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Mechanical Properties of a High-Modulus Polyamide-Hydrazide Fiber in Composites and of the Polyamide-Hydrazide Fiber and Fabric Composites*

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ABSTRACT

Unidirectional, bidirectional, and fabric laminates were made of one type of X-500 fiber and fabric using, mainly, an epoxy-based matrix and other thermosetting and thermoplastic resins. This particular X-500 fiber (PABH-T), a polyamide-hydrazide, was found to be compatible with most of the resins tried, both with respect to inertness to the fiber and with respect to adhesion. Unidirectional composite properties, including longitudinal tensile modulus and strength, transverse modulus and strength, and shear modulus and strength, were measured. From the measured

*Contribution from the Chemstrand Research Center, Inc., a subsidiary of Monsanto Company.

transverse and shear unidirectional laminate moduli, the transverse modulus and shear modulus of the PABH-T X-500 fibers were measured. To reduce the amount of sample preparation and testing, and to make comparisons of PABH-T X-500 composite stiffness properties to glass fiber and other composites, computational procedures for estimating the stiffness properties of various laminates were worked out so that the comparisons could be made on an equal volume fraction basis with any matrix whose modulus and Poisson's ratio is known. At the 60% volume fraction level, the PABH-T X-500 composite's specific longitudinal tensile Young's modulus was typically 170×10^6 in. while the transverse specific Young modulus was 10×10^6 in., which would produce a quasi-isotropic laminate with a specific tensile Young's modulus of 72×10^6 in. and a specific in-plane shear modulus of 24×10^6 in. Properties measured on bidirectional and fabric laminates are also given.

1. INTRODUCTION

The chemical structure of the PABH-T X-500* molecule is

The Young's modulus of the oriented fiber, 13.9×10^6 psi according to our mechanical measurements, is remarkably high for an organic polymer and is presumably due to the stiff molecular chain. The Young's modulus of this particular chain configuration should be approximately one-half again that of the polyethylene terephthalate (PET) chain due to the reduced number of aliphatic groups in the chain. The theoretical modulus of the PET chain is 22×10^5 psi as calculated by Lyons [1] in 1958. Treloar [2] calculated a value

*PABH-T X-500 is one member of the X-500 family, a generic term denoting high modulus organic fibers made by Monsanto Co. The polymer is derived from p-aminobenzhydrazide (PABH) and terephthaloyl chloride (T), thus the specie name, PABH-T.

of 18×10^6 in 1960 for the PET molecule. Dulmage and Contois [3] measured a value for PET of 15.7×10^6 psi by x-ray techniques. We should then expect the modulus of the X-500 chain to be about 25×10^6 psi. The fact that actual fibers can be made which have half of this value is quite remarkable for a synthetic fiber. Theoretically, the rupture stress ought to be at least 3% of the actual modulus of the material [4, 5], which would be 420×10^3 psi. Since theoretical values are often obtained in real materials, the measured value for PABH-T X-500 (230×10^2 psi) is considerably below what we would expect for this material which indicates it contains many fiber flaws. The theoretical strength of the X-500 chain should be about 750×10^3 psi.

2. MATERIALS

The PABH-T X-500 fibers used in this work were made so as to achieve a high modulus material consistent with spinning methods economically reasonable at the time. Fiber properties are shown in Table 1. Fabric laminate and composites made with resins other than epoxy and polyester were made from PABH-T X-500 yarns which may have slightly different properties. A "noncommercial" S-glass roving, which had an epoxy compatible; high tensile strength, finish on it, was purchased from Owens Corning.

The PABH-T X-500 yarn that was used was typically 640 den, 90 filament, and had directly measured properties as follows: den/filament, 3.92 ± 4.77% (coefficient of variation); tenacity, 207 ksi ± 4.4%; elongation to break, 3.5 ± 8.7%; initial Young's modulus, 10.1 msi ± 4.3%; and energy to break, 5.8 ksi ± 10.0% at 1 in. gauge length, 20% elongation/min, 70°F, and 65% RH (ksi and msi represent thousand and million pounds per square inch, respectively).

It was found that a number of corrections had to be applied to these data. First, the high modulus of these fibers calls for a stiffness correction to the vibrascope denier. This effect amounted to about 10% increases of the apparent denier. Also, clamp effects and machine compliance were found to result in a low value for the modulus and a high value for the elongation.

The overall vibrascope correction brought the vibrascope and weighed deniers into agreement within 2%. The clamp/compliance correction is more uncertain however. Applying these corrections, an elongation of 2.8%, a tenacity of 240 ksi, and a modulus of 13.9 msi was obtained for the yarn properties.

TABLE 1. Tensile Tests of Impregnated Yarn

Notes	Weight unit length (mg/cm)	Fracture load (lb)	Slope (lb/%)	Gauge length (in.)	Fracture strain (%)
PABM T/X 500, not wiped, 50%/min	1.35 ± 0.17%[a]	15.5 ± 2.8%	5.3 ± 3.4%	2.0	3.13 ± 2.4%
PABM T/X 500, wiped, 20%/min, 700 den	1.70 ± 3.5%	17.0 ± 5.4%	6.8 ± 5.2%	1.0	3.72 ± 10.5%
	1.64 ± 6.1%	17.3 ± 2.4%	7.8 ± 9.4%	2.5	2.65 ± 3.2%
PABM T/X 500, wiped while hot, 20%/min, 700 den	1.87 ± 4.3%	17.3 ± 5.4%	9.3 ± 4.1%	2.5	3.40 ± 12.4%
	1.76 ± 10%	16.95 ± 3.4%	10.2 ± 4.3%	5.0	2.40 ± 9.8%
S glass, wiped while hot, 20%/min, 3743 den, occasional clamp slip	12.8 ± 7.3%	130. ± 1.7%	32. ± 2.4%	5.0	4.5 ± 27%

[a] Coefficient of variation.

Epoxy resins were obtained from the Shell Co. Epon 828 was used mainly, but Epon 826 and Epon 815 were used in some cases. m-Phenylene diamine (MPDA) was used as a curing agent at a concentration of 14 phr. The cure schedule was 2 hr at 85°C followed by 4 hr at 150°C. This cure schedule is relatively long and hot, and should therefore give a satisfactory test for any degradation of the fiber due to interaction with the epoxy.

MPDA oxidizes readily, and it was found that the dark color of the mixed resin could be avoided by subliming the MPDA.

3. NOL RINGS—FABRICATION, v_f, AND v_v

Test specimens were fabricated in accordance with ASTM D 2291-67 "Fabrication of Ring Test Specimens for Reinforced Plastics."

A bobbin of yarn, which had been stored in the dark at room conditions, was mounted on a shaft against which a split cork could be pressed to control the tension. From the bobbin the yarn passed over a 2-in. diameter ceramic pulley on ball bearings and into a resin pot. The pot was surrounded by a water bath at 60°C and contained three fixed 1/2 in. diameter Teflon guides which served to spread the fibers and improve the impregation. The yarn turned through about 180° at each guide. From the pot the yarn passed through, but was not deflected by, a ceramic guide with a 1/16 in. slot which served to remove some of the excess resin. Two more pulleys were used to pass the yarn to a traverse guide from which the yarn passed to the ring mold. The bearing of the second of these pulleys was mounted on a spring with a dial gage attached so that the tension could be measured. The ceramic traverse guide had a 1/16-in. slot with rounded corners and was driven at the same speed both ways. Ring molds were used which were each constructed from three stainless steel circular plates held together by six screws. The inside surfaces of the mold slot were given a "mirror" finish and treated with mold release (Dow Corning) DC-20. The mold and the traverse guide were geared to the same electric motor, the speed of which was controlled manually. The mold speed was 7.5 rpm (13.5 ft/min yarn speed), there were 9.2 revolutions per traverse, and the tension was 240 g. The resin mix was degassed before it was poured into the pot, and the winding operation was started when the resin temperature reached 59°C The resin temperature increased to a few degrees above the bath

temperature during the course of winding thicker rings due to the exothermic reaction. The working pot life under these conditions was about 1 hr. A limit was reached when the viscosity was so high that excessive broken filaments appear at the guides. The mold temperature was held at 85°C by means of an IR lamp.

The thickness of the winding was monitored by a dial gage equipped with a Teflon plunger. The depth of the slot was greater than the desired thickness of the ring and the excess resin was wiped off, by hand, with a Teflon wiper. This left a small fillet of resin which may have led to slightly low fiber volume fraction measurements. The ring was rotated for a further 30 min under a heat lamp before oven curing at 85 and 150°C for 2 to 4 hr. This allowed the resin to set up without first running out of the winding. After curing and cooling, the rings were removed from the mold and weighed in and out of water. The outside surface of some rings was machined with a 24,000-rpm hand grinder equipped with a 1/8-in. diameter tungsten carbide burr (square end, spiral flute) and mounted, with the ring, in a lathe.

The volume fraction of fiber and apparent volume fraction of voids were calculated from the number of turns on the ring, denier, volume of ring, densities, etc., using the formulas (see the Appendix for the meaning of symbols):

$$v_f = V_f / V_c$$

and

$$V_c = (W_c - W_c')/\rho_{H_2O}$$

where the prime indicates the weight in water

$$V_f = W_f/\rho_f$$

where

$$W_f = (D + t)\,\text{den} \times N \times 8.867 \times 10^{-9}\ \text{g}$$

and

$$v_v = 1 - (1/V_c)[(W_c/\rho_r) - W_f(1/\rho_r - 1/\rho_f)]$$

which may be derived from the formulas:

$$\rho_c = \rho_r v_r + \rho_f v_f + \rho_v v_v$$

$$v_f = V_f/V_c$$

$$\rho_c = W_c/V_c$$

and

$$v_r + v_f + v_v = 1$$

and assuming $\rho_v = 0$.

Values of density in g/cc used for PABH-T X-500, S-glass, and resin were 1.46, 2.485, and 1.204, respectively. Results for PABH-T X-500 and S-glass rings are incorporated into Table 4. The lower volume fraction of the glass is probably due to lower tensile stress during winding. The higher void content of the glass probably reflects the increased difficulty in impregnating the heavier yarn.

4. FABRICATION OF UNILAMINATES

Unilaminates of PABH-T X-500 were made by substituting a rotating flat plate for the ring mandrel and winding resin-dipped yarn in a manner similar to that of making the NOL rings. The wound unilaminates were B-staged like the NOL rings but their final cure was between press plates with shims and side plate to eliminate resin flow traverse to the fibers. The unilaminates were cut off the flat mandrels with a diamond saw.

5. FABRICATION OF MULTILAMINATES

Laminates were made by winding from one, or a few, bobbins onto a drum, cutting the lamina off, and flattening it. The laminae are then cut to the shape of a flat mold which had a few mils clearance between the male and female parts. After stacking the laminae in the mold and placing shims in position, the assembly was pressed to controlled thickness at the cure temperature. The fiber volume was calculated from the final thickness of the laminate, the weighed denier of the yarn, and the number of turns per inch. A fiber density of 1.46 g/cm^3 was assumed. No correction was made for either voids within the fibers or for moisture regain of the fiber. The settings of the Goldsworthy filament winding machine were calibrated in turns of yarn per inch of tape. Any lateral expansion or contraction after removal from the drum was ignored, and any clearance between the cut tape and the sides of the mold was allowed for if it amounted to more than a 1% correction.

The void content was calculated from the measured density of the composite assuming a resin density of 1.204 g/cm^3.

Details of laminates made from PABH-T X-500 fiber and from S-glass fiber are shown in Table 6. The fiber volume of the S-glass laminates was determined by burn off and shows agreement with the value determined by counting within ±5% without any systematic error apparent.

Visual observation of the laminates showed that lack of collimation of the fibers in some parts of some laminates was present. This was probably due to what has been termed fiber "wash," and it seems to be more of a problem when large amounts of resin are present. In extreme cases it seemed that a discontinuity in the degree of fiber wash had led to a completely fiber-free part of an inner lamina.

Deviations of the angles of the lamina up to a few degrees away from the target values have been observed. Systematic nonuniformity of thickness has been seen; some samples were thick in the middle and others were tapered to the end.

6. PREPARATION OF FABRIC LAMINATE

The PABH-T X-500 yarn used was 13.3 msi modulus having a Z-twist of 0.65 turns/in. The satin fabric made from the yarn had

56 ends/in. in the warp and 54 ends/in. in the fill to simulate a widely used glass fabric. Fabric weight was 5.3 oz/yd^2, breaking strength was 432 lb/in. in the warp and 512 lb/in. in the fill directions. The initial modulus of the fabric was 2.83×10^3 and 2.74×10^3 lb/in./oz/yd^2 in the warp and fill directions, respectively. The fabric was impregnated with epoxy resin of the type used in most of the previously described composites and cured into panels using the laminating technique similar to that described for the preparation of laminates.

7. OTHER TEST SPECIMENS

NOL rings were fabricated using a polyester resin commonly used in glass composite fabrication in a manner similar to that used for the epoxy-impregnated NOL rings except that the resin was applied cold.

Phenol-formaldehyde PABH-T X-500 composite laminates were made by techniques similar to those used in preparing the epoxy-impregnated laminate. The yarn was passed through a phenol-formaldehyde resin thinned with solvent. The winding was partially cured by heating to 100°C for 10 min after solvent evaporation. The laminate was then made by plying 20 layers of the coated roving in an open end mold, cold pressed at 200 psi, and then heated for 30 min at 107°C and then at 163°C for 1 hr under 500 psi. Melamine-formaldehyde resin impregnated samples were made by a similar technique with suitable modification of curing temperatures.

Polyimide impregnated PABH-T X-500 composites were prepared by using a 25% solution of an aromatic polyimide resin at room temperature instead of epoxy, and the solvent was removed from the unilayers by evaporation. The resin was then partially cured for 30 min at 120°C and the unilayers stacked in an open-end mold, hot pressed at 260°C at 15 psi for 5 min after which the pressure was released momentarily, then raised to 100 psi at 260°C for 1 hr. Another specimen was prepared in the same way except that an aromatic polyimide prepolymer was used.

8. IMPREGNATED YARN PROPERTIES

By impregnating a length of yarn with resin and curing it, a composite can easily be made which is adequate to judge the

magnitude of any degradation of the fiber tensile properties due to the heat treatment in a resin environment. Pirzadeh [6] has examined many of the variables involved in this test with single-ended glass rovings. He found them all to be unimportant except the tensile properties of the resin. The 828, MPDA resin used here is rather brittle and may have lead to lower strengths on this account. No information was found on the effect of unequal tension among the various fibers of the yarn. Because of the lack of finish on the PABH-T X-500 yarn and the pronounced tendency to splay due to static electrification, it was felt that some attempt should be made to control the tension distribution. This was done, on some samples, by wiping the excess resin off with one end unclamped. It was found that extending a 5-m length of yarn did not seem to equalize the tensions. An Instron machine without an extensometer and with compressed asbestos in rubber based clamps was used. Results are shown in Table 1. Figure 1, Curve A, shows the stress-strain curve of a typical PABH-T X-500 impregnated yarn. A gauge length correction can be applied to the fracture load by assuming Weibull statistics apply to the fracture loads. From the theory of assemblies [7] of tensile bodies obeying Weibull statistics, one can calculate the Weibull exponent, β, from test data of various length specimens and then use it to compute the strength of any length specimen. When the procedure is done for the data of Table 1 for 1-in. gauge length specimens, an average value of 18.3 lb fracture load is obtained.

Overall average properties for a sample of spun drawn PABH-T X-500 and also for a control sample of S-glass were derived using estimated corrections (as described below) and are shown in Table 4 alongside values obtained by other methods.

Average tensile properties were estimated from the data in Table 1 as follows. The PABH-T X-500 fiber will be dealt with first. A reasonable figure to choose for P^* is the 18.3 lb determined above. The weighted average of the fiber weighed denier measurements was 641 den. W_c was 1.6 mg, cm and ρ_f and ρ_r were taken as 1.46 and 1.204 g, cc, respectively.

Using

$$w_f = \text{den}, 900\ \hat{W}_c \ (\text{mg, cm})$$

$$w_r = (1 - w_f)$$

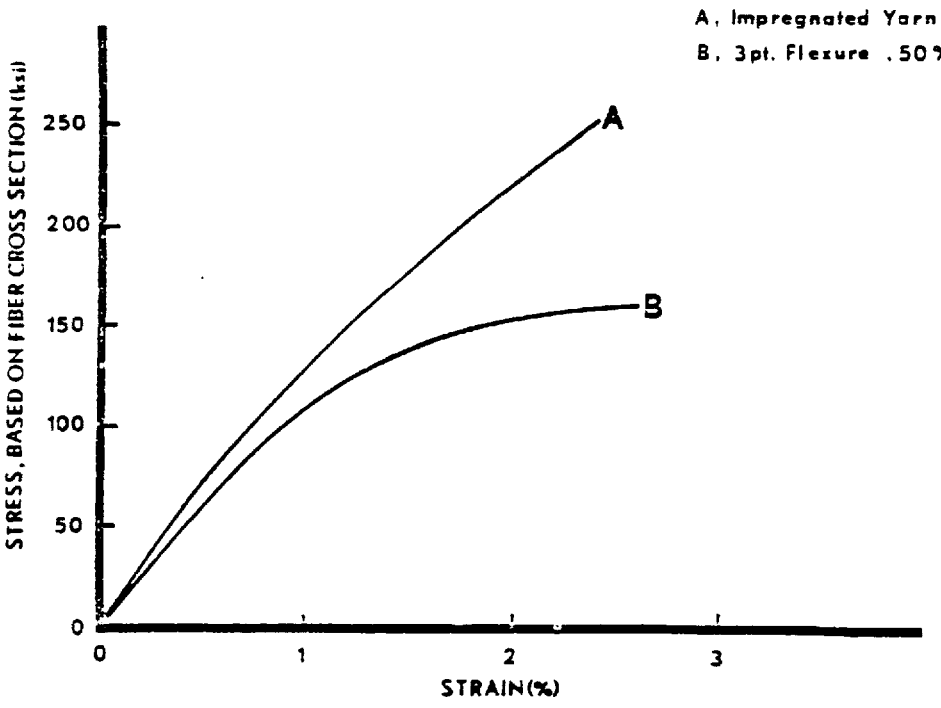

FIG. 1. Comparison of tensile and flexural stress-strain curves of PABH-T X-500 composites. Stress has been normalized by rule of mixtures to 100% fiber.

$$v_f = (1 - v_r)$$

and

$$v_f \rho_f / w_f = v_r \rho_r / w_r$$

which combine to give

$$V_f = 1/\{1 + (\rho_f/\rho_r)[(900\hat{W}_c/\text{den}) - 1]\}$$

It must be noted that the samples had blobs of resin on them at intervals so that this value of v_f is a little high, but the error may be neglected for the present purposes.

$$\sigma_c^* = v_f\sigma_f^* + v_r\sigma_r^*$$

Using

$$\sigma = P/A$$

$$Ac = A_f/V_f$$

and

$$A_f = (den/5.806 \times 10^5\rho_f)\ \text{in.}^2$$

gives

$$\sigma_f^* = 5.806 \times 10^6 P^*\rho_f/den - \sigma_f^*[(900\hat{W}_c/den) - 1]\rho_r$$

Substitution of the numerical values, and assuming $\sigma_r^* = 10$ ksi, gave $\sigma_f^* = 230$ ksi, with a resin contribution of 6.5%.

The modulus was calculated similarly, taking a value of 10.5 lb/% for the slope. A high value was chosen from Table 1 in order to allow for the gauge length effect which is evident in the data. The final formula used was

$$E_f = 5.806 \times 10^5\rho_f(dP/d\epsilon)/den - E_r(\rho_f/\rho_r)[(900\hat{W}_c/den) - 1]$$

and gave $E_f = 13.1$ msi with a resin contribution of 5.8%.

No attempt was made to correct the data for the elongation at break for the clamp error, but a value of 2.5% was judged reasonable.

The data for the S-glass sample was treated similarly using $\rho_f = 2.485$ g/cm^3 (not measured, ignoring presence of finish),

W_c = 12.3 mg/cm, ρ^* = 139 lb, dP/dϵ = 3.2×10^3 lb, $\epsilon_c^* = \epsilon_f^* = 5\%$, den = 3743, and ρ_r = 1.204 g/cm^3.

It must be noted that the load extension curves were not linear and that one sample slipped in the clamps. This was a 12-end yarn, and it is felt that the clamping arrangement was highly unsatisfactory and led to low modulus values and high ultimate strains. The results were v_f = 19.8%, σ_f^* = 496 ksi (resin contribution 8.1%), and E_f = 10.3 msi (resin contribution 19.6%).

As mentioned above, the main results from this experiment have been tabulated in Table 4. Other interesting results evident in Table 1 are as follows. Both the slope and the fracture load for the S-glass showed much less scatter than for the PABH-T X-500. The attempt to equalize the tension distribution by wiping with loose ends did not show any significant increase of slope or fracture load. The W_c data show that the unwiped sample retained less resin than the others. This was unexpected and the reason for it is not known.

9. NOL RING SPLIT D TEST

The procedure for this test follows ASTM D2290 64T, "Apparent Tensile Strength of Parallel Reinforced Plastics by Split Disk Method." The nominal ring thickness was 0.060 in. and the bearing surfaces of the test fixture were greased.

Results obtained with this test are shown in Table 2. The resin contribution was accounted for by assuming the rule of mixtures and σ_r^* = 10 ksi. For some rings which were not machined, the cross-sectional area was not measured, and the formula used for σ_f^* reduces to

$$\sigma_f^* = 5.806 \times 10^6 \rho^* / (2N\text{den}) - (1 - v_f)\sigma_r^* / v_f$$

The fracture was accompanied by a fraying or delamination in most cases. Sometimes the broken sample could be pulled out into a helix. Some samples showed a slight drop in load before continuing upward to a maximum load at fracture. These events are called partial fractures in Table 2. Partial fractures could be heard

TABLE 2. Results of NOL Ring Split D Tests

Fiber	Treatment	No. of samples	V_v (%)	Mean V_f (%)	Resin contribution to σ_c^* (%)	σ_c^* (ksi) Mean ± coefficient of variation	Mean σ_f^* (ksi)	Predominant failure mode
PABH-T X-500	Machined	4		68	2.7	130 ± 4.5%	186	Helical fracture, one partial fracture
	Machined and boiled	1		68	2.9	119	170	Helical, 2 partials
		1		68	2.4	142	204	Helical, no partials
	Not machined	7		67	2.8	121 ± 3.5%	176	Severe to helical delamination. Partial fractures inaudible. Location indeterminate
S-Glass	Machined	5	4 ± 33%	58 ± 3.8%	1.7	270 ± 5.4%	437	Severe delamination, all at gap. Partial fractures slight on chart but audible

just before the final fracture in all the glass rings which were tested.

The results in Table 2 show that machining the PABH-T X-500 rings produced no loss of strength and that a limited boiling treatment (2 hr followed by several hours drying at room conditions) had no effect. The tensile strength of the spun drawn PABH-T X-500 was about 180 ksi based on the fibers and as measured in this test.

10. NOL RING DIAMETRIC COMPRESSION

A value for the longitudinal Young's modulus was obtained by compressing NOL rings along a diameter between two parallel plates. The following formula based on simple beam theory and neglecting any anisotropic effects was used:

$$E_c = 1.786(dP/dH)(D - t)^3/bt^3$$

Each ring was compressed and recompressed along two orthogonal diameters. No deviation from linearity could be detected in the curves, and the four values of dP/dH agreed within 2%.

The results are shown in Table 3 where the fiber modulus has been calculated assuming that the rule of mixtures holds and using $E_r = 0.5$ msi.

11. DISCUSSION OF LONGITUDINAL TENSILE PROPERTIES

The results from the various tests have been collected in Table 4. PABH-T X-500 showed 94 and 96% retention of its single filament modulus and strength, respectively, in the impregnated yarn tests.

TABLE 3. NOL Ring Diametric Compression

Fiber	E_c (msi)	v_f	E_f (msi)	Resin contribution (%)
PABH-T X-500	7.74	0.68	11.2	2.0
S-Glass	6.98	0.59	10.9	3.2

A noticeable strength loss occurred in going to the split D test, but the same was true for S-glass, and this may well have been due to the stress concentration inherent in this test. The PABH-T X-500 modulus by diametric compression was 80% of the single filament value. Some of this loss may have been due to the assumptions involved in interpreting the test and the fact that the test was essentially a flexure test in which a reduced compressional modulus would reduce the value for modulus obtained. On the whole, there was no evidence of any serious loss of longitudinal properties in going to a fully cured epoxy composite.

It is important to note that the stress-strain curves for PABH-T X-500 fibers and for the corresponding composites are not linear (Fig. 1), the tangent modulus decreasing smoothly at increasing strains. At high loads the curvature means that the effective (secant) modulus is less (by about 20%) than the initial modulus.

12. MODULUS OF MATRIX

To ascertain approximately the modulus of the matrix resin used throughout these experiments, a block of resin with parallel sides was cut out of a large piece of cured resin. As positioned in the testing machine, the sample was 0.313 in. high and had a cross-sectional area of 0.1098 in.^{2}. Reversible moduli and secant moduli were determined up to 3.8% compression. The initial modulus was not determinable in these experiments because of two factors: the inherent softness of the Instron machine in the particular setup that was used with it, and the fact that the top and bottom of the samples could not be made perfectly flat and smooth. Results are shown in Table 5.

The secant modulus was measured by fixing the deformation and letting the stress relax. The average value over a period of 1-10 min was taken as the secant modulus.

Whereas the contribution of the resin to the longitudinal properties of the composite amounts to only a few per cent, in transverse properties the resin can support an appreciable fraction of the load, and the time-dependent properties become very important.

13. TRANSVERSE MODULUS OF PABH-T X-500 COMPOSITE

Satisfactory specimens of cut lengths for transverse modulus and strength measurements could not be made due to difficulties

TABLE 5. Transverse Modulus of PABH-T X-500 Epoxy Composites

Sample	Transverse elastic modulus (msi)	Transverse secant modulus (1-10 min) (msi)	Volume fraction fiber (%)	Strain rate (%/min)
PABH-T X-500,				
Ring A	0.73 ± 0.02	0.52 ± 0.03	68	2.0
Ring B	0.71 ± 0.05	0.43 ± 0.01	66	2.0
Resin	0.55 ± 0.03	0.28 ± 0.05	0	1.6

of cutting the material without introducing gross defects in the samples due to delamination; therefore, a compression technique like that used to determine the compressional modulus of the matrix was used. Specimens of NOL rings of the same size that were used for the short beam shear test were used in this determination. They were compressed parallel to the axis of the original ring. Elastic modulus was again calculated rather than initial modulus for the same reasons as was given for the matrix. Two different samples having a dimension in the compression direction of 0.26 in. and an area of around 0.08 $in.^2$ were used. One ring, A, had a 68% volume fraction of PABH-T X-500 fiber and the other ring, B, had a 66% volume fraction of PABH-T X-500 fiber. Values are given for the average elastic (reversible) modulus at strains below 4%. At strains higher than 4% the elastic modulus increased rapidly, possibly due to the collapse of very small voids within the fibers. Since no high modulus composite will experience strains greater than 4% due to the fact that other failures will occur below 4% strain, the modulus below 4% is the proper one to use in composite design calculations. Again the secant modulus was computed and the same considerations about its meaning apply to the composite as apply to the matrix. The data are given in Table 5.

To compute the transverse modulus of the fiber from the transverse modulus of the composite, E_{22}, several assumptions must be made. Two methods may be used to obtain the transverse modulus of the fiber, each method giving about the same results.

The results of Tsai [8] obtained for a square array and reported to give fairly good results yield a transverse modulus for PABH-T X-500 fibers of 0.83 msi for one specimen and 0.77 msi for another specimen as obtained from the elastic modulus properties. Another method, that of Whitney [9], gives 0.8 msi for one specimen and 0.78 msi for the other from the elastic modulus properties. Taking the secant modulus for the matrix and of the composites, the secant modulus of the fiber may be computed. Whitney's method gives a secant transverse modulus of PABH-T X-500 as 0.66 msi in one case and a 0.50 msi in the second case, showing that there is likely to be considerable stress relaxation under transverse strains and that multidirectional laminates could be expected to show a certain degree of time-dependent stiffness in spite of the almost time-independent moduli observed in fiber tension.

14. TRANSVERSE STRENGTH AND FIBER FAILURE

Polished sections of transverse (90°) flexural fracture surfaces showed fiber failure in specimens with strengths greater than 4.5 ksi. Failure in transverse flexure occurs in one of two modes, interface or fiber failure. In interface failure the fracture surface makes tortuous detours in order to avoid going through a fiber. In fiber failure the surface follows a straight course with no regard to whether the material is fiber or matrix.

In specimens that showed interface failure, a transverse flexural strength of 3.3 ksi ± 23% coefficient of variation was observed while those that showed fiber failure showed a strength of 5.2 ksi ± 11% coefficient of variation with a peak value of 5.7 ksi.

Although the failure modes observed were quite distinct, regions of interface failure could always be found in a predominantly fiber failure type specimen and vice versa.

The specimens came from two different flat plates which were directly filament wound. The modulus of all specimens from all samples was in the range 0.4 to 0.5 msi. The strength showed much greater variability, from 2 to 6 ksi, the five samples within each specimen having a coefficient of variation of 7 to 23%. Fiber volume was 49 to 53%. The samples taken from the edges of the plate were weakest in some cases but not in all.

The fabrication variables from plate to plate included the degree of vacuum during impregnation, the amount of volatiles added to facilitate degassing after winding, and the fiber type

(highly oriented or medium-highly oriented). No positive conclusions regarding the effect of these variables could be resolved within the scatter of the data. However, it was observed that the two weakest plates did not have vacuum impregnation.

It is possible that the process of machining the specimens with a water-cooled diamond saw contributes significantly to the large scatter in the strength data. In one experiment 90° tube specimens were wound and broken in four-point bending. None of the surfaces were machined. The strength values were 3.5 to 4.9 ksi. There were too few samples to judge the scatter, and it was found to be quite difficult to make a specimen so built up at the ends that it would be free from stress concentrations. One sample appeared to break satisfactorily but its strength, 4.5 ksi, was not unusually high.

In summary, the transverse strength shows a strong dependence on unknown factors. Machining flaws may be contributing to the scatter and limiting the values, but there is strong evidence that values much above 5 ksi will never be achieved because of transverse fiber failure. It may be noted that 5 ksi is much lower than the strength (15 ksi approx) of the highly cross-linked resins used.

15. NOL RING HORIZONTAL SHEAR

The ASTM test D-2344-65T, "Apparent Horizontal Shear Strength of Reinforced Plastics by Short Beam Method," was used to give a rough measure of the degree of adhesion between PABH-T X-500 and an epoxy resin.

The main results were that PABH-T X-500 with no surface treatment or finish gave a shear strength of 9.2 ksi. This may be compared with values of up to 12 ksi which can be obtained with some systems [10-12] although an upper limit of 10 ksi may be set by the particular resin used. An S-glass sample showed 9.9 ksi. The PABH-T X-500 shear strength was not reduced by boiling water treatments nor by the application to the fiber of certain finishes which aid handling of the yarn. A polyvinyl alcohol finish reduced the shear strength to 3 ksi and it fell to 1 ksi after boiling. Postcure times of at least 2 hr were necessary to realize the maximum shear strength.

The shear strength increased with decreasing concentration of curing agent (MPDA). The optimum concentration has not been ascertained, but it seems that the bulk of the samples were

prepared with a concentration which was too high. (This result is subject to a possible effect of variable volume fraction discussed below.)

The detailed results of these tests are shown in Fig. 2. The average coefficient of variation for all the tests was 5.5%, ranging from 2.1 to 13%.

A series of NOL rings were made in which the major variable was the concentration of MPDA curing agent to see if this variable affected the shear strength. It appears that a maximum in short beam shear strength occurred at a concentration of 10 phr (10 parts of curing agent per hundred parts of epoxy resin by weight). This corresponds to a molar ratio of 1:0.7 of epoxy:amine hydrogen. The result is consistent with the possibility that the epoxy group can react with the amide hydrogen of the PABH-T X-500 molecule when all the primary and secondary amine hydrogens of the curing agent have been used up. PABH-T X-500 is generally unreactive, and one would anticipate that a high temperature would be needed to make this happen. Accordingly, it was observed that the 150°C postcure was necessary to achieve the best shear strength.

A striking difference was observed between the modes of failure of the strong and the weak specimens numbered A and B, respectively, in Fig. 2. As shown in Fig. 1, the weak specimen had a multiple fracture surface, whereas that of the strong sample was single.

Examination of polished cross sections of the fracture surface indicated that the reason for this could be that in the strong sample a large amount of fiber failure had occurred and that the crack could proceed in a straight line. On the other hand, the crack in the weak sample had been strongly deflected by the fibers during the interfacial failure mode. As in the transverse flexural studies, the failure modes are not perfectly clearcut; one can always find some regions of interfacial failure in specimens in which fiber failure predominates and vice versa.

Referring to Fig. 2, note that fiber failure was observed in A and interface failure was observed in B. Also note that the failure was interfacial at 8 ksi shear strength. Therefore, it may be concluded that the threshold for fiber failure was between 8 and 9 ksi short beam shear strength and that improvements of fiber-matrix bonding are not likely to increase the shear strength much above 9 ksi unless it is possible to improve the degree of order of the packing of the filaments to remove stress concentrations. Evidently the shear strength in the fiber direction of PABH-T X-500 fibers was about 8 ksi.

Although data are very limited as to the effect of void content on the shear strength, there is some evidence that voids lower the shear strength. Some NOL rings were prepared by passing the yarn into a vacuum chamber in which they passed through the resin while under a vacuum, with more resin being used as a vacuum seal as the yarn entered and left the chamber through capillary holes. The average of three rings, two of which had a spin finish, and without boiling in water, gave 8.00 ksi shear strength prepared by the vacuum technique compared to 7.74 ksi, the shear strength for an average of 6 like rings prepared with resin impregnation in air.

16. SHEAR MODULUS

A unidirectional composite with transverse isotropy has five independent elastic constants. In terms of the compliance matrix with the z-axis along the fiber axis, they are s_{11}, s_{33}, s_{44}, s_{12}, and s_{13}, with

$$s_{66} = 2(s_{11} - s_{12})$$

s_{33} and s_{11} are, respectively, the reciprocals of the longitudinal and transverse moduli which have already been discussed. Of the remaining three, s_{44}, which is the reciprocal of a shear modulus, G, was measured.

The Greszczuk-Douglass [13] ring test for shear modulus of composite materials was done on two PABH-T X-500 rings and one S-glass ring. The Young's modulus of the ring in the longitudinal direction is determined first by using the ring as a proving ring (diametric compression, Section 6). A small hole is then drilled through the ring at one point, and the ring is sawed in two on an acute angle through the hole to divide one side of the ring and provide a place to connect hooks for the shear modulus test. The derived [13] formula for the shear modulus of the ring is

$$G = (3/J)[8H/\pi P(D + d)^3 - 1/E_{11}I]$$

The torsional moment of the ring equals βbt^3 where β is a geometric factor between 0.14 and 0.33 depending upon the ratio of b to t. I, the

moment of inertia for bending the ring section in a direction parallel to the ring axis of symmetry, equals ($tb^3/12$). The ring is deflected by pulling the two cut ends apart in a direction parallel to the ring's axis of rotation. The other end of the ring is supported by a spring mechanism so that there is very little, if any, moment to twist the ring due to its own weight. For most materials the EI term is far smaller than the torsion term, and for the materials tested here, it approached insignificance. The rings were deformed at a strain rate of 5.5%/min based on the ratio $H/\pi(D - t)$. The shear modulus of PABH-T X-500 NOL rings was measured to be 0.320 msi with a fiber volume fraction of 67%.

The shear modulus of the PABH-T X-500 fiber was read off from the plotted tabulation given by Tsai [14] of the ratio of shear modulus of the unidirectional composite to the matrix shear modulus as a function of fiber volume fraction and the ratio of fiber shear modulus to matrix shear modulus which was computed for a square array of fibers and reported (private communication, Tsai) to give good predictions. To obtain the shear modulus of the matrix tested under similar conditions, NOL rings of S-glass were made of about the same fiber volume fraction (62%) and their shear modulus determined. Using 4.8 msi as the shear modulus of S-glass, the shear modulus of the resin was 0.23 msi. A fiber shear modulus for PABH-T X-500 was then determined to be 0.40 msi. It should be noted that the final result is very insensitive to the matrix shear modulus when the fiber shear modulus is near the value of the matrix modulus.

17. TESTING OF LAMINATES

Conventional tensile and flexural tests were performed on specimens cut from the laminates in a variety of orientations. Machining was by water-cooled diamond saw only. Fibrillation at the edges of some of the PABH-T X-500 specimens was removed with emery cloth by hand. Three specimens were used in each test. The average value is reported except for some of the ultimate properties where, if two out of three agreed, the mutual value was reported. The tensile specimens were 3/8 in. wide, had 3 in. between tabs, and an overall length from 5 to 9 in. Using aluminum tabs, it was found that superior results could be obtained by using a somewhat flexible epoxy resin as adhesive. The formulation used was equal parts by volume of Shell V-40 (polyamide), Epon 871, and

Epon 826 with a cure of 1 hr at 85°C and 1 hr at 150°C. The thickness was about 10 mil/ply. An Instron testing machine and extensometer were used at room conditions with a nominal strain rate of 5%/min. Flexural specimens were 1/2 in. wide, had a span to depth ratio of approximately 20:1, and the loading nose radius was 0.125 in. Room conditions and a surface strain rate of nominally 5%/min were used.

The results of the tests are shown in Tables 6 and 7. The modulus values are later compared with theoretical predictions. We did not compare strength to any available strength theories. The unidirectional strength achieved in the straight tensile test represents a fiber efficiency of only 63%. This is about the same as is calculated from the flexural strength figure and is less than the value achieved in the NOL ring split "D" test. The failure mode involved a rather large amount of longitudinal splitting. As was expected, the off-axis tests showed a nonlinear stress-strain curve for glass as well as for PABH-T X-500, and a cleavage failure mode [15].

The transverse modulus of the unidirectional laminate, 0.47 msi, agreed with the value previously deduced from compression tests of NOL ring sections. The transverse flexural strength measured was 5 ksi, which is at the upper boundary of the unilaminate tests. The unidirectional flexural strength was 65 ksi, which yields a fiber strength of about 160 ksi, its fiber volume fraction being 40%. The failure observed was in compression.

18. LONGITUDINAL COMPRESSION MODULUS

Unidirectional composites of glass and other isotropic fibers are known to fail by buckling of the fibers when a compressive force is applied along the fiber direction. With highly drawn PABH-T X-500 it is conceivable that a similar instability can occur on a molecular scale within the fibers. If such a mechanism can proceed at a low-yield stress, then it will be important in the use of PABH-T X-500 composites in compression members including the compression side of beams or plates subjected to bending moments. The effect would be to give a low strength and, possibly, a high toughness.

A certain amount of substantiation for such an intrafiber buckling failure in compression came from microscope observations of

TABLE 6. Nonwoven Laminate Data

Code	Density (g/cm³)	Fiber volume fraction (%)		Void content (%)	Layup (°)
		By turns	By burning		
U3-G[a]	1.921	63	60	7.4	0,0,0
U6-G	1.871	57	56	5.2	0,0,0,0,0,0
C4-G	1.865	55	57	4.6	0,90,90,0
3,6-G	1.999	65	65	3.1	0,-30,30,30,-30,0
U3-X[b]	1.304	54		3.2	0,0,0
U6-X	1.174	40		11.	0,0,0,0,0,0
C4-X	1.322	55		1.9	0,90,90,0
3,6-X	1.330	61		2.5	0,-30,30,30,-30,0
U6-X2[c]	1.286	55		8.9	0,0,0,0,0,0
U3-X2	1.333	61		6.3	0,0,0

[a]G series: S-glass, 12 end, 3700 den, Owens Corning, HTS-901 finish, 2.485 g/cm³ in., Epon 828/MPDA-14 phr, cure; 1 hr at 80°C and 4 hr at 150°C.

[b]X series: PABH-T X-500, 367 den, 1.46 g/cm³, Epon 828/MPDA-14 phr, cure; 1 hr at 80°C and 4 hr at 150°C.

[c]X2 series: PABH-T X-500, 367 den, 1.46 g/cm³, Epon 826/MPDA-10 phr, cure; 2 hr at 85°C and 4 hr at 150°C.

TABLE 7. Nonwoven Laminate Test Results

	Code[a]	Stress angle	Strength (ksi)	Modulus (msi)	Fracture strain (%)
Tensile	U3-G	0°	>210	8.1	>2.7
	U6-G	90	9	1.8	0.5
	C4-G	0	120	4.0	1.2
	C4-G	45	14	1.7	1.9
	3,6-G	0	84	5.8	1.8
	3,6-G	30	80	3.9	-
Flexure	U6-G	0	210	6.6	3.2
	U6-G	90	11	1.6	0.7
	C4-G	0	240	6.4	3.9
	C4-G	45	44	2.4	3.9
	3,6-G	0	220	7.4	3.0
	3,6-G	90	18	2.0	3.1
Shear			6:1[b]	4:1[b]	3:1[b]
	U6-G	0	11.1[c]	11.7[c]	13.0[c]
Tensile	U3-X	0	-	6.8	-
	U6-X	90	2.0	0.50	0.40
	C4-X	0	56	3.8	1.8
	C4-X	45	9.6	0.58	3.1
	3,6-X	0	58	5.0	1.4
	3,6-X	30	30	2.8	1.5
	U3-X2	0	93	7.1	1.45

Flexure	U6-X	0	65	4.8	2.8
	U6-X	90	5.0	0.47	1.1
	C4-X	0	48	4.4	3
	C4-X	45	25	0.83	6.0
	30-X	0	79	6.3	2.5
	30-X	90	10	0.38	5.0
Shear			6:1[b]	4:1[b]	3:1[b]
	U6-X	0	5.0[d]	7.4[d]	10.2[d]

[a]G = glass, X = PABII-T X-500.
[b]Short beam shear strength (ksi) at span to depth ratio indicated.
[c]Shear failure.
[d]Tensile failure.

deformation bands within the fibers similar in gross appearance to kink bonds observed in plastically strained metals [16] and oriented crystalline polymers [17].

Flexure involves both tension and compression of the materials in a beam, and the compressive properties of an extended chain polymeric material could conceivably be different than its tensile properties. Flexure of unidirectional laminates of PABH-T X-500 gave a Young's modulus in the fiber direction lower than enrichment of the surface layer by resin would be expected to give. For example, for the thickness of the fiber used here, the worst case calculation of surface enrichment would only lower the modulus of a beam such as ours by 0.2%. Figure 1 shows the stress-strain curve, A, of an impregnated yarn sample calculated on the basis of stress on the fiber cross section. Curve B is that of a unidirectional beam in flexure calculated on the same basis for the outermost fibers from a 3-point flexure test, showing both a lower initial modulus and a yield effect.

There is a bending stiffness reduction effect due to shear compliance which can become a large effect in anisotropic materials such as fibrous composites. One can compute this effect for a particular composite from the formula

$$E_{approx} = 2E_t S^2 G / (2S^2 G + 3E_t)$$

G can be derived from Timoshenko's [18] equation (g + 1), p. 173. At the 20-1 span to depth ratio used, the reduction of bending stiffness due to the shear coupling for PABH-T X-500 turned out to be only about 5%. The remainder of the effect observed in the case of flexure test unidirectional laminates and NOL ring diametric compression tests are accounted for as a difference between tensile and compressive Young's modulus.

If it is assumed that the material has a compressional modulus E_c different than the tensile modulus E_t, one can calculate the position of the neutral axis from the force equilibration condition and the apparent modulus E from the sum of the moments. The result is

$$E_a = 4[E_t r_n^3 + E_c(1 - r_n)^3]$$

where

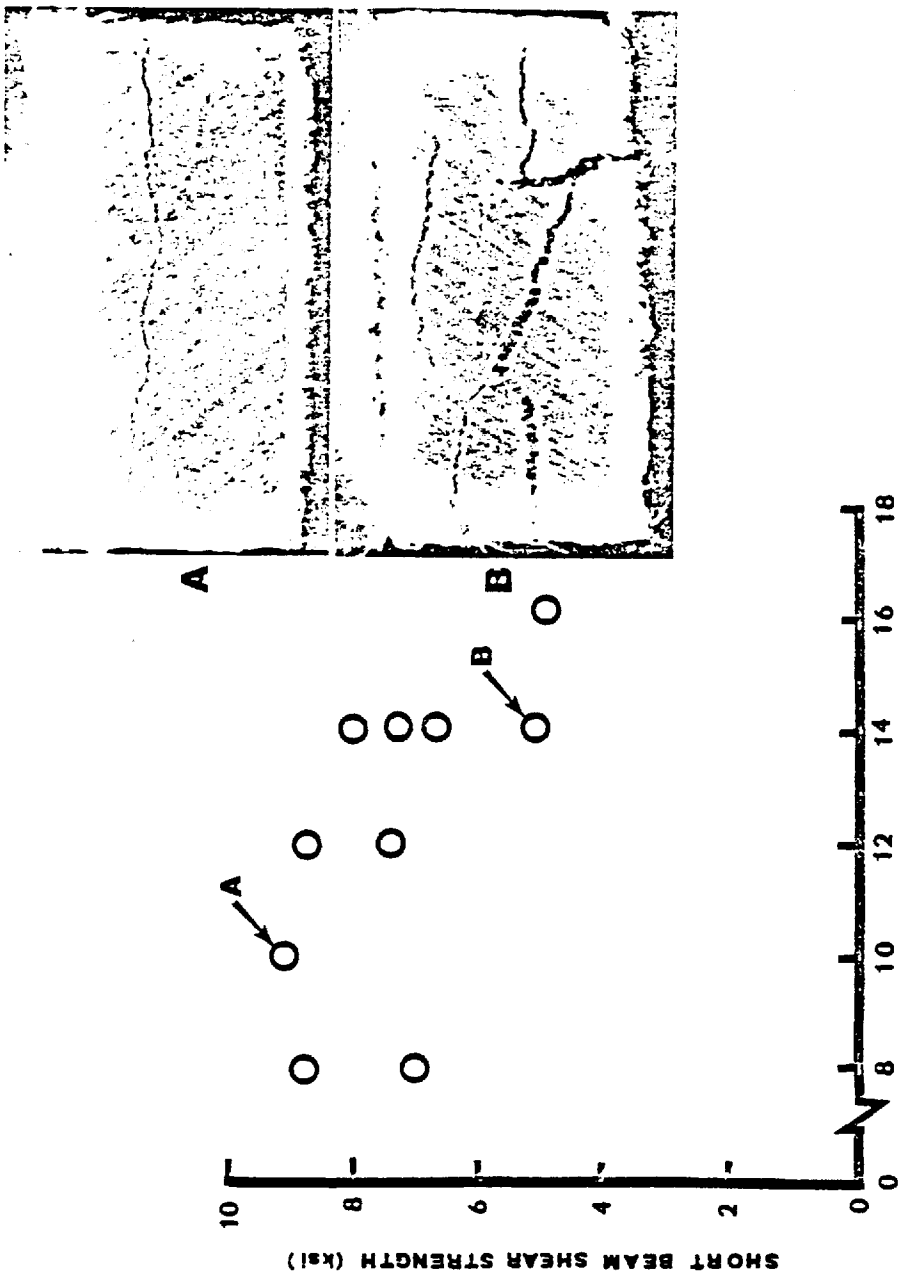

FIG. 2. Short beam shear strengths of PABH-T X-500 EPON 828/MPDA composites. Point A exhibits fiber failure, B exhibits bond failure.

$$r_n = \frac{x_n}{t} = 1/[1 + (E_t/E_c)^{1/2}]$$

The result is that the compressive longitudinal modulus of the PABH-T X-500 fiber in the beam is 10.8 msi whereas the tensile longitudinal modulus of the impregnated yarn is 12.5 msi, assuming the tensile modulus is the same both in the beam and impregnated yarn and taking the average of flexural measurements on several samples (whose data appear in Table 8).

It will be noted that Curve B in Fig. 1 shows a yield phenomenon at about 1% strain, which is greater than the lowering of the slope (presumably due to viscoelastic effects) in the impregnated yarn under tension, Curve A. This yielding is probably due to a compressive plastic yield phenomena and is accompanied by criss-crossing strain marks mentioned earlier in the fibers seen only on the compressive side of the flexural samples. Also the beams fail by compression rather than by tension.

In making practical composites it is convenient to have the fibers in the form of fabric. Flexure and tensile tests were performed on PABH-T X-500 fabric laminates. The specimens were cut with their long axis in the fill direction. The fiber volume fraction was 52.4% and the composite had a 13.5% void volume, and its short beam shear strength was 4.3 ksi. Normalized to 60% fiber volume fraction, its tensile modulus and strength were 4.2 msi and 52 ksi while its flexural stiffness was 3.3 msi. Correcting for the shear coupling effect gives a flexural stiffness of 3.4 msi, and computing the compressive modulus as before with the unidirectional laminates, the compresional Young's modulus of the PABH-T X-500 fibers is 8.8 msi. Some of the discrepancy with the 10.2 msi calculated from the unidirectional laminate data may be due to the fact that not all of the fiber is oriented at 0° in a fabric. It is not likely that this effect is large due to the fact that the Young's tensile modulus of the fiber calculated from this data is 13 msi, about that measured on fibers (the modulus of the fibers used for these particular laminates is not available). Considering all factors, the compressive Young's modulus of typical high modulus PABH-T X-500 fibers is estimated to be about 9.6 msi.

TABLE 8. Properties of X-500 and S-Glass Composites in Other Resins

	Fiber volume (%)	Flexural strength (ksi)	Flexural modulus (ksi)	Shear strength (ksi)	Density (g/cc)
PABH-T X-500—phenol—formaldehyde resin	72.5	77.5	6.8	6.5	1.55
S-Glass—phenol—formaldehyde resin	68.0	61	7.5	2.6	2.35
PABH-T X-500—melamine—formaldehyde resin	71	90	8.2	6.6	1.55
S-Glass—melamine—formaldehyde resin	72.7	130	8.8	5.3	2.22
PABH-T X-500—polyimide resin	72.5	70	6.0	5.3	-
PABH-T X-500—polyimide prepolymer resin	69.0	66.5	5.7	4.8	-
PABH-T X-500—polyester (NOL rings)	68	129	7.1	2.3	1.38

19. PROPERTIES OF OTHER PABH-T X-500 COMPOSITES

The results of flexure testing unilaminates of PABH-T X-500 fibers and S-glass fibers in phenol-formaldehyde, melamine-formaldehyde, and polyimide matrixes are given in Table 8 along with their short-beam shear strengths and density. Their specific properties normalized to 60% fiber volume fractions are given in Table 9 along with the ratios of the specific flexural strengths and flexural moduli of the PABH-T X-500 composite to the S-glass composite. Included in the table are corresponding calculated specific properties of epoxy composites of PABH-T X-500 and S-glass from data obtained in this work. On the average, the ratios of specific strengths are about 1, and those of the specific moduli indicate about a 40% greater specific moduli than S-glass. The S-glass used in this study was quite fresh and was stored at fairly low humidities. The strength of S-glass is very often less than the strength observed in this work. It can be shown that the figure of merit for the stiffness of weight penalized flexural members, such as nonsandwich construction of aircraft fairings, etc., is the modulus divided by the cube of the density rather than the specific modulus. The figure of merit for strength considerations of the same type of usage would be the strength divided by the density squared. This effect is due to the fact that for equal weights the lower density material is thicker, and the thickness enters into the strength and stiffness of flexural beams as the inverse square and cube, respectively. On this basis, PABH-T X-500 60% fiber value composites have a 20% greater figure of merit for the NOL ring tests and about equal for the laminate flexural strength tests, while the stiffness figure of merit for PABH-T X-500 is about threefold that of the S-glass.

20. COMPUTATION OF COMPOSITE PROPERTIES

Fibrous composites have many possible variations in composition and orientation. In the use of fibrous composites an engineer will take his force conditions and strain limits and, for a particular composite system, design the composite article with respect to number of lamini, fiber orientation, and fiber concentration to withstand his forces (with an appropriate safety factor for overstresses, material flaws, and fatigue lifetime) and remain within his strain limits. The stress and strain limits are determined from

the required stiffness of his article, which is determined by the geometric arrangement of the fibers in the composite. The concentration of fibers in a composite has some practical limits also, generally being between 15-70% volume of fiber. Random fibers do not pack well enough for high performance usage, so that in practice the fibers are made parallel and in laminations. In considering using a new material, one would need to compare properties of composites available with these materials on either equal volume or equal weight basis or ratios of certain powers of moduli compared to the composite density. To gather the vast amount of information needed for design and comparison studies would be an overwhelming task. The approach of using mathematical expressions for moduli and densities from the measured uniaxial properties of a few specimens of actual composites to calculate the expected moduli of uni- and multilaminates has been taken. Calculations of strengths have not been undertaken due to the inadequacy of the present state of theories.

A small degree of explanation of the unique character of transverse properties of fibrous composites and particularly of composites made of anisotropic fibers such as PABH-T X-500 is in order. Transverse stress on a unidirectional fibrous composite does not apply any stress along the fibers except for the minute amount due to the Poisson's ratio effect, and the fibers do not give any reinforcement to the matrix due to their length. The fibers reinforce in the direction only as if they were cut into infinitesimal slices of their cross sections, or only as disks in a thin slice of the composite cut transverse to the fiber direction. In recent years several theories and approaches to the mathematical expression of the transverse stiffness of a fibrous composite have appeared [19]. The equation we have chosen to use is not the best for matching the properties of good, voidless composites, but it gives better matching of transverse modulus for practical composites. It was proposed by Whitney [9] and is:

$$E_{22} = 2k(1 - \nu_c)/(E_{11} + 4k\nu_c^2)$$

where

$$k = [k_r(k_f + G_r) + (k_f - k_r) G_r V_f]/[k_f + G_r - (h_f - k_r) V_f]$$

$$k_f = E_f/2(1 - \nu_f - 2\nu_f^2)$$

$$k_r = E_r/2(1 - \nu_r - 2\nu_r^2)$$

TABLE 9. Specific Properties of Various Composites Based on 60% Fiber and Rule of Mixtures

Material			Specific strength $\times 10^6$ in.	Specific modulus (E_{11}) $\times 10^6$ in.	R (PABH-T X-500/ S-Glass)	
Resin	Test	Fiber			Specific strength	Specific modulus
Epoxy	Theoretical	PABH-T X-500	3.54	174		
Epoxy	Theoretical	S-Glass (best)	4.25	108		1.61
Epoxy	Theoretical	S-Glass (practical)	2.14	108		
Epoxy	NOL ring	PABH-T X-500	2.32	140		
Epoxy	NOL ring	S-Glass	2.34	95	0.99	1.47
Epoxy	Impregnated yarn	PABH-T X-500	2.89	163		
Epoxy	Impregnated yarn	S-Glass	4.25	94	0.68	1.73
Epoxy	All 0° laminate, tensile	PABH-T X-500	1.85	151		
Epoxy	All 0° laminate, tensile	S-Glass	2.82	110	0.66	1.37

Epoxy	All 0° laminate, flexure	PABH-T X-500	1.85	140		
Epoxy	All 0° laminate, flexure	S-Glass	2.52	97	0.66	1.44
Phenol-formaldehyde	All 0° laminate, flexure	PABH-T X-500	1.18	102		
Phenol-formaldehyde	All 0° laminate, flexure	S-Glass	0.65	79	1.81	1.29
Melamine-formaldehyde	All 0° laminate, flexure	PABH-T X-500	1.39	125		
Melamine-formaldehyde	All 0° laminate, flexure	S-Glass	1.36	91	1.02	1.37
Polyimide	All 0° laminate, flexure	PABH-T X-500	1.07	90		
Polyester	NOL ring	PABH-T X-500	2.31	126	0.98	1.32[a]
				Average:	0.97	1.43

[a]Ratio based on epoxy—S-glass NOL ring test.

The computation gives the modulus parallel and transverse to the fiber direction, and the properties of a quasi-isotropic laminate where fiber directions are all 60° from each other in multiples of 3 layers of equal properties, calculated by using the approximating equations of Tsai [8] which are:

$$E_{iso} = 3E_{11}/8 + 5E_{22}/8$$

$$G_{iso} = E_{11}/8 + E_{22}/4$$

The corresponding specific moduli were also obtained by dividing the moduli by the density. These properties were computed by this program, called COMPOS, for 5% increments of volume fraction. The specific composite properties for PABH-T X-500 in epoxy matrix are given in graphical form in Fig. 3.

The laminate properties for other layups than the quasi-isotropic type can also be computed by the FLEX program whose description follows. Figure 3 shows the computed specific Young's modulus in the fiber direction ($\hat{E}_{11}$) and transverse to the fiber direction ($\hat{E}_{22}$), and of a quasi-isotropic laminate ($\hat{E}_{iso}$) and the in-plane shear modulus of a quasi-isotropic laminate ($\hat{G}_{iso}$). Two measured $\hat{E}_{11}$ values and two $\hat{E}_{22}$ values for PABH-T X-500 and one $\hat{E}_{11}$ and one $\hat{E}_{22}$ value are plotted. The PABH-T X-500 fiber properties used for the computation were the highest experimental values measured at the time of the computation and were slightly higher tensile properties than the fibers used to make the measured specimens shown as data points.

21. THEORY OF LAMINATE MODULUS

As a first step towards this objective, we have set out to calculate the Young's modulus E, the flexural stiffness E_{flex}, and the in-plane shear modulus G. These quantities are numbers which would come out of the appropriate ASTM type of test by using the standard formulas. For a test specimen cut at an arbitrary angle from an arbitrary multidirectional laminate, E, E_{flex}, and G serve as a valuable guide to the mechanical response of a new type of laminate

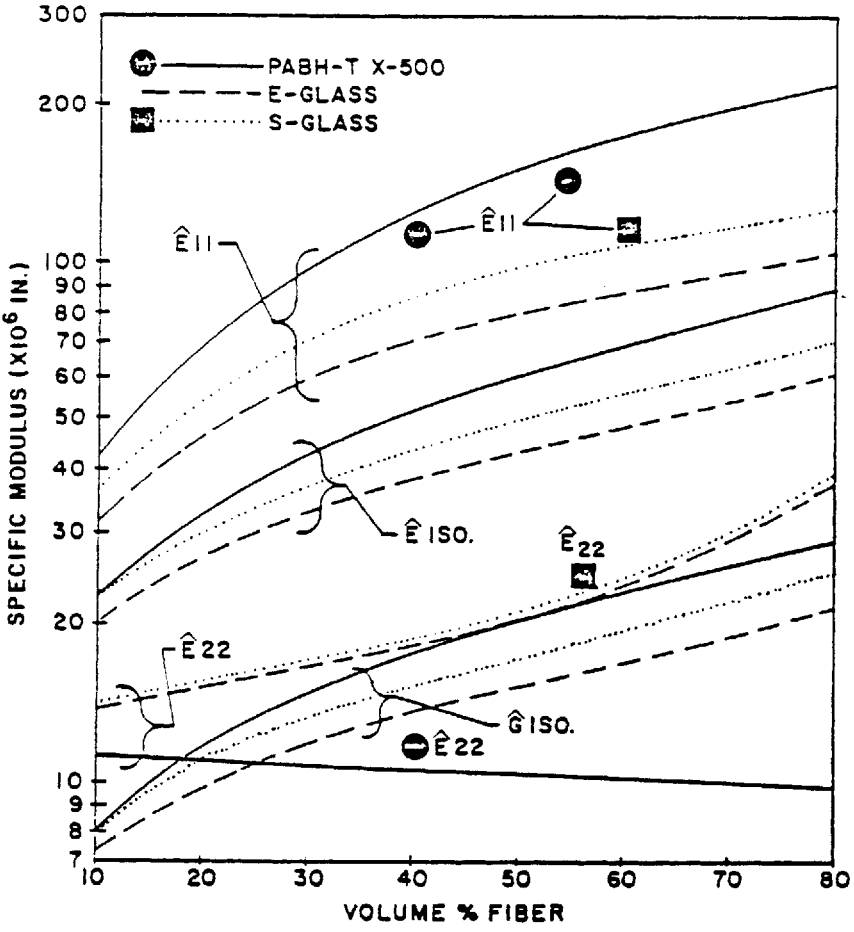

FIG. 3. Computed specific moduli of PABH-T X-500, E-Glass and S-Glass unidirectional and quasi-isotropic laminate composites.

and simulate in-use applications. Furthermore, the computations are easily done.

Significant literature on the theory of the elasticity of anisotropic laminates exists (see, e.g., Refs. 20-22). In order to reduce the theory to practice, it is necessary to consider the various assumptions which are made at each level of the theory. A rigorous solution making no assumptions would have been too time consuming for the needs present here. A "strength of materials" approach

	Code	Stress angle[a]	fiber volume (%)	Modulus (msi) Observed	Modulus (msi) Calculated	% Difference from calculated
Tension	U3-X	0	61	7.1	8.5	-16.47
	U3-X	0	54	6.8	7.9	-13.92
	U6-X	90	40	0.50	0.50	0
	C4-X	0	55	3.8	4.2	- 9.52
	C4-X	45	55	0.58	1.1	-47.27
	3,6-X	0	60	5.0	4.9	2.04
	3,6-X	30	61	2.8	3.8	-26.32
Flexure	U6-X	0	40	4.8	5.8	-17.24
	U6-X	90	40	0.47	0.50	- 6.00
	C4-X	0	55	4.4	7.0	-37.14
	C4-X	45	55	0.83	1.0	-17.00
	3,6-X	0	61	6.3	6.8	- 7.35
	3,6-X	90	61	0.38	0.6	-36.67
Tension	U3-G	0	60	8.1	7.7	5.19
	U6-G	90	56	1.8	1.6	12.50
	C4-G	0	57	4.0	4.4	- 9.09
	C4-G	45	57	1.7	2.6	-34.62
	3,6-G	0	65	5.8	6.0	- 3.33
	3,6-G	30	65	3.9	4.9	-20.41
Flexure	U6-G	0	56	6.6	7.1	- 7.04
	U6-G	90	56	1.6	1.6	0
	C4-G	0	57	6.4	6.4	0
	C4-G	45	57	2.4	2.4	0
	3,6-G	0	65	7.4	7.2	2.78
	3,6-G	90	65	2.0	2.1	- 4.76

[a]The stress angle and the lay-up angle (Table 7) are referenced to the same base.

was taken and assumed everything possible, within reason. By modifying one of these assumptions, a fit was obtained ±12%, with experiment (Table 10).

The assumptions made are very similar to those made by Timoshenko [18]. Each lamina was considered to be made of a material which was transversely isotropic. Together with the assumption of plane strain, this meant that we had to deal with only four elastic constants. Expressed in the form which is most amenable to direct measurement, these are longitudinal Young's modulus E_L, transverse Young's modulus E_T, longitudinal shear modulus G_L, and major Poisson's ratio, ν_{12}. The calculations were set up in the form of a computer program, and provision has been made to input a different set of values of the four elastic constants for each lamina (or ply). Also, each lamina can have its own individual thickness and orientation.

As output, the program gives values of the modulus of the laminate as the direction of the applied stress (i.e., direction of the beam axis in the case of flexure) is incremented at 5° intervals.

The first approach was to average the Young's modulus, which is tantamount to assuming that when the laminate is stressed each lamina is free to contract transversely at will. This would be the case if there were no adhesion between the laminae. The assumption would also be good if the transverse contraction effect were negligible. This approach does not give an invariant angular Young's modulus for a quasi-isotropic laminate, which has been shown to be the case experimentally [20].

To improve the theory, the assumption that the transverse strains were the same in each lamina was used instead. For flexure the transverse strain varies uniformly across the laminate thickness in proportion to z/r (r = radius of curvature of the flexed laminate) but without regard to the lamina material. This assumption is implemented by taking the appropriate average of the stiffness instead of the Young's modulus and is set out in Eq. (9) of Ref. 20:

$$[A_{ij}, B_{ij}, D_{ij}] = \int_a^b Q_{ij}[1, z, z^2]\, dz$$

Rather lengthy equations to give the transformed Q_{ij} ($= b_{ij}$), the reduced stiffness matrix in terms of the E's, G's, and ν's, are readily available.

In the program the stress direction is incremented at 5° intervals. The lamina properties are returned, transformed, and averaged each time. Tsai and Pagano [20] give the transformation equations for the laminate, but these were not used because they would involve the restriction that all laminae had the same Q_{ij}, and composites of two or more different materials are also of high interest.

To simplify the procedure from here on, only layups which have a mirror plane of symmetry in the plane of the laminate are considered. In practice such laminates do not warp although they may contain residual stress and are termed "balanced construction." This restriction fixes the origin of coordinates (neutral axis) at the center of the laminate. Then for the limits of integration in Ref 18, $-b = a$ ($= h/2$ in Ref. 20). It can be shown analytically [20] that the restriction makes

$$B_{ij} = 0$$

The task of getting the strains and curvatures from the applied forces and moments by using Eq. (7) of Ref. 20 now becomes more manageable:

$$N_i = A_{ij}E_j$$

$$M_i = D_{ij}k_j \qquad (7)$$

A_{11}/h is the ratio of the tensile stress to the tensile strain when the transverse strains are zero. To get the Young's modulus, which is valid when the transverse stresses are zero, it is necessary to calculate the reciprocal of the 11 component of the inverse of the matrix A_{ij}. This quantity is E_{xh}.

To calculate the flexural stiffness, the assumption was made that all $M_i = 0$ except M_1. Equations (7) can then be solved for k_1. That the contribution of the curvature k_1 to the deflection of the beam overwhelmed the contributions of all other k_i was then assumed by putting $k_1 = 1/r$ in the simple beam theory [18].

It is interesting to compare the laminate program, FLEX, with an approximate formula [20] of the Young's modulus of a

quasi-isotropic laminate. The difference is 3% for the glass and 8% for the PABH-T X-500. The laminate program predicts isotropy for these cases, agreeing with experimental observations.

22. LAMINATES—COMPARISON OF THEORY WITH PRACTICE

Theoretical values of Young's modulus and flexural stiffness were obtained using the computer program together with input data used (Table 11). Properties of E-glass were included for convenient comparison.

TABLE 11. Basic Component Properties Used to Compute Laminate Properties

	Epoxy resin	PABH-T X-500	S-Glass	E-Glass
Longitudinal Young's modulus (msi)	0.5	13.9	12.5	10.5
Transverse Young's modulus (msi)	0.5	0.5	12.5	10.5
Major Poisson's ratio	0.3	0.3	0.3	0.3
Density (g/cm^3)	1.204	1.46	2.484	2.550

The properties of the glass fibers are those commonly reported in the literature. The composite properties of each lamina were obtained from these data and from the desired fiber volume as follows:

Composite density: from rule of mixtures.
Composite longitudinal Young's modulus: from rule of mixtures.
Composite transverse Young's modulus: from equations of Ref. 19.
Composite longitudinal shear modulus: estimated from computations found in Ref. 15: glass, 0.9 msi; PABH-T X-500, 0.3 msi.

Composite major Poisson's ratio: estimated as 0.3.

The experimental and calculated values are shown in Table 10. There seems to be a degree of agreement sufficient to enable us to use the theory to explore the performance of PABH-T X-500 composites, on a specific modulus basis, over a wide ranging field of laminate constructions and stress directions. This has been done by means of polar plots (Figs. 4, 5, 6, and 7). In Table 10 it will be noted that isolated data points show disagreements up to 47%. In some cases, at least, the poorest agreement occurs where sensitivity to angle errors is high, and in all cases the experimental error was expected to be rather high. The computation also assumes the tensile and compressive moduli of the fibers are the same, which for PABH-T X-500 fibers is apparently not true.

23. A COMPARISON OF THE SPECIFIC MODULI OF PABH-T X-500 AND S-GLASS LAMINATES

The chief virtue of PABH-T X-500 is its high Young's modulus in the fiber direction and its low density. This can be expressed as a single number by the specific modulus with a value of 263×10^6 in. This advantage is progressively reduced as more and more matrix material is added to the composite, and also as the structural configuration moves away from the simple unidirection. For sheet-type structures the limit, or other extreme case where the specific modulus advantage of PABH-T X-500 is lowest compared to glass, is in the quasi-isotropic case [20]. The developed computational methods and experimental verification now allow us to compare PABH-T X-500 composites to S-glass or other composites easily. This has been done for example, by plotting polar diagrams (Figs. 4 to 7) of the specific modulus of selected laminates which, in order of increasing degree of isotropy, are unidirectional, cross-ply, and isotropic. A standard fiber volume of 60% was chosen and the component moduli figures which were used are given in Section 8.

The specific flexural stiffness as well as the specific Young's modulus has been calculated. The shape of the flexure curves can be qualitatively rationalized by bearing in mind that the flexural stiffness is more heavily weighted toward the stiffness,

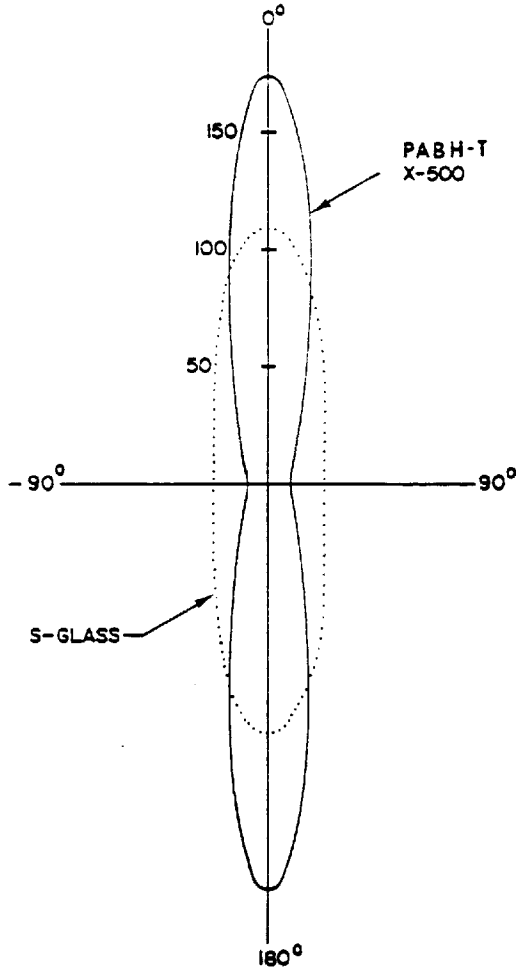

FIG. 4. Specific Young's modulus of unidirectional laminate (10^6 in.), (0°, 0°), 60% fiber volume.

in the stress direction, of the outer plys. The inner plys act as dead weight to some extent.

In addition the flexural figure of merit, $\hat{E}_{flex}/\rho^2$, referred to earlier, has been plotted for the two composite materials in unidirectional, cross-ply, and quasi-isotropic laminates. These

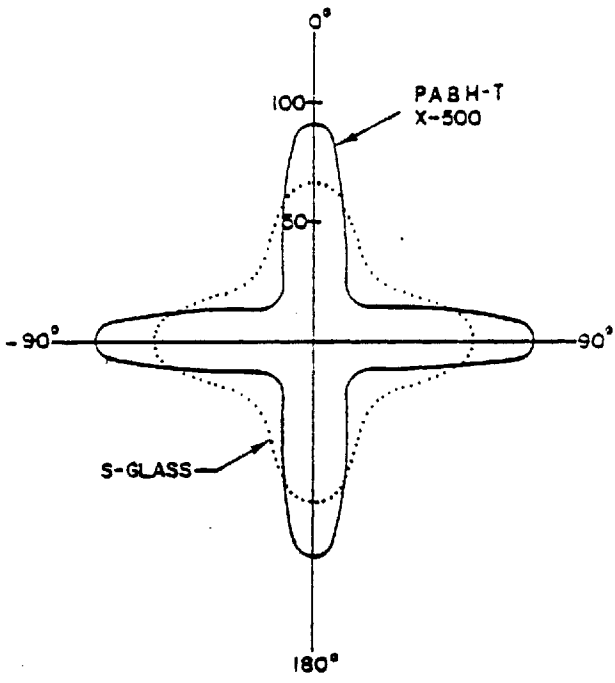

FIG. 5. Specific Young's modulus of cross-ply laminate (10^6 in.), 60% fiber volume (0°,90°,90°,0°).

appear as Figs. 8, 9, and 10, respectively. In these it can be seen that the PABH-T X-500 composites are almost everywhere stiffer than the S-glass composites on a minimum weight basis. The greater anisotropy of PABH-T X-500 composites can also be seen, due to the anisotropic nature of the fibers themselves as opposed to the isotropic glass fibers.

APPENDIX

Symbols have been used in the text according to the following scheme, and the abbreviations ksi and msi have been used to denote 10^3 psi and 10^6 psi, respectively.

Main Line Symbols

A = cross-sectional area (in.)
b = width (in.)
D = inside diameter of NOL ring (in.)
den = denier (g/9000 m)
E = Young's modulus of elasticity
G = shear modulus
H = head position of testing machine (in.) or velocity (in./min)
I = moment of inertia of section
J = torsional moment
N = number of turns of yarn
P = load (lb)
r = fractional position of neutral axis
s = compliance
S = span of depth ratio of a beam
S_H = ASTM horizontal shear strength (ksi)
t = thickness (in.)
v = volume fraction
V = volume (cc)
w = weight fraction
W = weight (g)
x = distance from compressive edge
ϵ = tensile strain
ρ = density (g/cc)
σ = tensile stress (psi)
ν = Poisson's ratio

Subscripts

a = actual or measured
app = apparent
c = property of composite, compression
f = property of fiber
iso = quasi-isotropic laminate
n = neutral axis
r = property of resin
t = tension, true
v = property of voids
11 = property of composite in the fiber direction
12 = property in 2 direction while stressed in the 1 direction, sheared in the 12 plane
22 = property of composite transverse to the fiber direction

Superscripts

$\hat{}$ = specific property (divided by density in $lb/in.^3$) or per unit length (cm)
* = value at fracture of the composite

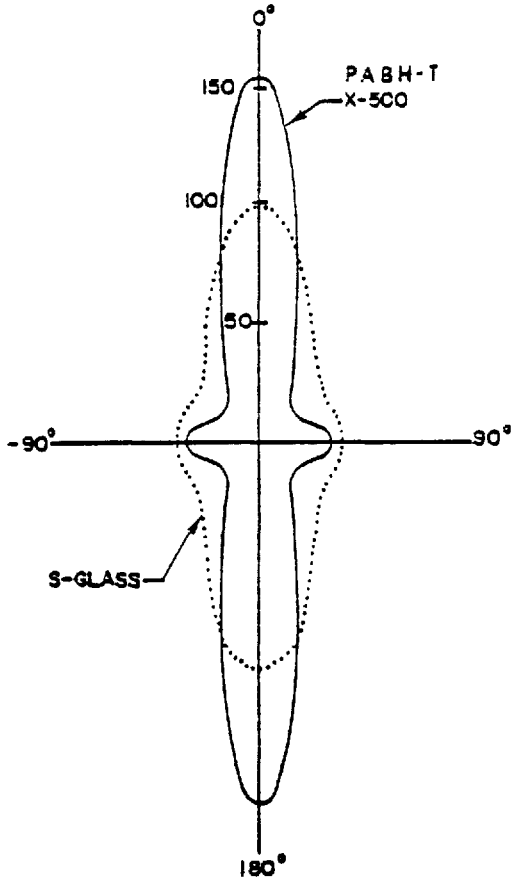

FIG. 6. Specific flexural stiffness of cross-ply laminate (10^6 in.), 60% fiber volume (0°,90°,90°,0°).

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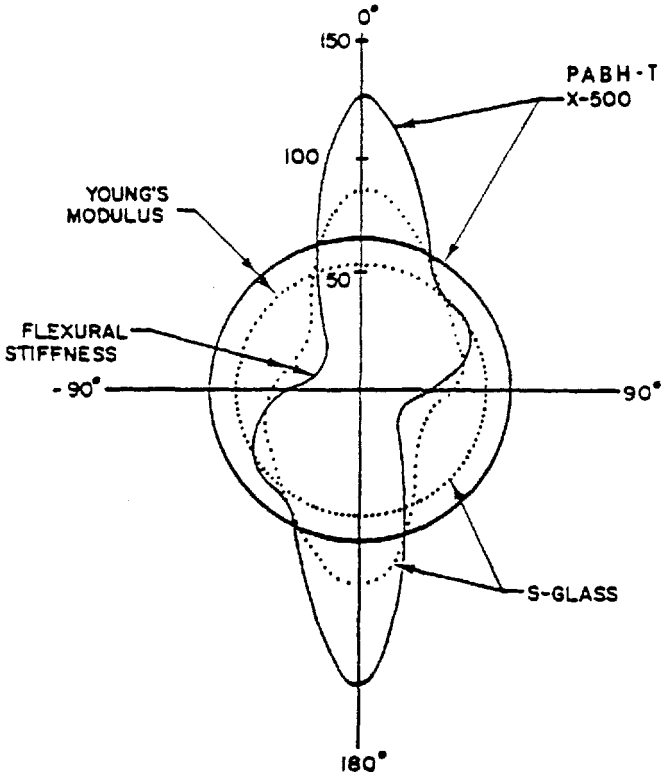

FIG. 7. Specific Young's modulus and flexural stiffness of isotropic laminate (10^6 in.), 60% fiber volume (0°,60°,-60°,-60°, 60°,0°).

melamine-formaldehyde, and polyimide resins; to P. A. Tranghber for fabrication of laminates; to H. P. Holladay for fabrication of the fabric laminate; to H. Morgan for providing the PABH-T X-500 yarns; to M. R. Lilyquist for providing the PABH-T X-500 fabric; to J. W. Ausley, M. C. Readling, and M. L. Woodcock for the bulk of the remainder of the laboratory work; and to J. W. Freeman, J. M. Peterson, J. D. Calfee, J. P. Bell, and J. R. Holsten for many valuable discussions.

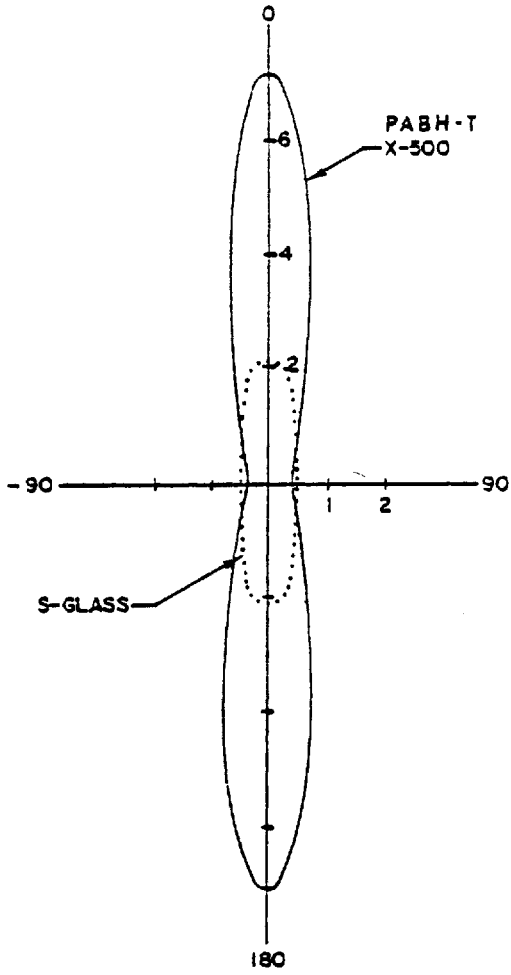

FIG. 8. Flexural stiffness figure of merit of unidirectional laminate (10^{10} in.^{7}, lb^2), 60% fiber volume.

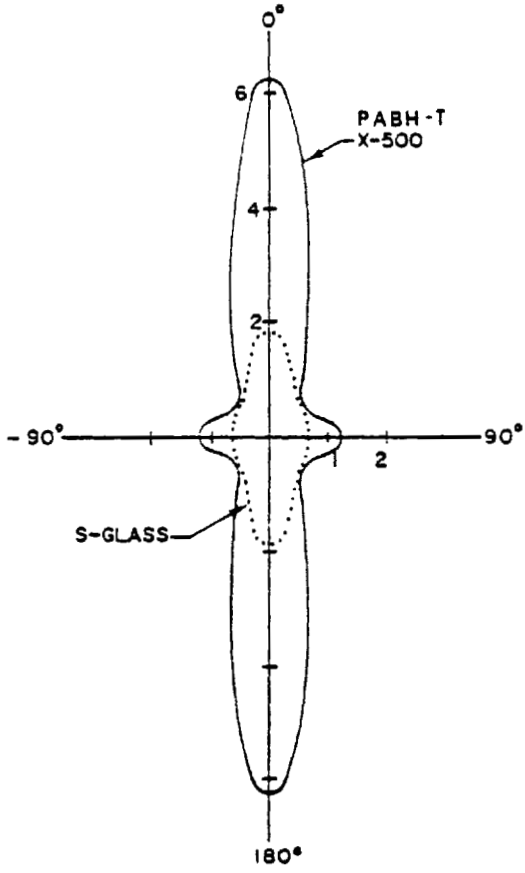

FIG. 9. Flexural stiffness figure of merit of cross-ply laminate (10^{10} in.^{7}/lb^2), 60% fiber volume (10°,90°,90°,0°).

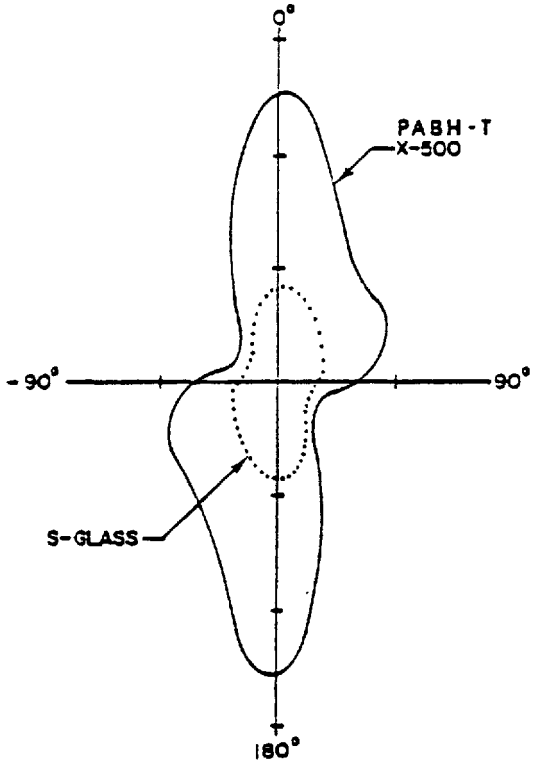

FIG. 10. Flexural stiffness figure of merit of quasi-isotropic laminate (10^{10} in.^{7} lb^2) (0°,60°,-60°,-60°,60°,0°), 60% fiber volume.

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