MECHANICAL PROPERTY CHARACTERIZATION AND ENHANCEMENT OF RIGID ROD POLYMER FIBERS

 \mathbb{R}^N

by

MAUREEN THERESA FAHEY

submitted to

THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

in partial fulfillment of the requirement for the degree of

BACHELOR OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1990

@ Massachusetts Institute of Technology 1990 All rights reserved

LIBRARIES

MECHANICAL PROPERTY CHARACTERIZATION AND ENHANCEMENT OF RIGID ROD POLYMER FIBERS

by

MAUREEN T. FAHEY

Submitted to the Department of Materials Science and Engineering on May 11, 1990 in partial fulfillment of the requirements for the degree of Bachelor of Science.

ABSTRACT

Despite promising tensile behavior, the use of rigid rod polymer fibers such as Kevlar™ 49 and PBO is limited by fiber compressive strength. By depositing thin coatings of high modulus materials on the fiber, ultimate compressive strength as well as average ultimate tensile strength is increased.

Tensile and tensile recoil tests were performed on pretreated fibers with coating thicknesses ranging from 3000A to 900oA. Kevlar fibers were more fully characterized than PBO because of the difficulty obtaining lengths of unkinked PBO fibers. Property enhancement is related to coating thickness, with greatest UCS increase around 3300 and 6900 A and greatest UTS increase near 6200A for Kevlar. Improvement for PBO is seen most clearly around 4000 and 6800 A (UCS) and 4000 A (UTS).

Thesis supervisor: Frederick J. McGarry Title: Professor of Materials Science and Engineering

TABLE OF CONTENTS

 $\ddot{}$

List of Illustrations and Figures

 \mathcal{L}

Å

List of Tables

Acknowledgements

The members of Professor McGarry's research group, especially John Moalli, Rodrigo Rubiano have been essential to the progress of this research. Along with Maria Raposa and Ramnath Subramanian, they have been an anchor of reason and a welcome source of advice.

Most of this work could not have been accomplished without the help of the staff of the Microelectronics Laboratory: Rich Perilli, Darrell Roan, Tim McClure and Brian McDonald. Arthur and Stephen Rudolph provided design advice and fine workmanship at all stages. Also, David Greenberg, Mike Groleau and Shari Schuchmann cheerfully helped out when I needed an extra pair of hands.

The support and commiseration of my friends Raquel D'Oyen and Daniel Aalberts have helped me avoid many pitfalls on the way to a complete thesis. Raquel has been an important companion, assistant and "babysitter" during my stay at MIT.

I will always remember the friendship and good times shared with the brothers of Phi Gamma Delta. Their camaraderie and quest for fun despite the Institute has kept a smile on my face.

The adventuresome Jeff Drake has changed the way I see the world. I can only hope he knows how much his love, support and tolerance mean to me.

I appreciate all the effort my father, the one who dared me to try MIT, has put in to learning about polymers and fibers. His love and concern, as well as that of the rest of my family, Mom, Katie, Mike, Tim and Pat, have been major motivating factors all along.

I would like to dedicate this work to my biggest fan, the woman who had commissioned hosts of angels to keep me safe and happy, my Grandma, Nell Fahey.

Additionally I would like to acknowledge The Dow Chemical Co. for providing materials and funding for this project.

1.INTRODUCTION

1.1 Composite materials

The desire for strong, lightweight materials for applications such as transportation structures has spawned research in the area of composite materials. Composites consist of a reinforcing agent, such as fibers, surrounded by a matrix. In the case of fiber reinforced polymers, the weight-saving advantage of the polymer matrix is combined with load-bearing fibers along the stressed directions of the material, so no material strength capabilities are wasted. A comparison of the properties of 60% unidirectional Kevlar in epoxy, to high strength steel and to an aluminum alloy is shown in Table 1.

Material	Density (g cm ⁻³)	UTS (MPa)	specific strength
60% Kevlar/ epoxy	1.4	1240	886
High-strength steel	7.8	1000	128
Aluminum alloy	2.8	500	179

Table 1. A comparison of materials for design. [1]

Usually, composite strength and performance are limited by matrix and fiber properties, geometry and interfacial interaction. With rigid rod fibers as the reinforcing agent, composite strength, especially in compression, is limited by the fiber. For example, Kevlar fibers yield at 0.7% bending strain, according to elastica loop measurements. The yield strain of a typical epoxy resin is 2.8% while the composite yields at 0.3% compressive strain, brought down by the limitations of the fiber [2]. For this reason, it is important to quantify and develop techniques for enhancing fiber properties. This study focuses on the rigid rod polymer fibers Kevlar[™] 49 and experimental PBO, which have excellent axial tensile properties, but poor axial compressive properties due to fiber microstructure.

1.2 Literature Survey

A variety of tests have been developed to measure the compressive strength of fibers. Direct testing is not usually an option because a fiber's aspect ratio, length compared to diameter, is very large. Compressing a single fiber of reasonable length results in out- ofcolumn bowing, or Euler buckling. Therefore, a number of indirect testing methods have been developed. The Elastica Loop test [3] involves both tensile and compressive loads by tying a knot in the fiber. The validity of this test is questionable because of the dual nature of the stress field [4], however, it is useful for comparing fibers [5].

The Bending Beam test is performed by vertically deflecting a bar with the fiber adhered to the compressive face and measuring the strain to first kink. Beam deflection must be small compared to length to assure small curvature and validate the assumption of linear beam behavior.[2] Failure load cannot be accurately determined from this test unless the compressive modulus is assumed equal to the tensile modulus and Hooke's law is applied [4].

Tensile Recoil testing is a bracketing technique which uses a reflected tensile wave of known magnitude to determine the compressive threshold of a fiber. The severity of kinking, indicated by depth and spacing, is related to the intensity of applied compression [6]. Compressive modulus and strain cannot be determined from this test, but the results agree with those determined by composite testing and with the Micro-Tensile Testing Machine at Air Force Wright Aeronautical Labs [4, 5].

Fiber modifications to improve compressive strength have been attempted. It has been shown that increasing the modulus of a particular fiber does not affect its compressive strength [7]. A change in density, however, can provide some increase. Fibers close to their ideal crystal density, like Kevlar™ 49 and PBO, have low compressive strengths and high moduli [8]. Lower density, caused by entanglements and crosslinking, gives higher compressive strength by preventing microfibrillar buckling. Unfortunately, this decrease also yields lower tensile modulus, a product of high crystallinity [8].

The compressive strength of Kevlar 49 unidirectional/ epoxy composites has been shown to decrease with temperature [9]. By extrapolating to zero strength, a temperature very close to the glass transition temperature for Kevlar is obtained, suggesting that compressive failure may involve buckling of the amorphous regions between Kevlar

crystallites [9]. The actual percent crystallinity of Kevlar has not been detennined, [10] but this suggests that a 100% crystalline fiber would have a higher compressive strength. Kumar and Helminiak [7] suggest achieving compressive strength improvement by providing the support of primary bonds between the fibrils, inhibiting microfibrillar buckling. In contrast, the study reported herein seeks improvement by physically reinforcing the outer fibrils, thus increasing the load carrying ability of the fiber before instability causes buckling.

1.3 Outline of Work

Tensile recoil testing was used in addition to standard tensile testing of single fibers to determine ultimate compressive and tensile strengths of Kevlar™ 49 and PBO fibers. The baseline values were then used to evaluate the improvement in properties from the application of a high modulus coating. Coating thickness was varied to determine which provides the greatest strength increase. The primary goal was to increase fiber ultimate compressive strength above 100 ksi without decreasing ultimate tensile strength.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1 Fibers

Fibers of highly crystalline, oriented polymers have low densities compared to traditional materials, but they still exhibit good axial strength. Both Kevlar[™] 49 (poly (phenylene terephthalate)) and PBO (poly (phenylene benzobisoxazole)) are composed of rigid rod molecules, sketched in Figure 1. This stiff backbone promotes chain packing, which X-ray diffraction and transmission electron microscopy indicate results in highly crystalline

Figure 1A. Chemical structure of poly(phenylene terephthalate) monomer.

Figure lB. Chemical structure of poly(phenylene benzobisoxazole) monomer.

structures conforming to the monoclinic (psuedo-orthorhombic) unit cell [10,11]. Orientation and crystallinity contribute to high tensile modulus and strength, but significant anisotropy occurs due to the fibrillar microstructure of these fibers, illustrated in Figure 2. Table 2 shows the resulting drastic difference between tensile and compressive strengths.

Fiber	Density	Modulus	Tensile Strength	Comp. Strength
	(g/cc)	(Msi)	(Ksi)	(Ksi)
SPECTRA	0.97	25	435	24
Kevlar [™] 49	1.44	18	515	57
PBO	1.58	52	830	29

Table 2. Properties of highly crystalline. oriented polymer fibers [12l.

Lateral strength between fibrils is provided by secondary Van der Waals forces. The outer fibrils are not supported on all sides, like the inner ones, so defects or an uneven load distribution can cause the initiation of kinks. As the first fibril buckles, it pulls its neighbors along [6]. Energy is absorbed as the fiber deforms, reducing the stress intensity, so the cascading effect will result in kinkbands of varying severity. This process is shown schematically in Figure 3. Small kink band formation and a fully developed kink are seen in

Figure 3. Kink band formation, macro- and microscale.

Micrograph 1, Appendix B. In some cases, the fiber appears to explode instead of kink. This is likely the result of multiple initiation sites at approximately the same axial location, so the fibrils broom out. Fibers which have been recoil tested exhibit kinks at the reflecting interface. At the compressive threshold, high magnification is necessary to identify the single, barely formed kink at the reflecting interface. Above the threshold, kinks occur with random spacing, but more frequently near the interface.

2.1.1. SPECfRA

This study was to include the high perfonnance fiber, SPECfRA, Allied Signal's extended chain, ultra high molecular weight polyethylene fiber. Like Kevlar and PBO, this fiber also fails by kinking, but the kinks tend to be circumferential rather than V-shaped, a result of the much weaker interfibrillar strength. Preliminary coating runs on SPECfRA show excellent adhesion, possibly due to fiber softening during coating. Because the fibers could not be reliably separated from the tow, nor successfully gripped for testing, baseline property values and effects of coating were not established.

2.1.2. PBO

Initially, the improvement of PBO was the primary concern of this study. This experimental fiber is both stronger in tension and weaker in compression than the commercially available Kevlar™ 49. Its large diameter and dark purple color made sample preparation easy, but because it is not made on a large scale, the drawing process does not yet produce a consistent fiber diameter. Also, sections of the tow which were not visibly kinked or damaged were difficult to find. This led to the batch approach to fiber testing: coated fiber improvement based on baseline values from the same section of tow. As seen in Micrograph 2, Appendix B, the coating adheres very well to this fiber. Still, difficulty in obtaining enough undamaged fiber to make the necessary number of test specimens changed the main thrust of experimentation toward Kevlar™ 49.

2.1.3. Kevlar[™] 49

Kevlar™ 49 is duPont's aramid fiber. These fibers are more difficult to see than PBO because they are smaller and yellow. However, recoil testing produces more valid results because the necessary instantaneous load release is easier to achieve with the smaller diameter. Also less stiff, the primary drawback to handling Kevlar is being able to watch its movement until both ends can be securely fastened. A second drawback is the necessary pretreatments for good coating adhesion. Kevlar has many hydrogen bonds, which attract and hold moisture. This water is released as the fiber nears 100°C, and causes a slight change in diameter. Since the coating machine operates near this temperature, excess moisture must be removed before coating.

The manufacturing process employs sulfuric acid and sodium carbonate. These combine and appear in elemental analysis as sodium sulfate, 0.2% to 1.0% by weight [10]. This finding is supported by XPS and neutron activation [12], which show a sodium content of approximately 0.85% to 1% by weight, present as sodium sulfate. Also found on the surface of Kevlar are textile lubricants such as stearic acid. All of these inhibit the excellent adhesive behavior exhibited between the coating and the other fibers. Pretreatments, described later, are used to overcome these barriers to good adhesion and the resulting compressive improvement.

2.2 Rack Systems

Fiber coatings are applied under vacuum, which places restraints on fiber holding devices. Base plate size is defined by the holder in the coating chamber, the use of mechanical feedthroughs is limited, and gear friction cannot be compensated by lubricants. Also, materials must be nonmagnetic and free of volatiles, making only very few metals and no plastics appropriate for rack construction. Coating thickness has been found to vary along both the length and width of the rack; differences range widely, usually between 100 and 100oA, depending on the surface condition of the coating material before application. Because rack design cannot compensate for this variation, thickness measurement locations have been standardized, and an average is used to describe the coating thickness of a particular run. During the period of this research the rack system used has been changed and modified a number of times. The main rack systems used are described.

2.2.1 Alligator Clip Rack

The original rack system consisted of two thin stainless steel rectangular frames with copper alligator clips secured by epoxy (see Figure 4A). The base plate is stainless steel with brass slotted posts (see Figure 4B). When both racks are in the slots, fibers do not overlap and the two layers are separated by one half inch. Since coating is a line-of-sight, distance dependent process, the fibers on each rack have a different coating thicknesses. Also, the racks must be removed from the chamber, turned over and coated again. Not only is this inefficient, but the circumferential coating distribution, as seen by backscattered electron analysis, is uneven. This distribution is shown schematically in Figure 5.

Figure 5. Schematic of coating distribution.

$2.2.2$. Prong Rack

The next step was to provide a more uniform coating by rotating the fibers. Since a mechanical feedthrough was not yet an option, manual means were employed. Prongs (see Figure 6A) were made to replace the alligator clips on the smaller rack. The fiber holding section could be rotated with a "tool" (see Figure 6B) which fit over prong pairs, preventing fiber twist. While this helped the distribution, the number of fibers coated per run was reduced because only one rack was used. Also, four coating periods, at approximately three hours pumpdown and run time each, were needed for each batch. Use of the "tool" was awkward because fiber spacing limited range of motion.

Figure 4. Fiber-holding prong, part of John's rack system

Figure 5. "The Tool" used for rotating prongs.

The choice was made to coat, turn the rack over, coat, rotate the prongs one quarter turn, coat, turn the rack over and coat. This kept more fibers intact, but still resulted in circumferential thickness variations as well as large time and equipment costs.

2.2.3. The R^3 Rotating Rack

Finally, a rack was designed which would allow fifteen fibers to be uniformly coated during one run period. After all minor adjustments were made, this system, named after designer and co-worker Rodrigo R. Rubiano, consisted of fifteen gear pairs, of alternating brass and aluminum, press fit onto brass slotted shafts which fit through a split block. The gears are protected from the coating process by steel cover plates. Fibers are secured with aluminum shims. A removeable drive shaft is employed to allow the rack to fit in a desiccator for pretreatment. (See Figure 7.) An additional system of bevel gears connects the rack with a mechanical feedthrough, by which the fibers can be rotated. Alternating gear material is an attempt at reducing gear sticking, while the blocks are split to allow full cleaning without removing the press fit gears. Cleaning makes a noticeable difference in the ease of turning the fibers, but even with thorough cleaning after every run, without lubrication, there is a significant amount of gear friction to overcome. In extreme cases this can lead to gear lock or slippage. Gear lock results in the original problem of uneven circumferential distribution, while fiber twist is a result of the far side gears slipping. The solution has been to reduce the number of gear pairs. Currently, nine to eleven four inch fibers can be coated per run.

Figure 7. The R^3 Rack System.

2.3. Fiber Preparation

Single fibers, four inches long, are removed from the fiber tow with tweezers and secured in the slotted shafts of the rotating rack. These fibers are then coated. Microscopy shows excellent adhesion between PBO and the coating, but coating on Kevlar is not as well bonded. The nature of the bond between the two surfaces is still being studied. Meanwhile, pretreatments to promote adhesion between Kevlar and the coating have been tried. Mentioned earlier, two main problem sources are moisture held by hydrogen bonds and processing residue.

To remove the moisture, the fiber-loaded rack, without drive shaft, shields or connecting gears, is placed in a desiccator and heated under vacuum for 1.5 to 2.5 hours. The desiccator is sealed, allowed to cool and taken to the coating machine. When the machine is ready for loading, the rack is removed from the desiccator, fully assembled and loaded into the machine. This process allows the fibers to be exposed to a clean room atmosphere for approximately ten minutes. Adhesion with this pretreatment has been inconsistent, but fibers with this pretreatment constitute the bulk of current results.

Adhesion may be prohibited by the presence of processing residues. First brought to our attention was sodium sulfate. According to the CRC Handbook of Chemistry and Physics, sodium sulfate is soluble in hot water, approximately 42 g per 100 cc. So, a beaker of 200 cc of water is heated to boiling and the heat source reduced. The section of tow to be separated and coated is added and kept at the same temperature for 30 minutes. The tow is then removed with tweezers and placed in a second beaker of water similar to the first. It remains for ten to fifteen minutes, is removed and dipped in acetone for one to three minutes. The resulting section of tow is less shiny and the fibers do not slide past each other as well. The change in physical appearance and handling may be a result of removing any lubricants. The CRC indicates that stearic acid is soluble in acetone, so this may have been inadvertently removed in trying to remove sodium sulfate. Tests are still being conducted to determine if this pretreatment reduces the sodium sulfate content and if it improves coating adhesion.

2.4 Coating

A fiber in compression, due to its aspect ratio will bow. If a high modulus material is deposited on the surface of the pretreated fibers, the composite fiber is much stiffer (see

Figure 8). Bowing is prevented because the high modulus coating is far from the neutral axis of the fiber, creating an effect similar to that of an I-beam. In the case of fibrillar structure, the rigid coating assists lateral hydrogen bonds and reduces fiber anisotropy. At first glance, it would appear that regardless of adhesion, coating can increase the compressive strength of the fiber as long as it is intact. Currently, tests of compressive capacity are being run after the fiber has been stressed to 80% of its tensile strength. As seen in Micrograph 3, Appendix B, radial and some axial cracks are obvious after loading. Residual compressive strength is unknown. Shown in Figure 9, the coating, an isotropic material, withstands compression along the fiber axis in addition to opposing the effective outward force of buckling fibrils. Coating adhesion is important because of the local nature of buckling. Without good adhesion, coating forced off by a kink at one location will cause the rest of the coating to crack and come off the fiber. With adhesion, a damaged area is localized, and the rest of the fiber can still exhibit the superior behavior associated with the coating.

Figure 9. Forces on fiber coating .

Coating thickness is an important parameter. As thickness increases, the fiber behaves more like the brittle coating, eventually exhibiting mechanical properties unlike those sought. Too thin of a coating will not act in a way to inhibit buckling and increase compressive strength. A main goal of this study has been to determine the optimal coating thickness. This value will not be absolute, because the three thickness measurements are taken 0.5" closer to the the coating source than the fibers, near the corners of the 9.4" x 6.3" rack. The values are averaged and compared. With this in mind, actual coating thickness is lower than reported, but how much so is determined by the fiber's position on the rack during coating. This could account for anomalous results when recoil testing (no failure seen well above the bracketed threshold) as well as the large variation in tensile strengths above that of the uncoated fiber.

2.5 Sample Preparation

Single fibers are removed from sections of tow cut to a length of five to seven inches. Those to be coated are pretreated if necessary and coated in four inch lengths. Coated or uncoated, fibers are placed across paper sample tabs and secured with epoxy. The gage length used for all tests is one inch. Tensile samples (Figure lOA) also require RTV silicone rubber to reduce the stress concentration at the fiber/ epoxy interface and to insure failure equidistant from the ends. For proper recoil, on the other hand, the fiber epoxy interface must be sharp (Figure lOB). The epoxy cannot be drawn onto the fiber, or be present as droplets along the gage length, especially near the interface because the

Figure 10. (A) Tensile specimen, (B) tensile recoil specimen.

effective diameter of the fiber, which appears in the calculation of stress, is altered. These two conditions are identified before testing by low magnification light microscopy, and invalid samples are discarded.

2.6 Tensile Testing

Early tests were run on an Instron 1122, while recent testing has employed an Instron 4505. All tests use a 2000g load cell and pneumatic grips. An axial load is applied by lowering the crosshead at a rate of 0.125 mm/ min. The load at fracture is recorded, then the fiber diameter is measured. Initially measurements were made using scanning electron microscopy, but satisfactory measurements are obtained with a light microscope. Ultimate tensile strength for the fiber is then determined according to Equation 1, the basic

$$
\sigma = \frac{F}{A} = \frac{L}{\pi r^2} \tag{1}
$$

equation for stress, where L is the measured failure load and r is the measured fiber radius. Since tensile strengths always occur as a distribution, at least thirty samples are needed to reliably describe it [13]. This was attainable for uncoated fibers, but the limited number of coated fibers usually kept the number of samples near five. The purpose of tensile testing is to ensure there is no drop in ultimate tensile strength when a coating is applied, so the limited tensile results from each batch are compared to uncoated values; average batch value for PBO, average batch and total average for Kevlar™ 49.

2.7 Tensile Recoil Testing

Tensile recoil testing, first developed by S. Allen at duPont, makes use of a reflected stress wave to fail the fiber in compression. The fiber is axially loaded in tension to a known value. It is then cut halfway between the ends so that the load drops instantaneously. The tensile stress wave released travels away from the cut site, is reflected by the epoxy, and returns as a compressive wave. If the stress is greater than the fiber ultimate compressive strength, kinking occurs. Fibers can be visually characterized as failed or unfailed, and the

compressive strength bracketed within a few kilopounds per square inch. In the appendix to Allen's paper [5], the analysis is given in full, featuring the standard wave equation (Eqn. 2) where u is displacement, t is time, x is axial location ($x = 0$ at the fiber ends) and $a²$ is the ratio of modulus to density, or specific modulus. Boundary conditions are 1) fixed fiber end,

$$
\frac{\partial^2 u}{\partial t^2} = a^2 \frac{\partial^2 u}{\partial x^2}
$$
 (2)

2) zero initial wave velocity, 3) zero stress at the fracture surface and 4) initial displacement equal to the initial tensile strain. For complete reflection, specific density must be noticeably different between the fiber and reflective material. Table 3 compares modulus, density and this specific modulus for steel, epoxy, Kevlar™ 49 and PBO. The grips have steel faces, so this option was first explored, but the sample cannot be adequately gripped due to the presence of the epoxy adhesive. Instead, the faces are coated with silicone rubber to increase the reliability of holding paper specimen tabs and epoxy is used to reflect the stress wave. Specific modulus is satisfactory, and the epoxy is already incorporated into the sample to hold the fiber in place.

Material	Density (g/cc)	Modulus (Msi)	Sp. Mod. $(10^4 \text{ m}^2/\text{s}^2)$
Kevlar [™] 49	1.44	18	8.62
PBO	1.58	52	22.69
Epoxy	$1.2 - 1.4$	$2.1 - 5.5$	$1.03 - 3.16$
Steel	7.9	210	18.33

Table 3. Material suitability parameters for stress wave reflection [l, ¹²¹

Tensile recoil testing is performed using essentially the same set up as for tensile testing. The hold feature on the Instron 4505 keeps the fiber load at a pre-programmed value. FI-RE-CUT, a device designed by John MoalIi, is attached to a backplate and positioned to

cut the loaded fiber in half. FI-RE-CUT uses scalpel blades on blocks which slide along linear bearings and are moved by connected left- and right-handed screws. The assembly, seen in Figure 11, is mounted on a micrometer stage which can be fine adjusted to center the fiber

Figure 11. FI-RE-CUT

between the blades. This device makes the test easier in practice than the spring-loaded scissors used by Allen [5]. A test is not valid if the load spikes by ten percent or more during cutting. Spikes are usually a result of uneven cutting, a problem with the scissors which can be overcome with practice aligning the fiber in FI-RE-CUT, or blade mismatch. Seen in Figure 12, mismatch occurs when the cutting line of the scalpel blades does not lay

Figure 12. End-on view of scalpel blade: (a) centered cutting edge, (b) off- center cutting edge. [As seen with SEM.]

along the center line of the edge. The blades should appear reflected across the plane which cuts through the fiber longitudinally; asymmetry creates shearing similar to that of the scissors. Another advantage of FI-RE-CUT is the low speed at which the cut is made and recorded. Load spikes can go undetected if the pulse is too rapid.

2.8 Microscopy

2.8.1 Scanning Electron Microscopy

A Cambridge Stereoscan 240 electron microscope was used extensively in the early stages of research to determine ifkinking failure had occurred and to measure the fiber diameter of the failed specimen. For these purposes, no conductive gold coating was applied to the fiber on the sample stub, and an acceleration voltage of 5 keV was used. While a noticeable amount of sample charging occurs under these conditions, kinks can be easily identified. Diameter measurements were taken at a number of locations along the fiber to determine a typical value and the degree of inconsistency. Economically, it is impractical to view every tested specimen under the SEM. Especially for PBO, which has widely varying diameters, it is desirable to get an idea of the failure stress instead of bracketing DCS by failure load. Light microscopy is now employed for these purposes.

The SEM is still used for high magnification analysis of coating characteristics. Fiber failure condition is also confirmed with the SEM if light microscopy information is inconclusive. Backscattered electron images indicate areas of different chemical composition, giving greater contrast between fiber and coating at low acceleration voltages, so cracks or coating spalling is easily identified. When in depth analysis of a specific feature is desired, a conductive gold coating of approximately 50A is sputtered onto the sample. Sample charging, which gives a fuzzy image, is reduced. Also, higher acceleration voltages can be used and corresponding higher resolution obtained.

2.8.2 Light Microscopy

Fibers that do not appear kinked are examined under a Nikon light microscope at 40x magnification immediately after a test is performed. All tested fibers are then measured using a Riechert light microscope at 900x magnification with measuring reticule in one eyepiece. Each gfidline corresponds to 1.3 microns, determined by comparing measurements from the SEM. One problem associated with this method is the small depth of field. The optimal measuring location for the fiber diameter is right at the fiber/ epoxy interface.

However, the height of the epoxy droplet does not allow the lens to approach the fiber ends. If the fiber is severely kinked, locating and focussing a measurable section can be difficult. Many times, one half of a tensile specimen will be too short to measure and stress calculations must be based only on diameters from the other half. Fortunately, Kevlar diameters are consistent enough that this does not make much of a difference. Most PBO measurements were made with the SEM, but those made with the light microscope are very similar. By comparing the diameter of KevlarTM 49 fibers calculated from denier (11.9) microns) to those measured (usually 11.7 to 12.0 microns), we conclude that a fiber diameter can be accurately measured with the light microscope to within 0.2 microns of the actual diameter.

3. RESULTS AND DISCUSSION

Raw data for tensile and tensile recoil tests of PBO and Kevlar™ 49 are presented in Appendix A. Thickness measurements for PBO fiber sets were made across the rack from the drive gears and at the other end of the rack on the same side as the gears to allow averaging of maximum thickness variation. A third measurement, from the comer diagonally opposite the drive gears is added for the Kevlar fiber sets. Earlier data are not presented because they cannot be satisfactorily incorporated into the main body of information. This includes runs made with the alligator clip and prong racks, as well as sets in which the fibers were damaged in handling, used for other tests or insufficient in number to complete the recoil bracketing sequence.

3.1 PBO

The ultimate compressive strength of PBO measured by tensile recoil testing is 23 ± 1 ksi, as bracketed by the C series. Incomplete results from other sets cluster near this value, which is lower than that reported in Table 2. Use of FI-RE-CUT is likely to give lower but

more accurate UCS values because load spikes are better detected. Figures 13A and 13B

show the effect of coating thickness on compressive strength. DCS values shown are the average of the highest unfailed specimen and the lowest failed specimen. Because of the variation in fiber diameter and the limited number of fibers in a set, the range can be ± 7 or 8 ksi. These graphs show greatest UCS improvements near 4000\AA , which is approximately 4% of the fiber radius.

Tensile strength is not degraded when the coating is applied. Figures *14A* and 14B show the tensile strength of coated fibers compared to uncoated fibers from the same section of the tow. There are fewer points on the graphs because most of the coated fibers were used to determine ultimate compressive strength. In the tested range, average UTS appears to be increasing as the thickness approaches 4000Å, but it is important to recall the scatter usually associated with tensile tests and to discount improvements of less than 10-20% as no appreciable change.

3.2 Kevlar™ 49

Reported results are associated with the previously mentioned pretreatment to remove moisture from the fibers. Coating adhesion was not complete in all cases, and it is possible that the scattered change in compressive strengths with coating thickness (Figures 15A and 15B) is a direct result of this lack. Ultimate compressive strength for uncoated

Figure 15A. UCS of coated Kevlar 49 (uncoated value: 44 -46 ksi)

Figure 15B. Percent UCS increase, coated Kevlar 49.

Kevlar™ 49 is bracketed between 44 and 46 ksi. As for PBO, this is lower than the value reported in Table 2. Compressive strengths near 65 ksi occur at 3287A and 6881A, thicknesses which represent 6% and 11% of the fiber radius. At 8474A, the DCS drops slightly below the baseline value.

Tensile results are displayed in Figures 16A and 16B. At 8474A, the tensile strength of the fiber, like the compressive strength, is actually reduced. Other changes are less than ten percent, and therefore insignificant. Since the modulus of Kevlar is much lower than that of PBO, the small percent increase in mechanical properties may be a result of the choice of coating. A lower modulus rigid material may be better suited to providing the large increase in DCS seen with PBO. If the 140% increase exhibited by coated PBO were to occur with coated Kevlar™ 49, DCS would be 108 ksi, which is above the target value of 100 ksi. Also, instead of having so much load carried by the brittle coating, which has a much lower tensile strength than the fiber, a less rigid coating may allow more of the fiber to be loaded in tension.

Figure 16A. Coated Kevlar 49 tensile strengths (uncoated value: 562 ± 19 ksi, average of 31 samples)

Figure 16B. Coated Kevlar 49 UTS increase with thickness.

Table 4 and Figure 17 show ultimate compressive strength as a function of thickness. Both fiber types are combined to show that regardless of fiber, DCS can be tailored to a specific value. As testing continues, these will become more complete and empirical relations between fiber, UCS and coating thickness can be developed.

Coating thickness	UCS (ksi)	Fiber type
3455	35	P
2618	37	P
3267	42	P
3357	43	P
8474	45	K
3448	46	K
4577	50	K
5887	50	K
6269	50	$\bf K$
6772	52	P
3965	55	P
3287	64	K
6881	65	K

Table 4. UCS increase for both Kevlar[™] 49 (K) and PBO (P).

Figure 17. Coated Kevlar and PBO

4. CONCLUSIONS

Tensile recoil testing, especially with FI-RE-CUT is an effective means for determining the compressive strength of high performance fibers such as Kevlar™ 49 and PBO. With a large enough sample set, ultimate compressive strength can be bracketed to within a few thousand pounds per square inch. The results match the performance exhibited in composites.

The application of a high modulus coating can significantly increase the ultimate compressive strengths of Kevlar™ 49 and PBO by providing lateral support for fibrils and restraining kink band formation. Mechanical property alteration is dependent on coating thickness. For thin coatings, DCS improvements of up to 140% are seen with PBO, with no accompanying loss in tensile strength. Improvements in Kevlar™ 49 are less dramatic due to irregular coating adhesion and a greater mismatch between fiber and coating moduli.

5. SUGGESTIONS FOR FUTURE WORK

Current research should be continued. First, the adhesion problem with Kevlar needs to be solved, so greater DCS improvement may be obtained. Second, the range of coating thicknesses tested on PBO should be expanded. This can only be accomplished if large quantities of undamaged PBO fiber with consistent diameters can be produced.

Other fiber types, such as SPECTRA, should be coated. A rigid coating should increase the ultimate compressive strength of any fiber which fails by kink band formation. Also, fiber behavior with a variety of coatings should be explored.

Complete results for tensile and tensile recoil tests will be more easily obtained if the fiber coating process is modified. The variation of coating thickness for a single run will need to compensated. A rack with less friction is needed to allow more fibers to be coated per run than is currently possible. Eventually, this coating process will need to be scaled up and modified for continuous coated fiber production.

6. APPENDIX A- TENSILE AND TENSILE RECOIL TEST RESULTS

 $\mathcal{L}^{\text{max}}_{\text{max}}$ and $\mathcal{L}^{\text{max}}_{\text{max}}$

Comments:

Recoil Test Information

Comments: Top gear slipped in last minute of coating

UNCOAT

 $\mathcal{L}^{\text{max}}_{\text{max}}$

Tensile Test Information

Recoil Test Information

6. APPENDIX A- TENSILE AND TENSILE RECOIL TEST RESULTS

Comments: 2hr/ 120C pretreat.

Recoil Test Information

6. APPENDIX A- TENSILE AND TENSILE RECOILTEST RESULTS

Tensile Test Information

 \sim ϵ

 43.4 x \times x at top

 $\mathcal{A}^{\mathcal{A}}$

 $\hat{\boldsymbol{\beta}}$

 $\ddot{}$

 $\ddot{}$

6. APPENDIX A- TENSILE AND TENSILE RECOILTEST RESULTS

Comments: *2hrl* 120C pretreat.

Recoil Test Information

Tensile Test Information

UNCOATED

Fiber type: Kevlar Series: U Operator: M1F Comments: *2hr/120C* pretreat. Run with 5 11-30-892H and half a Si wafer for E. Murphy Recoil Test Information Test Date 3-Feb Operator MTF Coating: TYPE 1 date: *1/26/90* Measured thicknesses: 8315A, 8320A, 8787 A average: 8474A Instron 4505 Crosshead Spee .125 *mm/min* Full Scale Loa 2000g \overline{a}

6. APPENDIX A- TENSILE AND TENSILE RECOIL TEST RESULTS

Comments: AI feedthrough overtightened and destroyed

Recoil Test Information

UNCOATED

Fiber type: Kevlar Series: S Operator: MTF/RRR Coating: TYPE 1 date: *1/12/90* Measured thicknesses: 3905A, 4923A average: 4414A

Comments: i hr./ 100°C pretreat, high deposition rate

Recoil Test Information

Test Date 19-Jan Instron 4505 Crosshead Spee .125 mm/min Operator MTF Full Scale Loa 2000g coated

7. APPENDIX B- SCANNING ELECTRON MICROGRAPHS

 \mathbb{R}^2

 \sim

 \mathbf{r}

7. APPENDIX B- SCANNING ELECTRON MICROGRAPHS.

Micrograph 1. Small kink band formation approaching a fully developed kink.

Micrograph 2. Tensile side of kink in coated PBO: good adhesion.

49

2,85KX 15KV ND:11MM $S: 00000 P: 00002$ $\mathcal{C}(\mathcal{C})$ $\mathcal{L}=\{1,2,\ldots,n\}$. The set of $\mathcal{L}=\{1,2,\ldots,n\}$

7. APPENDIX B- SCANNING ELECTRON MICROGRAPHS,

'0,

Micrograph 3. Coated Kevlar loaded to 80% UTS and unloaded. Cracks multiply and open with beam heating.

References:

- 1. Ashby Michael F., and Jones, David R.H. Engineering Materials 2. An Introduction to Microstructures. Processing and Design. 2nd ed. Pergamon Press, New York, 1988.
- 2. DeTeresa, S.J., Allen, S.R., Farris, R.1. and Porter, R.S. "Compressive and Torsional Behaviour of Kevlar 49 Fibre." J Mat Sci **19** (1984) 57-72.
- 3. Greenwood, 1.H. and Rose, P.G. "Compressive Behaviour of Kevlar 49 fibres and composites." J. Mat. Sci. 9 (1974) 1809-1814.
- 4. Fawaz, Scott *A.,* Palazotto, Anthony N. and Wang, Chyi-Shan. Compressive Properties of High Performance Polymeric Fibers. AFWAL-TR-88-4262. Interim report for April 1988- December 1988. Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. March 1989.
- 5. Allen, S.R. "Tensile Recoil Measurement of Compressive Strenght for Polymeric High Performance Fibers." J. Mat. Sci. 22 (1987) 853-859.
- 6. DeTeresa S.J., Farris, R.J. and Porter, R.S. "Behavior of Aramid Fiber Under Uniform Compression." Polym. Comp., April 1982, vol 3, No 2.57-58.
- 7. Kumar, Satish and Helminiak, T.E. "Compressive Strength of High Performance Fibers." in The Materials Science and Engineering of Rigid-Rod Polymers, W.W. Adams, RK Eby, and D.E. McLemore, eds., Materials Research Society Symposium Proceedings, vol. 134, Pittsburgh, PA 1989.
- 8. Kumar, Satish, Adams, W.W. and Helminiak, T.E. "Uniaxial Compressive Strength of High Modulus Fibers for Composites" J Reinf. Plas. and Comp. vol. 7, 1988.
- 9. Wilfong, R.E. and Zimmerman, 1. "Strength and Durability Characteristics of Kevlar Aramid Fiber." 1. Appl. Polym. Sci., Appl. Pol. Symposium 31, 1-21(1977)
- 10. Dobb, M.G., Johnson, D.J., and Saville, B.P. "Supramolecular Structure of a High-Modulus Polyaromatic Fiber (Kevlar 49)" 1. Polym. Sci., Polymer Physics ed. 15, 2201-2211 (1977).
- 11. Penn, L. and Larsen, F. "Physicochemical Properties of Kevlar 49 Fiber." J. Appl. Polym. Sci. 23 59-73 (1979).
- 12. McGarry, FJ. 3.92 lecture notes, 1990.
- 13. Dally, 1., Rielly, W., and McConnell, K. Instrumentation for Engineering Measurements. New York: Wiley and Sons. 1984.