AFWAL-TR-86-4003

ADA171620

PBT

THE INTERFACIAL AND COMPRESSIVE PROPERTIES OF POLYBENZOTHIAZOLE FIBERS

L. T. Drzal

Mechanics and Surface Interactions Branch
Nonmetallic Materials Division

June 1986

Final Report for Period January 1984 to December 1984.

Approved for public release; distribution unlimited

MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AFB, OHIO 45433-6533

20040219245

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

L. T. Drzal

L. T. DRZAL
Materials Research Engineer
Mechanics & Surface Interactions Br

SW Tsai

STEPHEN W. TSAI, Chief
Mechanics & Surface Interactions Br
Nonmetallic Materials Division

FOR THE COMMANDER

Merrill L. Minges

MERRILL L. MINGES, Chief
Nonmetallic Materials Divison

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/MLBM *, W-PAFB, OH 45433 to help us maintain a current mailing list".*

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS
N/A

2a. SECURITY CLASSIFICATION AUTHORITY
N/A

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE
N/A

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
AFWAL-TR-86-4003

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Mechanics & Surface Interactions Branch

6b. OFFICE SYMBOL *(If applicable)*
AFWAL/MLBM

7a. NAME OF MONITORING ORGANIZATION
N/A

6c. ADDRESS *(City, State and ZIP Code)*
Materials Laboratory
Wright-Patterson AFB OH 45433-6533

7b. ADDRESS *(City, State and ZIP Code)*
AFWAL/MLBM
Wright-Patterson AFB OH 45433-6533

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
Materials Laboratory

8b. OFFICE SYMBOL *(If applicable)*
AFWAL/MLBM

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N/A

8c. ADDRESS *(City, State and ZIP Code)*
Wright-Patterson AFB OH 45433-6533

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61102F	2303	Q3	07

11. TITLE *(Include Security Classification)* The Interfacial and Compressive Properties of Polybenzothiazole Fibers

12. PERSONAL AUTHOR(S)
L. T. Drzal

13a. TYPE OF REPORT
Final

13b. TIME COVERED
FROM Jan 84 TO Dec 84

14. DATE OF REPORT *(Yr., Mo., Day)*
June 1986

15. PAGE COUNT
35

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB. GR.
11	04	
11	05	

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
PBT
Polybenzothiazole
Fiber
Compressive Strength
Shear Strength
Interface
Graphite Epoxy
Composite
Kevlar 49

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This report evaluates the interfacial and compressive properties of polyparaphenylene-benzobisthiazole (PBT) fibers in an epoxy matrix (Epon 828, Shell Chemical Co., cured with metaphenylenediamine). The interfacial shear stress was measured by the single fiber tensile coupon method, while wettability of the fiber was determined from the contact angle. A technique was developed for measuring compressive strength of single fibers by placing a matrix-embedded fiber in axial compression, and observing microscopically the onset of kinking or fracture in the fiber.

The difficulty in developing adhesion between PBT fibers and epoxy matrices appears to be due to three factors: (1) the surface of the PBT fiber is thermally stable and very non-reactive making traditional methods of improving fiber-matrix adhesion inoperative; (2) the Poisson's ratio of the PBT fiber is greater than that of the typical structural matrices used in advanced composites, which results in a net tensile interfacial force

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. T. E. Helminiak

22b. TELEPHONE NUMBER *(Include Area Code)*
513-255-9154

22c. OFFICE SYMBOL
AFWAL/MLBP

Block 19 Cont'd:

causing separation of the fiber and matrix under tensile loading conditions; (3) the fibrillar nature of the fiber causes interfibrillar failure under shear loading which is the upper limit axial shear strength.

The interfacial shear strength attainable with the PBT fibers and epoxy is only of the order of 1.5 ksi versus the value of 3.6 ksi obtained with Kevlar-49 in the same matrix.

The compressive strength of PBT fibers is substantially below that of the tensile strength of the same fibers. The highly oriented structure of the fibers, its fibrillar nature and its lack of transverse coupling between fibrils contribute to the generation of a microbuckling type of instability causing formation of helical surface folds which propagate at very loads. The compressive strength of PBT fibers measured by the single fiber compressive coupon method is about 50 ksi. A Kevlar-49 aramid fiber has a compressive strength of about 123 ksi and a graphite AS-4 fiber has a compressive strength of 1000 ksi in the same matrix.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

SECTION I

INTRODUCTION

The Polymer Branch of the Air Force Materials Laboratory has developed a new class of high performance materials based on aromatic-heterocyclic rigid-rod polymers. These polymers have been spun into fibers which have demonstrated properties superior to many common reinforcing elements of composites in use today.

One composition, polyparaphenylene benzobisthiazole (PBT) has exhibited a high degree of order as well as excellent heat and moisture resistance. Fibers spun from this material and heat treated, produce a material with a tensile modulus of 40 million psi (280 GPa) and a tensile strength of 400,000 psi (2.8 GPa). Further optimization of critical process parameters of PBT offers the possibility of creating a polymeric reinforcing fiber exceeding these initial values.

Evaluation of this polymeric reinforcement in an advanced composite requires that the fiber properties be effectively coupled to the matrix. Therefore the interfacial shear strength between the PBT fiber and the matrix is important. Likewise the ability of the PBT fiber to withstand compressive loadings as well as tensile loadings is crucial to composite performance. This study was directed at evaluating the interfacial and compressive properties of these PBT fibers so that appropriate steps could be taken to concurrently optimize the PBT mechanical property values as well as the PBT processing parameters.

SECTION II

EXPERIMENTAL

Two sources for the PBT fibers were used in these experiments. One source was PBT fiber designated AF Tech I and was produced by the Celanese Research Company (Reference 1). The fiber was used 'as received' after overnight vacuum drying at 125°C. The other fiber labelled AF Tech II was produced by the E. I. duPont de Nemours Company (Reference 2). It was pretreated in the same manner as AF Tech I. The average diameter, Young's tensile modulus and the tensile strength of these fibers are listed in Table 1. PBT fibers taken from these lots and surface treated in various ways were also evaluated in this program. Their identification is included at the appropriate point in the text.

TABLE 1

MECHANICAL PROPERTIES OF THE PBT AND ARAMID FIBERS

	Dia(u)	(Msi)Ey(GPa)		(Ksi)T.S.(GPa)	
AF Tech I	13.4	37	258	414	2.85
AF Tech II	16.4	41	280	435	3.00
Kevlar 29	13	9	62	400	2.76
Kevlar 49	13	18	124	400	2.76

A baseline for comparison of the interfacial and compressive behavior of the PBT fibers was established by including two aramid reinforcing fibers (Kevlar 29 & 49) in these investigations. The aramid fibers have a lower tensile modulus than the PBT fibers with a similar tensile strength and were obtained from the duPont company. The sizing present on these fibers was removed by repeated washing with absolute ethyl alcohol followed by overnight drying under vacuum at 125°C.

2. MATRIX

The matrix used in this investigation was a stoichiometric mixture of a diglycidyl ether of bisphenol-A (Epon 828, Shell Chemical Company) cured with 14.5 phr meta-phenylene diamine (m-PDA, Aldrich Chemical Company). The m-PDA was of high purity and was kept in a cool, dark, inert environment to prevent deterioration. A previous study has shown that a "darkened" m-PDA can affect the interfacial properties while leaving the bulk properties of the epoxy unchanged (Reference 3). The Epon 828 was likewise kept in a cool, inert environment to prevent deterioration during the course of these experiments. The matrix system was vacuum melted, mixed, debulked, and then processed for two hours at 75°C and for two hours at 125°C followed by an overnight cooldown.

3. INTERFACIAL SHEAR STRENGTH

The adhesion between fiber and matrix was characterized through measurement of the interfacial shear strength. This is accomplished by embedding the fiber in a tensile coupon of matrix resin and subjecting the specimen to tensile loading. Since the tensile forces are transferred to the fiber through shear forces at the fiber-matrix interface and because the maximum strain of the fiber is much less than that of the matrix, the fiber will fracture into small segments within the matrix. As higher tensile loads are applied the fracture process continues until the interfacial forces no longer induce fracture in the fiber. At this point a minimum segment length is attained known as the critical transfer length (ℓ/d) which allows the interfacial shear strength to be determined.

The relationship between fiber tensile strength (σ_f) critical length to diameter ratio (ℓ/d) and the interfacial shear strength (τ) is given by

$$\tau = \frac{\sigma_f}{2}\left(\frac{\ell}{d}\right) \qquad (1)$$

Since a distribution of lengths is observed experimentally, this relationship has been altered to reflect Weibull statistics to the form

$$\tau = \frac{\sigma_f}{2\beta} \, \Gamma\left(1 - \frac{1}{\alpha}\right) \qquad (2)$$

where (α) is the shape factor, (β) is the scale factor (i.e., the mean value of (ℓ/d) and (Γ) is the Gamma function. This relationship is used to evaluate the interfacial shear strength between fiber and matrix. Details of the technique and the data accumulation and reduction schemes have been published (Reference 4).

4. MICROSCOPY

Two microscopic techniques were used to investigate the interfacial response between graphite fiber and matrix as a function of shear loading. Optical microscopy with transmitted polarized light was used to detect fiber fracture within the epoxy specimen and to document the load transfer from fiber to matrix near the region of the fiber break. Transmitted electron micrographs (TEM) of 70 nm thick sections of graphite fiber-epoxy specimens cut parallel to the fiber axis with an ultramicrotome were used to document the failure path at the interface. Details of the techniques have been published (Reference 5).

5. CONTACT ANGLE

A precursor to formation of a coherent void-free composite is wetting of the reinforcing fiber by the matrix. The measurement of contact angles by selected organic liquids of known polar and dispersive surface free energy is the preferred method for wetting evaluation. This approach is not possible with these PBT fibers because some of the wetting liquids can be absorbed into the fiber giving an erroneous contact angle. In order to avoid this difficulty, droplets of the epoxy matrix itself were placed on the fiber surface and cured. The contact angles were measured optically.

Individual fibers were mounted on a stainless steel frame and fixed in position with cyanoacrylate adhesive over a two centimeter span. The epoxy matrix (a stoichiometric mixture of Epon 828 and m-phenylene diamine) was deposited on the fiber surface at various points and 20 micron diameter droplets were formed. The apparatus was transferred to a vacuum oven and given the standard epoxy cure cycle. After removal from the oven, the frame was transferred to the stage of a transmitted light microscope and the contact angle formed between the matrix and fiber was determined optically.

6. COMPRESSIVE STRENGTH

The compressive strength of small fibers is a difficult property to measure. Buckling of unsupported fibers tends to occur before true compressive failure. In a development program such as this where large amounts of fiber are not available to fabricate composite specimens single fiber techniques must be used. A special compressive single fiber specimen and loading fixture was prepared which allows the compressive strength of individual fibers to be measured. The sample consists of an 18mm long curved neck epoxy specimen. The specimen is cast with a single fiber centered axially. The sample thickness is about 3mm and the cross sectional area at the minimum diameter in the necked region is about six square mm.

The sample is loaded at the ends and compressed slowly until the first indication of compressive failure is detected in the necked region. For these polymeric fibers the appearance of a fold in the fiber surface is the first indication. This process is observed with the aid of transmitted light at about 200 x. The load at the observation of this first compressive event can then be related to the fiber compressive strength through the following relationship (Reference 10)

$$\sigma_c = \frac{P}{A_f + \frac{E_m}{E_f} A_m} \tag{3}$$

where (σ_c) is the fiber compressive strength, A_m is the matrix cross sectional area at the center of the specimen, A_f is the fiber cross sectional area, E_m is the matrix tensile modulus and E_f is the fiber tensile modulus.

SECTION III

SURFACE TREATMENTS

Fiber surface treatments were used in an attempt to enhance the interfacial shear strength. Three different approaches were tried. Coupling agents were used. These silane and titanate type coupling agents function through the promotion of a surface chemical bond between the agent and both the reinforcement surface and the matrix.

Fiber finishes can be used to promote adhesion. Because of the large modulus mismatch, finishes that were intermediate in modulus between the fiber and matrix were tried. Since the strain response of the PBT fiber was different than the brittle reinforcements commonly used for advanced composites, compliant finishes were also used. In all cases, the finishes were dissolved in an appropriate solvent and applied to about 1% by weight to the fiber surface. This created a coating about 200 nm in thickness.

A third approach was to modify the fiber surface and surface chemistry through the use of cold plasma treatments. Argon, oxygen, ammonia, and water plasmas were created and used to treat the fiber surface at various power levels and for increasing periods of time. The onset of fiber mechanical property degradation was used as the upper limit for termination of the plasma treatments.

SECTION IV

RESULTS AND DISCUSSION

1. PBT FIBER WETTABILITY

The contact angle that a 25 micron droplet of epoxy matrix forms after being deposited on a single PBT fiber was measured. The value of the contact angle was used to compute the Work of Adhesion (Wa). The value of the Work of Adhesion is given by the expression

$$Wa = \gamma_{LV} (1 + \cos \theta) \tag{4}$$

where (γ_{LV}) is the surface free energy of the epoxy matrix and θ is the value of the contact angle. For the case where the contact angle is zero, that is spreading of the epoxy on the fiber, the value of the cosine of the contact angle is 1 and the Work of Adhesion is just twice the surface free energy of the epoxy or for this formulation, 84.6 ergs/square cm.

The results of these measurements are listed in Table 2.

The first section of data in Table 2 compares the PBT fibers with two common commercial reinforcements, AS-4 an intermediate modulus graphite fiber and Kevlar-49 an aramid reinforcing fiber. The graphite fiber is wet by this epoxy matrix and gives a value for the contact angle of 27°. The aramid fiber is also wet by the epoxy and has a value for the contact angle of 15°. Both PBT fibers (AF Tech I and II) are indistinguishable from each other in their wetting behavior and have a value (∿28°) which is the same as that obtained on the graphite fiber. Comparing the Work of Adhesion shows that thermodynamic wetting is most favorable for the aramid fiber with the graphite and PBT fibers being about equal.

In an effort to improve the wettability of the PBT fibers, various surface treatment methods were applied to the PBT fiber surfaces. Since the wettability of both PBT fibers was almost identical the surface treatment experiments were conducted on the AF Tech I fibers only.

TABLE 2

CONTACT ANGLE AND WORK OF ADHESION
OF EPOXY AT 70°C

Fiber	Contact Angle (θ)	Work of Adhesion (ergs/cm)
AS-4 (graphite)	27^{0}+/-4^{0}	80.0
Kevlar-49 (avamid)	15^{0}+/-3^{0}	83.0
AF Tech I (PBT)	27^{0}+/-6^{0}	80.0
AF Tech II (avamid)	29^{0}+/-3^{0}	79.3
Treated AF Tech I		
	'PLASMA'	
NH_3/5min/50watt/100u	19^{0}+/-3^{0}	82.3
O_2/5min/10watt/150u	26^{0}+/-1^{0}	80.3
H_2O/15min/50watt/200u	26^{0}+/-4^{0}	80.3
	'CHEMICAL TREATMENTS'	
Steam/240min/125°C/Vac	26^{0}+/-4^{0}	80.3
$HClO_4$	28^{0}+/-7^{0}	79.7
	'COUPLING AGENTS'	
DOW Corning #1	58^{0}+/-4^{0}	64.7
DOW Corning #2	39^{0}+/-4^{0}	75.2
DOW Corning #3	27^{0}+/-4^{0}	80.0
DOW Corning #4	44^{0}+/-9^{0}	72.7
DOW Corning #5	56^{0}+/-5^{0}	66.0
	'FINISHES'	
Epon 828	26^{0}+/-4^{0}	80.3
Epon 828-190°C	30^{0}+/-6^{0}	78.9
MY720	47^{0}+/-12^{0}	71.1
MY720-190°C	24^{0}+/-7^{0}	80.9

A large body of published information exists of the treatment of polymers with cold plasmas. Three types of plasma were tried with the PBT fiber. Oxygen was used in order to oxidize the fiber surface and introduce surface oxygen groups capable of interacting with the epoxy matrix. Water was used as the active agent for the second plasma treatment in order to add surface hydroxyl groups. If the fiber surface could by hydroxylated, silane or titanate coupling agents could be used to alter the fiber matrix adhesion. The third approach was to use ammonia as the plasma agent in order to aminate the surface as had been reported as promoting adhesion to Kevlar fibers (Reference 6).

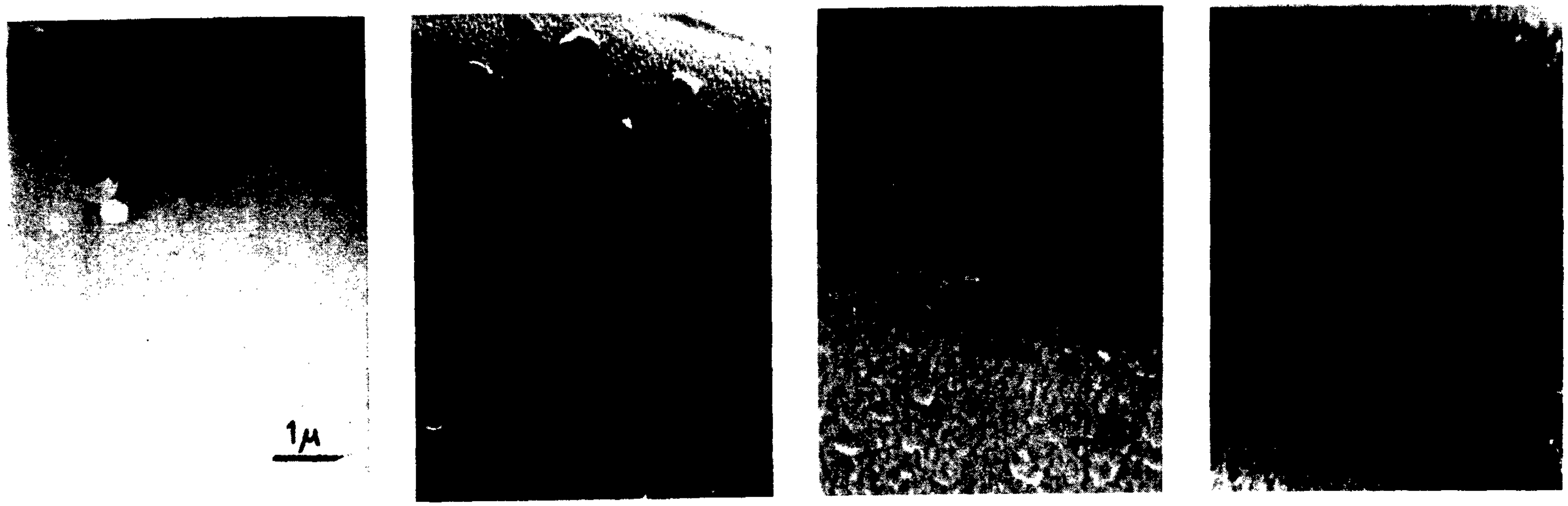
The plasma conditions are as listed in Table 2.

Both the oxygen and water plasma treatments did not improve the fiber wetting characteristics with this epoxy. Prolonged treatments at longer times and higher pressures and/or power levels produced a deep etching of the fiber surface as shown in Figure 1. These prolonged plasma treatments also gave indications of differences between the structure of the PBT fiber surface and the core of the fiber. The Argon c) and Oxygen d) plasma show remnants of the original fiber surface that is attacked by the plasma in a different way. Strength measurements of these fibers showed that the surface etching was accompanied by a severe loss in fiber tensile properties. A listing of the other plasma treatments tried and the effect of these treatments on the fiber tensile strengths and Young's modulus is included in Table 3.

For the treatments listed in Table 2, within the experimental scatter of the measurements, no changes were detected in the fiber contact angles. However, for the ammonia plasma a small but experimentally significant reduction in contact angle and hence a measurable increase in the Work of Adhesion was detected.

Other chemical treatments were used to change the fiber surface chemistry. Steam and acid treatments were tried but did not alter the fiber wettability.

The Dow Corning Company (Midland, MI) was asked to provide some coupling agents for use with these fibers. Five surface coupling agents were applied to samples of the fiber by Dow Corning and the contact angle with the epoxy was measured. The silane coupling agents furnished in all cases either reduced the fiber wettability by the epoxy or had no measurable effect. Silane agents were also tried on the



a) As Received

b) Ammonia
50w 150u 150m

c) Argon
50w 150u 30m

d) Oxygen
50w 150u 150m

Figure 1. Surfaces of Plasma Etched AF Tech I Fibers

TABLE 3

AF TECH I TENSILE STRENGTH
(1", Single Filament)

TREATMENT	Dia(u)	(Msi)Ey(GPa)		(Ksi)T.S.(GPa)	
NONE	12.7	37.6	259	414	2.85
c.v.	+/-4%	+/-5%		+/-7%	
Argon Plasma					
30min/50W/150u	11.0	31.1	214	174	1.2
Ammonia Plasma					
5min/50W/1000u	12.7	38.2	263	395	2.72
150min/50W/150u	12.1	34.3	236	272	1.88
Oxygen Plasma					
5min/10W/150u	12.7	37.4	258	387	2.67
5min/25W/150u	12.7	37.0	255	362	2.5
5min/50W/150u	12.5	35.9	248	360	2.48
30min/50W/150u	12.5	32.0	221	224	1.54
Water Plasma					
5min/50W/50u	12.6	36.8	254	403	2.78
15min/50W/200u	11.6	35.3	243	277	1.91
Steam					
240min/125°C/VAC 125°C	12.7	37.6	259	426	2.94

water plasma and steam treated fibers. The amino functional and epoxy functional silanes did not alter the fiber wettability.

An alternate approach to alteration of the fiber surface chemistry is to apply a finish to the fiber surface. The finish is usually a polymer compatible with the matrix applied from solution to about one weight percent. Previous studies have shown the epoxy resin itself or in combination with the curing agent can have a beneficial effect on fiber-matrix adhesion (Reference 7). Two types of epoxy resin, the di- and tetra- functional types were applied and dried in air or under elevated temperature conditions. Neither method caused a significant improvement in fiber wettability.

Other studies have shown that the PBT polymer is extremely resistant to solvents and chemical attack except for protonated acids (Reference 8). The difficulty in altering the PBT fiber surface chemical functionality must be due to the inert nature of the fiber making chemical attachment of either coupling agents or polymeric finishes very difficult.

SECTION V

INTERFACIAL SHEAR STRENGTH

One of the primary goals of the surface modification of the PBT fiber was to increase its shear strength in an epoxy matrix. Actual composite testing is not feasible in a fiber development program because of the limited number of samples produced and the variability of the fiber. The single fiber interfacial shear strength test developed at the Materials Laboratory provides quantitative comparisons with other fibers for interfacial shear strength and in addition can give additional insight into the fiber behavior under shear loading.

Both AF Tech I and II were fabricated into single fiber samples and tested for interfacial shear strength along with the AS-4 graphite fiber and the aramid fiber.

The determination of the single fiber interfacial shear strength requires measurement of the fiber fracture length. While this quantity can be easily measured for the graphite fiber because of its brittle nature the actual fracture locus is impossible to determine for the aramid or PBT fibers. The fracture area could be located however by the large degree of local interfiber fracture seen under transmitted light as indicated by the region between the arrows in Figure 2. (An enlargement of this region for the AF Tech I fiber is shown in Figure 3.) For the aramid and PBT fibers, the number of fracture regions in a fixed fiber length were used to calculate the fiber critical transfer length, while the lengths could be measured directly for the graphite fiber.

The measured fiber critical length to diameter ratios are listed in Table 4 along with the interfacial shear strength calculated from Equation 2. Also listed is the fiber tensile strength which was measured independently for each fiber or fiber surface treatment. This quantity also determines the interfacial shear strength as shown by Equation 2 and must be independently measured at the actual fiber critical length to diameter ratio. Surface treatments can reduce fiber strength and/or change the fiber strength with gage length. These changes must be accounted for if an accurate value for the interfacial shear strength is desired.

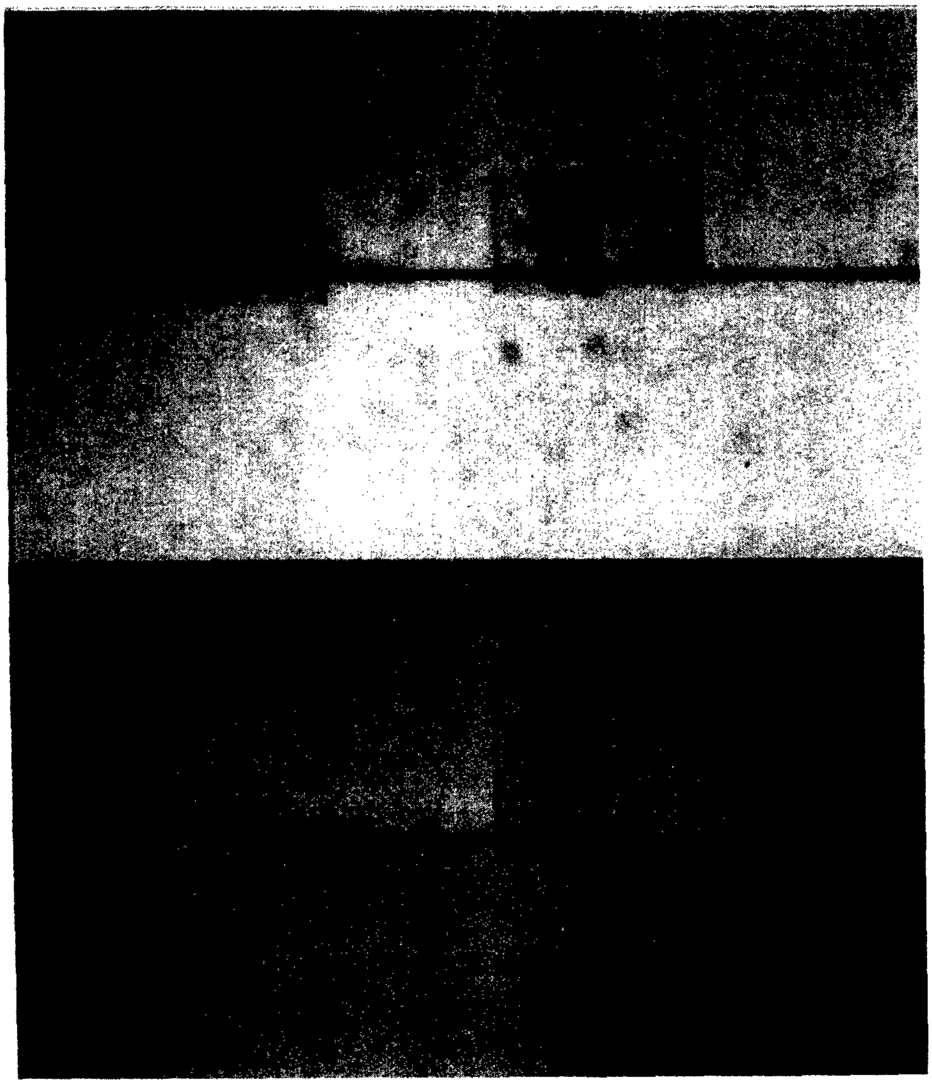
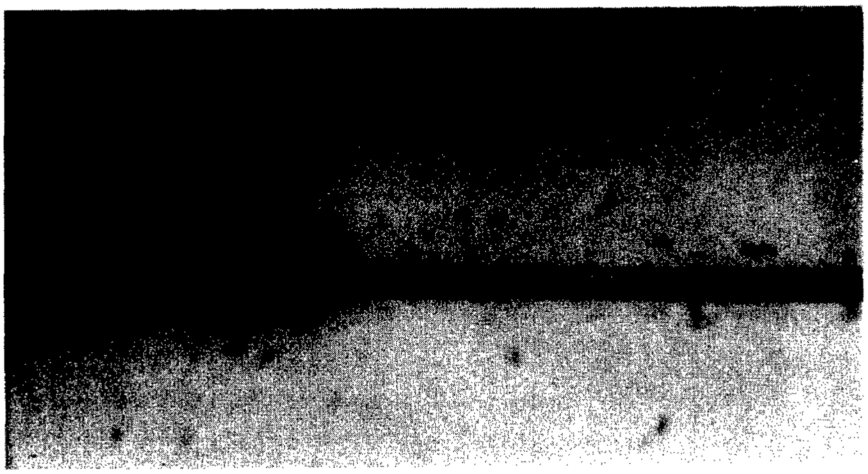
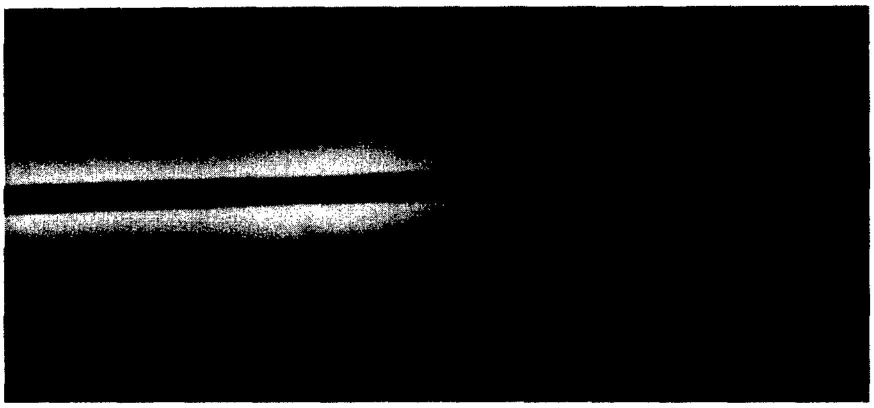


Figure 2. Fibrillar Fracture of Polymeric Fibers



a) Transmitted Light (400x)



b) Polarized Light (400x)

Figure 3. AF Tech I Fiber in Epoxy at 4% Strain

TABLE 4

INTERFACIAL SHEAR STRENGTH IN EPON 828/14.5 phr mPDA

Fiber	ℓ/d	σ_f(ksi)	τ(ISS)
AS-4	57+/-6	845	9.9
Kevlar-49	75+/-5	400	3.4
AF Tech I	139+/-14	414	1.5
AF Tech II	157+/-20	435	1.3
Treated AF Tech I			
PLASMA			
NH_3/5min/50W/1000u	139	395	1.5
O_2/5min/10W/150u	157	387	0.9
O_2/30min/50W/150u	50	224	2.2
H_2O/15min/50W/200u	140	277	1.0
Ar/30min/50W/150u	41	174	2.1
TREATMENTS			
Steam	153	426	1.4
$HClO_4$	139	414	1.5
COUPLING AGENTS			
DOW Corning #1	161	414	1.3
DOW Corning #2	165	414	1.3
DOW Corning #3	160	414	1.3
DOW Corning #4	149	414	1.4
DOW Corning #5	150	414	1.4
A189 (epoxy-silane)	131	414	1.6
Z6040(amino-silane)	144	414	1.4
KR52S (titanate)	201	414	1.0
FINISHES			
Epon 828	136	414	1.5
Epon 828/190°C	155	414	1.5
MY720	136	414	1.5
MY720/190°C	122	414	1.7
C1000-Vulcup	117	414	1.8
Eponol 55-B-40	122	414	1.7

As shown in Table 4, the AS-4 graphite fiber has the shortest length to diameter ratio and has the highest interfacial shear strength. The aramid fiber has a longer ℓ/d and a lower interfacial shear strength. Both PBT fibers have a very large ℓ/d and consequently a very low interfacial shear strength. Although there is a difference in the ℓ/d and the interfacial shear strength between AF Tech I and II this difference is not significant based on the scatter experienced in conducting these measurements on the PBT fibers.

An interesting feature of the single fiber interfacial shear strength test is that the fiber can be observed under load with transmitted light. Figure 3 is a micrograph of a PBT fiber under load in the epoxy matrix under both transmitted and polarized transmitted light. Under transmitted light a large number of irregular fractures are observed to occur within the fiber. The fractures are concentrated in one region of the fiber. Catastrophic failure is not detected. A progressive increase in the fracture density is observed with increasing shear load on the fiber. Observation of the same area under polarized transmitted light highlights some of the fractures and shows regions of epoxy matrix that are under stress as indicated by the photoelastically active areas. Most of the fractures in the fiber are internal but some extend to the outer surface of the fiber.

The internal fracturing process occurring in the fiber can be seen in transmission electron micrographs (TEM) of the stressed fiber. Figure 4 is an ultramicrotomed section of a PBT fiber in the epoxy matrix. Before loading, the sample is cohesive and shows a remarkable regularity in structural features reflecting the axial morphology of the fiber (Figure 6). After loading in shear, fracture has taken place within the fiber as evidenced by the regions of discontinuity in the fiber.

Figure 5 is a sequence of micrographs of the same area of a PBT (AF Tech I) fiber encapsulated in the epoxy matrix and observed as a function of increasing strain. In photographs a) to e) the strain on the sample is increasing. Axial internal fracture of the fiber can be observed. Figure 5 sections e) to h) show another remarkable feature of the PBT fiber. During the unloading of the sample, a folding or kinking of the outer skin of the fiber is observed. Apparently the fiber has moved in relation to the matrix under the tensile loading conditions. When unloading starts, the outer part of the fiber is loaded in compression causing folds in the outer skin to appear. The folds are seen to grow in a helical manner around the circumference of the fiber with an axial shift resulting in a helical pattern.

Figure 4. TEM of Ultramicrotomed Section of AF Tech I Fiber in Epoxy after Straining to 6%

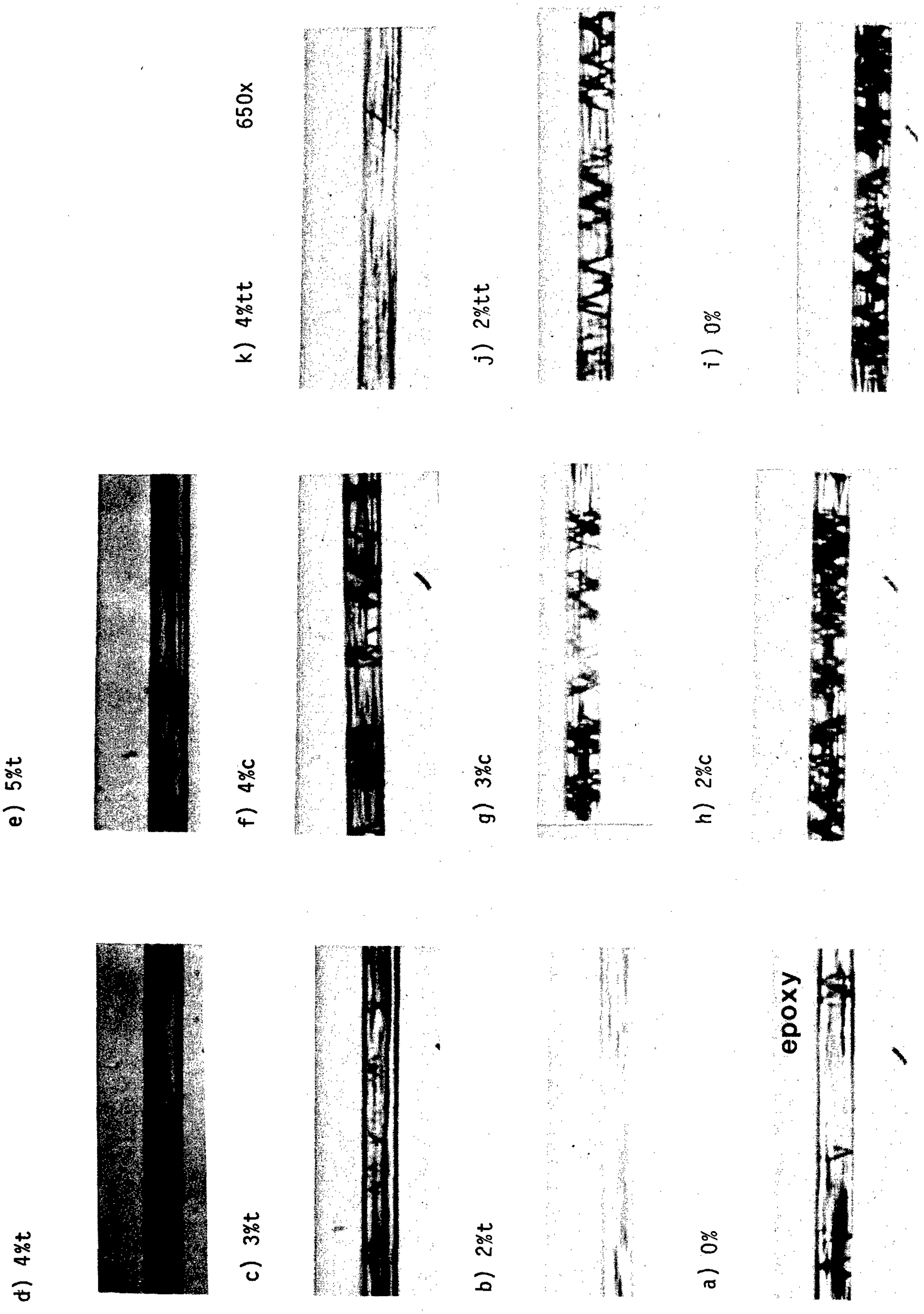


Figure 5. EPON 828/mil DA/AF Tech I Fiber

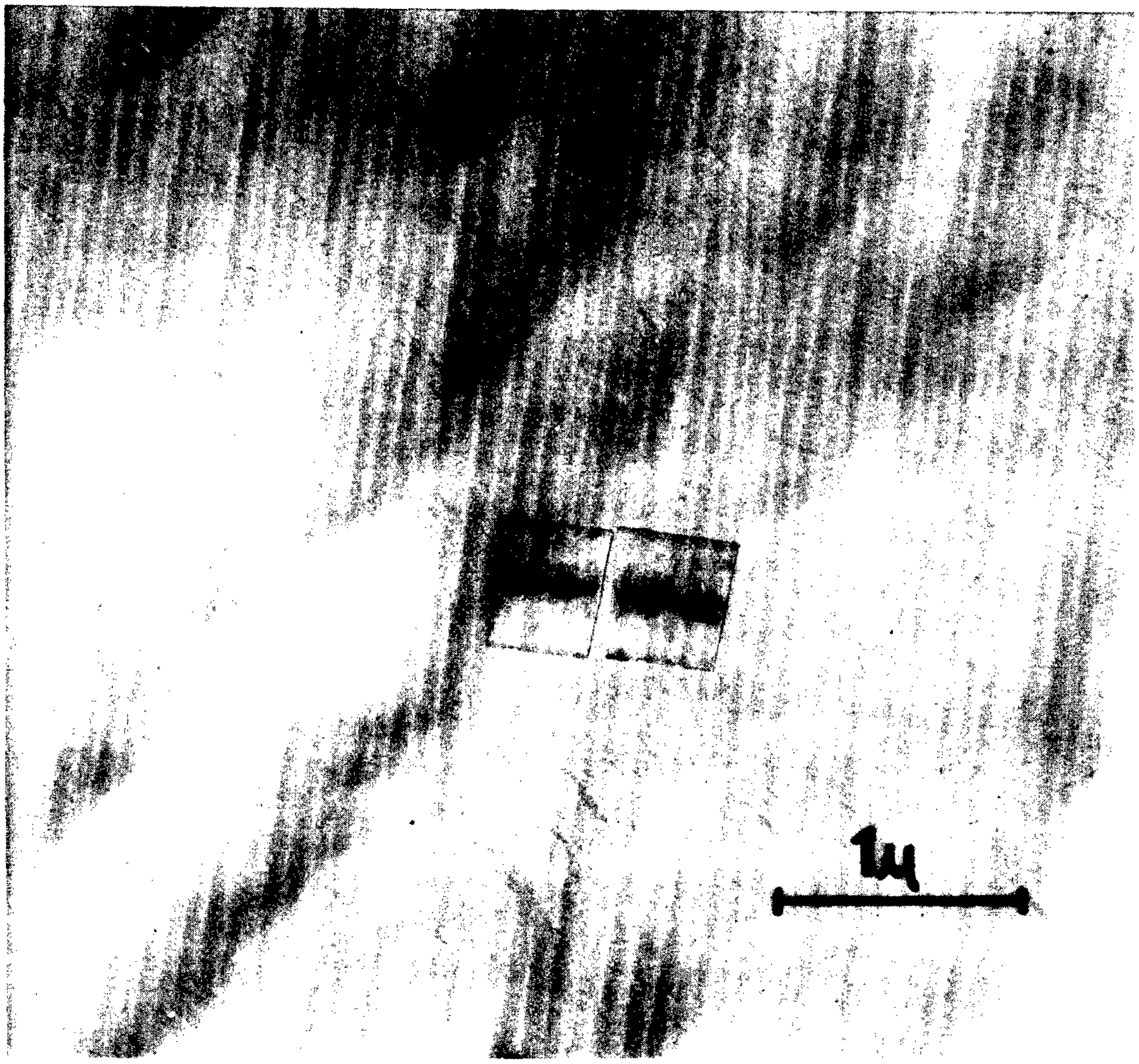


Figure 6. TEM of Ultramicrotomed Section of PBT Fiber

The growth of this folded outer fiber skin is reversible (sections i) to k)) and subsequent reloading of the sample causes it to disappear. The process is reversible with no discernible permanent fiber damage detectable. Similar behavior has been documented for the aramid fibers (Reference 9).

The interfacial shear strength for the AF Tech I and II fibers is lower than other fibers currently used in conventional composites. The various surface treatments, plasma treatments, finishes, and coupling agents applied to the PBT fiber in the wettability studies were tested for their effect on interfacial shear strength. The remaining rows of Table 4 summarize this data.

The overall lack of any significant change in the interfacial shear strength with surface treatment is immediately obvious. The 1.5 ksi value obtained for the untreated fibers is not substantially changed by any method listed. Some of the more severe plasma methods which are altering the fiber topography do cause the ℓ/d ratio to decrease giving a rise in the interfacial shear strength. The tensile properties of these treated fibers are quite poor however, so as to make them unsuitable for use as a reinforcement.

In addition to the Dow Corning supplied proprietary coupling agents, three of the common silane coupling agents were evaluated. A189 and Z6040 are amino and epoxy functional silanes respectively. The KR52S is a titanate coupling agent advertised as effective with aramid fibers in epoxy matrices. None of these coupling agents exhibited a change in either level of interfacial shear strength or a change in interfacial failure mode when applied according to the manufacturers directions. Two additional finishes were tried with the PBT fibers. The C1000-Vulcup was a high shrinkage resin applied to induce a large radial compressive force on the fiber to retard fiber fibrillation and increase the interfacial shear strength. The Eponol 55-B-40 is a thermoplastic epoxy based coating designed to increase the interfacial toughness. While some slight decreases in the ℓ/d were noted statistically significant decreases in the ℓ/d and increases in the interfacial shear strength were not detected.

An explanation for the lack of any significant change in the interfacial shear strength can be proposed. The PBT fiber's Poisson's ratio was calculated from composite data (Reference 2). The value for this fiber was around 0.4. The Poisson's ratio for most polymers and for the epoxy matrix used here is about 0.35. This leads to the conclusion that there is a net tensile force acting on the PBT fiber-epoxy interface acting to pull the two materials apart under tensile loading, which is the case in the interfacial shear strength testing. Irregardless of the approaches taken to change the fiber surface chemistry or to improve the interaction with the matrix material, the tensile mode at the interface due to the Poisson's ratio mismatch would act counter to the hoped for effect. This leads to the conclusion that a matrix with a Poisson's ratio greater than 0.4 would be a more effective matrix for the PBT fiber. This unfortunately is out of the realm of most structural polymeric matrices and can be achieved only with material having a high elastomeric character.

In addition to the mismatch in Poisson's Ratio that exists between fiber and matrix, the fibrillar nature of the fiber itself observed in the microtomed sections, contributes to the limitation preventing an increase in interfacial shear strength. Figure 6 is a TEM of an ultramicrotomed section of an untreated PBT fiber. 40-50 nm fibrils are clearly visible aligned parallel to the fiber axis. The fibrils act independent of each other within the fiber. Under axial shear loading interfibrillar failure can occur.

Evidence for interfibrillar failure is available. Figure 7 is a TEM of an ultramicrotomed section of the PBT fiber-epoxy interface after straining to 5%. At the point of epoxy-PBT separation many PBT fibrils can be observed to be pulled out of the fiber and still attached to the epoxy matrix.

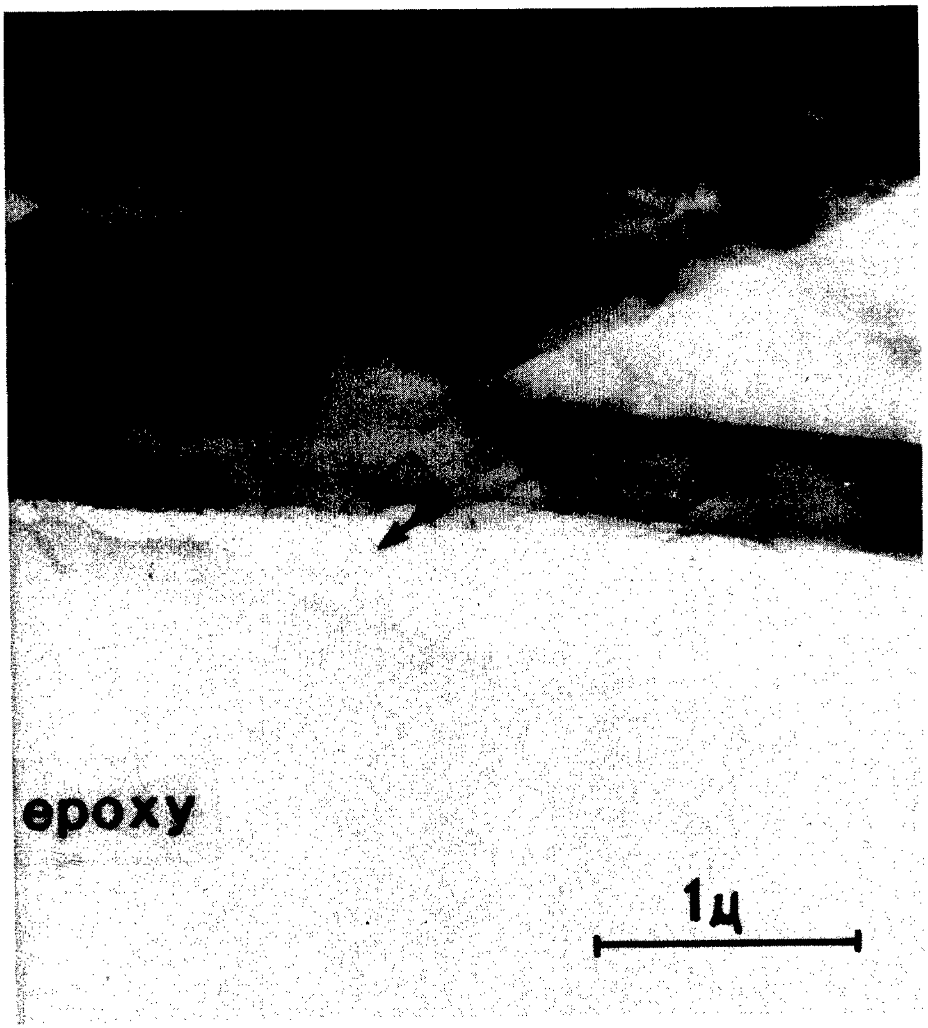


Figure 7. TEM of Ultramicrotomed Section of PBT Fiber-Epoxy Interface after Straining

SECTION VI

COMPRESSIVE STRENGTH

The folding or kinking of the PBT fiber skin detected in the interfacial shear strength testing suggests that the compressive properties of the PBT fibers might be similar to that of the aramid fibers. Compression testing of composite materials is difficult because of sample alignment, preparation, testing methodology, etc. A single fiber compression test developed as part of this effort appears to offer a reproducible method of measuring the actual fiber compressive strength using single fiber specimens.

Using the data analysis discussed earlier, the compressive strengths of 20 specimens each of Kevlar-29, Kevlar-49, AF Tech I, and AF Tech II were measured. The same epoxy matrix used in the wettability and interfacial shear strength determinations was also used here. The results were tabulated according to Equation 3 and listed in Table 5.

TABLE 5

SINGLE FIBER COMPRESSIVE STRENGTHS

Fiber	σc(ksi)
Kevlar-29	63+/-5
Kevlar-49	123+/-21
AF Tech I	40+/-17
AF Tech II	61+/-27
AS-4	1020+/-14

Both aramid fibers had a greater compressive strength than the PBT fibers. The AF Tech II fiber compressive strength was greater than the AF Tech I fiber although the scatter in the measurements is high. None of the polymeric fibers exhibited a compressive strength close to that of graphite fiber.

The reason for the large disparity between the aramid and PBT fibers versus the graphite fibers has to do with the compressive failure modes. Figure 8 shows a micrograph of a single fiber of each of the three types under compressive loading after failure. The graphite exhibits the shear compressive failure expected for brittle materials. The aramid and the PBT fibers however show a progressive helical folding of the outer fiber skin with increasing load as described earlier. The angle of the helix changes with the fiber composition. The load at the generation of the first fold is taken as the load from which the compressive strength is calculated using Equation 3. This value is quite low and on the order of 150 Ksi for the PBT, 123 ksi for the aramid, and over 1,120 ksi for the graphite fiber.

The helical folds disappear after unloading of the specimen indicating that the folds are on the surface of the fiber and that no permanent damage results from repeated loading and unloading. Bundles of either aramid or PBT fibers behave in a similar fashion with all fibers exhibiting the same behavior under the same loading conditions.

AS4

Kevlar 49

AF Tech 1

Figure 8. Compressive Failure Mechanisms of Single Fibers in Epoxy

SECTION VII

CONCLUSIONS

The difficulty in developing adhesion between PBT fibers and epoxy matrices appears to be due to three factors. First, the surface of the PBT fiber is thermally stable and very non reactive making traditional methods of improving fiber-matrix adhesion inoperative. Second, the Poisson's ratio of the PBT fiber is greater than that of the typical structural matrices used in advanced composites. This results in a net tensile interfacial force causing separation of the fiber and matrix under tensile loading conditions. Third, the fibrillar nature of the fiber causes interfibrillar failure under shear loading which is the upper limit axial shear strength.

The interfacial shear strength attainable with the PBT fibers and epoxy are only of the order of 1.5 ksi versus the value of 3.6 ksi obtained with Kevlar-49 in the same matrix.

The compressive strength of PBT fibers is substantially below that of the tensile strength of the same fibers. The highly oriented structure of the fibers, its fibrillar nature, and its lack of transverse coupling between fibrils contribute to the generation of a microbuckling type of instability causing formation of helical surface folds which propagate at very low loads.

The compressive strength of PBT fibers is about 50 ksi. A Kevlar-49 aramid fiber has a compressive strength of about 123 ksi and a graphite AS-4 fiber has a compressive strength of 1000 ksi in the same matrix.

REFERENCES

1. Celanese Research Company, New Jersey, work performed under Air Force Contract No. F33615-81-C-5052.

2. E. I. duPont de Nemours Company, Wilmington, Delaware, work performed under Air Force Contract No. F33615-81-C-5148.

3. K. Gutfreund and D. Kutscha, Interfacial Investigations in Advanced Fiber Reinforced Plastics, AFML-TR-67-275, 59 (1967).

4. L. T. Drzal, M. J. Rich, J. P. Camping, and W. J. Park, Proceedings of the 1980 Conference of RP/Composites Inst., Paper 20-C, (1980).

5. L. T. Drzal, M. J. Rich, and P. F. Lloyd, J. Adhesion, 16, 1 (1983).

6. R. E. Allred, "Surface Chemical Modification of Polyaramid Filaments," D.Sc dissertation, Massachusetts Institute of Technology, (1983).

7. L. T. Drzal, M. J. Rich, M. F. Koenig and P. F. Lloyd, J. Adhesion, 16, 133 (1983).

8. E. L. Thomas, R. J. Farris, D. L. Hsu, S. Allen, A. Filippov, J. Minter, E. Roche, K. Shimamura, T. Takahashi, and G. Venkatesh, Mechanical Properties Vs. Morphology of Ordered Polymers, V. II, AFWAL-TR-80-4045, (1980).

9. S. J. Deteresa, S. R. Allen, R. J. Farris and R. S. Porter, J. Material Science, 19, 57 (1984).

10. M. J. Pagano, personal communication.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1986 - 646-067/40917