against fiber oxidation.

The resultant three-point flexural strength data are listed in Appendix B, Table 12; the average flexural strengths were 9.7 and 14.8 MPa for specimens of 4 and 16 plies, respectively. In every case the specimens appeared to fracture at the tensile surface and crack propagation occurred across the specimen thickness. Fracture did not occur, however, at the mid-span in each case. This was particularly true of the 4 ply thick composite specimens (GC 208) and can be readily understood when one considers the importance of microstructure and the location of weaker and stronger material regions on transverse properties. Calculated composite strengths ranged from approximately 6.8 MPa (1000 psi) to 22.2 MPa (3240 psi) with the single high value occurring for a thicker specimen. These low levels of transverse strength are expected because of the low bond strength between the HMS graphite fiber and 7740 glass.

HTS and Celanese DG-102 fiber unidirectionally reinforced 7740 specimens were fabricated for 90° flexural strength measurement. The data for the HTS containing specimens are also presented in Table 12, Appendix B; the average transverse strength was 10.8 MPa and ranged from 4.7 to 18.0 MPa. As expected, the transverse strengths measured were quite low. The DG-102 fiber composite data were not obtained because the fabricated panels fractured during handling and cutting, thus also evidencing a very low transverse strength. As was previously noted, these data point clearly to the importance of multiaxially reinforced specimens for most applications. Furthermore, since these composites were prepared using a 7740 matrix hot pressed at 1473 K, the data should be viewed as preliminary. Improvements might be obtained from composites pressed at 1723 K, the optimum temperature for longitudinal strength.

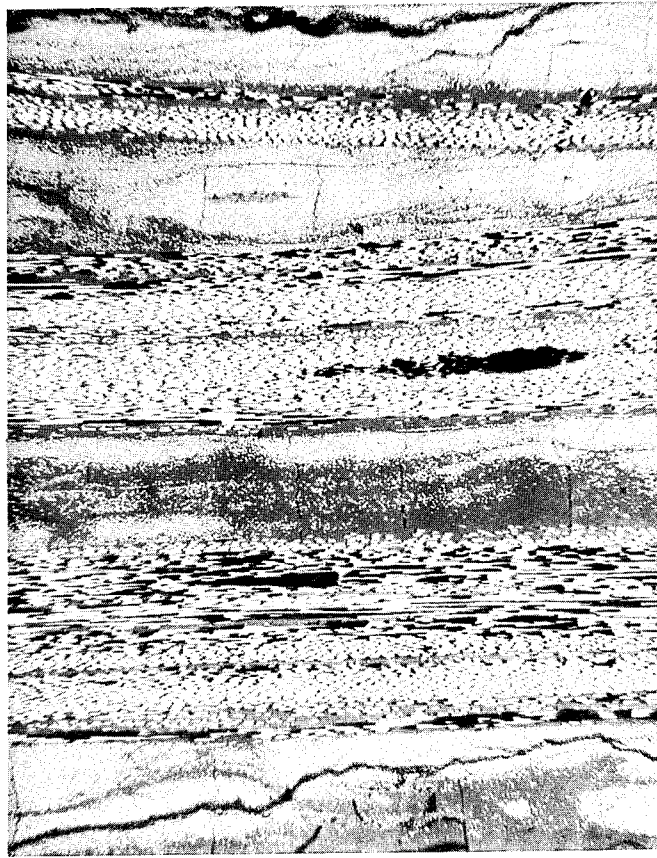
### Cross-Ply Composites

Cross ply constructions of HMS and Celanese DG-102 fiber reinforced composites were fabricated by the same procedures used for uniaxially reinforced specimens (hot pressed at 1473 K). The composite lay-up consisted of a sequence of alternating 2 ply thick strata that were stacked symmetrically with respect to the composite mid plane. The abbreviated notation for this lay-up sequence is  $[(90_2, 0_2)_2]_S$  and consists of a total of 16 plies.

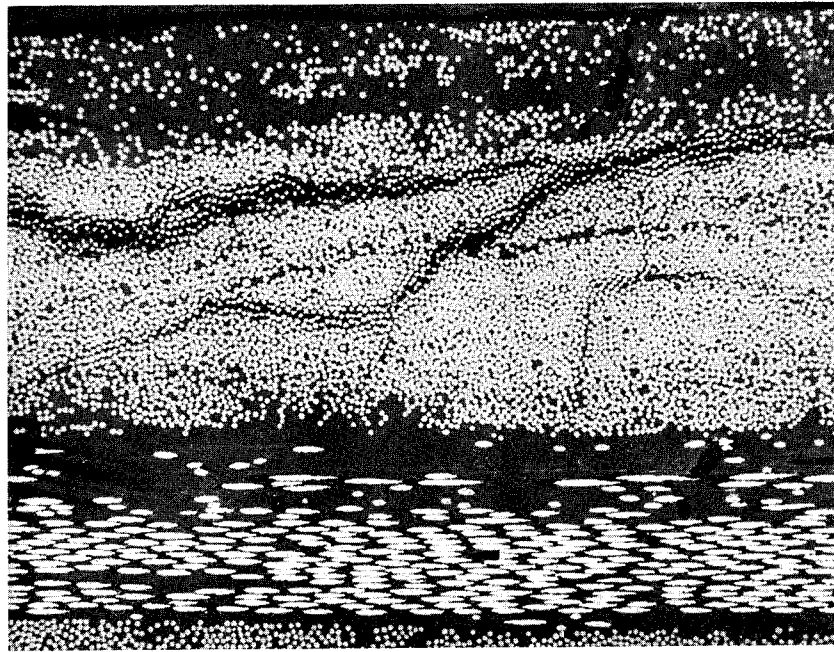
The microstructure of the composite containing DG-102 fiber is shown in Fig. 28. Besides the obvious fiber distribution, the most notable feature is the presence of many microcracks running through the plies. Many of these cracks are evenly spaced, run at  $90^\circ$  to the ply plane, and may be associated with the mismatch in thermal expansion between the two ply orientations. On a macro scale, however, the as-fabricated composites looked excellent and uncracked. The  $90^\circ$  direction has a higher coefficient of thermal expansion and thus, on cooling from the hot pressing temperature, it could crack because of the tensile stresses induced within the ply and at  $90^\circ$  to the fiber direction. Careful examination of composites, however, has demonstrated that any observed cracks are due more to the preparation of the metallographic sections rather than any other reason. Thus, specimens which were cut and polished by the standard technique exhibited a large population of microcracks, while those which were surface ground and polished to remove approximately 0.25 cm of material after cutting, were almost completely crack free. This is shown in the cross-ply composite, GC 215, in Fig. 29 which was prepared with a ply lay-up scheme of  $[(0/90)_4]_S$ . In addition, the matrix was leached out of samples of each composite and the freed fibers examined to ascertain whether any fiber fragmentation had occurred. This could conceivably occur during the application of pressure at the contact points of neighboring crossed fibers. No evidence of fiber fragmentation was found, however, and all of the extracted fibers exhibited lengths equivalent to the dimensions of the original specimens.

Mechanical testing of samples was carried out in the three-point bend mode. The specimens were cut such that the surface ply fibers were parallel to the major span of the bend test apparatus and no surface preparation was used prior to testing in order to avoid grinding through the  $0^\circ$  primary load bearing plies. Because of this lack of grinding, and also the fact that the as-fabricated panels were not very uniform in thickness, the bend tests were not well controlled. Nevertheless, the objective was to make a first attempt at gaining data for cross ply material, and this was achieved.

The measured strengths are given in Table XIV, along with other pertinent information. In the case of the Celanese fiber reinforced specimens, an average strength of 115 MPa (16,700 psi) is somewhat lower than that expected since the average room temperature bend strength of unidirectionally reinforced  $0^\circ$  specimens has been approximately 270-320 MPa (40-45,000 psi). This difference, however, may be attributable to a lower fiber content (40%) than has been typical in the past (50-60% by volume). All of these specimens fractured in a tensile mode and, as previously reported for  $0^\circ$  Celanese reinforced specimens, the fracture did not exhibit much fiber pull out. In contrast, the HMS fiber reinforced specimens failed by interlaminar cracking at regions generally remote from the mid-span of the specimens. These cracks then propagated along interlaminar ply bond lines toward the centers of the specimens. The specimens, however, did not separate into pieces and instead retained substantial fractions of their original



400 μ m



100 μ m

Figure 28. Microstructure of Specimen GC 30 203 Celanese DG 102 Reinforced  
7740, [ ( 90<sub>2</sub> O<sub>2</sub> )<sub>2</sub> ]<sub>s</sub>, Slurry B

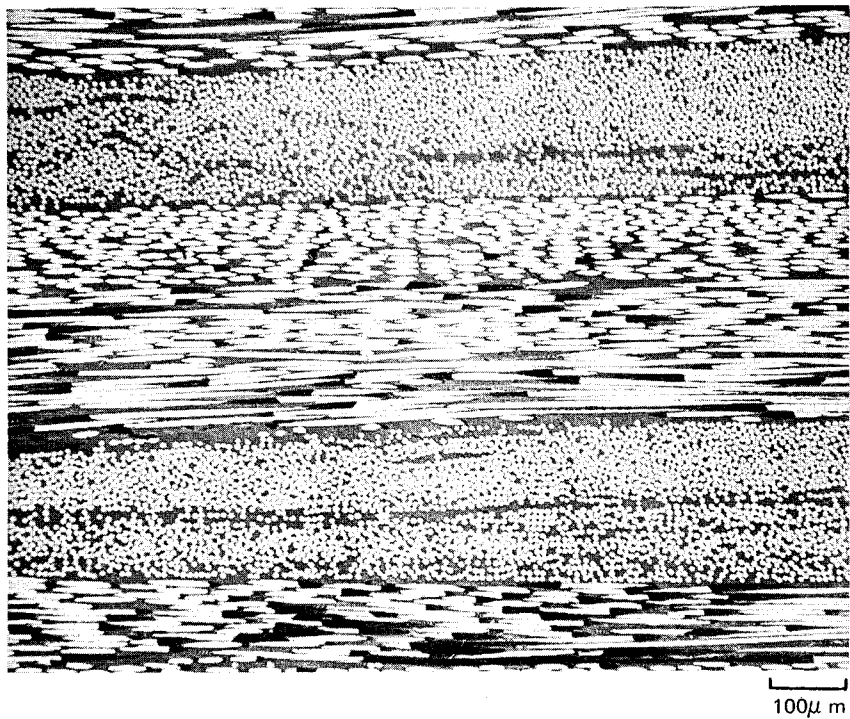
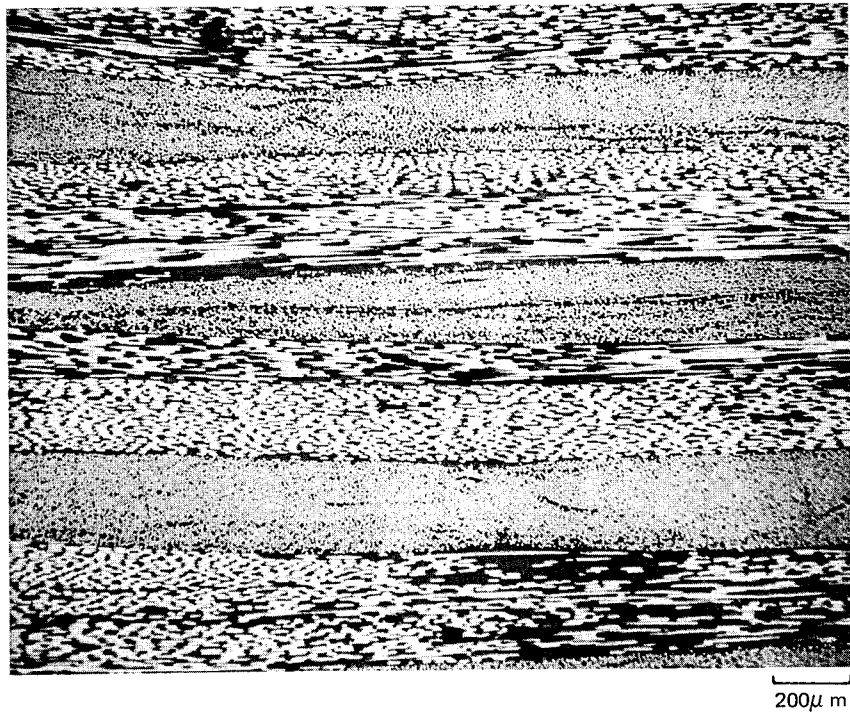


Figure 29. Microstructure of Specimen GC 215-5 HMS Reinforced 7740, [(0/90)<sub>4</sub>]<sub>s</sub>  
samples Surface Ground and Polished, Slurry B

Table XIV

Three Point Bend Data for Cross Ply Specimens  
Slurry B

Specimen	Fiber	Lay-up <sup>1</sup>	v/o Fiber	Calc. Max. Flex. Stress		S/D <sup>2</sup>	Fracture
				10 <sup>3</sup> psi	MPa		
GC 202-1	DG-102	[(0 <sub>2</sub> 90 <sub>2</sub> ) <sub>2</sub> ] <sub>S</sub>	40	24.6	170	28	Tensile <sup>3</sup>
-2	"			7.7	53	30	
-3	"			17.7	122	29	
			Avg	16.7	115		
GC 203-1	HMS	[(0 <sub>2</sub> 90 <sub>2</sub> ) <sub>2</sub> ] <sub>S</sub>	50	28.7	198	14	Interlaminar <sup>4</sup>
-2	"			33.1	228	15	
-3	"			32.6	225	14	
			Avg	31.5	217		
GC 210	HMS	[(0/90) <sub>4</sub> ] <sub>S</sub>		35.4	244	16	Tensile <sup>3</sup>
				33.1	228	16	Interlaminar <sup>4</sup>
				25.0	172	15	"
			Avg	31.2	215		
GC 214	HMS	[(0/90) <sub>4</sub> ] <sub>S</sub>		25.1	173	6.5	Interlaminar <sup>4</sup>
				29.6	204	6.5	
				37.6	259	10	
				36.8	253	10	
			Avg	32.3	222		
GC 215	HMS	[(0/90) <sub>4</sub> ] <sub>S</sub>		32.3	223	6.4	Interlaminar <sup>4</sup>
				34.0	234	6.4	
				41.2	284	10	
				31.1	215	10	
			Avg	34.6	239		

<sup>1</sup>In these tests the outer 0° plies were oriented with fibers parallel to the major span

<sup>2</sup>Span-to-depth ratio for 3 point bend test

<sup>3</sup>Specimens separated at mid point of span into two pieces

<sup>4</sup>Specimens remained in tact after test. Interlaminar cracks occurred between 0° and 90° layers. These cracks started at the free ends of the specimens and propagated inward.

strength after test. This observed failure mode may have been aggravated by the use of a smaller value of span-to-depth ratio (14) than has been typical in the past (30). The tabulated specimen flexural strengths were not widely spread and averaged 217 MPa which again appears somewhat low when compared with a value of 550-700 MPa for all 0° material.

Composites GC 210, 214 and 215, slurry B, were fabricated using the [(0/90)<sub>4</sub>]<sub>S</sub> lay-up scheme and HMS as the fiber. GC 214 was pressed in vacuum and GC 215 was slow cooled from 1473 K to minimize residual stresses. The strengths of these composites are also tabulated in Table XIV, were similar to the alternate HMS ply lay-up, and were not affected by changes in the fabrication procedures. A higher hot pressing temperature would be expected to improve the strength of the cross-plyed composites.

### Woven Cloth

A two dimensionally woven cloth of Thornel 300 fiber was used to fabricate cross ply specimens. The cloth contained 12 fibers per inch in both the 0° and 90° directions, woven in a simple weave, and was easily cut and handled. The fabrication procedure involved dipping the layers of cloth in a standard slurry of glass followed by stack up of plies and hot pressing. The resultant composite microstructure is shown in Fig. 30 where it can be seen that the fiber content is very high. Glass did, however, penetrate the woven cloth and this type of procedure will be pursued further in the coming months. The major difficulty is that the woven nature of the cloth prevents spreading of the individual tows and hence it is more difficult to get the glass slurry to penetrate the fiber bundle.

A specimen was also prepared wherein the PVA fiber sizing was removed prior to glass impregnation. The surface appearance of this composite is shown in Fig. 31. The fabric weave is clearly visible through the thin glass surface layer and the general appearance was excellent. The degree of internal densification and bonding was not measurably superior, however, to the specimens fabricated without a fiber precleaning step. The fiber-matrix bond was very weak, and the specimens failed by delamination at a shear stress on the order of 3 MPa. The specific data are shown in Table 13 of Appendix B.

### Thermal Expansion

One of the most interesting and important aspects of graphite fiber reinforced composites is their coefficients of thermal expansion. Because of the very low axial coefficient of thermal expansion of graphite fibers, it has been possible to make resin matrix composites that are exceptionally dimensionally stable in thermal gradients. This has been accomplished despite the high thermal expansion of resin matrices. Based on this successful experience, glass matrix composites would be expected to offer superior dimensional stability due to the much lower thermal expansion of glass, as compared to resins.

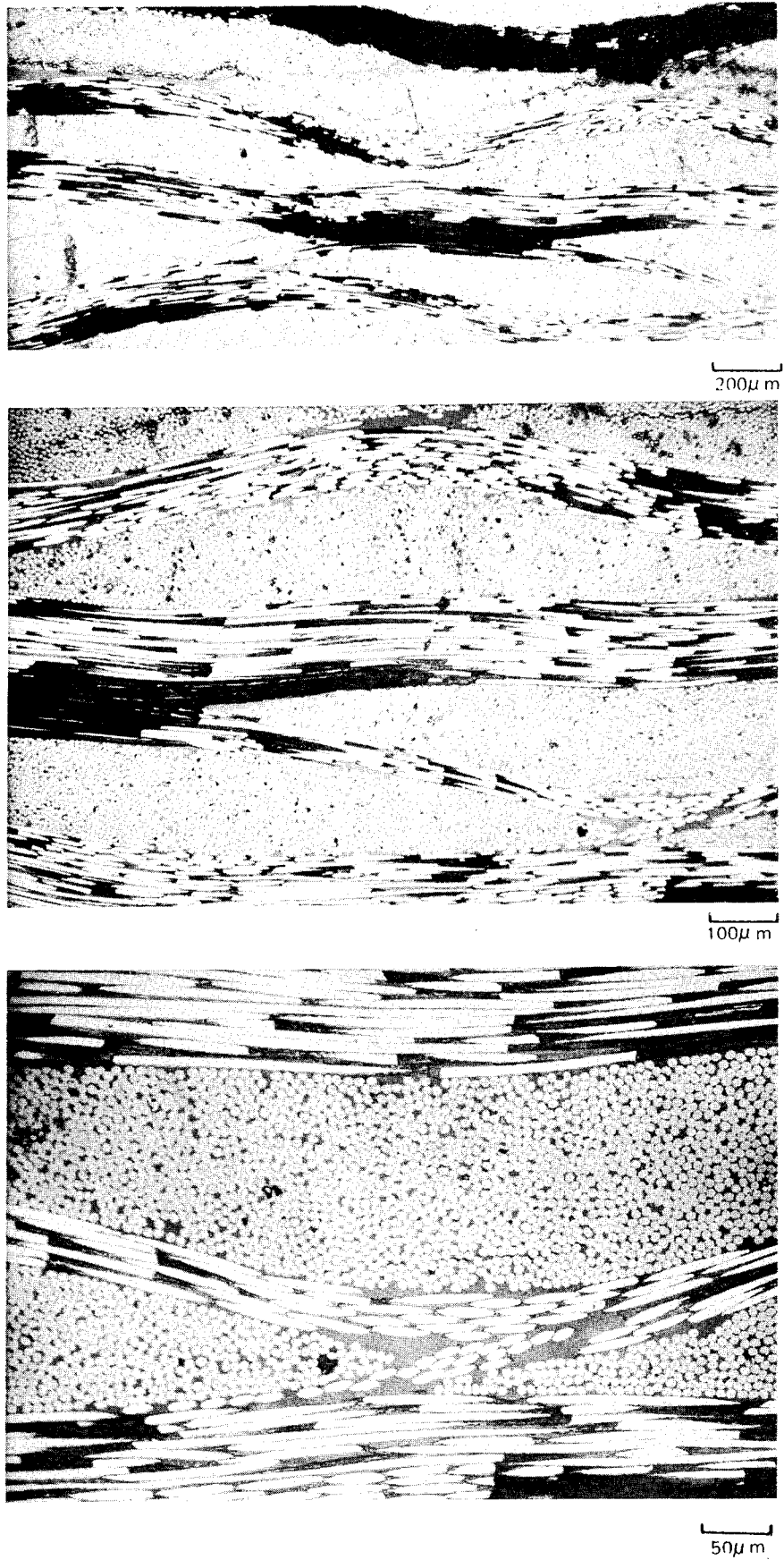
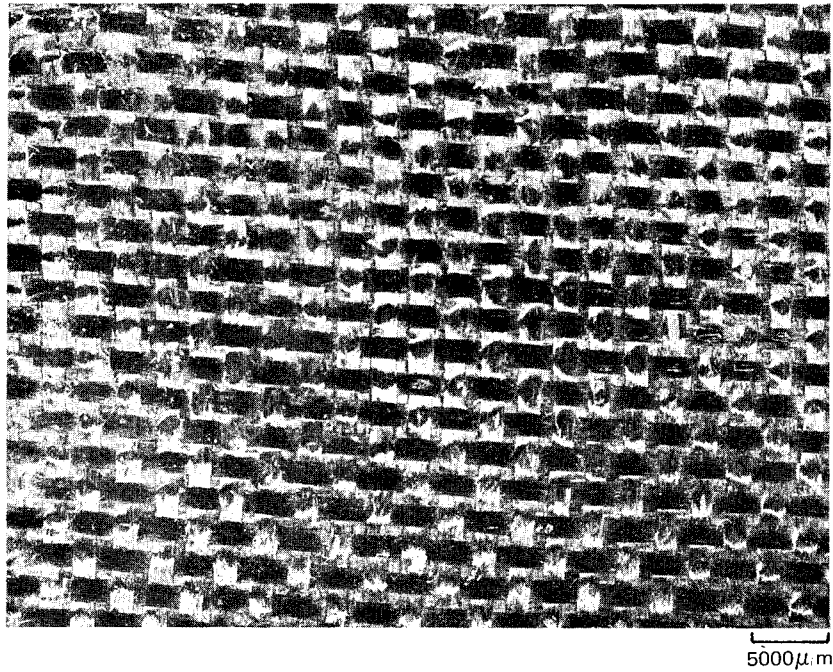
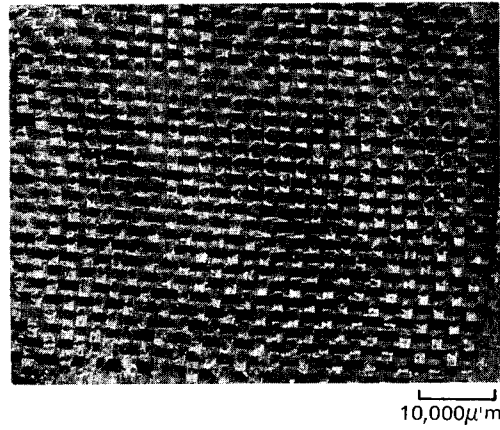


Figure 30. Microstructure of Specimen GC 218-5 Thornel 300 Cloth Reinforced 7740, Slurry B



**Figure 31. Transparent Glass Surface of Specimen GC 220 0° / 90 Thornel 300 Reinforced 7740 Fabricated Using Woven Cloth, Slurry B**

Unidirectionally reinforced 7740 matrix composites were fabricated with Thornel 300 (LB 161E), Celanese DG-102 (LB 97L), and Hercules HMS (GC 216) reinforcements. Elongation of  $0^\circ$  and  $90^\circ$  oriented specimens was measured, and the resultant data are presented in Figs. 32-38 in the form of thermally induced specimen strain as a function of temperature. All tests were begun at room temperature and were repeatedly run up to approximately 823-848 K for at least two complete cycles. There did not appear to be any significant difference in material performance due to cycling so that the data presented, which were taken from the final cycle, are typical of stable material behavior.

The data in Figs. 32 and 33 are for  $0^\circ$  and  $90^\circ$  oriented Celanese DG-102 reinforced 7740, respectively. The  $0^\circ$  data are particularly interesting because they reflect the unique ability of graphite fibers to contract in the axial direction during heating. This negative expansion is reversed at about 573 K so that a net zero change in dimension is the resultant of heating to 823 K. The  $90^\circ$  thermal expansion is always positive and of much larger magnitude than the  $0^\circ$  characteristic primarily due to the glass which essentially controls the transverse expansion.

The thermal expansion of Thornel 300 reinforced glass specimens is presented in Figs. 34 and 35. The  $0^\circ$  data are nonlinear and small in value; however, no evidence of composite contraction was obtained illustrating the importance of fiber type in controlling expansion. As in the case of the Celanese fiber reinforced composite, the  $90^\circ$  expansion is considerably larger than that for the  $0^\circ$  orientation.

The thermal expansion data for the HMS reinforced 7740 are similar to those of the DG-102 reinforced glass. In the case of the  $0^\circ$  orientation, Fig. 36, the composite contracts initially on heating due to the negative thermal expansion of the fibers. The expansion is reasonably linear up to a temperature of approximately 423 K at which time the rate of contraction decreases with a complete reversal to expansion taking place between 573 and 623 K. Although the maximum temperature was 848 K, a net zero change in length would be expected at a temperature of 923 K. Because the glass is reasonably soft at this temperature, permanent deformation of the specimen would be expected, however. The transverse composite thermal expansion, Fig. 37, is much more linear, and positive at all temperatures. The value of coefficient of thermal expansion is dependent on both the radial fiber expansion, and the expansion of the matrix, with the latter having the predominant role.

Values of composite coefficients of thermal expansion were obtained from the above described data and are presented in Table XV. In the cases of nonlinearly expanding  $0^\circ$  specimens, the coefficient of expansion varies significantly with temperature range and each calculation was based on drawing a straight line between the low temperature and high temperature strain values.

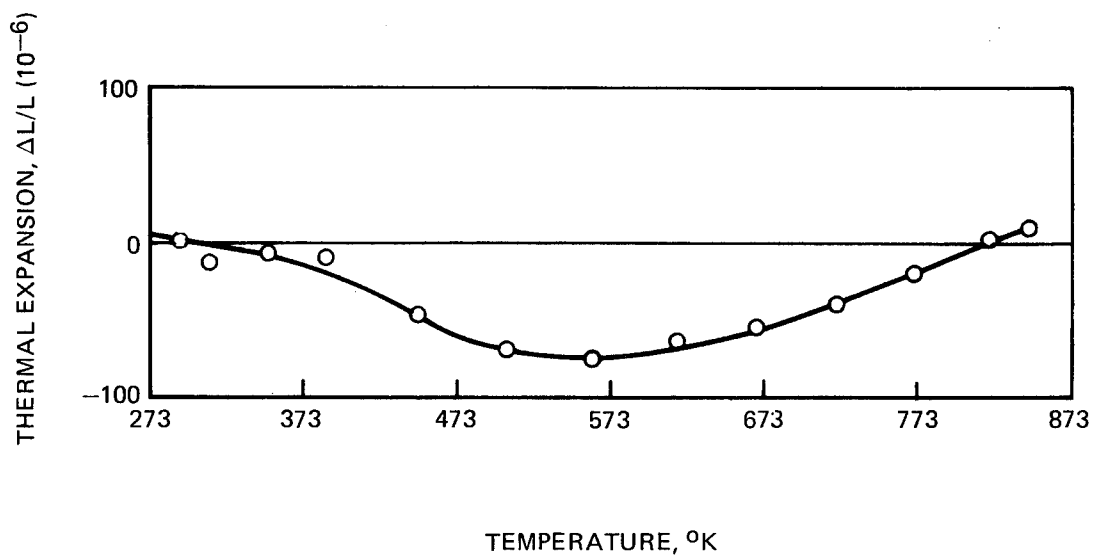


Figure 32. Thermal Expansion of 0° Celanese DG – 102 Fiber Reinforced 7740 , Slurry B

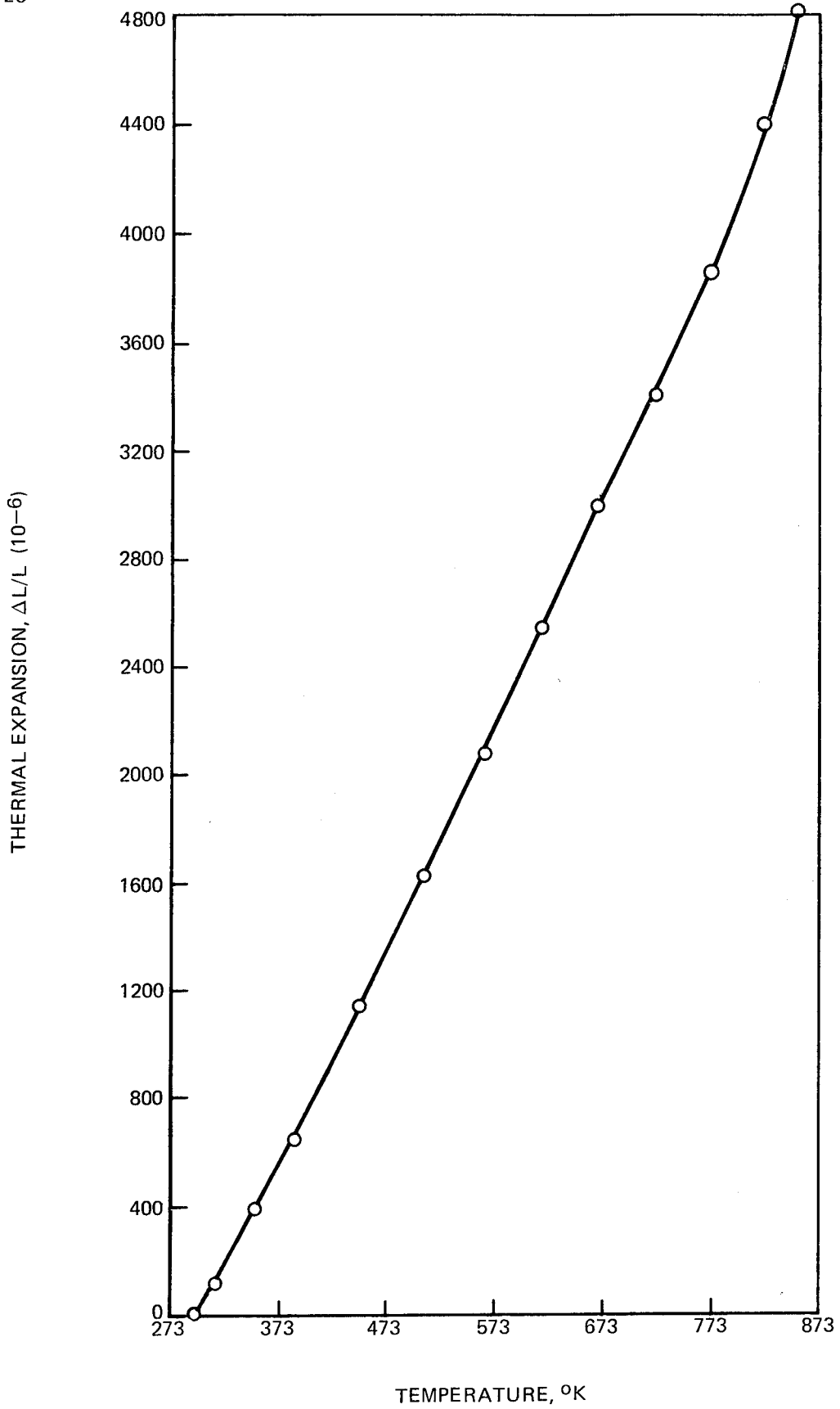


Figure 33. Thermal Expansion of 90° Celanese DG – 102 Fiber Reinforced 7740, Slurry B

77-08-157-4

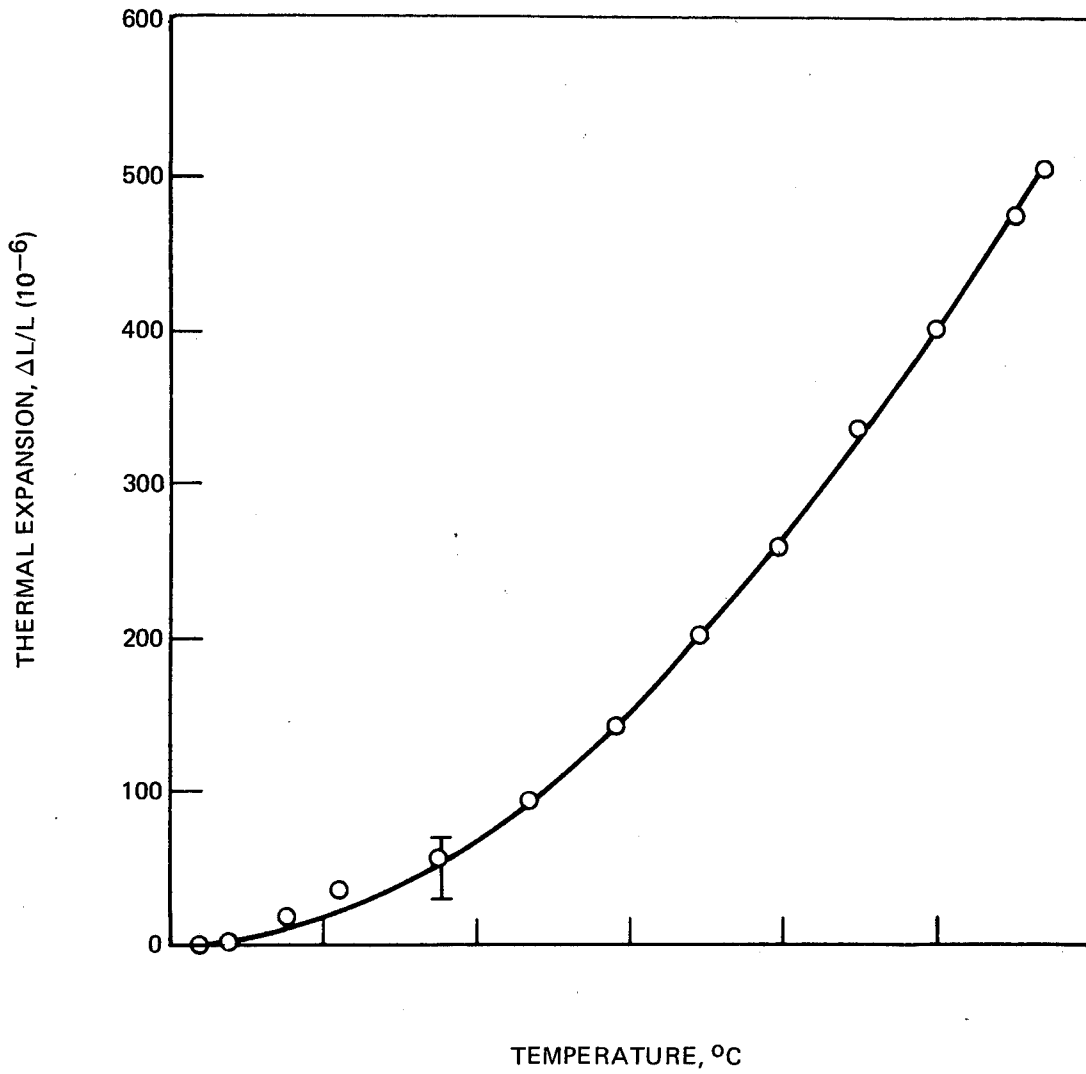


Figure 34. Thermal Expansion of 0° Thornel 300 Reinforced 7740, Slurry B

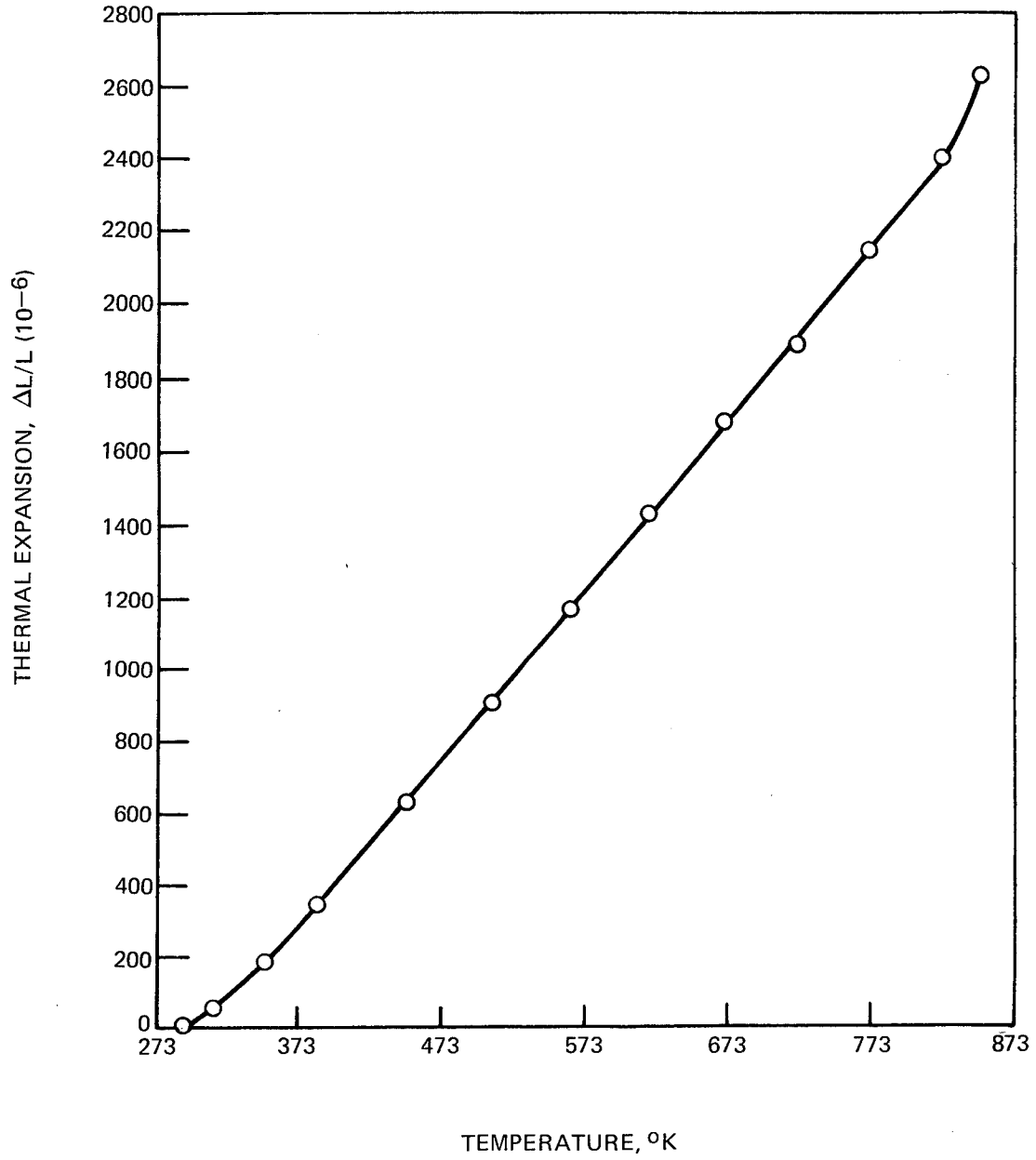


Figure 35. Thermal Expansion of 90° Thornel 300 Fiber Reinforced 7740, Slurry B

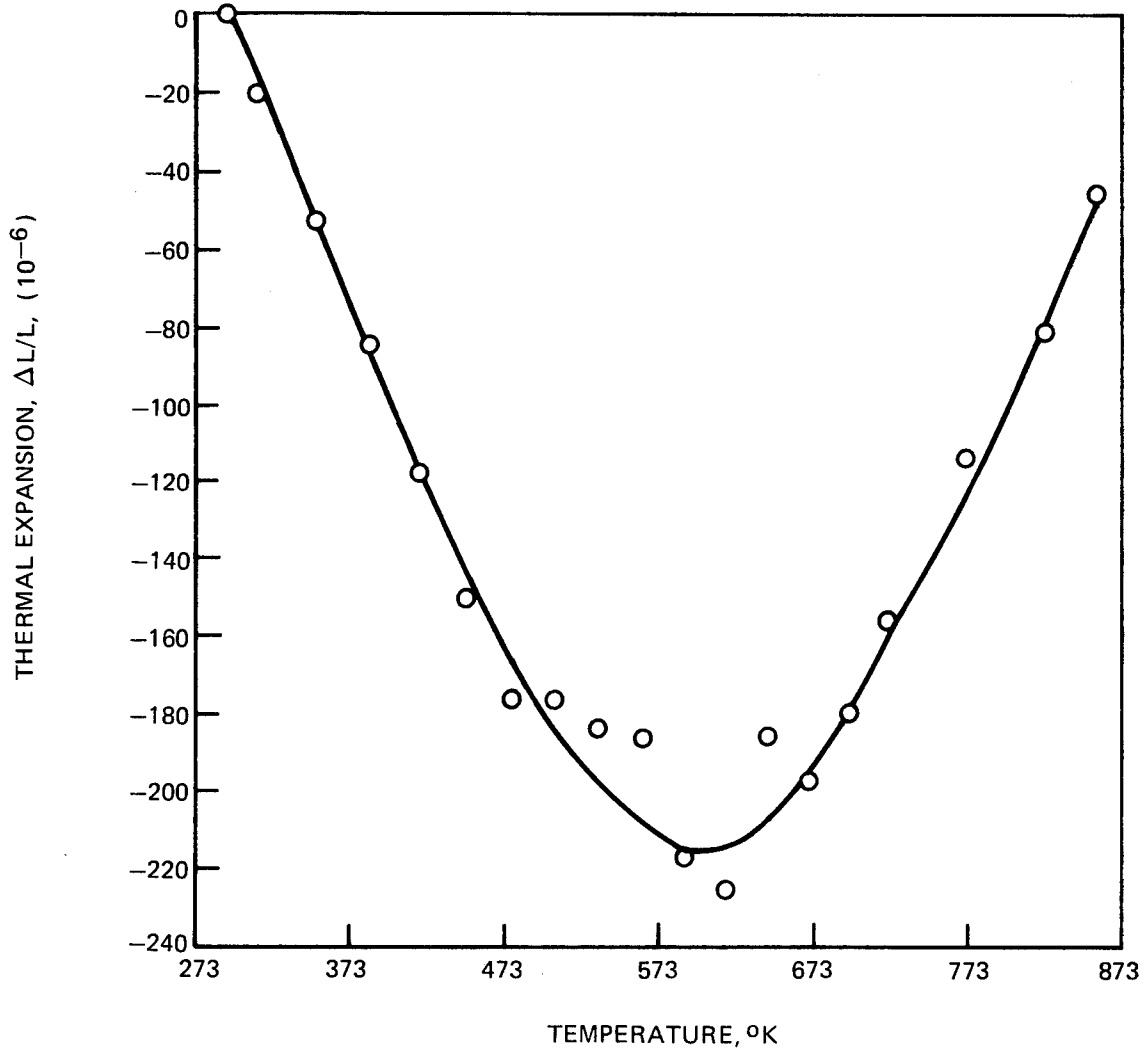


Figure 36. Thermal Expansion of 0° HMS Reinforced 7740, Slurry B

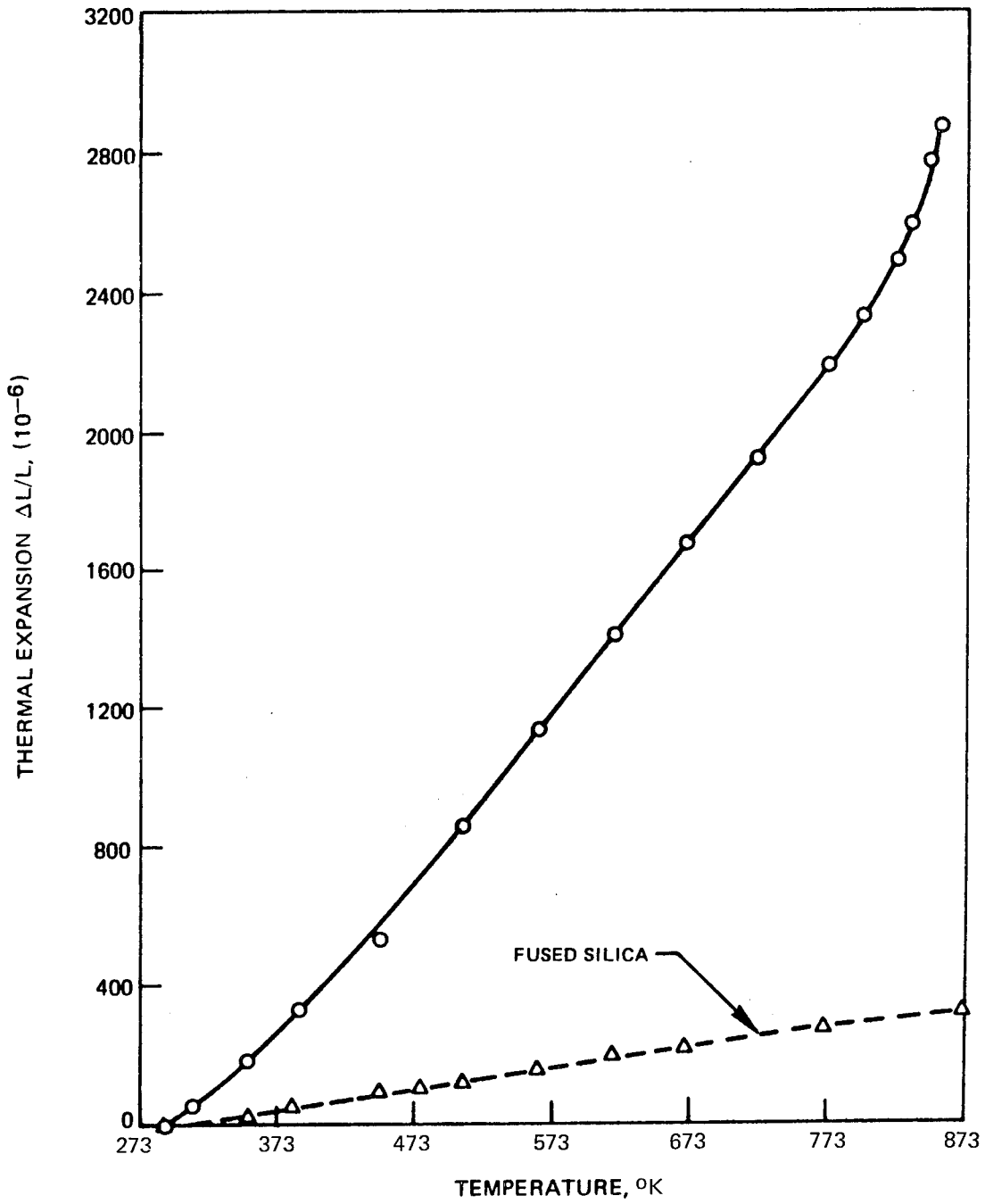


Figure 37. Thermal Expansion of 90° HMS Reinforced 7740 Spec. GC 216 ,  
Slurry B

Table XV

## Comparison of Composite Coefficients of Thermal Expansion

<u>Material</u>	<u>Specimen &amp; Orientation</u>	<u>Temp. Range</u> K	<u>Coefficient of Thermal Expansion</u> $\alpha$ ( $K^{-1}$ )
50% Thornel 300 Reinforced 7740 Slurry A	LB 161E-90 <sup>0</sup>	295-823	$4.3 \times 10^{-6}$
	LB 161E-0 <sup>0</sup>	295-823 295-423	$0.9 \times 10^{-6}$ $0.38 \times 10^{-6}$
50% Celanese DG-102 Reinforced 7740 Slurry A	LB 97-90 <sup>0</sup>	295-823 295-423	$7.6 \times 10^{-6}$ $7.6 \times 10^{-6}$
	LB 97-0 <sup>0</sup>	295-823 295-423 295-573 295-673	0 $-0.29 \times 10^{-6}$ $-0.29 \times 10^{-6}$ $-0.14 \times 10^{-6}$
60% Hercules HTS Reinforced 3002 Resin	90 <sup>0</sup> 0 <sup>0</sup>	295-423 295-423	$30 \times 10^{-6}$ * $-0.4 \times 10^{-6}$ *
50% Hercules HTS Reinforced ERLA 4617 Resin	90 <sup>0</sup> 0 <sup>0</sup>	- -	$33.9 \times 10^{-6}$ ** $-0.06 \times 10^{-6}$ **
50% Hercules HMS Reinforced ERLA 4617 Resin	90 <sup>0</sup> 0 <sup>0</sup>	- -	$33.9 \times 10^{-6}$ ** $-0.5 \times 10^{-6}$ **
50-60% HMS Reinforced 7740 Slurry B	GC 216-90 <sup>0</sup>	295-823 295-423	$4.7 \times 10^{-6}$ $3.6 \times 10^{-6}$
	GC 216-0 <sup>0</sup>	295-823 295-423 295-573 295-673	$-0.2 \times 10^{-6}$ $-1.0 \times 10^{-6}$ $-0.8 \times 10^{-6}$ $-0.5 \times 10^{-6}$
50% HMS Reinforced ERLA 4617 Resin	90 <sup>0</sup> 0 <sup>0</sup>	- -	$33.9 \times 10^{-6}$ * $-0.5 \times 10^{-6}$ *

\*Freeman &amp; Campbell, ASTM-STP 497, p 121, 1972

\*\*Rogers, et al, J. Mat. Sci., Vol. 12, p 718, 1977

Also presented in the table are data for several resin matrix systems. A comparison between resin and glass matrix composites reveals a major difference in  $90^\circ$  values of  $\alpha$ , with a factor of up to eight decrease in expansion ascribable to the 7740 matrix composites. In all cases the  $0^\circ$  values are quite low. Another important point is that the glass matrix data extend up to a temperature of 823 K while resin matrix composite data are limited (by matrix properties) to a maximum temperature of about 423 K.

The above described data have confirmed the unique qualities of graphite reinforced glass matrix composites for use in the construction of dimensionally stable structures. They also confirm the major anisotropy of expansion which can cause microcracking in cross ply composites.

The thermal expansion of a cross ply ( $0/90^\circ$ ) HMS reinforced 7740 composite was measured; the results are displayed in Fig. 38. The measurement was repeated several times, and in no case was there any permanent change in dimension after a full heating and cooling cycle. The measured thermal expansion of the cross ply material is quite low over the entire temperature range and particularly between 295 and 573 K. In this range, a hysteresis effect is also maximized. The hysteresis arises from the significant thermal expansion mismatch of the  $0^\circ$  and  $90^\circ$  directions.

#### Oxidation Properties

The effect of oxidation on the strength of graphite fiber reinforced glass matrix composites is summarized in Fig. 39. The specimens from which these data were collected were nominally 0.2 x 0.5 x 6.4 cm in size. After oxidation exposure the surfaces of the specimens assumed a whitish color. Nonetheless, the most important path for oxidation is along the fiber direction. This accounts for the majority of the weight loss experienced by the composites. Therefore any application which minimizes edge exposure should exhibit superior oxidation resistance.

Specific data on the oxidation properties of the graphite fibers at 823 K, the flexural strength and weight loss in HTS and HMS graphite fiber reinforced 7740 and the flexural strengths of DG-102 and pitch type graphite fiber reinforced 7740 are tabulated in Appendix B, Tables 19-31.

As shown in Fig. 39 and the tabulated data, the HMS graphite fiber reinforced 7740 + 2% silica, hot pressed at 1723 K, exhibits superior resistance to oxidation. After 24 hrs at 813 K, the percentage weight loss is 5.6; after 100 hrs, 12.6. In comparison, this matrix reinforced by HTS fiber and hot pressed at 1623 K exhibits a weight loss of 9.7% after 24 hrs and 28.8% after 100 hrs. At an oxidation temperature of 723 K, the weight loss is accordingly much less for the HMS fiber reinforced composite. After 24 hrs, the loss is 0.6% and after 100 hrs, 1.8%.

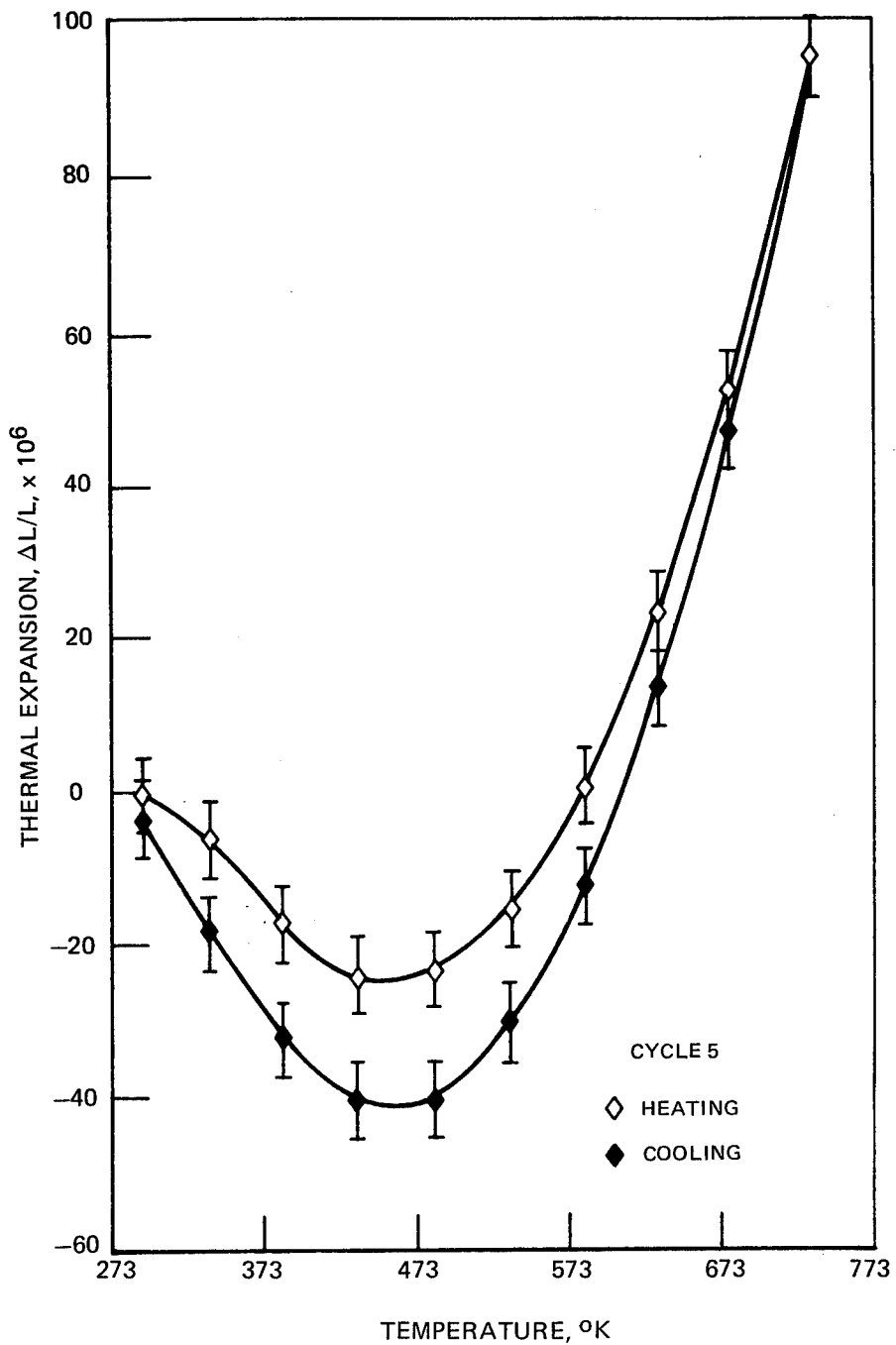


Figure 38. Thermal Expansion of  $0^{\circ} / 90^{\circ}$  HMS Reinforced 7740, Bars Represent Confidence in these Data Points for this Cycle

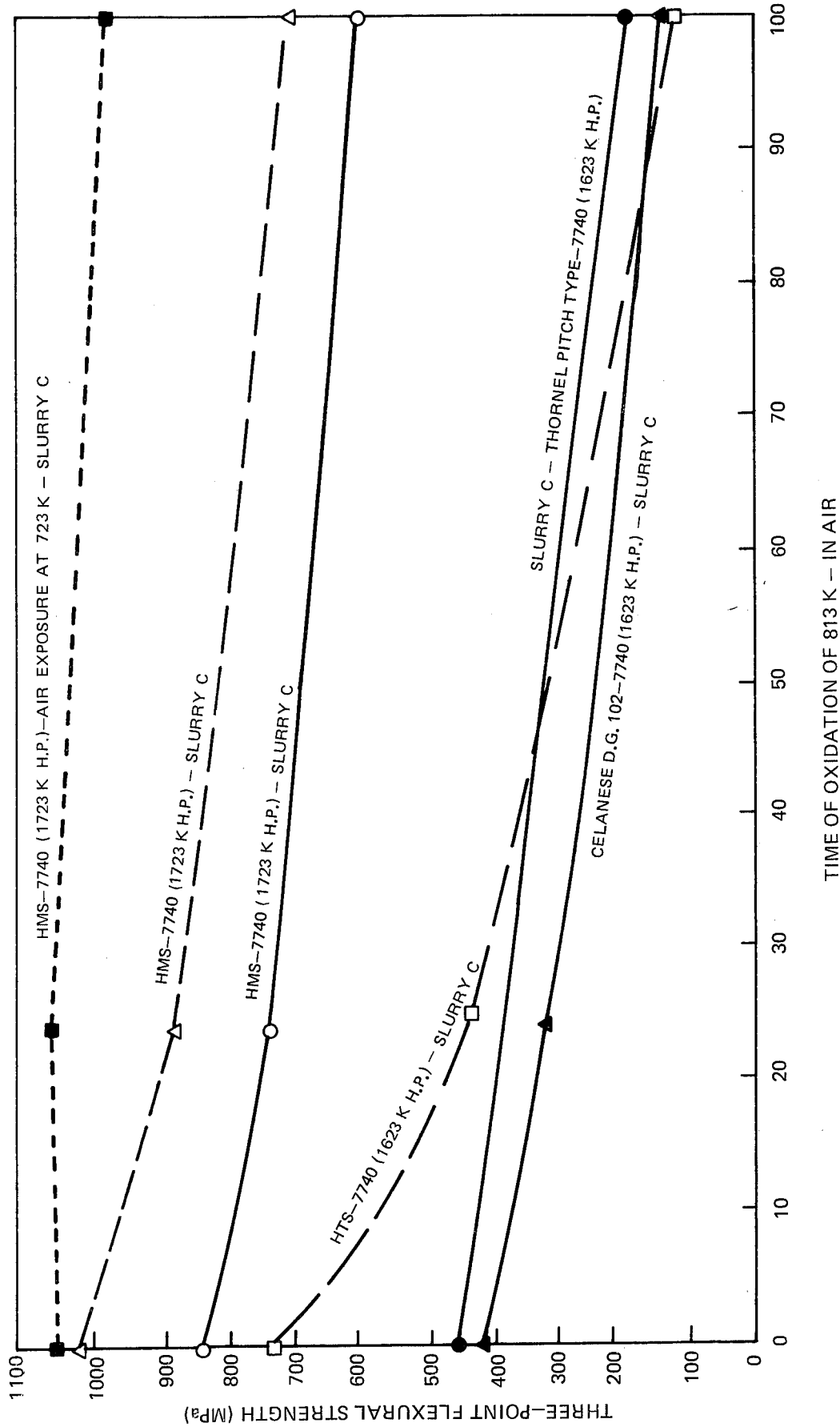


Figure 39. Effect of Oxidation on Three -- Point Flexural Strength of Graphite Fiber -- 7740 Glass Matrix Composites with added Silica, Slurry C

In the case of composites fabricated with fibers of the Thornel pitch and Celanese DG-102 types, strength losses of 57 and 68% were suffered after 100 hrs at 813 K. In both cases these results are disappointing since, based on oxidation studies of the bare graphite fibers (Appendix B, Tables 19 and 20), these materials were expected to yield better, not worse, oxidation resistance than found for the HMS graphite reinforced glass composites. These results are not conclusive, however, since composites pressed at 1723 K, found optimum for the HMS composites, need to be evaluated.

In comparing the data in Table 27 of Appendix B which represents recently made samples of HMS graphite fiber reinforced C.G.W. 7740 glass + 2% silica with that of Table 28 of Appendix B for similar samples made a year ago and with a slurry without added silica, two facts must be considered. First, the making of strong graphite fiber reinforced C.G.W. 7740 + 2% SiO<sub>2</sub> has been a gradual learning process and secondly, not only did the older samples lack the beneficial effect of the 2% added silica but they were also hot pressed at 200 K higher temperature. These same two factors must also be considered in comparing Tables 29 and 30, Appendix B, for Celanese graphite fiber reinforced glass matrix composites where Table 29 represents year old data and here the 4 hr data of Table 29 is certainly less accurate than the 24 and 100 hr data of Table 30.

## CONCLUSIONS

High strength graphite fiber reinforced borosilicate glass matrix composites can be prepared by hot pressing tapes of powdered glass which has been introduced into graphite yarn from a slurry. By employing colloidal silica as part of the slurry vehicle, a modified borosilicate glass which contains an additional 2% silica has been identified as a composite matrix. With such a matrix, Hercules HMS graphite fiber and a very high hot pressing temperature (i.e. 1723 K), uniaxially reinforced composites have exhibited room temperature flexural strengths on the order of 1000 MPa, elastic moduli of 200 GPa and failure strains of 0.005; furthermore, strengths have been retained after 100 hrs of air exposure at 723 K. These results represent substantial improvements over what has been previously accomplished with graphite fiber reinforced glass matrix composites.

From other data which have been obtained on graphite fiber reinforced glass matrix composites, the following conclusions can be made:

- the flexural strength of borosilicate glass matrix composites increases with temperature up to 875 K which is the softening point of the glass;
- the uniaxially reinforced composites exhibit surprisingly high values of fracture toughness only 40% less than that of a graphite reinforced epoxy composite;
- the composite strength is not reduced by flexural fatigue cycling or by short term thermal cycling between 383 and 833 K; and
- extremely low values of thermal expansion and attendant dimensional stability result from the properties of the composite components.

By suitable orientation of tapes, uniaxial, biaxial and multiaxially reinforced composites can be prepared in the graphite fiber reinforced glass matrix system.

## REFERENCES

1. Siefert, August, C.: Fiber-Reinforced Ceramics, U.S. Patent 3,607,608, Sept. 21, 1971.
2. Siefert, August C.: Method of Making Glass-Metal Fiber Composites, U.S. Patent 3,792,985, Feb. 19, 1974.
3. Sambell, R. A. J., D. H. Bowen, D. C. Phillips: Carbon Fibre Composites with Ceramic and Glass Matrices, Part I, Discontinuous Fibres Journal of Materials Science, 7 (1972) pp 663-675.
4. Sambell, R. A. J., A. Briggs, D. C. Phillips, and D. H. Bowen: Carbon Fibre Composites with Ceramic and Glass Matrices, Part II, Continuous Fibres Journal of Materials Science, 7 (1972) pp 676-681.
5. Phillips, D. C.: The Fracture Energy of Carbon-Fibre Reinforced Glass, Journal of Materials Science, 7 (1972) pp 1175-1191.
6. Phillips, D. C., R. A. J. Sambell, D. H. Bowen: The Mechanical Properties of Carbon Fibre Reinforced Pyrex Glass, Journal of Materials Science, 7 (1972) pp 1454-1464.
7. Levitt, S. R.: High Strength Graphite Fibre/Lithium Aluminosilicate Composites, Journal of Materials Science, 8 (1973) pp 793-806.
8. Phillips, D. C.: Interfacial Bonding and the Toughness of Carbon Fibre Reinforced Glass and Glass Ceramics, Journal of Materials Science, 9 (1974) pp 1847-1854.
9. Lange, F. F.: Fracture Energy and Strength Behavior of Sodium Borosilicate Glass- $Al_2O_3$  Composite System, Journal American Ceramic Society, Vol. 54, No. 12, pp 614-620, Sept. 1971.
10. Harris, Bryan: The Nature and Properties of Carbon Fibres and Their Composites, Carbon Fibres in Engineering, Editor, Marcus Langley, McGraw-Hill, London, 1973, pp 1-45.
11. Sambell, R. A. J., D. C. Phillips and D. H. Bowen: The Technology of Carbon Fibre Reinforced Glasses and Ceramics, Harwell Materials Bulletin, AERE-R7612, Feb. 1974.
12. Donald, I. W. and P. W. McMillan: Review, Ceramic-Matrix Composites, Journal of Materials Science II (1976) pp 949-972.

13. Prewo, K. M. and J. F. Bacon: Glass Matrix Composites I - Graphite Reinforced Glass. A paper presented at the Second International Conference on Composite Materials (ICCM 2), April 16-20, 1978, Toronto, Canada. To be published by the Metallurgical Society of AIME, New York, NY.
14. Bacon, J. F. and K. M. Prewo: NASA Contract Report 145245, June 1977.

APPENDIX A

Summary of Graphite Fiber Reinforced  
Glass Matrix Composites Made

Table A1

## Summary of Graphite Fiber Reinforced Glass Matrix Composites

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Highest Density Achieved in Similar Composite (kg/m <sup>3</sup> )
			Pressure (MPa)	Temp. (K)		
GL 10	7913	Thorne1 75	13.8	1823	1585	2138
LB 11	↓	↓	↓	1873	1695	↓
12	↓	↓	↓	1923	1605	↓
13	↓	↓	↓	1823	1585	↓
53	7913+7740	↓	↓	1873	2138	↓
53B	7913	↓	↓	1873	1732	↓
90	7740	Celanese DG-102	13.8	1393	2011	2060
91	↓	↓	↓	1393	2046	↓
92	↓	↓	↓	1388	2060	↓
93	↓	↓	↓	1383	2043	↓
94	↓	↓	↓	1298	1936	↓
95	↓	↓	↓	1323	1997	↓
96	↓	↓	↓	1348	1911	↓
97	↓	↓	↓	1373	1969	↓
97B	↓	↓	↓	1373	1980	↓
97C	↓	↓	↓	1373	1969	↓
97D	↓	↓	↓	1473	2025	↓
97E	↓	↓	↓	↓	2049	↓
97F	↓	↓	↓	↓	Cracked	↓
97G	↓	↓	↓	↓	↓	↓
97H	↓	↓	↓	↓	↓	↓
97I	↓	↓	↓	↓	↓	↓
97J	↓	↓	↓	↓	↓	↓
98	↓	↓	↓	1393	1969	↓
107	7913	↓	↓	1873	↓	↓
108	7913	↓	↓	1923	↓	↓
112	7913	↓	↓	2123	1375	↓
131	7740	↓	↓	1373	1952	2060
132	7740	↓	↓	1373	2000	2060
135	7740	Hercules HMS	13.8	1373	1960	1976
135B	↓	↓	↓	↓	1972	↓
135C	↓	↓	↓	↓	↓	↓
135D	↓	↓	↓	↓	1976	↓
135E	↓	↓	↓	↓	1920	↓
135F	↓	↓	↓	↓	1939	↓
135G	↓	↓	↓	↓	1957	↓
135H	↓	↓	↓	↓	1955	↓
135I	↓	↓	↓	↓	1949	↓
135J	↓	↓	↓	↓	1943	↓
135K	↓	↓	↓	↓	1937	↓
135L	↓	↓	↓	↓	1955	↓
135M	↓	↓	↓	↓	1951	↓
135N	↓	↓	↓	↓	1958	↓
135O	↓	↓	↓	↓	↓	↓

All samples with numbers lower than GC 175 are slurry A. Samples GC 175 through GC 294 are slurry B, higher numbered samples are slurry C. Exceptions are noted.

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Highest Density Achieved in Similar Composite (kg/m <sup>3</sup> )
			Pressure (MPa)	Temp. (K)		
LB 136	7740	Hercules HMS	13.8	1373	1960	1977
137	↓	↓	↓	↓	1957	↓
138	↓	↓	↓	↓	1952	↓
139	↓	↓	↓	↓		↓
140	↓	↓	↓	↓		↓
157	↓	↓	↓	↓		↓
158	↓	↓	↓	↓	1977	↓
159	↓	↓	↓	↓		↓
171	1723	↓	↓	1393	1963.7	↓
172	↓	↓	↓	↓		↓
173	↓	↓	↓	↓	1948.9	↓
174	↓	↓	↓	↓		↓
147	7740	Hercules HTS	13.8	1373	1902	1902
148	↓	↓	↓	↓	1597	↓
148B	↓	↓	↓	↓	1858	↓
148C	↓	↓	↓	↓	1886	↓
148D	↓	↓	↓	↓	1865	↓
148E	↓	↓	↓	1473	1800	↓
148F	↓	↓	↓	1473		↓
149	↓	↓	↓	1373		↓
150	↓	↓	↓	↓		↓
151	↓	↓	↓	↓		↓
152	↓	↓	↓	↓		↓
C2639-23	7740	Thornel 300	13.8	1373		2013
C2658-1,2	↓	↓	↓	1373	1931	↓
GL 1-1,2	↓	↓	↓	1498	1603	↓
2a,b	↓	↓	↓	1873	1955	↓
3a,b	↓	↓	↓	1923	2013	↓
4a,b	↓	↓	↓	1823		↓
5a,b	↓	↓	↓	1423		↓
6a,b	↓	↓	↓	1323		↓
LB 75	↓	↓	↓	↓	1757	↓
78	↓	Thornel 300S	↓	↓	1829	↓
79	↓	Thornel 300	27.6	↓		↓
80	↓	↓	↓	1373		↓
81	↓	↓	↓	↓	1780	↓
82	↓	↓	↓	↓		↓
133	↓	Thornel 300S	13.8	↓	1566	↓
160	↓	↓	↓	1393		↓
161	↓	↓	↓	↓		↓
161B	↓	↓	↓	↓	1700	↓
161C	↓	↓	↓	↓	1674	↓
161D	↓	↓	↓	↓	1640	↓
161E	↓	↓	↓	↓	1675	↓
161F	↓	↓	↓	↓	1673	↓
162	↓	↓	↓	↓	1823	↓
163	↓	↓	↓	↓	1829	↓
134	↓	↓	↓	1373		↓

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Remarks
			Pressure (MPa)	Temp. (K)		
GC 200	7740	DG-102	13.8	1473		
201	↓	HMS	↓	↓		
202		DG-102				Biaxial
203		HMS				
204	↓	HMS	↓	↓		
205	7740	DG-102	13.8	1473		Biaxial (Die Broke)
206	↓	HMS	↓	↓		
207		↓				
208	↓		↓	↓		
209	↓	↓	↓	↓		
210	7740	HMS	13.8	1473		Biaxial
211	↓	DG-102	↓	↓	1926	
212		300S			1840	
213		300				
214	↓	HMS	↓	↓	1970	Biaxial
215	7740	HMS	13.8	1473	1990	Biaxial, Annealed
216	↓	HMS	↓	↓	1980	
217		300 cloth				Failure
218		↓			1660	Biaxial
219					1689, 1618	Biaxial
220	↓	↓	↓	↓	1638	Biaxial
221	7740	HTS	13.8	1473	1700	
222	↓	HTS	6.9	↓	1800	
223		DG-102	13.8			Failure
224	↓	DG-102	13.8	↓		Failure
225	7740+50% Ludox	HTS	13.8	1473	1840	
226	"	HTS	13.8	↓	1858	
227	7740	HMS	6.9		1950	Biaxial
228	↓	HTS	13.8		1890	
229a		HTS	13.8	↓	1790	
229b	↓	HTS	13.8	↓	1820	
230a	7740	Ni Coated C	13.8	1473		
230b	↓	Ni Coated C	↓	↓		
231		Pitch				
232	7940+25% Pyrex	HMS		1523		
233	Vycor+20% Pyrex	HMS	↓	1623	1733	
234	7740	HMS	6.9	1473		
235	7940+25% Pyrex	↓	13.8	1573		
236	7940+25% Pyrex		↓	1623	1684	
237	7940+4% Pyrex			1623	1173	
238	100 ml Ludox, 12.9 gm Pyrex	↓	↓	1673	1786	

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Remarks
			Pressure (MPa)	Temp. (K)		
GC 239	100 ml Ludox, 12.9 gm Pyrex	HMS	13.8	1673	2249	
241	"	↓	↓	1723	1996	
242	7940+5% Pyrex	↓	↓	1723	1575	
243	Vycor+5% Pyrex	↓	↓	1673		
244	Vycor+25% Pyrex	↓	↓	1673	1885	
247	"	↓	↓	1723	1902	
248	Vycor+10% Pyrex	↓	↓		1796	
249	"	↓	↓		1878	
250	"	↓	↓		1866	Not useful
251	7740	↓	↓			
252A		↓	↓		1582	
252B		↓	↓		2133	
254A	Ludox+5% Pyrex	↓	↓			
254B	"	↓	↓			
255	"	↓	↓			
256	7740	↓	↓	1473		53.7 v/o graphite
GC 257a	7740	HMS	6.1	1473		
b	↓	↓	↓	↓		
c	↓	↓	↓	↓		
258		↓	↓		2000	
259a		↓	↓			49.1 v/o graphite
b		↓	↓		1940	
c		↓	↓		1920	
271		↓	13.8		1900	
272a		↓	13.8			
b		↓	13.8			
273	7740	HMS	13.8	1773		Die Broke
274	↓	↓	↓	1773		
275	↓	↓	↓	1473	1989	
277	↓	↓	↓	1473	1989	
278	↓	↓	10.3	1473	1932	64.9 v/o graphite
279	7740	HMS	10.3	1473	1920	64.4 v/o graphite
280	↓	↓	4.1	1473	1918	60 v/o graphite
281	↓	↓	13.8	1473	1950	
282	↓	↓	13.8	1823		
283	↓	↓	13.8	1473	1977	
284	7740	HMS	13.8	1473		
285	↓	↓	13.8	↓		
286	↓	↓	13.8			
287a	↓	↓	6.9	↓		Biaxial
b			6.9			Biaxial
288	7740	HMS	13.8	1473	1970	Biaxial
289a	↓	↓	↓	↓	1978	
289b		↓	↓	↓	1968	
289c		↓	↓	↓	1966	
290		↓	↓	↓		
291		↓	↓	↓	1780	
292	7740+2% SiO <sub>2</sub>	HTS				
293A	7740	HMS			1800	
293B	↓	↓	↓	↓	1690	
294A	↓	↓	↓	↓		
294B	↓	↓	↓	↓		

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Remarks		
			Pressure (MPa)	Temp. (K)				
GC 295A	7740+2% SiO <sub>2</sub>	HTS	13.8	1473	1760			
B					1770			
C					1790			
296A							1800	
B							1830	
C							1820	
297A							1814	
B							1820	
C							1790	
298A							1810	
B							1800	
C							1830	
299A							1790	
B							1830	
C							1800	
300A							1670	
B							1820	
C							1820	
301A						6.9		Broken
B						6.9		Broken
C						6.9		Broken
302A						13.8		1660
B						13.8		1540
C						13.8		1720
303A						6.9		1820
B+								1829
C								1828
304A							1623	1820
B							1623	1800
C							1623	1820
305A							1473	Broken
B							1473	Broken
C							1473	Broken
306A	7740+2% SiO <sub>2</sub>	Celanese	6.9	1473	1910			
B					1870			
C					1920			
307A							1780	
B							1840	
C							1820	
308A							1990	
B							1960	
C							1970	
309A	7740+2% SiO <sub>2</sub>	Thornel Pitch	6.9	1623	2050			
B					2090			
C					2060			
310A							2100	
B							2100	
C							2050	

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Remarks				
			Pressure (MPa)	Temp. (K)						
GC 311	7740+2% SiO <sub>2</sub>	HMS	6.9	1623						
312B										
C										
313A										
B										
C										
314A								1930		
B								1910		
C								1880		
315A								1850		
B								1890		
C								1900		
316A								1930		
B								1900		
C								1920		
317A							1673	1900		
B							1673	1920		
C							1673	1890		
318A							1623	1910		
B							1623	1900		
C							1623	1930		
319A							1573	1888		
B							1573	1900		
C							1573	1860		
320A							1523	1870		
B							1523	1860		
C							1523	1860		
321A							1473	1840		
B							1473	1840		
C							1473	1850		
323A				7740+2% SiO <sub>2</sub>	HMS	6.9	1623		No composite	
B										"
C										"
326A							1723	1910		
B							1723	1920		
C							1723	1920		
327A							1773	1870		
B							1773	1870		
C							1773	1880		
328A							1723	1910		
B							1723	1900		
C							1723	1890		
329A							1743	1910		
B							1743	1850		
C							1743	1890		
330A	7740+2% SiO <sub>2</sub>	Celanese Multi	6.9	1623	1990					
B						1940				
C						2000				
331A							1970			
B							1960			
C				1960						

Table A1 (Cont'd)

Sample No.	Glass Type	Fiber Type	Hot Pressing Conditions		Density (kg/m <sup>3</sup> )	Remarks
			Pressure (MPa)	Temp. (K)		
GC 332A	9608	HMS	6.9	1623		Lost most glass
B	↓	↓	↓	1623		"
C	↓	↓	↓	1623		"
333A	↓	↓	↓	1548		Lacked glass
B	↓	↓	↓	1548		Reacted with Mo
C	↓	↓	↓	1548		"
336A	7740+2% SiO <sub>2</sub>	Celanese Multi	6.9	1723	2010	
B	↓	↓	↓	↓	2020	
C	↓	↓	↓	↓	2030	
337A	↓	↓	↓	↓		
B	↓	↓	↓	↓	1870	
C	↓	↓	↓	↓	1970	
338A	7740+2% SiO <sub>2</sub>	HMS	6.9	1723	1880	
B	↓	↓	↓	↓	1880	
C	↓	↓	↓	↓	1890	
339A	↓	↓	↓	↓	1890	
B	↓	↓	↓	↓	1880	
C	↓	↓	↓	↓	1890	
340A	↓	↓	↓	↓	1880	
B	↓	↓	↓	↓	1900	
C	↓	↓	↓	↓	1900	
341A	7740+2% SiO <sub>2</sub>	HMS	6.9	1723	1900	
B	↓	↓	↓	↓	1890	
C	↓	↓	↓	↓	1850	
342A	↓	↓	↓	↓	1910	
B	↓	↓	↓	↓	1920	
C	↓	↓	↓	↓	1930	
343A	↓	↓	↓	↓	1910	
B	↓	↓	↓	↓	1920	
C	↓	↓	↓	↓	1930	
344A	↓	↓	↓	↓	1880	
B	↓	↓	↓	↓	1890	
C	↓	↓	↓	↓	1900	
356A	S	HMS	6.9	1723		Insufficient glass
B	↓	↓	↓	↓		"
C	↓	↓	↓	↓		"
357A	↓	↓	↓	↓	1850	
B	↓	↓	↓	↓	1860	
C	↓	↓	↓	↓	1900	
358A	1723	HMS	6.9	1723	1910	Much flash,
B	↓	↓	↓	↓	1910	samples
C	↓	↓	↓	↓	1930	unusable
359A	↓	↓	↓	↓	1940	Composite not
B	↓	↓	↓	↓	1910	fully infiltrated
C	↓	↓	↓	↓	2140	with glass
360A	7740+2% SiO <sub>2</sub>	HMS	6.9	1623	1950	Biaxial
B	↓	↓	↓	↓	1950	"
C	↓	↓	↓	↓	1960	"

APPENDIX B

Properties of Selected Graphite Fiber  
Reinforced Glass Matrix Composites

Table B1

Flexural Strength of HMS Reinforced 7740  
Slurry A


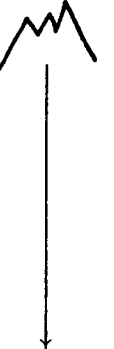
Sample Number	Thickness cm	Hot Pressing Temperature K	Type of Load Curve	Three-Point Flexural Strength	
				MPa	psi x 10 <sup>3</sup>
LB 135 RC	0.152	1373		673	97.7
CB	0.142			663	96.2
LC	0.150			705	102.0
CC	0.124			734	106.0
TC	0.081			640	92.9
TR	0.084			705	102.0
TL	0.086			733	106.0
LB	0.084			746	108.0
RB	0.137			614	89.0
Average				689	99.98
LB 135FRC	0.150	1473		1070	155.0
CB	0.150			1010	146.0
LC	0.173			1050	152.0
CC	0.150			1140	165.0
TC	0.152			903	131.0
TR	0.157			946	137.0
TL	0.160			698	101.0
LB	0.152			1050	152.0
RB	0.155			983	143.0
Average				977	142.0

Table B2

Hercules HMS-10K Reinforced 7740 LB 139  
Slurry A

3 Point Flexural Strength Tested at Temperature in Argon

Test Temperature (K)	Flexural Strength	
	MPa	10 <sup>3</sup> psi
295	863	125
295	785	114
773	793	115
823	1081	157
873	706	102
873	1292	187
923	1134	164
973	772	112
	347*	50.3*

\*Specimen highly deformed so that this number is not strictly valid

Table B3

Flexural Strength of Celanese Graphite Fiber DG-102 Reinforced  
C.G.W. 7740 Glass Composite at Elevated Temperatures  
Slurry A

<u>Specimen</u>	<u>Temperature at Which Flexural Strength was Measured (K)</u>	<u>3-Point Flexural Strength Span 5.0 cm</u>	
		<u>MPa</u>	<u>ksi</u>
LB 98 BL	295	374	54.2
CR	295	250	36.2
TL	773	515	74.7
BR	773	481	69.7
CL	823	565	82
TR	873	196	28.4
TC	973	292	42.3
CC	973-908	305	44.3

Table B4

Thermal Cycling

HMS Reinforced 7740 Spec LB 135 G  
Slurry A

Condition	4 Point Bend Strength		*Elastic Modulus	
	MPa	10 <sup>3</sup> psi	GPa	10 <sup>6</sup> psi
As Fabricated	896	130	185	26.8
	938	136	196	28.5
	800	116	201	29.2
	Average	876	127	194
After 20 Cycles**	917	133	196	28.5
	910	132	203	29.4
	834	121	189	27.4
	Average	889	129	196
After 100 Cycles***	786	114	174	25.2
	614	89	167	24.2
	758	110	185	26.9
	Average	717	104	175

\*Tested with major and minor spans of 5 cm and 1.27 cm

\*\*Cycled while in argon containing glass tube between 863-903 K and 383 K  
Target temperature 833 K or annealing point of glass matrix

\*\*\*The 100 cycles extended overnight with result that temperature exceeded  
target temperature (annealing point of glass matrix is 833 K or 1040°F) by 33K

Table B5

Four Point Flexural Fatigue  
(Major and minor spans of 5 cm and 1.27 cm)  
HMS Reinforced 7740 Spec LB 135 H  
Slurry A

Condition	4 Point Bend Strength		Elastic Modulus	
	MPa	10 <sup>3</sup> psi	GPa	10 <sup>6</sup> psi
As Fabricated	548	79	200	29.0
	532	77	195	28.3
After 3 cycles between 484 and 48 MPa	325	47	185	26.8
After 20 cycles between 337 and 34 MPa	519	75	186	26.9
After 20 cycles between 390 and 39 MPa	658	95	194	28.1
After 20 cycles between 450 and 45 MPa	574	83	210	30.5
After 20 cycles between 520 and 52 MPa	638	92	208	30.1
After 100 cycles between 430 and 43 MPa	575	84	207	30.0
After 100 cycles between 445 and 44 MPa	573	83	201	29.1

Table B6

Four Point Flexural Strength Data for HMS Graphite Fiber  
Reinforced Glass Matrix Composite\* (C.G.W. 7740 + SiO<sub>2</sub>)  
Made from New Slurry C  
Span 6.35 cm to 1.90 cm

<u>Sample</u>	Four Point Flexural Strength		Flexural Modulus		<u>% <math>\epsilon_f</math></u>
	<u>MPa</u>	<u>ksi</u>	<u>GPa</u>	<u>10<sup>6</sup> psi</u>	
GC 326 B3	896	130	195	28.3	0.43
B6	1131	164	144	21.0	0.62
B9	803	116	213	30.8	0.46
B11	931	135	207	30.0	0.48
C2	853	124	202	29.3	0.50
C5	950	138	211	30.6	0.45
C7	1105	160	217	31.5	0.53
C10	1041	151	206	29.9	0.67
Mean	964	140	199	28.9	0.52
Std Dev	118	17.1	23	3.3	0.085

\*Hot pressed at 1723 K, 6.9 MPa pressure, 1 hr dwell time in argon

Table B7

Relation of Hot Pressing Pressure to Three Point Flexural Strength  
of HMS Graphite Fiber Reinforced 7740 Glass Matrix Composites  
All Samples Made at 1473 K  
Slurry B

GC-280 - 4.1 MPa

GC-257 - 6.1 MPa

<u>Sample</u>	Three Point Flexural Strength		<u>Sample</u>	Three Point Flexural Strength	
	<u>MPa</u>	<u>ksi</u>		<u>MPa</u>	<u>ksi</u>
TL	595	86.4	1	558	80.9
LC	553	80.2	2	646	93.7
LB	481	69.8	3	473	68.6
TC	387	56.5	4	674	97.8
CC	507	73.5	5	474	68.8
CB	471	68.3	6	753	109
RB	513	74.3	7	407	59.1
RC	489	70.9	8	496	72.0
TR	563	81.6	9	471	68.3
			10	513	74.4
Avg	507	73.5		548	79.5

GC-278 - 10.1 MPa

GC-281 - 13.8 MPa

<u>Sample</u>	Three Point Flexural Strength		<u>Sample</u>	Three Point Flexural Strength	
	<u>MPa</u>	<u>ksi</u>		<u>MPa</u>	<u>ksi</u>
LC	644	93.4	RB	965	140
TR	585	84.8	RC	674	97.7
RC	553	80.2	TR	688	99.8
RB	644	93.5	CB	752	109
TL	633	91.8	CC	786	114
CB	785	114	TC	745	108
TC	690	100	LB	793	115
CC	552	80.0	LC	800	116
LB	582	84.4	TL	660	95.7
Avg	630	91.3		765	111

Table B8

Properties of Three Composite Samples of HMS-7740 Produced Simultaneously  
 (Hot Pressed at 1473 K, 13.8 MPa)  
 Slurry B

GC-289 - Top Sample				GC-289 - Center Sample				GC-289 - Bottom Sample			
Specimen	Three Point Flexural Strength		Specimen	Three Point Flexural Strength		Specimen	Three Point Flexural Strength		Specimen	Three Point Flexural Strength	
	MPa	ksi		MPa	ksi		MPa	ksi		MPa	ksi
1	660	95.8	1	852	124	1	746	108	1	746	108
2	895	130	2	839	122	2	491	91.2	2	491	91.2
3	928	135	3	939	136	3	799	1.6	3	799	1.6
4	759	110	4	908	132	4	799	1.6	4	799	1.6
5	652	94.6	5	572	83.0	5	710	103	5	710	103
6	692	100	6	913	132	6	968	140	6	968	140
7	747	108	7	642	93.1	7	908	132	7	908	132
8	658	95.4	8	905	131	8	778	113	8	778	113
9	1030	149	9	680	98.6	9	774	112	9	774	112
10	757	110	10	819	127	10	841	123	10	841	123
Avg		113			118			113			113
Std Dev		18.9			19.0			18.5			18.5
Std Err		5.78			6.00			5.85			5.85

Table B9

Effect of Hot Pressing Temperature on Three-Point Flexural Strength of H<sub>2</sub>S Fiber Reinforced-7740 Composites Made with New Slurry C at a Pressure of 6.9 MPa

GC 321 - 1473 K Hot Press			GC 320 - 1523 K Hot Press			GC 319 - 1573 K Hot Press			GC 318 - 1623 K Hot Press		
Three-Point Flexural Strength			Three-Point Flexural Strength			Three-Point Flexural Strength			Three-Point Flexural Strength		
MPa	ksi		MPa	ksi		MPa	ksi		MPa	ksi	
A1	284	41.1	A1	372	54.0	C1	352	51.1	A1	767	111
A2	284	41.2	A2	365	53.0	C2	381	55.3	A2	746	108
A3	205	29.8	A3	419	60.7	C3	446	64.7	A3	628	91.0
A4	203	29.5	A4	372	54.0	C4	350	50.7	A4	615	89.2
A5	174	25.3	A5	509	73.8	C5	658	95.5	A5	515	74.7
A6	227	32.9	A6	467	67.8	C6	609	88.3	A6	630	91.4
A7	228	33.1	A7	391	56.7	C7	578	83.9	A7	637	92.5
A8	267	39.1	A8	332	48.2	C8	615	89.1	A8	667	96.8
A9	223	32.3	A9	441	63.9	C9	496	72.0	A9	456	66.1
A10	278	40.3	A10	404	58.6	C10	417	60.5	A10	622	90.1
A11	176	25.5	A11	302	43.7	C11	524	76.0	A11	682	98.9
A12	148	21.4	A12	293	42.6	C12	508	73.7	A12	712	103
Avg	225	32.6	Avg	389	56.4	Avg	494	71.7	Avg	639	92.7
Std Dev	46.3	6.71	Std Dev	64.2	9.31	Std Dev	106	15.4	Std Dev	87.6	12.7
Std Err	13.4	1.94	Std Err	18.5	2.69	Std Err	30.8	4.46	Std Err	18.5	2.68
GC 317 - 1673 K Hot Press			GC 326 - 1723 K Hot Press			GC 329 - 1743 K Hot Press			GC 327 - 1773 K Hot Press		
Three-Point Flexural Strength			Three-Point Flexural Strength			Three-Point Flexural Strength			Three-Point Flexural Strength		
MPa	ksi		MPa	ksi		MPa	ksi		MPa	ksi	
A1	no result		A1	1110	162	A2	1097	159	A4	644	93.5
A2	873	127	A2	1150	166	A6	923	134	A6	786	114
A3	944	137	A3	1240	180	A8	737	107	A8	644	93.5
A4	1048	152	A4	1170	170	A11	910	132	A10	666	96.6
A5	903	131	A5	1060	153	B2	1019	148	B4	702	102
A6	806	117	A6	931	135	B6	1153	167	B6	672	97.5
A7	812	118	A7	835	121	B8	1026	149	B8	813	118
A8	762	110	A8	942	137	B11	1115	162	B10	684	99.2
A9	782	113	A9	1020	147	C2	706	102	C4	978	142
A10	645	93.5	A10	823	119	C6	1061	154	C6	1236	179
A11	778	113	A11	1040	150	C8	957	139	C8	1085	157
A12	806	117	A12	1070	155	C11	1161	168	C10	1000	145
Avg	834	121	Avg	1034	150	Avg	989	143	Avg	825	120
Std Dev	107	15.5	Std Dev	130	18.9	Std Dev	150	21.7	Std Dev	200	289
Std Err	32.2	4.67	Std Err	37.6	5.46	Std Err	43.2	6.27	Std Err	57.8	8.35

Table B10

Check of Consistency of Test Results Obtainable in Measuring the Three-Point Flexural Strength of HMS Fiber Reinforced-774- Composites Made With 7740 + 2% Silica Slurry C at a Temperature of 1623 K, 6.9 MPa Pressure

	GC 318		GC 312		GC 311	
	Three-Point Flexural Strength MPa	ksi	Three-Point Flexural Strength MPa	ksi	Three-Point Flexural Strength MPa	ksi
A1	767	111	B1	565	A1	700
A2	746	108	B2	689	A2	755
A3	628	91.0	B3	623	A3	521
A4	615	89.2	B4	727	A4	563
A5	515	74.7	B5	668	A5	563
A6	630	91.4	B6	774	A6	691
A7	637	92.5	B7	466	A7	538
A8	667	96.8	B8	586	A8	642
A9	456	66.1	B9	818	A9	720
A10	622	90.1	B10	536	A10	556
A11	682	98.9	B11	635	A11	547
A12	712	103	B12	733	A12	642
Avg	639	92.7		651		616
Std Dev	87.6	12.7		103		87.9
Std Err	18.5	2.68		29.8		25.1

Table B11

Three Point Flexural Strength of Thornel Pitch VS 0032  
 Fiber Reinforced 7740 + 2% SiO<sub>2</sub> Glass Composite (GC-209)  
 Hot Pressed at 1623 K, 6.9 MPa, 1 Hr Dwell Time  
 Slurry B

Specimen	Three Point Flexural Strength	
	MPa	ksi
A1	539	78.2
A3	465	67.6
A5	491	71.2
A7	579	84.0
A9	399	57.8
A11	335	48.6
B1a	574	74.5
B3	396	57.4
B5	489	70.9
B7	523	75.8
B9	294	42.7
B11	349	50.6
Avg	448	65.0
Std Dev	95	13.8
Std Err	39	5.6

Table B12

## Three Point Bend Data for Transversely Oriented Specimens

<u>Specimen</u>	<u>Fiber</u>	<u>Lay-up</u>	Max. Flex. Stress		<u>S/D*</u>	<u>Fracture</u>
			<u>10<sup>3</sup> psi</u>	<u>MPa</u>		
GC 208	HMS (4 plys in thickness) 13.8 MPa	90 <sup>o</sup>	1.4	9.3	40	Tensile
			1.3	9.1	40	"
			1.0	6.8	40	"
			2.0	13.6	40	"
			Avg	1.4	9.7	
GC 209	HMS (16 plys in thickness) 13.8 MPa	90 <sup>o</sup>	1.8	12.7	10	Tensile
			3.2	22.2	10	"
			1.4	9.5	10	"
			Avg	2.15	14.8	
GC 221**	HTS 10 plys thick	90 <sup>o</sup>	1.8	12.6	14	Tensile
			0.7	4.7	14	"
			1.3	9.1	14	"
			1.6	11.2	14	"
			1.4	9.8	14	"
			Avg	1.4	9.5	
GC 222***	HTS 10 plys thick	90 <sup>o</sup>	2.1	14.7	12	Tensile
			1.4	9.3	12	"
			1.8	12.1	12	"
			1.0	6.9	12	"
			2.6	18.0	12	"
			Avg	1.8	12.0	

\*span-to-depth ratio for 3 point bend test

\*\*fabricated using 13.8 MPa pressure

\*\*\*fabricated using 6.9 MPa pressure

Table B13

Three Point Bend Data for  
Thornel 300 Fabric Reinforced 7740 Glass  
Slurry B

<u>Specimen</u>	<u>Precleaned Fiber</u>	<u>Flexural Strength</u>		<u>Shear Strength</u>		<u>S/D*</u>
		<u>MPa</u>	<u>ksi</u>	<u>MPa</u>	<u>ksi</u>	
GC 218	No	99.6	14.4	2.24	0.32	5
		93.1	13.5	2.05	0.30	5
		80.4	11.7	1.81	0.26	5
		108.0	15.7	2.32	0.34	5
GC 219	No	94.8	13.8	5.6	0.81	8
		87.1	12.6	6.1	0.75	8
		48.4	7.0	3.0	0.44	8
		43.0	6.2	2.7	0.39	8
GC 220	Yes	105.0	15.2	3.3	0.48	16
		106.0	15.4	3.3	0.48	16
		102.0	14.8	1.6	0.23	16

\*Span-to-depth ratio of test

Table B14

## Oxidized Fiber Strength Loss

	<u>HMS</u>	<u>HTS</u>	<u>Celanese DG-102</u>
Vendor supplied fiber Average UTS (MPa)	2446	2873	1723
As-received average fiber UTS measured at UTRC (MPa)	2956	2777	2074
Average fiber strength after exposure to air at 823 K for 1 hr (MPa)	1550*	792*	1054*
% of fiber UTS lost based on UTRC measurements	48%	71%	49%
% weight loss of fiber after exposure to air at 823 K for 1 hr	20%	84%	16%

\*Strength calculated based on original unexposed average fiber diameter

Table B15

Air Exposure of Graphite Fibers at 823 K for  
Several Lengths of Time  
(% Weight Loss)

<u>Fiber</u>	<u>1 hour</u>	<u>2 hours</u>	<u>6 hours</u>	<u>Delivered Modulus &amp; Strength</u>		<u>Precursor</u>
				<u>GPa</u>	<u>MPa</u>	
Hercules HTS	83.8	96.9	100	255	2873	PAN
Hercules HMS	19.8	no data	no data	351	2446	PAN
Celanese DG-102	16.5	32.3	85.2	530	1723	PAN
Thornel 50	15.5	26.4	56.1	393	2170	Rayon
Thornel Pitch Type	10.0	17.3	47.3	413	*944	Pitch

\*Material currently shipped has strength greater than 1378 MPa

Table B16

Effect of Exposure to Air for 4 hrs at 833 K on the  
 3 Point Flexural Strength of HTS Graphite Fiber  
 Reinforced 7740, Hot Pressed at 1473 K  
 Slurry B

<u>Specimen</u>	<u>Specimen Surface Condition</u>	<u>Specimen Condition</u>	<u>Three Point Flexural Strength</u>	
			<u>MPa</u>	<u>ksi</u>
GC 228	Exposed Fibers	As Fabricated	254	36.8
			214	31.1
			272	39.5
			274	39.7
			Avg	250
GC 228	Exposed Fibers	Oxidized	195	28.3
			211	30.7
			198	28.8
			299	43.3
			274	39.8
Avg	236	34.2		
GC 229	Glazed on Two Surfaces	As Fabricated	342	49.5
			254	36.8
			466	67.5
			Avg	354
GC 229	Glazed on Two Surfaces	Oxidized	382	55.4
			264	38.3
			303	44.0
			Afg	317

Table B17

Effect of Heat Treatment in Argon and Air on 3 Point  
Strength of Hercules HTS Graphite Fiber in 7740  
Glass Matrix Hot Pressed at 1473 K  
Slurry C

<u>Specimen</u>	<u>Heat Treatment</u>	<u>3 Point Flexural Strength</u>	
		<u>MPa</u>	<u>ksi</u>
LB 148E-RB	none	344	49.9
-CB	none	338	49.0
-LC	none	384	55.7
		Avg	355
			51.5
LB 148E-TR	4 hrs, 833 K, argon	396	57.5
-CC	4 hrs, 833 K, argon	337	48.8
-TL	4 hrs, 833 K, argon	438	63.5
		Avg	390
			56.6
LB 148E-LB	4 hrs, 833 K, air	370	53.6
-RC	4 hrs, 833 K, air	318	46.2
-TC	4 hrs, 833 K, air	315	45.7
		Avg	334
			48.5

Table B18

Effect of Heat Treatment in Vacuum and in Air on 3 Point  
Flexural Strength of Hercules HTS Graphite Fiber  
in C.G.W. 7740 (Pyrex) Glass Matrix  
1473 K - Hot Pressed, Slurry B

<u>Specimen</u>	<u>Heat Treatment</u>	<u>Three Point Flexural Strength</u>	
		<u>MPa</u>	<u>ksi</u>
GC 293A	none ↓		
1		368	53.3
2		311	45.0
3		408	59.2
4		339	49.1
	Avg	356	51.7
GC 293A	4 hrs @ 833 K in air ↓		
1		345	50.0
2		321	46.6
3		342	49.7
4		343	49.7
	Avg	338	49.0
GC 293A	4 hrs @ 833 K in air ↓		
1		336	48.8
2		361	52.3
3		448	65.0
4		302	43.8
	Avg	362	52.5
GC 293B	none ↓		
1		412	59.7
2		432	62.6
3		287	41.6
4		330	47.9
	Avg	365	53.0
GC 293B	4 hrs @ 833 K in air ↓		
1		377	54.6
2		322	46.6
3		300	43.6
4		272	39.4
	Avg	318	46.1
GC 293C	4 hrs @ 833 K in vacuum ↓		
1		424	61.4
2		333	48.3
3		271	39.2
	Avg	343	49.6

Table B19

Effect of Air Exposure at 813 K on the Three Point Flexural Strength and Weight Loss of HTS Graphite Fiber Reinforced 7740, GC 304, Pressed at 1623 K, Slurry C

Sample	Time in Air at 813 K hrs	Initial Weight gms	Final Weight gms	3 Point Flexural Strength After Exposure				
				MPa	ksi			
A2	0	↓	↓	766	111			
A7				651	94.4			
A12				681	98.7			
B2				695	101			
B7				695	101			
B12				844	122			
C2				789	114			
C7				708	103			
C12				749	109			
				Avg			730	106
A1				24	↓	↓	530	76.9
A6							438	63.6
A11	514	74.5						
*B1	435	63.1						
B6	448	65.0						
B11	492	71.3						
*C1	304	44.0						
C6	343	49.7						
C11	357	51.9						
	Avg	1.938	1.750				429	62.2
A4	100	↓	↓				137	19.9
A5				160	23.2			
A9				120	17.4			
B4				171	24.8			
B5				93.2	13.5			
B9				165	23.9			
C4				88.4	12.8			
C5				78.5	11.4			
C9				42.1	6.1			
				Avg	1.955	1.392	117	17

\*Damaged sample. Damaged side closer to compression surface. All samples tested with 6.4 cm test span

Table B20

Effect of Air Exposure at 723 K on the Three Point  
Flexural Strength of HMS Graphite Fiber Reinforced  
7740 + 2% Silica, GC 328, Pressed at 1723 K  
Slurry C

Sample	Time in Air at 723 K hrs	Initial Weight gms	Final Weight gms	3 Point Flexural Strength After Exposure	
				MPa	ksi
A2	0	-	-	867	125.7
A6				860	124.7
A8				1062	154.0
A12				1046	151.7
B2				1110	161.0
B6				1200	174.0
B8				1150	166.8
B12				911	132.2
C2				935	135.6
C6				995	144.2
C8				1140	165.3
C12				923	133.8
Avg				1016	147.4
A3	24	1.6885	1.678	956	139
A7		1.7125	1.7025	930	135
A9		1.7195	1.706	859	125
A11		-	-	1021	148
B3		1.852	1.8405	1074	156
B7		1.831	1.820	1237	179
B9		1.823	1.809	1230	178
B11		1.850	1.836	1039	151
C3		1.651	1.638	910	132
C7		1.651	1.6425	1096	159
C9		1.6475	1.638	1220	177
C11		1.663	1.654	973	141
Avg			1.735	1.725	1045
A1	100	1.7000	1.6565	1150	167
A4		1.6875	1.655	824	120
A5		1.7015	1.6715	757	110
A10		1.7365	1.710	1020	148
B1		1.849	1.806	840	122
B4		1.8315	1.801	796	115
B5		1.820	1.789	971	141
B10		1.835	1.8025	1070	155
C1		1.6515	1.6065	856	124
C4		1.650	1.6275	987	143
C5		1.646	1.622	971	141
C10		1.653	1.6255	1050	153
Avg			1.730	1.698	941

Table B21

Effect of Air Exposure at 813 K on Weight Loss and Flexural Strength of HMS Graphite Fiber Reinforced 7740 + 2% Silica, GC 326, Pressed at 1723 K and GC 327, Pressed at 1773 K Slurry C

Sample	Time in Air at 813 K hrs	Initial Weight gms	Final Weight gms	Three Point Flexural Strength		
				MPa	ksi	
GC 326						
Avg	0			1034	150	
B1	24 ↓	1.687	1.590	867	126	
B4		1.693	1.6155	982	142	
B8		1.691	1.5685	748	109	
B12		1.685	1.5755	818	119	
C1		1.437	1.3575	925	134	
C4		1.445	1.3775	986	143	
C8		1.435	1.366	859	125	
C12		1.4475	1.369	920	133	
Avg			1.565	1.477	888	129
GC 327						
Avg	0			825	120	
A2	100 ↓	1.4525	1.170			
A3		1.534	1.282			
A9		1.501	1.248			
A11		1.502	1.255			
B2		1.722	1.417			
B3		1.731	1.478			
B9		1.724	1.480			
B11		1.715	1.453			
C2		1.7355	1.524			
C3		1.7475	1.5155			
C9		1.725	1.499			
C11	1.7175	1.496				
Avg		1.651	1.401			



Table B23

Effect of Air Heat Treatment on 4 Point Flexural Strength  
of Hercules HMS Graphite Fiber in 7740 Glass Matrix  
Spans 1.25 cm and 5.0 cm  
Slurry A

<u>Specimen</u>	<u>Heat Treatment</u>	<u>4 Point Flexural Strength</u>		<u>Modulus</u>		
		<u>MPa</u>	<u>ksi</u>	<u>GPa</u>	<u>10<sup>6</sup> psi</u>	
LB 135T-LC	none	596	86.5	176	25.6	
-BC	↓	699	101	187	27.1	
-CC		594	86.1	168	24.4	
-TC		487	70.7	186	27.0	
-RB		475	66.3	178	25.8	
		Avg	566	82.2	179	26.0
-LB	4 hrs, 833 K, air	345	50.0	175	25.4	
-RC	↓	286	41.5	167	24.2	
-TL		413	59.9	175	25.3	
-TR		476	69.1	174	25.2	
		Avg	380	55.3	173	25.0

Table B24

Effect of Heat Treatment in Argon on 4 Point Flexural Strength  
of Celanese DG-102 Graphite Fiber in 7740 Glass Matrix

<u>Specimen</u>	<u>Heat Treatment</u>	<u>4 Point Flexural Strength</u>		<u>Modulus</u>		
		<u>MPa</u>	<u>ksi</u>	<u>GPa</u>	<u>10<sup>6</sup> psi</u>	
LB 97E-TL	none	239	34.7	354	51.4	
-LC	↓	258	37.5	327	47.5	
-LB	↓	262	38.0	285	41.4	
		Avg	253	36.7	322	46.8
LB 97E-TR	4 hrs, 833K, argon	289	41.9	277	40.2	
-CR	↓	301	43.7	269	39.0	
-BR	↓	336	48.7	271	39.3	
		Avg	308.7	44.8	272	39.5



Table B26

Apparent Failure to Improve Oxidation Resistance of Pitch Type Fiber-7740  
Composites Made by New Process at 1623 K and 6.9 MPa  
Slurry C

	As Made		As Made		After 100 hrs in Air @ 813 K	
	GC 309 - Thornel Pitch Type Graphite Fibers Three Point Flexural Strength MPa	ksi	GC 310 - Thornel Pitch Type Graphite Fibers Three Point Flexural Strength MPa	ksi	GC 310 - Thornel Pitch Type Graphite Fibers Three Point Flexural Strength MPa	ksi
B1	490	71.0	A1	539	A2	200
B3	520	75.4	A3	465	A4	248
B5	449	65.2	A5	491	A6	180
B7	431	62.6	A7	579	A8	295
B9	394	57.2	A9	399	A10	206
B11	327	47.5	A11	335	B2	146
C1	661	95.9	B1a	514	B4	32.6
C3	555	80.6	B3	396	B6	261
C5	546	79.2	B5	489	B8	196
C7	482	69.9	B7	523	B10	113
C9	245	35.6	B9	294	B12	200
C11	214	31.0	B11	349		
AVG	443	64.3		448		192
Std Dev	131	19.0		95.0		72.3
Std Err	37.7	5.47		38.8		21.9
				5.63		3.18

NASA Contractor Report 158946  
Distribution List  
NAS1-14346

	<u>No. of Copies</u>
NASA Langley Research Center Hampton, VA 23665 Attn: Report and Manuscript Control Office, Mail Stop 180A Dennis L. Dicus, Mail Stop 188B	1 60
NASA Ames Research Center Moffett Field, CA 94035 Attn: Library, Mail Stop 202-3	1
NASA Dryden Flight Research Center P. O. Box 273 Edwards, CA 93523 Attn: Library	1
NASA Goddard Space Flight Center Greenbelt, MD 20771 Attn: Library	1
NASA Lyndon B. Johnson Space Center 2101 Webster Seabrook Road Houston, TX 77058 Attn: JM6/Library	1
NASA Marshall Space Flight Center Marshall Space Flight Center, AL 35812 Attn: Library, AS61L	1
Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, CA 91103 Attn: Library, Mail 111-113	1
NASA Lewis Research Center 21000 Brookpark Road Cleveland, OH 44135 Attn: Library, Mail Stop 60-3	1
NASA John F. Kennedy Space Center Kennedy Space Center, FL 32899 Attn: Library, NWSI-D	1
National Aeronautics and Space Administration Washington, DC 20546 Attn: RW-3	1

NASA Scientific and Technical Information Facility  
6571 Elkridge Landing Road  
Linthicum Heights, MD 21090

No. of  
Copies

30 plus  
original