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GRAPHITE FIBER/EPOXY RESIN MATRIX COMPOSITES

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FOREWORD

This report was prepared by the Plastics and Composites Branch, Nonmetallic Materials Division, and was initiated under Project Number 7340, "Nonmetallic and Composite Materials," Task Number 734003, "Structural Plastics and Composites." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division with R. J. Dauksys, N. J. Pagano, and R. G. Spain as Project Engineers.

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This report covers work conducted during the period of June 1966 through September 1967. The manuscript was released by the authors in December 1967.

This technical report has been reviewed and is approved.

R. G. Spain

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ABSTRACT

Four types of graphite fibers were utilized as reinforcements in a continuing experimental program of the fabrication and evaluation of epoxy resin matrix composites. Resultant composite data and analyses continue to demonstrate a high promise for graphite fiber reinforced resin composites as high performance materials.

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SECTION I

INTRODUCTION

The efforts reported here are an integral continuation of the fabrication and evaluation of previously reported data for graphite fiber reinforced epoxy resin matrix composites (Reference 1). Several reinforcements are currently the subject of research directed toward improved performance of resin matrix composites. Air Force requirements, in particular, emphasize the need for high mechanical-property-to-composite-density ratios. Although graphite fibers of sufficient mechanical property levels to generate interest as to their consideration as potential reinforcements for high performance level composites are a comparatively new material development, considerable progress has been realized in the preparation of graphite fibers and subsequent composites with increased mechanical property levels.

Much of the effort discussed in this report was concerned with the fabrication and evaluation of graphite fiber reinforced composites as to static mechanical properties, although the effects of composite "water boil" exposures and some preliminary dynamic evaluation data are also presented.

All composite evaluations in tension, flexure, shear, and compression were linear to failure.

SECTION II

DISCUSSION

FIBER CHARACTERISTICS

Mechanical and physical property data were obtained for four types of graphite fibers. (Table I). Samples A and B are Union Carbide products with the latter (Thornel 40) displaying increased modulus and strength properties compared to sample A (Thornel 25). Samples C and D were obtained from the Royal Aircraft Establishment (RAE) and consisted of 14-inch long samples of tow, a loose ropelike fiber bundle without definite twist, consisting of many thousands of filaments.

Since sample B was recently developed as a continuous yarn with greater fiber strength and higher modulus than those of other continuous graphitic yarns, considerable effort was devoted to yarn characterization and composite fabrication and evaluation.

Sample B (Thornel 40) handled as well as sample A (Thornel 25) during the winding of prepreg tapes. A difficulty encountered during fabrication when working with sample B was the number of adhesive splices per pound. Table II lists the number of breaks and splices encountered from two batches of Thornel 40 during impregnation and tape winding. Although the number of breaks directly attributed to splices seems small, a generous portion of the "other breaks" were due to accidental contact of yarn frays with the adhesive used in yarn splicing and with other parts of the yarn directly below the spliced section. As a result, the splice would have a tendency to adhere to the graphite at the point of takeoff, causing yarn pull, damage to many of the filaments, and overall poor integrity during impregnation and tape winding.

Although yarns C and D exhibited relatively high average tensile strength and modulus, fiber property data exhibited a large scatter, as illustrated by the maximum and minimum values shown in Table I. Also, due to the short lengths of fibers, it is obvious that prepreg fabrication would have been impossible by winding. Therefore, fiber alignment and impregnation were performed manually. This was time consuming and imparted poor control over fiber volume, spacing, and alignment in the resultant composites.

WATER BOIL EXPOSURE

As a means of simulating the effects of severe atmospheric conditions on composite performance, test specimens were subjected to a water boil environment prior to testing. A 2-hour water boil decreased the flexural strength of Thornel 25, epoxy matrix composites by less than 6% (Reference 1). Work at present (Table III) illustrated an average decrease in flexural strength of only 10%, even after subjection to water boil for prolonged exposure (72 to 144 hours). Flexural modulus was less affected, showing a decrease of about 1.5% compared to the control specimens.

In another series of experiments designed to study the effects of various epoxy yarn coatings as yarn finishes for Thornel 25 (Fiber A) on composite properties, 2-hour water boil data were also obtained. Table IV exhibits the fact that no obvious deleterious effects could be attributed to the coatings. The increases in mechanical property values were probably due to experimental error or variance in properties associated with the few fiber property tests allowable with the small quantities of fiber available.

TABLE I

GRAPHITE FIBER PROPERTIES*

Tensil' Strength PSI x 10^{-3}	A	B	C	D
Average*	173	205	231	296
Min.	158	172	59.9	163
Max.	195	256	355	370
Tensile modulus PSI x 10^{-6}				
Average*	25.7	43.0	39.1	47.3
Min.	24.1	34.8	30.0	33.3
Max.	26.8	49.0	45.2	54.9
Density g/cc	1.42	1.51	1.95	1.9 $\pm$.1
Finish	PVA	PVA	---	---
Construction				
No. of plies	2	2	(tow)	(tow)
Twist (turns/in.)	2.1	2.1	---	---
Filaments/ply	720	720	---	---

*Average property data are based upon five or more individual filament tests

TABLE II

YARN HANDLING CHARACTERISTICS DURING RESIN IMPREGNATION AND WINDING (FIBER SAMPLE NO. B)

Yarn	Total Yarn Length	Total Yarn Breaks	Breaks Directly Attributed to Splices	Other Breaks
Tube A	10,000	15	4	11
Tube B	16,000	14	4	10

TABLE III

AVERAGE FLEXURAL PROPERTIES OF 8-PLY BALANCED BIDIRECTIONAL GRAPHITE COMPOSITES AFTER PROLONGED WATER BOIL

(Fiber Sample No. A)[a]

As Prepared (Control)					After 72 Hours		After 144 Hours	
Weight % Resin	Volume % Fiber	Density g/cc	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}
36.8	59.3	1.34	71.9	6.6	64.4	6.[illegible]	65.5	6.6

[a]Average single filament properties: 184 x 10^3 PSI tensile strength; 24.1 x 10^3 PSI tensile modulus

TABLE IV

EFFECT OF 2-HOUR WATER BOIL ON EPOXY YARN COATINGS BALANCED 8-PLY BIDIRECTIONAL COMPOSITES

(Fiber Sample No. A)[a]

	As Prepared (Control)		2-Hour Water Boil	
Coating[b]	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}
Epon 834	74.4	8.3	74.4	8.7
Epon 1001	79.7	9.4	79.7	8.0
Epon 1010	73.0	8.4	75.5	8.9
Epon 1031	76.9	9.2	75.5	9.0
Eponol-53-B-40	76.3	8.4	75.5	8.6

[a]Single filament properties and composite fiber volumes are as listed in Table 8

[b]Coatings (Shell Chemical Co.) were in the range of about 0.6 to 0.9 weight percent based upon fiber weight

Table V demonstrated that the properties of the yarn C composites were also not significantly altered by a 2-hour water boil. Short-beam shear stress and flexural strength and modulus were virtually unchanged by the water boil.

Table VI shows that flexural modulus does not seem affected and strength parameters have decreased 11 and 14% after 2- and 24-hour periods, respectively, for the B fiber composites.

Thus, water boil tests on epoxy resin composites prepared with polyvinyl alcohol coated graphite fibers, epoxy resin coated graphite fibers, and uncoated graphite fibers indicate only mildly deleterious effects. Based on these results it appears that graphite fiber reinforced composites, unlike glass fiber reinforced composites, may not require fiber treatments to maintain composite mechanical properties during long periods of humid atmospheric exposure.

EPOXY COATINGS FOR GRAPHITE YARN

Graphite fiber coatings were supplied by the Plastics and Composites Branch (MANC) for application (during fiber preparation by Union Carbide Corporation) to 5-ply yarns of the Thornel 25 type. Initially, a 2% solid solution in trichloroethane of various epoxy resins was used as the coating medium. Most of the epoxy resins used in the coating investigation were of the epichlorohydrin, bisphenol A type and ranged in average molecular weight from about 470 to 80,000. Epon 1031 differed in structure and was tetra-functional with an estimated average molecular weight of about 1000. Union Carbide (U.C.C.) rated the handling characteristics during yarn fabrication and MANC rated them during tape winding. Table VII is indicative of handling characteristics as described by both organizations. Reexamination of the yarn coating procedures showed that mechanical handling during the coating procedure existed to at least some degree.

The yarn coatings were repeated with the elimination of mechanical handling prior to and during the application of epoxy resin coatings. This second set of yarns was of 2-ply construction and a 1% resin solution was used as the coating medium. Resin pickup was approximately 0.6 to 0.9% by weight. Accordingly, tapes using these yarns were wound and epoxy matrix composites were prepared and evaluated (Table VIII). All yarns coated by the second procedure handled satisfactorily during tape winding. Inspection of the data (Table VIII) indicates generally similar initial property levels for all the yarns coated with the epoxy resins as well as properties not significantly different from composites fabricated using similar yarns coated with 0.1% polyvinyl alcohol.

Although the choice of graphite yarn coatings would involve considerations of the coating compatibility with composite resin matrices, the data seem to indicate that materials of even very low molecular weights are adequate as coatings and impart good handling characteristics to graphite yarns if the coatings are applied to the graphite yarns prior to subjection of the yarns to mechanical contact.

FATIGUE, AND BALLISTIC IMPACT

Most of our effort to date has concerned the characterization of graphite/epoxy composites as to static properties. High performance composite structural elements are obviously subjected to dynamic and repeated loads. Thus, investigations were initiated to characterize graphite/epoxy composites under alternating loadings in tensile fatigue and under an induced high rate of strain as in ballistic impact tests. These evaluations are, as yet, in a very preliminary stage and have used only Fiber A (Thornel 25) as the composite reinforcement.

TABLE V

AVERAGE FLEXURAL AND SHEAR PROPERTIES OF A 10-PLY UNIDIRECTIONAL GRAPHITE YARN COMPOSITE AFTER 2-HOUR WATER BOIL

(Fiber Sample No. C)[a]

Before Water Boil			After Water Boil		
Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Short Beam Shear Stress PSI x 10^{-3}	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Short Beam Shear Stress PSI x 10^{-3}
80.3	21.6	2.97	77.3	20.9	2.98

[a]Average single filament properties: 231 x 10^3 PSI tensile strength
39.1 x 10^6 PSI tensile modulus

TABLE VI

AVERAGE FLEXURAL PROPERTIES OF 8-PLY BALANCED BIDIRECTIONAL GRAPHITE COMPOSITES AFTER 2 AND 24 HOURS' WATER BOIL

(Fiber Sample No. B)[a]

Composite	Weight % Resin	Volume % Fiber	Density (g/cc)	As Prepared		After 2 Hours	
				Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}
A	43.6	51.0	1.37	9.9	82.6	9.2	73.4
				As Prepared		After 24 Hours	
B	33.0	61.9	1.38	11.0	89.2	11.5	76.8

[a]Average single filament properties: 213 x 10^3 PSI tensile strength
32.0 x 10^6 PSI tensile modulus

TABLE VII

INITIAL EPOXY COATED GRAPHITE YARN HANDLING CHARACTERISTICS

(Yarns Subjected to Mechanical Handling During Resin Coating)

Coating	U.C.C. Yarn Characterization	MANC Tape Characterization
Epon 834	Poor	Very Poor
Epon 1001	Poor	Awful
Epon 1010	Good	Poor
Epon 1031	Poor	Poor
Eponol-53-B-40	Very Good	Good

TABLE VIII

EVALUATION OF EPOXY YARN COATINGS IN BIDIRECTIONAL COMPOSITES[a]

(Yarns Not Subjected to Mechanical Handling During Resin Coating)
(Fiber Sample A)

	Average Uncoated Single Filament Properties		Average Composite Properties				
Coating	Tensile Strength PSI x 10^{-3}	Tensile Modulus PSI x 10^{-6}	Fiber Vol. %	Flexural Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Short Beam Shear Stress PSI x 10^{-3}	Plate Shear Modulus PSI x 10^{-5}
Epon 834	174.5	25.2	50.9	74.4	8.3	3.2	6.1
Epon 1001	172.0	25.6	62.6	79.7	9.4	2.6	6.9
Epon 1010	169.0	26.5	54.3	73.0	8.4	3.1	6.1
Epon 1031	182.1	25.8	54.8	76.9	9.2	2.7	7.0
Epon-53-B-40	165.0	26.2	57.6	76.3	8.4	2.8	6.9

[a] Balanced 8-ply bidirectional composites evaluated in flexure and shear

Fatigue

Fatigue data are graphically illustrated in Figure 1, where curves are displayed which compare continuous beryllium and glass composites to a continuous graphite/epoxy composite. The graphite and beryllium composites used the same matrix and were fabricated as described in the fabrication section of this paper. The beryllium, glass (Scotchply), and graphite composites were of 12-ply, bidirectional (0°, 90°) balanced construction.

Although none of the specimens failed in the grip area, a good portion of the samples did fail outside the gage length, which would account for some of the data scatter. All stresses were calculated using the gage section area.

Table IX lists the ultimate static tensile strength of the beryllium, glass, and graphite/epoxy composites.

Throughout the repetitive tensile-tensile cycles, the graphite/epoxy composites were able to sustain a considerably greater percentage of their ultimate stress than either the beryllium or glass c mposites at similar numbers of cyclic loadings.

Both the beryllium and glass composites failed at about 10^4 cycles at 70% of the ultimate strength, but the graphite composite specimens resisted the same cycling while stressed to 90% of ultimate strength.

For the higher number of alternating cyclic loadings, it was observed that the graphite/epoxy composites were able to withstand 10^7 cycles when stressed to 70% ultimate strength. Conversely, the beryllium and glass composites maintained less than 45% of their ultimate strengths for the increased cycling.

Two of the continuous graphite/epoxy specimens which were cycled at 50 to 70% ultimate tensile strength for 26×10^6 and 17×10^6 cycles, respectively, without failure, were subjected to static tensile tests to determine the retention of ultimate strength. The tests indicated that the samples possessed over 92% of their original tensile strengths.

Ballistic Impact

Very preliminary data is presented showing the effect of high-speed projectiles striking graphite/epoxy panels (Table X). All panels were bidirectional and were of various thicknesses.

The criterion for failure is the formation of a crack which can be observed optically at 10X to 30X magnification on the reverse side or tension side of the impression. Impact resistance is defined as the maximum energy imparted to the specimens without inducing failure. Although data is sparse and no attempt has been made to correct the results to a normalized thickness, the difference in the thicknesses of the 7-ply graphite/epoxy composite and the beryllium and glass Scotchply panels is relatively small. Therefore, based on initial trials, it appears that the graphite composites are superior to the Scotchply composites, yet inferior to the bidirectional beryllium epoxy panel for the configuration tested.

MECHANICAL PROPERTIES OF GRAPHITE/EPOXY COMPOSITES

Tables XI through XIX are representative of the mechanical properties of epoxy matrix composites fabricated with graphite fiber reinforcements described in Table I. Each table also contains fiber property data, as sampled from the actual spool used in winding or on a batch basis as was the case with the RAE tow.

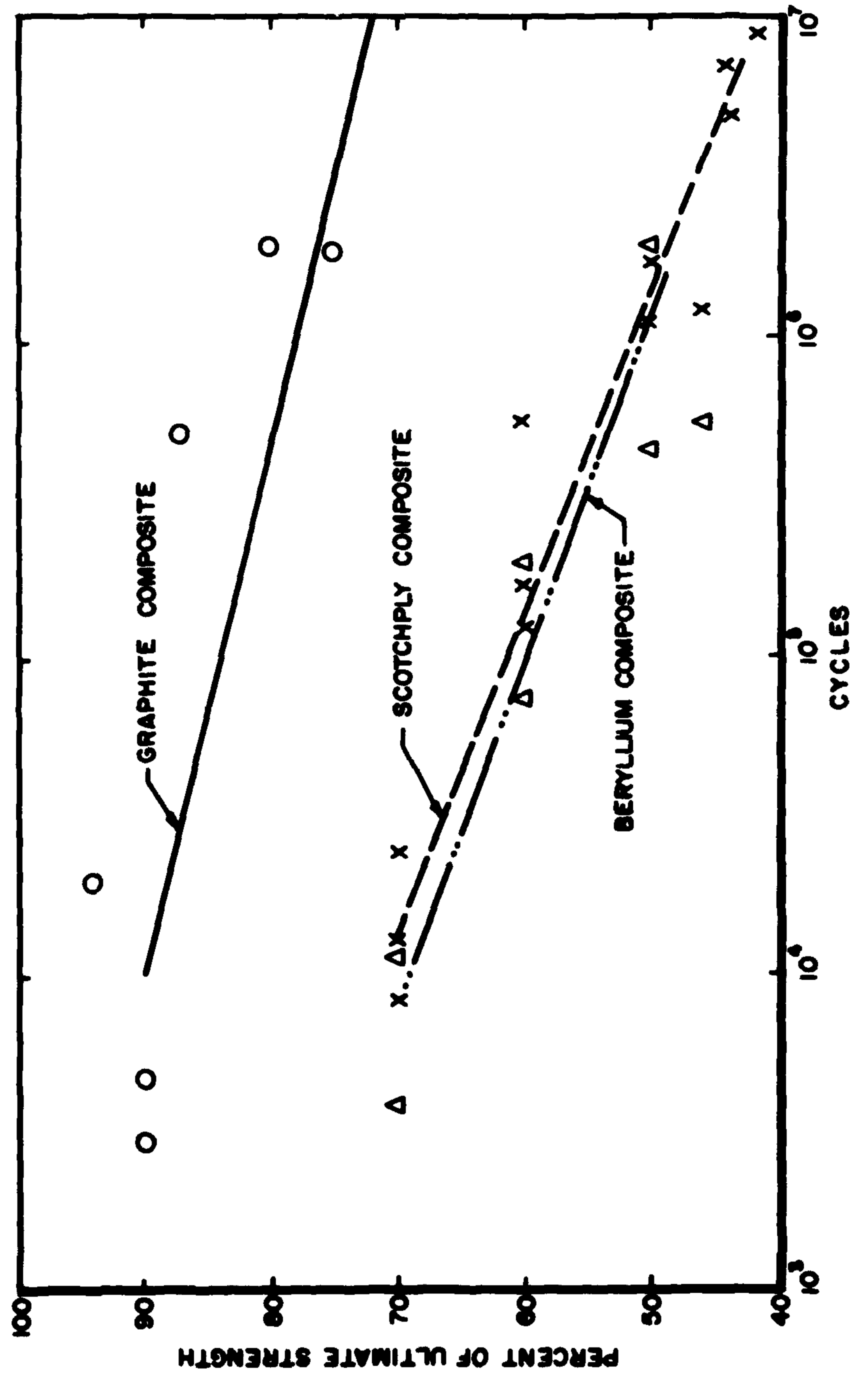

Figure 1. Comparison of S-N Curves of Graphite, Beryllium, and Scotchply Composites

TABLE IX

ULTIMATE TENSILE STRENGTH OF BERYLLIUM, SCOTCHPLY, AND GRAPHITE[a]/EPOXY BIDIRECTIONAL COMPOSITES

(Graphite Fiber Sample No. A)[a]

Composite	Gage Width	No. of Tested Specimens	Average Ultimate Strength PSI x 10^{-3}
Scotchply	1/2 in.	2	56.8
Beryllium	1/2 in.	2	43.0
Graphite	1/2 in.	2	38.9

[a]Average single filament properties: 158 x 10^3 PSI tensile strength
26.8 x 10^6 tensile modulus

TABLE X

BALLISTIC IMPACT RESISTANCE OF BIDIRECTIONAL COMPOSITES

Material	Thickness (inches)	Volume % Fiber	Impact Resistance (foot-pounds)
Graphite/epoxy (7 plies)	0.063 - 0.066	63.3	0.157
Graphite/epoxy (10 plies)	0.085 - 0.090	62.2	0.417
Graphite/epoxy (12 plies)	0.098 - 0.101	63.9	0.499
Scotchply	0.068 - 0.072	65.0	0.072
Be wire/epoxy	0.071 - 0.074	50.0	0.339

Fiber volume calculations were based on densities of 1.42, 1.50, 1.90, and 1.90 g/ml for Fibers A, B, C, and D, respectively. A density of 1.2 g/ml was used for the epoxy resin matrix.

Shear data were low for all composites and as true shear breaks were not clearly evident for the majority of the 0° unidirectional and bidirectional specimens, actual shear strength values can be expected to be somewhat higher than the reported shear stress values. The mode of failure appeared to be one of crushing or a combination of crushing on the face of the beam under the loading nose and tension on the opposite face.

Flexure specimens typically failed in a manner similar to that encountered in the shear tests.

Ultimate tensile strengths were extremely difficult to obtain as none of the breaks, except those reported for composites of Fiber B, occurred in the gage lengths.

Tables XI and XII are indicative of properties obtained from unidirectional and bidirectional composites using Fiber A (Thornel 25) as the reinforcement.

The data presented in Tables XIII and XIV consist of results obtained with the Fiber B (Thornel 40) reinforced composites. Both the unidirectional and bidirectional properties are higher than those obtained with the continuous Fiber A composites. It has been observed that as the longitudinal modulus of graphite filaments is increased, there is a noticeable decrease for short beam shear values. This is especially noticeable when comparing the Fiber A and B composites to the Fiber C and D composites, of which the latter have moduli that are significantly higher. The near circular cross-section of the C and D fibers, an outcome of the particular precursor employed, reduces the surface area and perhaps the possibility of mechanical interlock with the matrix. The cross-section of the B fibers are still highly irregular and although shear values are not extremely pronounced over the C and D fibers, they are greater. It seems obvious that different fiber morphologies and fiber finishes are also factors which may affect the shear values; however, coupling must be improved to realize high translation efficiencies of current and future graphite fiber reinforcements.

The only unidirectional tensile strength reported is for the B fiber composites. Special preparation of the specimens consisted of "dog-boning" the faces as well as the sides in order to facilitate a gage break. Attempts to obtain tensile strengths for the A, C, and D unidirectional composites did not use this method of specimen preparation and resulted in grip and shoulder breaks and low values.

Table XV depicts the properties of the Fiber C reinforced composites. As described earlier in this report and as apparent from the unidirectional data, control of fiber volume and, in turn, mechanical properties is a problem when fabricating with short lengths of tow. Short-beam shear stress values were particularly low for the bidirectional composites.

Although somewhat better control of fiber volume was obtained with the Fiber D composites (Tables XVI and XVII), the fabrication technique with graphite tow does not seem to lend itself to the fabrication of composite panels of significant size. The tensile and flexural moduli are higher than those of the Fiber A, B, and C composites. Notably, however, fiber strength translation as determined from flexural strength data, is low (about 40%) compared to the B composites (greater than 95%).

Tables XVIII and XIX are composed of unidirectional and bidirectional data, respectively, taken from the previous mechanical property tables and normalized to 60 volume percent to simplify comparison of the various composites.

TABLE XI

AVERAGE MECHANICAL PROPERTY DATA OF A 10-PLY UNIDIRECTIONAL GRAPHITE/EPOXY COMPOSITE[a]

(Fiber Sample No. A)[b]

Weight % Resin	Volume % Fiber	Density (g/cc)	Tensile Modulus PSI x 10^{-6}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Shear Modulus PSI x 10^{-5}	Short Beam Shear Stress PSI x 10^{-3}
34.0	62.1	1.36	13.9	13.1	117	7.8	3.8

[a]Specimens were cut from an 8-1/4 in. x 8-1/4 in. panel

[b]Average singlefilament properties: 195 x 10^3 PSI tensile strength
25.5 x 10^6 PSI tensile modulus

TABLE XII

AVERAGE MECHANICAL PROPERTY DATA OF A BIDIRECTIONAL COMPOSITE[a]

(Fiber Sample No. A)[b]

Weight % Resin	Volume % Fiber	Density (g/cc)	$(0°)^c$ Tensile Modulus PSI x 10^{-6}	$(0°)^c$ Flexural Modulus PSI x 10^{-6}	$(0°)^c$ Flexural Strength PSI x 10^{-3}	$(0°)^c$ Compression Modulus PSI x 10^{-6}	$(0°)^c$ Compression Strength PSI x 10^{-3}	$(0°)^c$ Short Beam Shear Stress PSI x 10^{-3}
32.8	62.8	1.35	7.1	7.2	73.4	7.0	44.4	3.1
			$(90°)^c$ Flexural Modulus PSI x 10^{-6}	$(90°)^c$ Flexural Strength PSI x 10^{-3}	$(90°)^c$ Short Beam Shear Stress PSI x 10^{-3}	$(0°-90°)^c$ Shear Modulus PSI x 10^{-5}		
			4.4	58.8	3.0	9.2		

[a]Specimens were cut from an 8-1/4 in. x 8-1/4 in. x 12 ply, balanced panel

[b]Average single filament properties: 185 x 10^3 PSI tensile strength; 26.8 x 10^6 PSI tensile modulus

[c]Denotes fiber direction of outer plies in relation to applied load

TABLE XIII

AVERAGE MECHANICAL PROPERTY DATA OF UNIDIRECTIONAL GRAPHITE YARN/EPOXY COMPOSITES

(Fiber Sample No. B)[a]

As Prepared Composite Description	Weight % Resin	Volume % Fiber	Density (g/cc)	Tensile[b] Modulus PSI x 10^{-6}	Tensile Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Short Beam Shear Stress PSI x 10^{-3}
6 in. x 1/4 in. x 8 plies	33.1	61.7	1.38	18.3		15.3	123.4	
6 in. x 1/4 in. x 8 plies	38.5	56.1	1.38	19.6		14.9	123.0	
6 in. x 1/4 in. x 8 plies	30.9	64.0	1.41	19.2		15.5	124.6	
4-1/4 in. x 4-1/4 in. x 8 in. plies	31.7	63.3	1.39	----		16.1	121.9	
8-1/4 in. x 8-1/4 in. x 10 plies	30.9	64.0	1.40	18.3		----	----	4.7
4-1/4 in. x 4-1/4 in. x 14 plies	40.1	54.5	1.40	18.9	116.5	----	----	----

[a]Average single filament properties: 205 x 10^3 PSI tensile strength; 35 x 10^6 PSI tensile modulus

[b]Only one test was performed for the 6 in. x 1/4 in. specimens. A minimum of 4 samples were cut, tested and averaged from the 4-1/4 in. x 4-1/4 in. and 8-1/4 x 8-1/4 in. panels respectively

TABLE XIV

BIDIRECTIONAL (0°, 90°) COMPOSITE MECHANICAL PROPERTY DATA

(Fiber Sample No. B)[a]

Panel A[b] Weight % Resin	Volume % Fiber	Density (g/cc)	$(0^o)^f$ Tensile Modulus PSI x 10^{-6}	Tensile Strength PSI x 10^{-3}	Compression Modulus PSI x 10^{-6}	Compression Strength PSI x 10^{-3}	Short Beam Shear Stress PSI x 10^{-3}
37.8	56.8	1.39	10.0	59.1	9.7	49.3	3.1[e]
			$(90^o)^f$				
			10.3	61.9	9.7	56.4	3.0[d]

Panel B[c] Weight % Resin	Volume % Fiber	Density (g/cc)	$(0^\circ)^f$ Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Short Beam Shear Stress PSI x 10^{-3}
39.3	55.2	1.37	10.8	93.4	3.5[e]
			$(90^o)^f$		
			5.5	73.3	2.9[d]

[a] Average single filament properties: 212 x 10^3 PSI tensile strength, 32 x 10^6 PSI tensile modulus

[b] Specimens were cut from an 8-1/4 in. x 8-1/4 in. x 8 ply balanced panel. Shear modulus = 1.31 x 10^6 PSI

[c] Specimens were cut from a 4-1/4 in. x 4-1/4 in. x 8 ply, balanced panel

[d] Interlaminar shear failures occurred

[e] Local failures occurred under concentrated load

[f] Denotes fiber direction of outer plies in relation to applied load

TABLE XV

AVERAGE FLEXURAL AND SHEAR PROPERTIES OF UNIDIRECTIONAL AND BIDIRECTIONAL[a] GRAPHITE YARN/EPOXY COMPOSITES

(Fiber Sample No. C)[b]

Configuration and Panel Number	Weight % Resin	Volume % Fiber	Density (g/cc)	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Shear Modulus PSI x 10^{-6}	Short Beam Shear Stress PSI x 10^{-3}
Unidirectional							
EY-4	62.4	27.6	--	5.9	50.3	0.3	3.4
EY-5	33.7	55.4	1.59	13.7	68.1	0.7	3.1
EY-7	25.1	65.4	1.66	21.6	80.2	1.0	3.6
Bidirectional							
EY-1	32.7	56.6	1.60	14.3	61.1	0.8	2.6
EY-2	24.4	66.2	1.64	15.7	57.8	0.8	1.9
EY-3	23.9	67.0	1.66	15.1	55.7	0.9	1.6

[a] 8 plies (0°, 90°), balanced

[b] Average Single Filament Properties: 231 x 10^3 PSI tensile strength
39.1 x 10^6 PSI tensile modulus

TABLE XVI

AVERAGE[a] MECHANICAL PROPERTY DATA OF 10-PLY UNIDIRECTIONAL GRAPHITE/EPOXY COMPOSITES[a]

(Fiber Sample No. D)[b]

Sample	Weight % Resin	Volume% Fiber	Density (g/cc)	Tensile Modulus PSI x 10^{-6}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Short Beam Shear Stress PSI x 10^{-3}
EY-15-1	29.9	59.8	1.63	26.0	20.9	92.9	3.5
EY-15-2	36.8	52.0	1.54	22.1	18.5	74.5	3.6
EY-15-3	31.0	58.5	1.63	28.3	22.1	97.3	4.0

[a] Each sample was 6 in. x 1/4 in.

[b] Average single filament properties: 296 x 10^3 PSI tensile strength
47.3 x 10^6 PSI tensile modulus

TABLE XVII

ELASTIC MODULI OF UNIDIRECTIONAL GRAPHITE YARN/EPOXY COMPOSITES

(Fiber Sample No. D)[a]

Sample	Configuration	Weight % Resin	Volume % Fiber	Density (g/cc)	Tensile Modulus PSI x 10^{-6}	Shear Modulus PSI x 10^{-5}
EY-11	0°	38.4	51.4	1.57	24.4	6.1
EY-14	90°	23.0	67.9	1.68	0.65	8.8

[a] Average Single Filament Properties: 296 x 10^3 PSI tensile strength
47.3 x 10^6 PSI tensile modulus

TABLE XVIII

COMPARISON OF UNIDIRECTIONAL COMPOSITE MECHANICAL PROPERTY DATA NORMALIZED TO 60 VOLUME PERCENT FIBER

	Tensile Modulus PSI x 10^{-6}	Tensile Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Shear Modulus PSI x 10^{-6}	Short Beam Shear Stress PSI x 10^{-3}
Fiber A	18.4	---	12.7	113.0	0.8	3.6 (5.2)
Fiber B	18.9	128	15.2	121.0	1.2	4.4
Fiber C	---	---	17.3	73.7	0.8	3.1
Fiber D	26.9	---	22.0	93.0	---	3.9

TABLE XIX

COMPARISON OF BIDIRECTIONAL (0°, 90°) COMPOSITE MECHANICAL PROPERTY DATA NORMALIZED TO 60 VOLUME PERCENT FIBER

	(0°)					
	Tensile Modulus PSI x 10^{-6}	Tensile Strength PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Compression Modulus PSI x 10^{-3}	Compression Strength PSI x 10^{-3}
Fiber A	6.82	---	6.95	70.8	6.7	42.8
Fiber B	10.5	62.5	11.7	101.5	10.2	52.1
Fiber C	---	---	14.3	55.7	---	---
	(90°)[a]					
	Short Beam Shear PSI x 10^{-3}	Flexural Modulus PSI x 10^{-6}	Flexural Strength PSI x 10^{-3}	Shear Strength PSI x 10^{-3}	Shear Modulus PSI x 10^{-6}	
Fiber A	3.0	4.23	56.7	2.9	0.9	
Fiber B	3.3	5.99	79.8	3.2	1.4	
Fiber C	1.9	---	---	---	0.8	

[a] Denotes fiber direction of outer plies in relation to applied load

The shear value expressed in parenthesis (Table XVIII) for the A composite is probably a more realistic average since it is based on a large number of tested samples from different populations (Reference 1).

FUNDAMENTAL MECHANICAL ANALYSES OF COMPOSITE DATA

The mechanical properties presented in each of the preceding tables have all been calculated from conventional equations for homogeneous materials; i.e., the difference in moduli of the individual plies and the geometry of the stacking sequence are not considered in these equations. Although the properties defined in this way are useful for quality control and comparison of materials, they do not represent intrinsic material properties of the composite material being tested. If the mechanical properties of the individual plies of a laminated beam are known, the response of the number can be predicted. Therefore, to obtain a measure of the accuracy of the experiments and the quality of the fabrication processes, it is important to correlate the data in a particular table. Furthermore, since it is difficult to measure the longitudinal strength of a composite containing high strength filaments in a tension test, one can estimate this property from the results of a flexural test. In view of this discussion, the flexure results will be analyzed by the equations presented in Reference 2.

The longitudinal and transverse moduli of a unidirectional ply, E_L and E_T, respectively, can be determined from the flexural moduli (moduli computed by the use of the homogeneous beam expression of the 0° and 90° bidirectional beams. However, E_T is very low, and the calculation for this quantity is subject to a large (percentage) error due to small variations in the measured data. Hence the value of E_T measured in the tension test was utilized, and the average value of E_L calculated from the flexural moduli of the 0° and 90° bidirectional beams was employed for subsequent calculations. The value E_L is determined by the expression

$$E' = \frac{F}{N^3} \tag{1}$$

where E_i is Young's modulus of the i^{th} ply in the direction of the beam axis,

$$F = 8 \sum_{i=1}^{n} E_i \, (3i^2 - 3i + 1) \tag{2}$$

and E' is the flexural modulus, $N = 2n$ is the number of plies, the top (and bottom) ply of the balanced laminate being represented by $i = n$.

The longitudinal tensile strength of a unidirectional composite can be estimated from the reported strength of the 0° bidirectional beam. Let σ' represent the maximum stress given by the homogeneous flexure formula, i.e., the value given in the preceding tables. The longitudinal strength of a unidirectional composite, σ_m, can be approximated by

$$\sigma_m = \frac{\sigma' N^3 E_n}{F} \tag{3}$$

Letting τ' represent the conventional calculation for interlaminar shear stress and τ_m, the corrected value as discussed in Equation 2, then τ' and τ_m and related by

$$\tau_m = \frac{\tau' NH}{F} \tag{4}$$

where

$$H = 4 \sum_{i=1}^{n} \varepsilon_i (2i - 1) \qquad (5)$$

Applying Equations 1 through 5 to the reported data yields results shown in Table XX.

The quantities in parentheses in Table XX represent experimental values reported for the unidirectional flexure tests in the present paper. Good agreement is observed here between theory and experiment. Poor correlation, however, is noted between the C composite unidirectional and bidirectional beams containing approximately 56% filaments (Table XV). This is evidently an example of the difficulties in fabrication and data scatter of filament properties, which were noted earlier in this report.

The flexural moduli of bidirectional laminates may be used as a means of comparing material performance; however, a stacking sequence of fixed identity should be used in the comparison. To compare the A composite flex properties to the analogous data for the other two materials, the former were recalculated through Equations 1, 2, and 3 on the basis of an 8-ply bidirectional laminate. The moduli of the Thornel 25 epoxy 0° and 90° bidirectional beams and the reported strength of the 0° beam are thus found to be 7.8×10^6, 3.8×10^6, and 79.7×10^3, respectively, which are more realistic figures for comparative purposes than the respective values of 7.2×10^6, 4.4×10^6, and 73.4×10^3 as reported in Table XII. The differences are not large in the present case but they would be more pronounced as the number of plies decrease.

Reasonable correlation seems to exist between the elastic moduli measured in the flexure and axial experiments. Typically, for the span-to-depth ratio of 20 employed, the longitudinal modulus measured in the flex tests is lower than that determined from the axial test. If the effect of shear deflection is considered (Reference 2), these values are brought into closer agreement.

FABRICATION

The epoxy resin matrix system utilized throughout this study consisted of 100 parts by weight ERL 2256 resin, and 27 parts by weight ZZL 0820 hardener, dissolved in 80 parts by weight methylethyl ketone (MEK).

The continuous graphite yarns were passed through a resin pot and wound about a mandrel covered with a removable Teflon-coated tape. A tension of approximately 1/4 lb was maintained from takeoff to mandrel take-up. The MEK was allowed to evaporate and the resin was B-staged at room temperature (usually 24 hours) which imparted good handling characteristics to the resultant prepreg tapes.

Since only short lengths of RAE tow were available, the tows were individually aligned on a Teflon-coated fabric, affixed at the two ends by means of masking tape, impregnated by spraying of the catalyzed resin solution, and B-staged to a handling consistency similar to those prepregs that were filament wound.

Prepreg tapes of both the continuous and discontinuous filaments were cut to fit various molds and laid-up in two configurations, i.e., unidirectional and bidirectional. The majority of the bidirectional panels were symmetrically laid-up with a 0° and 90° alternation of plies with respect to the central axis of the panel.

The curing cycle consisted of 2 hours at 180°F and 4 hours at 300°F. A pressure of 100 PSI was maintained throughout the cycle.

TABLE XX

MATERIAL PROPERTIES COMPUTED FROM FLEXURE TESTS
AND COMPARISON WITH EXPERIMENT

	E_L, 10^6 PSI	σ_m, 10^3 PSI	τ_m, 0°, 10^3 PSI	τ_m, 90°, 10^3 PSI
Fiber A Composite	10.5 (13.1)	111 (111)	2.89	3.22
V/F	63			
Fiber B Composite	17.0 [illegible]6.1)	127 (121)	2.80	3.45
V/F	62		56	
Fiber C Composite	22.1 (21.6)	81.7 (80.2)	----	----
V/F	66			

TESTING

Mechanical property data was obtained using procedures of Federal Test Specification L-P406b as a general guide. Flexural tests were conducted using the three-point loading method with a span-to-depth ratio of 20 to 1. Tensile modulus values were determined by testing rectangular coupons, whereas "dog-boned" specimens were employed for the determination of tensile strength. Short-beam shear values were obtained by the three-point loading method with samples of a 6-to-1 span-to-depth ratio. Shear modulus tests were performed on as-prepared panels according to the plate twist method discussed by Tsai (Reference 3). Compression moduli were obtained from rectangular coupons and strength values from "dog-boned" samples. Composite densities were measured by water immersion. Volume percent fiber calculations were acquired assuming a voidless composite, via a resin dissolution technique developed by Kuhbander (Reference 4). Data not reported herein has indicated that the graphite composites described have void contents of only a few tenths of a percent, or less.

Unless otherwise specified, tests performed on bidirectional composites were with the outer plies in the longitudinal (0°) direction of the specimen.

The fatigue tests were conducted using a Schenck fatigue machine which is equipped with automatic mean and alteration load maintainers. The fatigue cycling consisted of tensile loading to a particular stress level and returning to 1/10 of the original tensile stress imposed. All tests were performed at room temperature and at a frequency of approximately 2200 cycles per minute.

Generally, the ballistic impact test consisted of imparting a 0.174-inch-diameter copper-coated steel B-B projectile at a 2 in. x 2 in. panel clamped in a vise. A Benjamin air rifle which has been modified to utilize a compressed nitrogen gas supply was used. A pressure regulator was used to control the gas pressures which, in turn, determined the velocity of the projectile.

SECTION III

CONCLUSIONS

The previously reported contention that graphite fibers appear of high promise for the development of high performance plastic composites is felt to have been further substantiated by this more recent effort.

Fundamental mechanical analyses of current experimental graphite composite data appears to reinforce this assessment.

Prolonged water boil of Thornel 25 and Thornel 40 graphite fiber reinforced epoxy resin matrix composites did not result in substantial decreases in flexural properties.

Several uncatalyzed epoxy resins were applied as finishes to Thornel 25 graphite yarns during yarn preparation. The epoxy finishes varied both in molecular weight and epoxide equivalents and were applied in amounts of about 0.6 to 0.9 weight percent. Subsequent mechanical property determinations of epoxy composites yielded results equivalent to those obtained with yarns conventionally coated with 0.1 weight percent of polyvinyl alcohol. All the coated yarns were approximately equivalent in handling characteristics when mechanical handling was avoided prior or during resin coating application to the yarns.

Composites prepared from continuous Throนel 25 and Thornel 40 yarns by tape winding exhibited better general translation of fiber properties than did composites prepared from the short lengths RAE graphite tow. In part, at least, this seems attributable to the generally poorer composite quality associated with the hand lay-up technique which was used in fabrication of composites with RAE tow.

Short-beam shear tests of graphite composites typically results in failure modes other than interlaminar shear and were reported as shear stress values. However, a clear trend of decreasing composite shear values with increasing graphite fiber moduli seems evident. Accordingly, efforts are now underway to improve the shear values of graphite composites as well as other mechanical properties of composites by fiber treatments to promote fiber-resin bonding.

Initial fatigue data indicate epoxy resin graphite composites to be superior to comparable beryllium and glass filament reinforced composites.

Preliminary ballistic impact data show graphite composites to sustain higher impact loadings than glass composites and lower impact loadings than beryllium composites.

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13. ABSTRACT

Four types of graphite fibers were utilized as reinforcements in a continuing experimental program of the fabrication and evaluation of epoxy resin matrix composites. Resultant composite data and analyses continue to demonstrate a high promise for graphite fiber reinforced resin composites as high performance materials.

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