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LARGE-DIAMETER CARBON-COMPOSITE MONOFILAMENTS

by W. G. Bradshaw, P. C. Pinoli, and R. F. Karlak

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16. Abstract

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Section 1

SUMMARY

The objective of this program was to develop a process for producing large-diameter carbon composite monofilaments by impregnation of multifiber bundles with suitable matrix precursors and converting the resultant composite to all carbon by copyrolysis. Three types of fibers were used: fully graphitized Thornel 75, partially processed polyacrylonitrile copolymer having round filaments, and partially processed homopolymer having dog-bone-shaped filaments. Six matrix precursors were studied: high-char forming resins, modified phenolformaldehyde, two types of pitches, polyacrylonitrile, and polyvinyl chloride.

Best results were achieved by using processes and matrices to minimize matrix cracking and by using high-temperature heat treatment to equalize fiber and matrix strain-to-failure.

With Thornel 75, the highest composite properties were obtained by impregnating with high-temperature high-char-forming resins and heat-treating to 2873°K to form a composite monofilament with an average tensile strength of 1.449 GN/m^2 (210,200 psi) and elastic modulus of 264 GN/m^2 (38.2 x 10^6 psi).

Copyrolysis was studied with partially processed carbonized fibers produced from round polyacrylonitrile copolymer with 10,000 filaments per tow and dog-bone-shaped PAN homopolymer with 385 filaments per tow.

With the round filament, maximum elastic modulus could be achieved only at the expense of degradation in tensile strength, a characteristic apparently inherent in the precursor morphology and method of spinning.

In the GW-173 matrix, the highest composite tensile strength was obtained by copyrolyzing to 1673°K to produce a carbon composite monofilament with an average tensile strength of 0.415/GN/m^2 (60,000 psi), and composite modulus of 150 GN/m^2 (21.7 × 10^6 psi). The highest composite modulus was obtained in pitch by copyrolyzing to 1673°K and graphitizing to 2873°K to produce a composite monofilament with a composite elastic modulus of 348 GN/m^2 (50.5 x 10^6 psi), and a tensile strength of 0.635 GN/m^2 (92,100 psi). The deterioration in strength at high temperatures is a characteristic inherent in the polymer morphology.

Much better results were obtained with the dog-bone-shaped filament which does not undergo deterioration in tensile strength after graphitization. Optimum tensile properties were obtained with a fiber pretreatment to 1673°K, followed by copyrolysis with high-temperature, high-char-forming resins to 1673°K and graphitization to 2873°K to produce a monofilament with an average composite tensile strength of 1.438 GN/m^2 (208,600 psi) and elastic modulus of 293 GN/m^2 (42.5 x 10^6 psi).

Section 2
INTRODUCTION

Continuing improvement in the performance of air-breathing engines requires the development of materials with greater strength, elastic modulus, and high-temperature characteristics. One approach is to incorporate existing high-performance multifilament graphite bundles into large-diameter carbon-composite monofilaments for use in metal-matrix composites. Such monofilaments should be suitable for reinforcing oxidation-resistant alloys while retaining their inherent strength and structural integrity.

Carbon and graphite filaments (about 7×10^{-6} m in diameter) are competitive with other filaments such as boron or glass on the basis of specific strength or modulus. However, their use in metal-matrix composites has been limited because of their small diameter and by their reaction at the fiber-metal-matrix interface that may take place during service or fabrication resulting in the formation of a carbide or the dissolution of the carbon fiber by the metal (Refs. 1, 2). These difficulties should be mitigated by producing large-diameter carbon-composite monofilaments, $D \geqq 2.5 \times 10^{-4}$ m (10 mils), to minimize surface area subject to metal attack. Consequently, it was suggested that such monofilaments be produced by impregnating multifiber, high-strength, high-modulus carbon fiber bundles with suitable matrix precursor resins, curing, and pyrolysing the resultant product using the existing technology developed for carbon-carbon composites.

This approach had been attempted in a previous study (Ref. 3), and an apparent degradation in fiber tensile properties was observed with increasing heat-treatment temperature. The deterioration in fiber properties was associated with the development of voids, cracks, and blisters in the matrix. Such defects are caused by the rapid formation of volatile pyrolysis gases produced by the decomposition of matrix precursor resins (Ref. 4). However, crack-free monolithic materials can be produced in the form of glassy carbon from suitable precursor resins, provided that the processing cycles are carefully controlled and are slow enough (Ref. 5).

A new study (Ref. 6) was initiated in which the factors controlling fiber, matrix, and composite mechanical properties were carefully evaluated utilizing four thermosetting matrix-precursor resins, and nine high-strength, high-modulus carbon fibers. Various pregging procedures and processing cycles were evaluated.

Fiber degradation from exposure to volatile species liberated during pyrolysis was evaluated experimentally and considered thermodynamically. Apparent degradation in fiber tensile properties when exposed to the volatile matrix species generated in pyrolysis was measured. Fiber tensile properties as affected by matrix shrinkage and matrix strain-to-failure was evaluated. From these studies, it became clear that the apparent decrease in tensile strength was not due primarily to chemical attack by the vapor species released from the matrix, but to two factors inherent in the matrix precursors used. These were:

- Low matrix strain-to-failure after pyrolysis, a property inherent in matrices generated from state-of-the-art thermosetting resins, and
- The development of pyrolysis cracks as a result of differential shrinkage between the essentially stable carbonized fiber and the as-cured matrix, which underwent at least 20-percent linear shrinkage during pyrolysis

As previously discussed (Ref. 6), this differential shrinkage induces longitudinal tensile stresses in the matrix that lead to crack formation during pyrolysis to accommodate the matrix change in volume. Such pyrolysis cracks generally form as flaws perpendicular to the fiber axis and tend to reduce the effective matrix strain-to-failure.

As a consequence of the two factors, the possibility of realizing the full potential of the stiff strong carbon fibers was substantially reduced. Since the composite monofilaments are totally elastic, equal strains can be expected to prevail upon deformation when there is good interfacial bonding between fiber and matrix. Figure 1 shows the stess-strain behavior of several high-strength carbon fibers in a typical matrix. The intersection between a fiber stress-strain curve and the vertical dotted line represents the point at which a composite with that fiber may be expected to fail. Thus, a carbon-carbon monofilament formed from Thornel 75 in a matrix generated from GW-173, a modified phenolformaldehyde, can be expected to fail at a tensile stress no greater than 2.2 GN/m^2 (320,000 psi). Similarly, a composite monofilament of Thornel 400 in the same matrix should fail at a stress of 0.9 GN/m^2 (130,000 psi) or less. Pyrolysis cracks and flaws generated during pyrolysis tend to displace the matrix failure point to the left, resulting in even lower utilization of fiber reinforcement, i.e., a lower composite tensile strength.

This hypothesis was supported by experimental evidence. Of the nine fiber candidates and four matrix precursors examined, the highest composite tensile strength obtained was with GW-173, which had the highest matrix strain-to-failure (0.41 percent) after pyrolysis in monolithic form, and Thornel 75, which had the closest match in strain-to-failure (0.5 percent). After process optimization, the highest composite tensile strength observed was 1.47 GN/m (216,000 psi), which was equivalent to a fiber tensile stress of 1.66 GN/m (240,000 psi), i.e., 75 percent of the value predicted from the ratio of the matrix failure strain to the fiber failure strain (see Figure 1).

A study of the changes which take place during pyrolysis showed that the tensile strength of the composite monofilament modules decreases rapidly with increasing heat-treatment

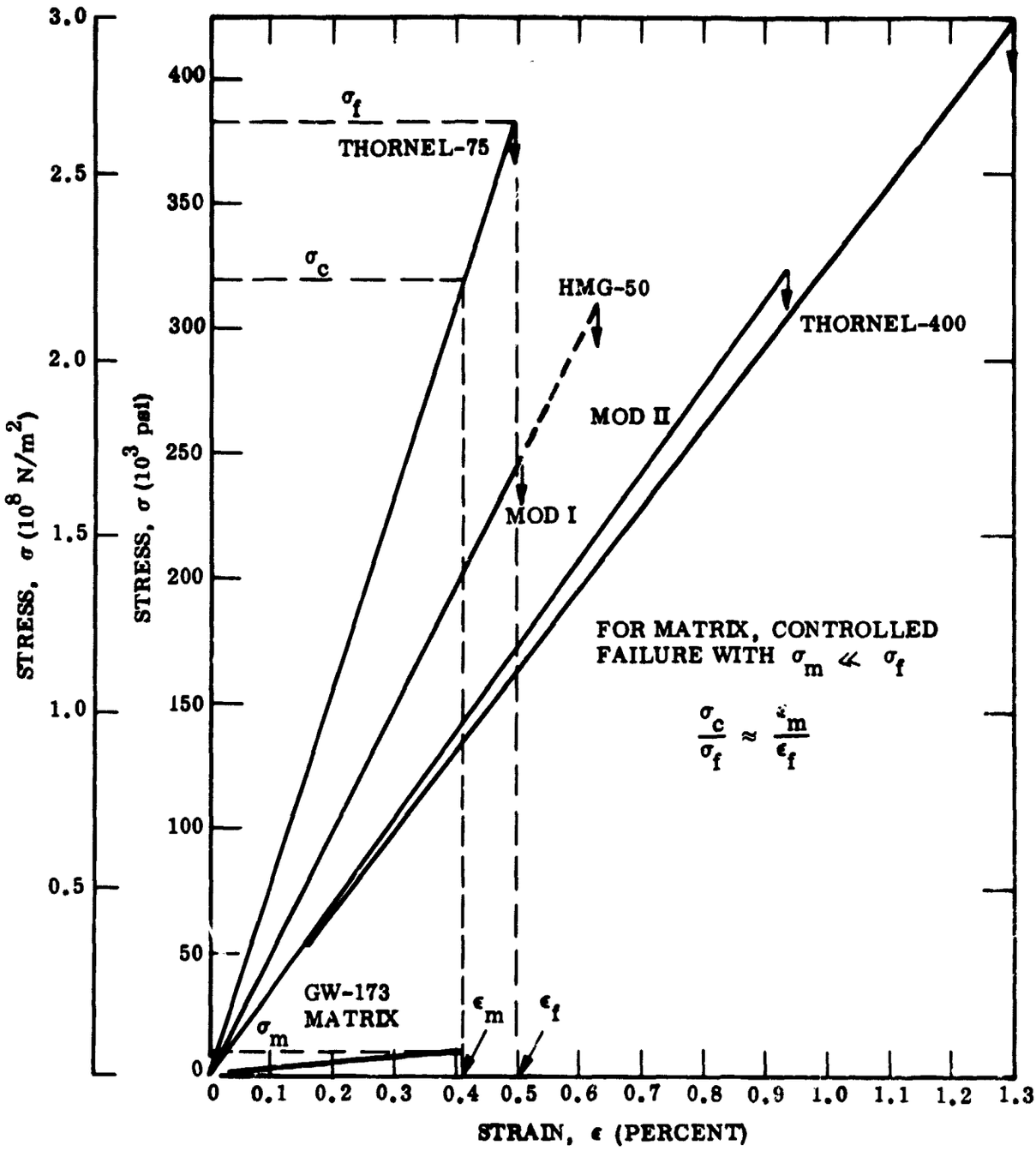

Figure 1. - Stress-Strain Relationship of Candidate Fibers and Matrix

temperature in the range of 673° and 773°K. This decrease was accompanied by a maximum rate of weight loss, 0.16 percent/°K, and the greatest shrinkage. Scanning electron microscopy and metallographic analysis indicated that pyrolysis cracking was initiated in this low-temperature range and became more severe with higher heat-treatment temperatures.

Because of the large difference in linear shrinkage (20 percent) between the stiff carbonized fibers and the matrix during pyrolysis, monofilaments free of matrix cracks could not be produced. Such carbon-composite monofilaments would not be useful in metal matrix composites because they were highly friable and pyrolysis cracks exposed individual carbon filaments to potential metal attack.

As a result of these studies, two approaches to solving these problems were suggested. One was modification of the matrix precursor to improve the matrix strain-to-failure, char yield, and graphitizability. In the second approach, called "copyrolysis," the matrix shrinkage problem would be reduced or eliminated by pregging partially processed carbon-fiber precursors with a suitable matrix resin, and pyrolysing and heat-treating the product to produce fully carbonized monofilaments. Preliminary studies (Ref. 6) had demonstrated the feasibility of this approach, monofilament bundles free of pyrolysis cracks with excellent fiber-matrix bonding were produced.

A new study was initiated in which matrix improvement, copyrolysis, and process optimization were to be further evaluated. The ultimate goal was a monofilament with a composite tensile strength of 4.0 GN/m^2 (580,000 psi), an elastic modulus of 400 GN/m^2 (58×10^6 psi), and a diameter of 2.54×10^{-4} m (10 mils). Since carbon fibers having such properties were not commercially available, interim goals and objectives were to be considered during the course of the study.

The program described consisted of four tasks: (a) matrix improvement, (b) copyrolysis, (c) process optimization, and (d) monofilament production and delivery.

However, all tasks were mutually independent and iterative so that the following could be accomplished:

- Evaluation of improved matrix precursors using copyrolysis and conventional techniques
- Copyrolysis studies using standard and advanced matrix precursors
- Process optimization of advanced matrices and copyrolysis monofilaments
- Shipment of the best monofilaments produced as representative products

Section 3

EXPERIMENTAL METHODS

The purpose of this program was to investigate methods of producing high-tensile-strength, high-modulus, large-diameter carbon composite monofilaments from suitable resin-base matrix precursors and multifilament carbon-fiber precursors. Emphasis was placed on matrix improvement, copyrolysis with reinforcing fibers at various stages of carbonization and process optimization.

3.1 MATERIALS

3.1.1 Matrix Precursors

In the previous study (Ref. 6), the matrix precursors tested were limited to resin systems that could be processed in monolithic form such that char yield, strain-to-failure, and tensile strength could be determined on the pyrolysed product.

In the current study, matrix precursors were not limited to readily processable, thermosetting resins but also included thermoplastic materials convertible into carbon char formers only by specialized processing techniques. The matrix precursors studied can be placed into four categories: (1) thermosetting cross-linking polymers such as a modified phenolformaldehyde (GW-173) used for reference purposes, (2) thermoplastic polymers (such as polyacrylonitrile and polyvinyl chloride) that can be stabilized under specialized processing conditions to form ladder polymers, (3) pitches which are graphitizable, and (4) HTR resin,* a highly aromatic thermosetting resin with a high char yield. Since all of these materials cannot be pyrolysed into monolithic form, matrix properties were estimated in-situ on the composite monofilament. Consequently, reference fibers such as Thornel 75 (or a characterized copyrolysis fiber) were used, and matrix properties were calculated from properties of the composite by assuming that the composite rule of mixture held with respect to elastic modulus, density, and area fractions.

Candidate matrix precursors evaluated in Task I, Matrix Improvement, are described in Table I. The characteristics of the reference matrix, GW-173, evaluated are described in detail in Refs. 5 and 6. When processed in monolithic form, this material forms a hard glasslike carbon with a char yield of 70%, an average tensile strength of 0.13 GN/m^2 (18,900 psi) and a density of 1.49 gm/cm^3 after pyrolysis. Its elastic modulus is 27.6 GN/m^2 (4×10^6 psi). It can be processed either in monolithic form or as a matrix precursor in carbon-carbon.

Pitches were selected because they are graphitizable to a form softer than glassy carbon. A representative petroleum pitch (No. 396) and a coal tar pitch (No. 385) were selected because they are totally or almost completely soluble in quinoline, thereby making them amenable to solvent pregging procedures. Moreover, high

*H-3 resin, produced by Haveg Industries, Inc., Santa Fe Springs, California.

TABLE I. - CANDIDATE MATRIX PRECURSORS

Matrix Precursor	Density As-Cured Condition (g/cm^3)	Char Yield[a] (%)	Solvent Used for Pregging	Comment
GW-173 Modified phenol-formaldehyde	1.29	70	Methanol	A modified phenol formaldehyde, a thermosetting resin that forms a cross-linked structure. Has a good char yield and is readily processable to form a glass-like carbon with a strain-to-failure of 0.41% when processed in monolithic form (Ref. 5).
Petroleum Pitch (No. 396)	1.23	62.7	Quinoline	A petroleum pitch, softening point = 396°K; quinoline solubles = 39.9%. Absence of low molecular weight solubles.
Coal Tar Pitch (No. 385)	1.33	53.0	Quinoline	A coal tar pitch, softening point = 385°K; quinoline solubles = 85.4%.
Polyacrylonitrile (PAN) $\left[CH_2\text{-}CHCN\right]_n$	1.52	50[b]	Dimethylformamide	An organic polymer that cyclizes to form a ladder polymer which can be processed in fiber form to strain-to-failure of 1% or greater.
Polyvinyl Chloride (PVC) $\left[CH_2\text{-}CHCl\right]_n$	1.40	75	Cyclohexanone	A graphitizable polymer that has a high char yield when oxidized, and up to 1% strain-to-failure when processed in fiber form (Refs. 14, 15).
HTR Resin[c]	1.145	90	Methyl Ethyl Ketone	A highly aromatic thermosetting resin. Absence of low molecular weight solubles.

(a) Char yield at 1283°K.
(b) When stabilized in a highly oxidizing environment.
(c) Product of Haveg Industries, Santa Fe Springs, California (H-A43)

quinoline solubility indicates a high molecular weight and a high degree of aromaticity, both characteristics that make them more graphitizable (Refs. 7, 8). When processed in the soluble form, pitches are thermoplastic and flow readily. However, char yield and cross-linking can be enhanced by oxidation, after which they become infusible (Refs. 9,10). Consequently, pitches were processed in situ utilizing a solvent pregging operation, followed by an air-cure (or by oxidation, in some experiments), then pyrolysis and heat treatment.

Polyvinyl chloride and polyacrylonitrile form long chainlike polymers without cross-linking and thus are readily processable into an oriented structure with high tensile strength. As indicated in Table I, polyacrylonitrile will cyclize under the influence of oxygen to form a ladder polymer that is thermally stable (Refs. 11,12). Polyvinyl chloride has been reported as graphitizable (Ref. 13). When processed in a strongly oxidizing atmosphere, it has a 75-percent char yield (Refs. 14, 15). Both polyacrylonitrile (Refs. 11,12) and polyvinyl chloride (Refs. 14,15) have been processed to form carbon fibers with a strain-to-failure of 1 percent or greater.

HTR resin is an aromatic, high-molecular weight thermosetting resin with a 90-percent char yield.

3.1.2 Fibers

3.1.2.1 Standard Fibers

Thornel 75, a completely carbonized fiber generated from cellulose,was used for control purposes with the most promising matrix precursors. This fiber is available as a 2-ply yarn of 1440 crenulated filaments per bundle, with a nominal density of 1.82 g/cm^3, a tensile strength of 2.7 GN/m^2 (392,000 psi), and an elastic modulus of 545 GN/m^2 (79 x 10^6 psi). This fiber has a strain-to-failure of 0.5 percent and has given the best results in monofilaments produced by conventional pyrolysis (Ref. 6).

3.1.2.2 Fiber Precursors for Copyrolysis

Fiber precursors were polyacrylonitrile (PAN), which was selected because it forms a linear rather than a cross-linked polymer. During spinning and subsequent oxidation, the polymer chain is readily oriented so that maximum tensile strength and elastic modulus are developed without stress graphitization.

Two types of fiber were evaluated: round PAN (Type-C)* available in 10,000 filament tow, and dog-bone shaped PAN (Type D)** available in much smaller bundles of 385 filaments per tow.

Type-C Fiber Precursor, 10,000 Filament Tow. Processes for producing high-strength, high-modulus fibers from Type-C fibers have been briefly described by Standage and Prescott (Ref. 16), and patents have been issued (Refs. 17, 18, and 19). Orientation in the fiber is developed during oxidation under tension while wound on a frame, after which the fiber is carbonized or graphitized (Ref. 20). The filaments are round in cross section and are available in 10,000 filaments per tow.

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*Obtained from Rolls Royce Ltd, England.

**Obtained from Bayer-Farbenfabriken, Germany, trade name – Dralon-T.

Limited copyrolysis data had been previously determined (Ref. 6) with Type-C fiber precursor. Data were obtained on the linear shrinkage, weight loss, and density of the oxidized fiber during carbonization from 473° to 1273° K. With the bare fiber, a tensile strength maximum of 2.18 GN/m^2 (316,000 psi) was obtained at 1673°K. However, available information (Refs. 21, 22, 23, 24) indicate that even though tensile strength starts degrading with higher temperature heat treatment, maximum elastic modulus is not developed without a heat treatment of 2773° K.

Evaluation was done (Ref. 6) on copyrolysis of Type-C fiber, oxidized and heat-treated to temperatures ranging from 473° to 1273° K, pregged with GW-173, and then copyrolysed to 1273° and 2273° K. Maximum tensile strength 0.69 GN/m^2 (99,000 psi), calculated on the basis of fiber cross section, and 0.51 GN/m^2 (74,000 psi), calculated on the basis of composite area, was obtained with fiber preheat-treated to 1273° K, copyrolysed to 1273° K, and heat-treated to 2273° K.

Type-D Fiber Precursor, 385 Filament Tow. This fiber, a commercially available homopolymer of polyacrylonitrile, designated Dralon-T, was selected because of its small bundle diameter, to facilitate ease of handling, and because available information (Refs. 25, 26) indicated that both tensile strength and elastic modulus increase with increasing heat-treatment temperature. Filaments of this type are dog-bone or Y-shaped in cross section.

No data were available on density and tensile strength of Dralon-T carbonized to less than 2473° K. However, the chemistry of degradation below 1273° K has been described by Fitzer et al. (Refs. 27, 28, 29), indicating that stabilization can be accomplished by preoxidation between 523° and 613° K. Data on graphite fibers produced from Dralon-T oxidized at 548° K indicate that both density and tensile strength increase in the range 2473° to 3073° K (Ref. 30).

Both PAN homopolymer and copolymer do not lose all their nitrogen below 1273° K, and carbonization is not complete until a heat-treatment temperature of 1573° K has been reached (Ref. 31).

3.2 METHODS

3.2.1 Matrix Properties

As indicated in Section 3.1, because monolithic chars could not be readily produced from the advanced matrix precursors to be studied, properties of composite monofilaments were determined and matrix properties were calculated from the difference between bare-fiber reference data and measured composite data. Actually, study of the matrix properties in this manner is more realistic because it has been found that unlike the case of monolithic chars, internal stresses developing during pyrolysis of a composite bundle can cause graphitization that must alter the properties.

Matrix weight fraction, after each step in the processing procedure, was calculated from the following:

After any processing step, the weight pickup of matrix, w_m, was calculated from the following:

$$w_m = w_c - w_f$$

where

w_c = unit-length weight of composite monofilament

w_f = unit-length weight of the bare fibers (determined separately) on reference fiber heat-treated to the same condition as the composite monofilament

Area matrix (A_m) was calculated from:

$$A_m = \frac{w_c - w_f}{d_m}$$

where

d_m = density of matrix in compatible units.

Also, with the precalculated fiber cross-sectional area (A_f), the fiber and matrix volume fractions can be calculated as follows:

$$V_f = \frac{A_f}{A_f + A_m} = \text{volume fraction fiber}$$

$$V_m = 1 - V_f = \text{volume fraction matrix}$$

The matrix density used was determined separately on monolithic material when it could be produced separately, or was estimated from composite density as follows:

$$d_m = \frac{d_c - V_f d_f}{V_m}$$

where

d_m = calculated matrix density,

d_c = measured composite density, and

d_f = reference fiber density.

3.2.2 Test Procedure

3.2.2.1 Density Determination

The method employed to determine bare fiber and composite monofilament densities was a variation of a density gradient technique. In lieu of a density gradient column, 10^{-4} m^3 (100 cc) solutions were prepared in density increments of 0.1 gm/cc using mixtures of benzene and 1, 1, 2, 2 tetrabromoethane. Density of the solutions was measured to five significant figures with a specific gravity balance. Individual specimens were then introduced into appropriate solutions to determine their gravity settling characteristics. The third significant figure was estimated on the basis of their sink-float action.

3.2.2.2 Evaluation of Room-Temperature Tensile Properties

Tensile tests were carried out on five to six specimens subjected to a particular processing condition. Specimens were epoxy-bonded into split slotted steel holders with slots aligned with 4.76×10^{-3} m (0.1875-in.) dowels in end holes as shown in Fig. 2. A 2.54-m length of monofilament specimen was bonded to each end tab to obtain sufficient strength to fracture the specimen during the tensile test.

Tests were conducted on a 4.5×10^4 N (10,000 lb) capacity testing machine. The high sensitivity range was used which allowed a selection of 0 to 178 N (0 to 40 lb) scale in 0.254 m (10 in.) of chart. Testing speed was in accordance with ASTM standards at 2.12×10^{-5} m/sec (0.05 in./min) using a 2.54×10^{-2} m gage length.

Axial alignment was obtained by using universal joints and double-pin ended connections between the specimen holders and clevises of the load train. An autographic recording of each test was obtained.

The elastic modulus of the composite monofilaments investigated was calculated from data obtained from static incremental loading and strain measured by the use of strain gages or by an optical cathetometer. Strain gages were used on the larger composite monofilaments produced from 10,000 filament Type-C tow. Sensitivity was 2.54×10^{-8} m^2 (1×10^{-6} in.). Micromeasurements type gages were bonded to the composite monofilament using a compatible epoxy adhesive. To eliminate damage to the composite, the strain gages were applied, and the three-wire system used was soldered to the gage before bonding the composite to the tensile end tabs. A digital strain indicator was used to obtain the incremental strain readings.

Optical measurements were made on composite monofilaments produced from 385 filament Type-D tow because they were too narrow to accommodate the smallest standard strain gage. The cathetometer was accurate to 254×10^{-8} m (100×10^{-6} in.). Sensitivity was increased to 85×10^{-8} m (33×10^{-6} in.) by using a 7.6×10^{-2}m (3.0 in.) gage length. A plot of the data was made as stress versus strain (m/m), and the elastic modulus was obtained from the slope of the line drawn through the data points. Samples were not loaded to failure. Specimens were epoxy bonded, using the same end holders described in tension tests (Fig. 2).

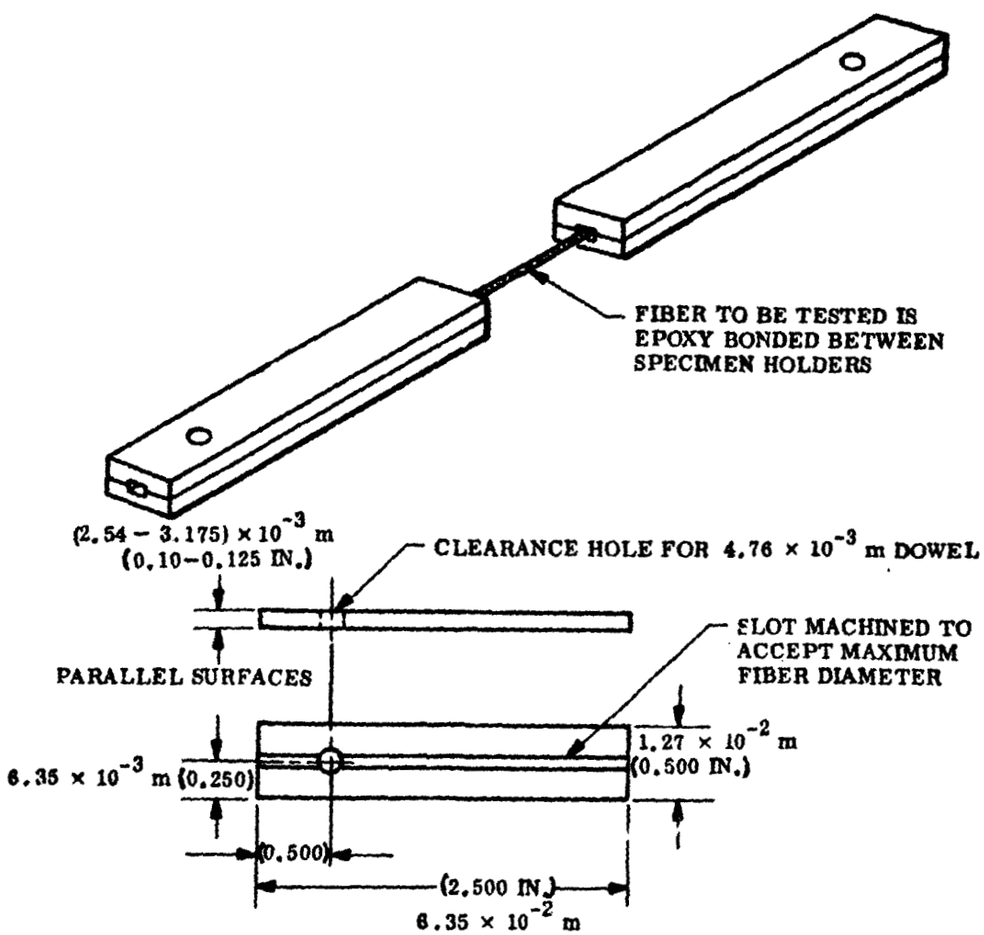

Figure 2. - Test Fixture for Determining Specimen Tensile Strength

Strain-to-failure was calculated from the ratio of the tensile strength, as determined in the 2.54×10^{-2} m gage-length specimen, to the elastic modulus determined with the longer specimen. The totally elastic behavior of the fibers permits such calculation. Calculation of strain-to-failure from the load deflection curve has been found to be highly inaccurate when the failure strain is low, as was the case in the monofilaments developed in the antecedent contract (Ref. 6).

3.3 MONOFILAMENT PREPARATION

3.3.1 Fiber Treatment

Both Type-C and Type-D fibers were stabilized by winding the tow on frames and oxidizing in air. Since the PAN shrinks 8 percent (Ref. 6) when oxidized in an unconstrained condition, tensile stresses that develop during constrained stabilization promote alignment of the polymer chain parallel to the filament axis.

A typical oxidation cycle was carried out using a long hold, $(5.76$ to $7.2) \times 10^4$ sec at 473°K, heating to 533°K in 3.6×10^3 sec (1 hr), and holding 3.6×10^3 sec (1 hr) at temperature. After stabilization, fibers were cut into 0.366-m lengths and processed to temperatures ranging from 673° to 1673° K in an inert atmosphere. Small weights (20×10^{-3} kg for Type-C fiber and 2.8×10^{-3} kg for Type-D fiber) were attached during pyrolyses.

3.3.2 Composite Monofilament Preparation

A batch solvent pregging procedure had been previously developed (Ref. 6) as the most desirable approach to impregnating multifiber bundles with candidate matrix precursors for screening purposes.

The process consisted of the following operations:

- Cut candidate fibers to a length of 0.366 m (14 in.)
- Apply 1.27×10^{-2} m (0.5-in.) masking tape to each filament end to prevent filament fraying
- Attach 2×10^{-2} kg weight to one end for tension
- Submerge weighted bundles vertically in a solution of the candidate resin for a minimum of 300 sec
- Air-dry pregged specimens for a minimum of 300 sec
- Cure weighted specimen vertically in oven
- After drying, remove heavy weights from samples and attach small weight
- Load fiber array into a graphite holder and process to desired final heat-treatment condition in an inert atmosphere.

Section 4
EXPERIMENTAL RESULTS

4.1 MATRIX IMPROVEMENT

The purpose of this task was to investigate and select from 3 to 10 resins which offer the greatest promise for the resin conversion and pyrolysis method of making carbon-carbon composite monofilament. Matrix selection criteria were high char yield and high failure strain.

4.1.1 Matrix Improvement/Copyrolysis Experiments

For the initial matrix characterization, the four thermoplastic matrix precursors listed in Table I were selected for evaluation. Because these materials melt and tend to dissociate when heated, it was necessary to stabilize them (i.e., render them infusible) after impregnation. Consequently, matrix characterization was carried out using the copyrolysis method described in the previous section, with two reference fibers for which bare fiber data had been established. These were:

- Oxidized Type-C tow
- Oxidized Type-C tow processed to 1273° K

To maximize char yield, each sample was given three cycles of solvent impregnation, air cure, and oxidation to 533° K. The cure was carried out at 339° K with an overnight hold. The oxidation cycle, one suggested by Otani (Ref. 15) for polyvinyl chloride, consisted of an overnight hold to 533° K. The weight percent pickup* per unit length of fiber is shown in Figure 3. The matrix pickup was close to 60 percent with the two pitches. There was loss in weight during oxidation stabilization so that only 39.4 wt percent matrix was retained with the No. 396 pitch and 32.2 wt percent was retained with the No. 385 pitch. Each successive impregnation and oxidation increased the matrix concentration slightly. After pyrolysis, the wt percent pickup was 59 percent or greater for both pitches because of concurrent fiber weight loss. With polyacrylonitrile (PAN) the weight pickup was only 24.7 percent after the first impregnation,

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*Wt percent pick = $\{(w_m - w_{f\,ref})/w_{f\,ref}\} \times 100$, where the fiber unit w_f is 14.2×10^{-4} kg/m (36.2×10^{-3} gm/in.) the reference value for 533°K oxidized Type-C tow, and 8.2×10^{-4} kg/m (20.8×10^{-3}) gm/in. is the value for 1273°K treated oxidized Type C tow.

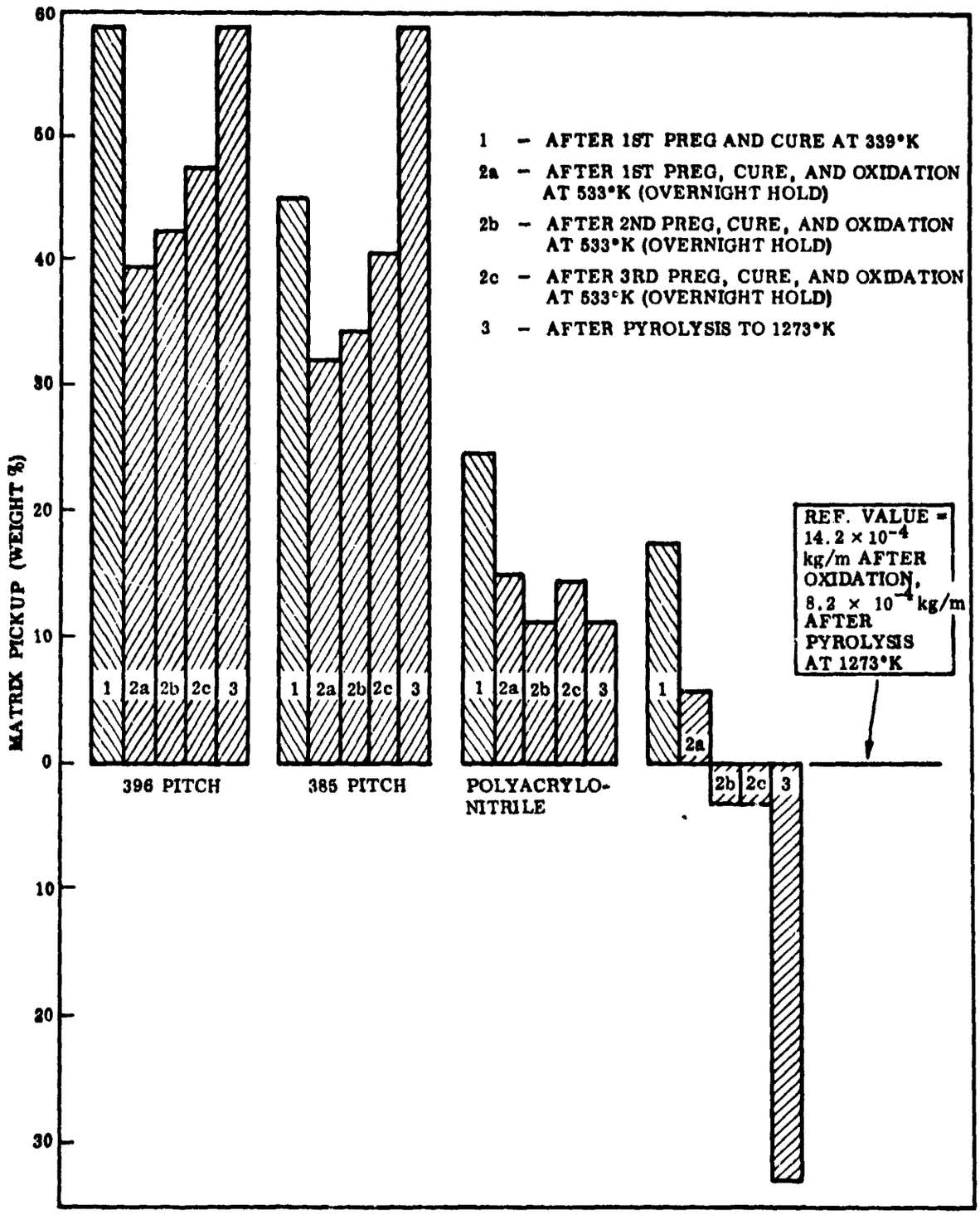

Figure 3. - Weight Pickup When Processing Oxidized (533°K) Type-C Tow With Four Candidate Matrix Precursors

and 15 percent after oxidation. Reimpregnation and oxidation resulted in no further weight gain. After pyrolysis, the weight pickup was only 10.7 percent. Results with polyvinylchloride (PVC) were poor. Resin pickup during the initial pregging was only 17.5 percent. After oxidation, the matrix pickup was 6.1 percent by weight. Further oxidation cycles caused the weight per unit length to decrease below the reference value. After pyrolysis, the decrease below the reference pyrolysis weight was -33.6 percent. The PVC matrix precursor candidate was abandoned because of its inconsistent performance.

The properties of the monofilaments after final oxidation and pyrolysis to 1273° K are listed in Table II. With both pitches, the content of matrix after final pyrolysis was 37 percent by weight. Metallographic examination indicated good bundle impregnation and wetting. Monofilament handling characteristics suggested that they were relatively weak. Testing for reference purposes yielded an average fiber tensile strength of only 0.050 GN/m^2 (7,150 psi) for monofilament produced with No. 396 pitch, and 0.037 GN/m^2 (5,370 psi) for monofilaments produced with No. 385 pitch. With the as-oxidized Type-C tow in GW-173 precursor without matrix oxidation, the results were somewhat improved, to a fiber tensile strength of 0.203 GN/m^2 (29,500 psi). Since the bare fiber tensile strength was 0.121 GN/m^2 (17,500 psi) after oxidation, and 1.815 GN/m^2 (263,000 psi) after pyrolysis to 1273° K, it appeared that some processing step caused a deterioration in fiber tensile strength, or that development of the strength-producing fiber structure was inhibited.

The possibility that strength degradation occurred by solvent attack during impregnation and drying was evaluated by testing oxidized Type-C tow exposed to representative matrix solvents and then dried (Table III). The loss in strength was 15 percent with quinoline, the pitch solvent; 10.4 percent with dimethylformamide (DMF), the PAN-matrix solvent; and 9.3 percent with cyclohexanone, the solvent used with polyvinylchlorides (PVC). The small losses in strength observed indicated that the 533° K fiber-oxidation cycle had effectively cross-linked and stabilized the polymer structure against solvent attack. Apparent weight loss observed with PVC during matrix oxidation and failure of expected tensile strengths to develop after pyrolysis could not be attributed to solvent attack.

Another possible reason for apparent strength reduction during processing is that the oxidation cycle was too severe, particularly since tensile strength was higher when the matrix was not oxidized, as with GW-173. Consequently, the oxidation cycle was modified. The cycle used for matrix oxidation, a short, high-temperature oxidation treatment (at 533° to 543° K), was one also used for polyvinylchloride fibers. However, unstabilized PAN softens at 463° K (Ref. 32), and in our previous experiments, fiber stabilization was accomplished by a long hold at 463° K followed by a short cycle to 543° K. Accordingly, the cure and oxidation cycles of the matrix were revised to effect oxidation and stabilization at the lower temperature. Matrix cure temperature was increased to 355° K, and oxidation was carried out on the same schedule as that used for the bare fiber.

TABLE II. - RESULTS OBTAINED WHEN COPYROLYSING OXIDIZED (533°K) TYPE-C TOW WITH FIVE MATRIX PRECURSORS

Component	Process Cycle	Weight % Length		Weight % Matrix	Char Yield (%)	Cross-Sectional Area of Component		Tensile Strength				Comments
								Fiber Area		Composite Area		
		(kg/m × 10^{-4})	(gm/in. × 10^{-3})			(m^2 × 10^{-7})	($in.^2$ × 10^{-4})	(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^3)	
Bare Fiber Type-C Fiber	• As oxidized, 533°K	[illegible].2	36.2	0	–	9.10	14.1	0.121	17.5	0.040	5.8	Value lower than previously obtained (Ref. 6).
	• After pyrolysis to 1273°K	8.2	20.8	0	57.5	4.68	7.26	1.815	263.0	1.000	144.9	Value comparable to previous value.
396 Pitch Matrix in Situ	• After 3rd preg, cure and oxidation	20.9	53.0	32.1	–	5.43	8.42	–	–	–	–	Only fiber/matrix combination which will support 0.620 kg/wt during oxidation.
	• After pyrolysis to 1273°K	13.0	33.1	37.2	72.5	2.76	4.28	0.050	7.15	0.031	4.50	Glassy outer surface, fracture is partially brittle, partially fibrous.
385 Pitch Matrix in Situ	• After 3rd preg, cure and oxidation	19.96	50.7	29.0	–	4.34	6.74	–	–	–	–	Good bundle impregnation, very few trans bundle cracks.
	• After pyrolysis to 1273°K	13.1	33.2	37.4	54.5	2.79	4.32	0.037	5.37	0.023	3.37	Very brittle monofilament.
Polyacrylonitrile Matrix in Situ	• After 3rd preg, cure and oxidation	16.22	41.2	12.6	–	1.31	2.03	–	–	–	–	Poor bundle impregnation, poor fiber matrix bonding, circumferential sheath of PAN.
	• After pyrolysis to 1273°K	9.17	23.3	10.7	47.0	0.56	0.87		Too weak to test			Circumferential sheath cracked perpendicular to roving axis.
Polyvinyl Chloride Matrix in Situ	• After 3rd preg, cure and oxidation	13.3	33.8	neg[a]	–	0	0	–	–	–	–	No matrix uptake.
	• After pyrolysis to 1273°K	5.44	13.8	neg[a]	neg	0	0	Too weak to test – falls apart on handling				Fiber bundle has longitudinal and transverse cracks.
GW-173 in situ	No matrix oxidation pyrolysed to 1273°K	14.4	30.15	29.75	70.0	2.58	3.61	0.203	29.5	0.113	16.33	Fiber brittle.

(a) No matrix – weight per unit length decreased below reference value.

TABLE III. - EFFECT OF SOLVENT SOAK ON TENSILE PROPERTIES OF BARE 533°K (260°C) OXIDIZED TYPE-C FIBER

Solvent Exposure	Function	Tensile Strength		Loss in Fiber Strength (%)
		(GN/m^2)	($psi \times 10^3$)	
None	Average	0.133	19.3	
	Maximum	0.137	19.8	
	Minimum	0.128	18.6	
Quinoline	Average	0.113	16.4	15
	Maximum	0.117	17.0	
	Minimum	0.110	16.0	
Cyclohexane	Average	0.121	17.5	9.3
	Maximum	0.134	19.5	
	Minimum	0.102	14.8	
Dimethyl-formamide	Average	0.118	17.1	10.4
	Maximum	0.132	19.1	
	Minimum	0.109	15.8	

The changes in matrix pickup observed with oxidized Type-C tow preheated to 1273° K, and the three most promising matrix precursors, are shown in Figure 4. With No. 396 pitch and 1273° K Type-C tow, the weight pickup after the first preg and cure was 90.4 percent. This decreased to 73.1 percent after oxidation (corresponding to a weight loss of only 20 percent). Each successive impregnation and oxidation cycle improved matrix yield. After pyrolysis, the weight pickup was 67.3 percent. The initial pickup with No. 385 pitch was lower, and each successive impregnation and oxidation cycle increased the matrix concentration. After pyrolysis, the weight pickup was 51.0 percent. With polyacrylonitrile, although the matrix retention on impregnation after oxidation was greater than previously observed (Figure 3), processing and pyrolysing directly to 1673° K (the temperature at which bare Type-C tow reaches maximum tensile strength) resulted in an ultimate weight pickup of only 10.1 percent.

The properties of monofilaments produced from 1273° K Type-C tow and the three most promising thermoplastic matrix precursors are summarized in Table IV. Char yields and matrix weight fractions are lower than with as-oxidized Type-C tow. The revised oxidation stabilization cycle was not used with the pitches, and monofilament properties are still low, e.g., fiber tensile strengths of 0.154 GN/m^2 (22,400 psi) for No. 396 pitch, and 0.118 GN/m^2 (17,100 psi) with No. 385 pitch. Fiber tensile strength was higher (0.573 GN/m^2 (83,000 psi) with PAN matrix and the revised oxidation cycle, but the matrix volume fraction was too low (9.2 percent).

Although the data obtained with multiple pregging and oxidation were not promising, limited additional studies were carried out utilizing No. 396 pitch and polyacrylonitrile matrix in which the multiple processing steps were eliminated or revised. These are reported in Section 4.2 on copyrolysis.

4.1.2 Matrix Improvements Using Fully Pyrolysed Fibers

During the program a thermosetting resin (HTR) was found with a char yield substantially greater than any of the candidate resin matrix precursors originally selected. Since pyrolysis shrinkage is inversely related to char-yield, such a resin could possibly be used to form a flaw-free matrix even with fully pyrolysed, high-strength, graphite-fiber reinforcements. A single trial run was made to verify this hypothesis and thereby indicate whether a more intensive series of tests was warranted.

The trial run was made using Thornel 75 roving impregnated once in a methyl-ethyl-ketone solution of the resin, cured, pyrolysed, and measured to yield the following properties.

Matrix Condition	Weight per Unit Length ($kg/m \times 10^{-4}$)	Weight per Unit Length ($gms/in. \times 10^{-3}$)	Matrix Cross-Sectional ($m^2 \times 10^{-8}$)	Matrix Cross-Sectional ($in.^2 \times 10^{-5}$)	Vol % Matrix	Char Yield
As cured at 450° K	1.26	3.21×10^{-3}	6.12	9.48	66.2	–
After pyrolysis to 1153° K	1.22	3.10×10^{-3}	4.58	7.10	58.4	93.7

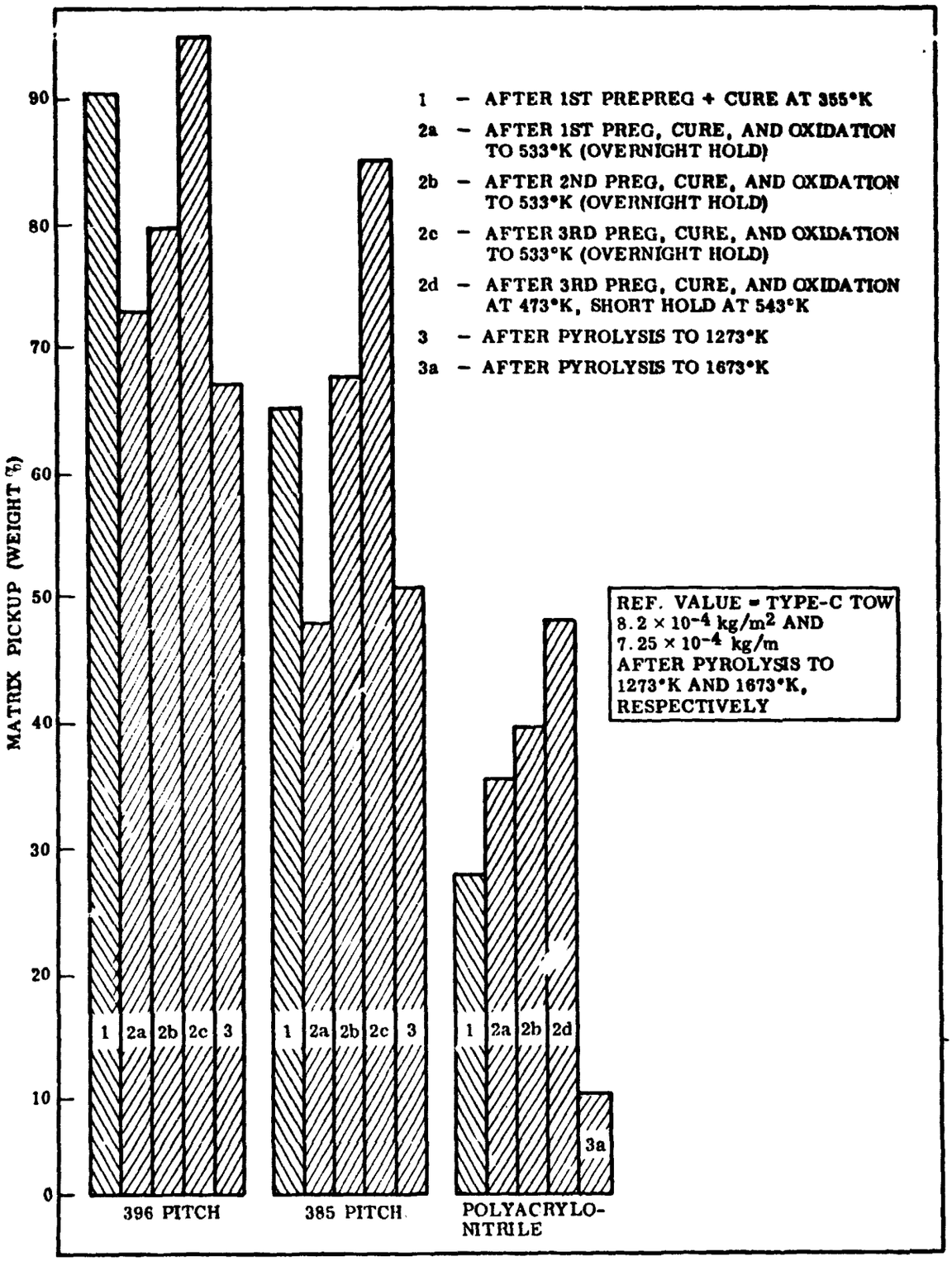

Figure 4. - Weight Pickup of 1273°K Grade Type-C Fiber in Three Candidate Matrix Precursors

TABLE IV. - RESULTS OBTAINED WHEN COPYROLYSING (1273°K) TYPE-C TOW AND THREE MATRIX PRECURSORS

Component	Process Cycle	Weight Per Unit Length		Weight % Matrix	Char Yield (%)	Cross-Sectional Area of Component		Tensile Strength			
								Fiber Area		Composite Area	
		(kg/m × 10^{-4})	(gm/in. × 10^{-3})			(m^2 × 10^{-7})	($in.^2$ × 10^{-4})	(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^3)
Oxidized Type C Tow	• Pyrolysed to 1273°K	8.2	20.8	0	57.5	4.7	7.26	1.815	263.0	–	–
	• Pyrolysed to 1673°K	7.25	18.35	0	50.6	4.16	6.42	2.04	315.0	–	–
No. 396 Pitch in Situ	• After 3rd oxidation at 533° K, short cycle	16.0	40.7	48.9	–	–	–	–	–	–	–
	• After 3rd oxidation and pyrolysis to 1273°K	13.7	34.8	40.2	70.5	3.14	4.87	0.154	22.4	0.133	13.45
No. 385 Pitch in Situ	• After 3rd oxidation at 533°K, short cycle	15.2	38.65	46.2	–	–	–	–	–	–	–
	• After 3rd oxidation and pyrolysis to 1273°K	12.36	31.4	33.75	59.4	2.38	3.69	0.118	17.1	0.078	11.3
PAN Matrix in Situ	• After 3rd oxidation at 533°K, standard cycle	4.41	11.2	32.7	–	–	–	–	–	–	–
	• After 3rd oxidation and pyrolysis to 1673°K	7.72	19.6	9.2	16.1	0.41	0.63	0.573	83.0	0.522	75.5

(a) Calculated from - $\left\{\left(\frac{w}{\ell}\right)_{form} - \left(\frac{w}{\ell}\right)_{f}\right\} \times 100$

Calculated from $\left(\frac{w_{c_{pyr.}} - w_f}{w_{c_{oxid}} - w_f}\right) \times 100$

Calculated from $\left\{(w_m)\ \text{pyrolysed}/(w_m)_{oxid}\right\} \times 100$

Furthermore, a micrographic cross section revealed no matrix cracks.

Additional experiments were made to determine the influence of resin/solvent ratio in the pregging bath, and heat-treatment temperature. A solution with 25-percent resin solids resulted in a low-matrix concentration after cure (35.6 percent), and 86 percent of the original fiber tensile strength was retained (Table V). Increasing the resin solids to 30 percent increased matrix content. After pyrolysis to 1160°K, the maximum fiber tensile strength was 1.852 GN/m^2 (268,600 psi), and monofilament properties increased with further heat treatment. A maximum fiber tensile strength of 2.436 GN/m^2 (353,300), 93.4 percent of the reference value, was obtained after a final heat treatment to 2873°K.

These results were better than any previously obtained (Ref. 6). Further development was carried out under Process Optimization, Task III, described in Section 4.3.

4.2 COPYROLYSIS

The purpose of this task was to study the copyrolysis of partially heat-treated precursor fibers after pregging with standard and experimentally improved matrix precursor materials.

Copyrolysis studies were carried out with two fiber precursors:

- Type C-fiber, 10,000-filament tow, with round filaments previously characterized (Ref. 6)
- Type D-fiber, 385-filament tow, with dog-bone shaped filaments

A standard matrix precursor was GW-173, a phenolformaldehyde which had given the best results in conventional pyrolysis (Ref. 6). Limited studies were done with No. 396 pitch, with polyacrylonitrile matrix, and with HTR thermosetting resin.

4.2.1 Copyrolysis With Type-C Fiber Precursor

The effect of low-temperature heat treatment on the tensile properties of Type C fiber when processed in an unconstrained condition, i.e., free of matrix, are shown in Figure 5. Substantial increase in tensile strength and elastic modulus occurs between 673° and 1273°K. After heat treatment to 1273°K, the fiber tensile strength is 1.82 GN/m^2 (263,000 psi), and the elastic modulus is 152 GN/m^2 (22.0 x 10^6 psi). Copyrolysis data obtained in GW-173 matrix precursor are summarized in Table VI. In all cases, tensile strength increased with increasing heat-treatment temperature. With oxidized Type-C tow, the maximum tensile strength obtained in this series was 0.204 GN/m^2 (29,480 psi), which is 9.1 percent of the bare fiber tensile strength. A higher tensile strength of 0.32 GN/m^2 (47,000 psi) had been previously obtained (Ref. 6) by copyrolysis to 1273°K, followed by a second heat treatment to 2273°K. Slight improvement in tensile strength was obtained with a fiber pretreatment to

TABLE V. - PROPERTIES OF MONOFILAMENTS PRODUCED FROM HTR RESIN AND THORNEL 75

Experiment No.	Run No.	Resin in Solution (%)	Composite Heat-Treatment Temperature (°K)	Volume Matrix (%)	Function	Tensile Strength (Fiber Area)		Strength Retention[a] (%)	Tensile Strength (Fiber Plus Matrix)	
						(GN/m^2)	(psi × 10^3)		(GN/m^2)	(psi × 10^3)
–	–	25	455	35.6	Maximum	2.344	339.9	89.9	1.563	216.6
					Average	2.137	309.9	86.0	1.365	198.0
–	VT-68	30	1160	56.2	Maximum	1.852	268.6	71.0	0.773	112.1
					Average	1.681	243.8	67.7	0.702	101.8
I	VT-68	30	1160[b]	58.4	Maximum	2.322	336.9	88.1	0.967	140.2
	C-119		2173		Average	2.250	326.4	86.3	0.869	126.1
R	VT-68	30	1160[b]	51.5	Maximum	2.436	353.3	93.4	1.256	182.1
	C-120		2073		Average	2.407	349.2	97.0	1.261	179.9

(a) % strength retention = $\frac{\text{Tensile strength (fiber area)}}{\text{Tensile strength of as-received fiber pregged with epoxy}} \times 100$

(b) Sample cooled to room temperature and transferred to another furnace for high-temperature treatment

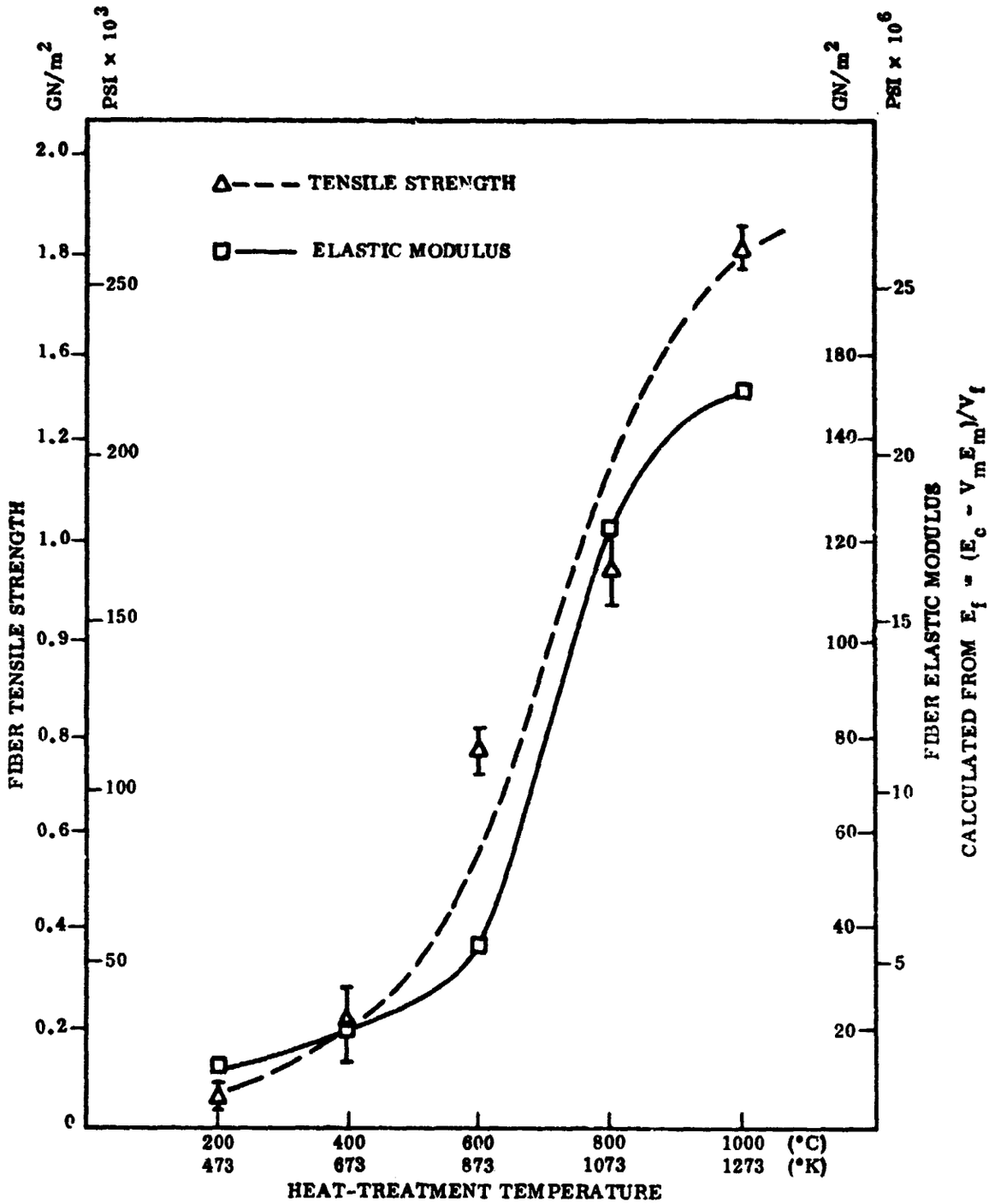

Figure 5. - Effect of Heat Treatment on Fiber Tensile Properties (Type-C Tow)

TABLE VI. - COPYROLYSIS OF TYPE-C TOW IN GW-173 MATRIX

Heat-Treatment Temperature (°K)		Volume % Matrix	Tensile Strength (Fiber Area)		% of As-Cured Value[a]	Tensile Strength (Composite)	
Fiber	Copyrolysis		(GN/m^2)	($psi \times 10^3$)		(GN/m^2)	($psi \times 10^3$)
455	470	33	0.121	17.5	100	0.040	5.813
455	673	35	0.0735	10.64	21.8	0.0477	6.92
455	873	42	0.0845	12.25	6.1	0.0493	7.15
455	1073	36	0.0843	12.22	4.5	0.0537	7.79
455	1273	45	0.204	29.48	9.1	0.112	16.3
455[a]	2273	62.5	0.32	47.0	19.2	0.12	17.0
673	470	39	0.337	48.9	100	0.132	19.165
673	873	35	0.0506	7.34	3.7	0.0329	4.77
673	1073	37	0.237	34.36	12.2	0.148	21.52
673	1273	37	0.285	41.46	12.8	0.181	26.24
673[a]	2273	60	0.36	52.0	21.2	0.17	24.0
873	470	36	1.370	198.5	100	0.493	71.35
873	1073	35	0.0732	10.62	5.3	0.0479	6.45
873	1273	42	0.2184	31.68	9.8	0.1265	18.34
1073	470	35	1.860	270.0	100	0.656	95.31
1073	1073	36	0.0843	12.22	4.5	0.0537	7.79
1073	1273	33	0.190	27.54	10.2	0.1269	18.4
1273	470	45	2.227	323.0	100	1.000	144.9
1273[b]	1273	46	0.428	62.2	19.3	0.233	33.9
1273[a]	1273	25	0.379	55.0	17.0	0.283	41.0
1273[b]	1673	43	0.752	109.0	34.7	0.430	62.4
1273[b]	1973	47	0.577	83.7	29.8	0.306	44.4
1273[b]	2273	41	0.703	102.0	36.0	0.414	60.1
1673[c]	470	--	2.178	316.0	100	–	–
1973	470	–	1.964	285.0	100	–	–
2273	470	–	1.834	266.0	100		

(a) Bare-fiber heat-treated to reference temperature. Table XXVI, Ref. 6.
(b) Table XXXI, Ref. 6.
(c) Fig. 38, Ref. 6.

673° K with a fiber tensile strength of 0.285 GN/m^2 (41,460 psi) after copyrolysis to 1273° K, and 0.36 GN/m^2 (52,000 psi) after heat treatment to 2273° K. No improvements were obtained with fiber pretreatments of 873° and 1073° K, but substantial improvement resulted from a fiber pretreatment of 1273° K. After copyrolysis at 1273° K, the fiber tensile strength was 0.428 GN/m^2 (62,200 psi). The maximum fiber tensile strength obtained was 0.752 GN/m^2 (109,000 psi) after copyrolysis and heat treatment to 1673° K. This was 34.7 percent of the bare fiber tensile strength which also was at a maximum at a heat-treatment temperature to 1673° K.

Metallographic and x-ray diffraction analysis showed that failure to develop optimum tensile properties with low-temperature fiber pretreatments is associated with a smaller shrinkage in filament diameter and failure to develop fully the crystallographic structure obtained when the bare fiber is heat treated (Table VII). With a fiber pretreatment of 1273° K, the fiber diameter approaches 7×10^{-6} m, the d-spacing is 3.48×10^{-10} m, approaching the minimum value of 3.45×10^{-10} m, and the crystallite size, L_c, is 21×10^{-10} m. Heat treatment to 2273° K causes no further detectable change other than an increase in crystallite size and preferred orientation caused by collapse of lenticular-shaped voids and alignment and dewrinkling of microfibrils within individual filaments (Ref. 33).

With a fiber pretreatment of 573° K, individual filaments crack during copyrolysis, and the fiber texture is not well defined (Figure 6a). The fracture path is linear, indicating a rapid glassy fracture, and it propagates across fibers without interruption. With a pretreatment of 773° K, no cracking of individual filaments was observed (Figure 6b). The fracture path is more random, but cracks propagate across fiber and matrix. The fiber modulus is less than 35 GN/m^2 (5×10^6 psi), so that it provides no reinforcement for the matrix. After a pretreatment of 973° K, cracks propagate primarily around filaments (Figure 6c) which have a definite texture. After a pretreatment to 1273° K, followed by copyrolysis to 1673° K, the fracture path is definitely more random, and crack propagation is around the fibers, indicating that the monofilaments are tougher. The texture or degree of preferred orientation is indicated by viewing typical cross sections under polarized light. (Optical activity, i.e., angular variation dependence of the intensity of reflected plane-polarized light, is an indication of fiber texture – Ref. 33 – and development of preferred orientation in conventional carbon on graphitic materials – Refs. 34-35.) With a fiber pretreatment of 773° K, neither fiber nor matrix shows evidence of preferred orientation on graphitization, but as the fiber is pretreated to higher temperatures, fiber texture develops and the matrix shows evidence of preferred orientation. The greatest degree of orientation observed in both fiber and matrix was with a fiber pretreatment to 1273° K followed by copyrolysis to 1673° K (Figure 7d).

The foregoing indicates that low-temperature fiber pretreatments are ineffective and that treatment to at least 1273° K is necessary to develop fiber texture and tensile properties. Also, post-copyrolysis heat treatments to temperatures greater than 1273° K are necessary to develop fiber texture, preferred orientation, and tensile properties. Therefore, additional studies were limited to 1273° K Type-C tow followed by heat treatments at higher temperatures.

TABLE VII. - STRUCTURE OF TYPE C TOW DEVELOPED DURING COPYROLYSIS

Heat-Treatment Temperature (°K)		d Spacing ($m \times 10^{-10}$)	Crystallite Size, L_c ($m \times 10^{-10}$)	Filament Diameter ($m \times 10^{-6}$)
Fiber	Copyrolysis			
573	1273	3.63	12.82	10.6
973	1273	3.48	13.49	9.0
1273	1273	3.48	21.08	6.7
1273	1673	–	–	6.7
573	2273	3.52	21.95	
773	2273	–	–	8.6
973	2273	3.45	26.8	7.84
1273	2273	3.45	25.92	6.05
Mod I	–	3.45[a]	45.21[a]	7.00

(a) Obtained at a heat-treatment temperature greater than 2873°K, Ref. 33.

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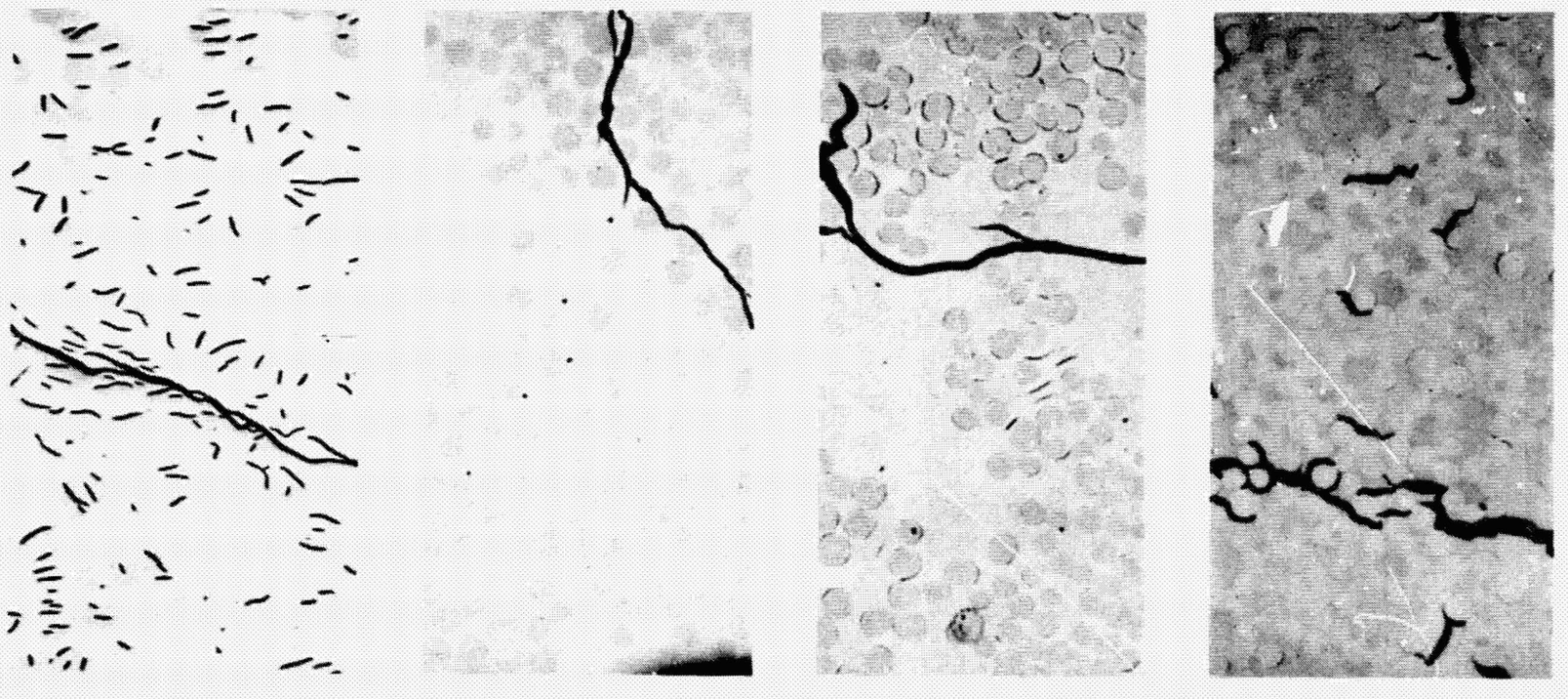

a. 573°K Fiber Copyrolysed to 1273°K

b. 773°K Fiber Copyrolysed to 1273°K

c. 973°K Fiber Copyrolysed to 1273°K

d. 1273°K Fiber Copyrolysed to 1673°K

Figure 6. - Microstructure of Copyrolysis Monofilaments, Type C Tow in GW-173, 500×

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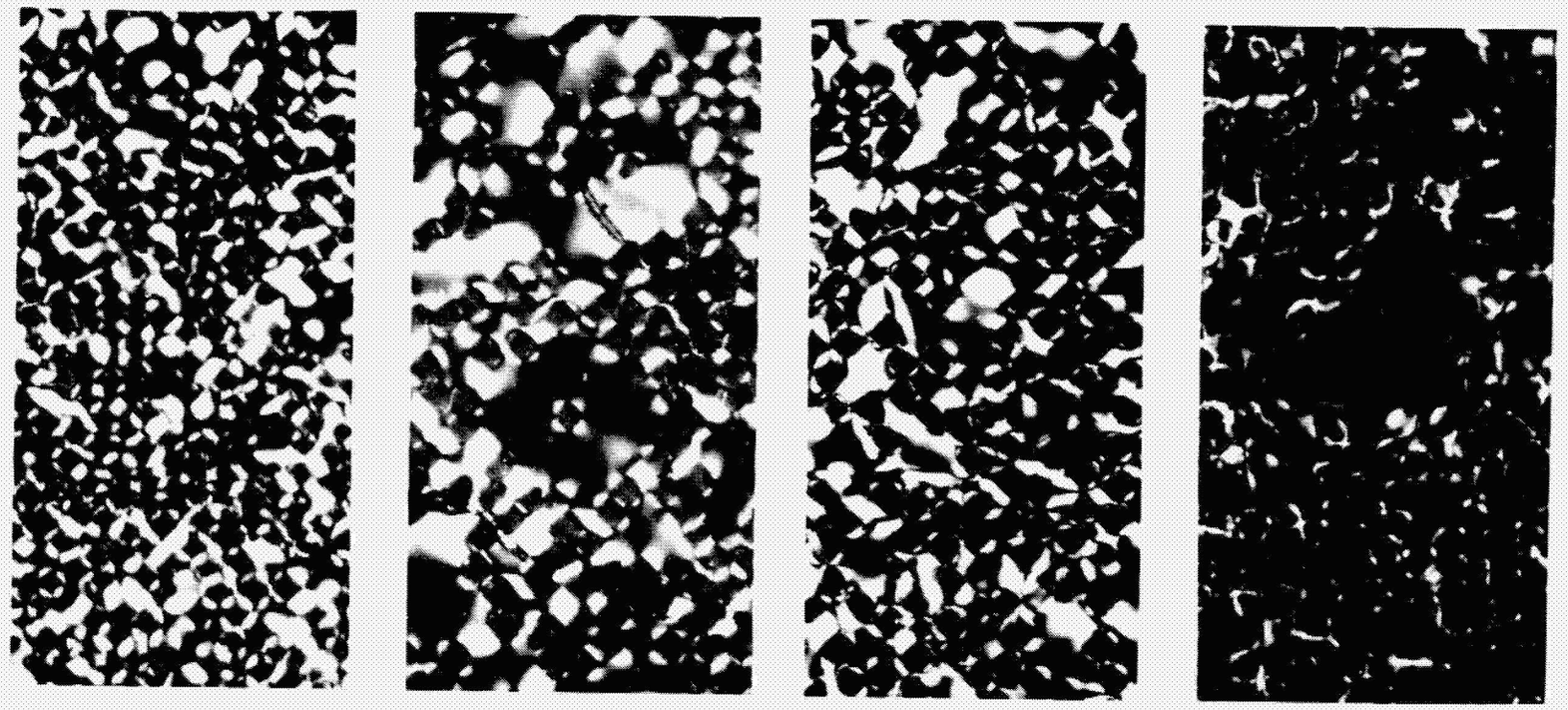

a. 773°K Fiber Copyrolysed to 1273°K

b. 973°K Fiber Copyrolysed to 1273°K

c. 1273°K Fiber Copyrolysed to 1273°K

d. 1273°K Fiber Copyrolysed to 1673°K

Figure 7. Copyrolysis Monofilaments, Type C Tow in GW-173, Polarized Light, 500×

Results obtained with 1273° K Type-C tow in various matrices are given in Table VIII. In the antecedent contract (Ref. 6), specimens were heat-treated to 1273° K in a slow pyrolysis cycle, 2.6×10^5 sec (72 hr), including a 4.33×10^4 sec (12-hr hold) at 1273° K. The samples were cooled, then recycled to 1673° K in 1.8×10^4 (5 hr) cycle B. The maximum fiber tensile strength observed was 1.503 GN/m^2 (218,000 psi), which is 69 percent of the value obtained with bare fiber.

In this series, the feasibility of direct copyrolysis to 1673° K was investigated. Results obtained with GW-173 matrix were considerably poorer, with maximum fiber tensile strength of 0.565 GN/m^2 (82,000 psi). A double preg to improve matrix concentration caused no improvement. Slightly better results were obtained with No. 396 pitch. Because the pitch was unoxidized, matrix concentration was low (28 percent),and increased slightly to 31 percent with a second impregnation. The maximum tensile strength was 0.731 GN/m^2 (106,000 psi), which is four times the value obtained with triple prepreg/oxidation (Table IV, Row 2).

With polyacrylonitrile (PAN) matrix, the maximum fiber tensile strength observed was 0.95 GN/m^2 (137,900 psi) with a single preg and oxidation (sample 14). With samples of Type 25, in which the tow was cycled through three pregging and oxidation steps to improve char yield, the matrix concentration was low, 6 vol percent, and the maximum tensile strength was only 0.65 GN/m^2 (94,000 psi). To determine whether the apparent strength reduction was due to deterioration of fiber properties during multiple processing, the excess matrix was stripped from the fibers and the tow was repregged with epoxy to determine inherent fiber tensile strength (sample 26). The maximum value obtained was 0.92 GN/m^2 (132,000 psi), indicating a 43-percent loss in strength during multiple processing.

Because variations in heat-treatment cycle might affect the tensile properties of the bare tow as well as that of the copyrolysis monofilament, control Type-C tow was utilized with succeeding experiments. Samples 16 and 24 are control samples for the 1673° K copyrolysis experiments. Results obtained are 25 to 32.5 percent lower than the 2.18 GN/m^2 (316,000 psi) previously observed (Ref. 6). Lower values are attributable to batch-to-batch variation or to the extended pyrolysis cycle.

When samples from run C-95 were heat-treated to 2873° K, improvements were noted in some cases (Table IX). The average bare fiber tensile strength was 1.296 GN/m^2 (188,000 psi), but the maximum value observed, 1.7 GN/m^2 (250,000 psi), was equivalent to reference fiber data (Ref. 6). With oxidized PAN matrix, sample 18, the maximum fiber tensile strength was 0.8 GN/m^2 (116,000 psi), indicating only a slight deterioration with higher heat-treatment temperature. With GW-173 matrix and No. 396 pitch, heat treatment to 2873° K resulted in improvement in monofilament properties. With GW-173 precursor and Cycles C and D, the best results were obtained with a single preg, fibers of Type 19. Maximum fiber tensile strength was 0.65 GN/m^2 (93,800 psi). With No. 396 pitch, the maximum fiber tensile strength was 0.97 GN/m^2 (140,000 psi) obtained with a single preg and no oxidation. With heat treatment from 1673° K to 2873° K, the GW-173 matrix exhibited no further weight loss. With pitch the matrix concentration decreased from 28 and 31 vol percent after

TABLE VIII. - TENSILE PROPERTIES OF COPYROLYSED MONOFILAMENTS OF TYPE-C TOW PRETREATED TO 1273°K, COPYROLYSED AND HEAT-TREATED TO 1673°K

Sample No.	Matrix	Composite Heat-Treatment Cycles	Final Temp (°K)	Volume (%) Matrix	Function	Load		Tensile Strength (Fiber Area)		Tensile Strength (Fiber Plus Matrix)		Strength Retention[d] (%)
						Newton	(lb)	(GN/m^2)	($psi \times 10^3$)	(GN/m^2)	($psi \times 10^3$)	
5	GW-173 - 60% solution	Cycle A[a] Cycle B[b]	1273[a] 1673[b]	51	Single Values	622.7 427.0	140 96	1.503 1.031	218.0 149.5	0.737 0.505	106.9 73.2	69
13	GW-173 - 70% solution single preg	Cycle C C-95[e]	1673[c]	47	Average Maximum	185.5 235.7	41.7 53	0.448 0.565	65.0 82.0	0.235 0.300	34.2 43.5	28
15	GW-173 - 70% solution double preg	Cycle C C-95[e]	1673[c]	53	Average Maximum	181.0 226.8	40.7 51.0	0.437 0.547	63.4 79.4	0.205 0.251	29.8 37.3	27.3
12	396 Pitch, single preg, matrix not oxidized	Cycle C C-95[e]	1673[c]	28	Average Maximum	183.7 213.5	41.3 48.0	0.443 0.516	64.3 74.8	0.321 0.374	46.6 54.2	27.8
17	396 Pitch, double preg, matrix not oxidized	Cycle C C-95[e]	1673[c]	31	Average Maximum	228.0 302.4	51.3 68.0	0.551 0.731	79.9 106.0	0.383 0.507	55.5 73.6	34.5
16	Epoxy Anhydride (Fiber HTT = 1673 °K)	C C-95[e] (Fiber Control)	1673[c]	0	Average Maximum	631.8 840.6	142.0 189.0	1.600 2.027	232.0 294.0	– –	– –	75.0
24	Epoxy Anhydride (Fiber HTT = 1673 °K)	C C-103[e] (Fiber Control)	1673[c]	0	Average Maximum	597.0 647.2	134.2 145.5	1.441 1.562	209.0 226.6	– –	– –	67.5
14	Oxidized PAN single preg, single oxidation	C C-95[e]	1673[c]	8	Average Maximum	316.7 393.6	71.2 88.5	0.765 0.951	111.0 137.9	0.687 0.855	99.7 124.0	47.5
25	Oxidized PAN - triple preg, triple oxidation	C C-103[e]	1673[c]	6	Average Maximum	236.2 267.8	53.1 60.2	0.573 0.648	83.0 94.0	0.522 0.589	75.5 85.5	39.8
26	Samples of Type 25 repregged with Epoxy Anhydride	–	–	na	Average Maximum	346.1 378.1	77.8 85.0	0.833 0.922	121.0 132.0	– –	– –	57.0

(a) Cycle A – standard cycle 60 1273°K – 2.2×10^5 sec (60 hr) to 1273°K.
4.3×10^4 sec (12 hr) at 1273°K.

(b) Cycle B – short cycle to 1673°K – 1.75×10^5 sec (5 hr) to 1673°K.

(c) Cycle C – continuous cycle to 1673°K – 2.2×10^5 sec (60 hr) to 1273°K.
1.45×10^4 sec (4 hr) to 1673°K.

(d) $\frac{\text{Measured fiber tensile strength}}{\text{Control bare-fiber tensile strength}} \times 100$

(e) Run Number

TABLE IX. - TENSILE PROPERTIES OF COPYROLYSED MONOFILAMENTS OF 1273° TYPE-C TOW, COPYROLYSED AND HEAT-TREATED TO 2873°K

Sample No.	Matrix	Composite Heat Treatment		Volume % Matrix	Function	Load		Tensile Strength (Fiber Area)		Tensile Strength (Fiber Plus Matrix)		Strength Retention[b] (%)
		Cycle	Final Temp (°K)			(Newtons)	(lb)	(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^3)	
23	Epoxy Anhydride (Fiber HTT = 2873 K)	D C-97[c] (Fiber Control)	2873	0	Average	489.3	110	1.296	188.0	–	–	77.5[c]
					Maximum	649.4	146	1.724	250.0			
18	Oxidized PAN (single preg, single oxid)	C C-95[d]	1673	6	Average	209.1	47.0	0.554	80.3	0.520	75.4	42.5
		D C-97[c]	2873		Maximum	301.6	67.8	0.800	116.0	0.752	109.0	
19	GW-173 - 70% solution (single preg)	C C-95	1673	45	Average	220.6	49.6	0.585	84.8	0.323	46.8	46.0
		D C-97[c]	2873		Maximum	244.2	54.8	0.647	93.8	0.337	51.8	
20	GW-173 - 70% solution (double preg)	C C-95	1673	54	Average	190.8	42.9	0.505	73.3	0.233	33.8	39.0
		D C-97[c]	2873		Maximum	216.2	48.6	0.573	83.1	0.263	38.2	
21	396 Pitch, single preg matrix not oxidized	C C-95	1673	21	Average	304.7	68.5	0.807	117.1	0.635	92.1	48.0
		D C-97[c]	2873		Maximum	364.7	82.0	0.967	140.2	0.760	110.2	
22	325 Pitch, double preg matrix not oxidized	C C-95	1673	26	Average	201.0	45.2	0.533	77.3	0.394	57.1	30.4
		D C-97	2873		Maximum	279.0	62.9	0.745	108.0	0.547	79.4	

(a) Run number.

(b) $\frac{\text{Measured fiber tensile strength}}{\text{Control fiber tensile strength}} \times 100$.

(c) Cycle D – fast cycle to 2873°K, 1.8×10^4 sec (5 hr rise) from 1673°K to 2873°K.

(d) Cycle C – copyrolysis, 2.232×10^5 sec (64 hr) to 1673°K.

heat treatment to 1673° K to 21 and 26 vol percent, respectively, after heat-treatment to 2873° K. In both cases, the composite tensile strength was greater. The highest composite tensile strength observed in this series was 0.76 GN/m^2 (110,000 psi) obtained with a pitch matrix, sample 21.

The elastic modulus of the series of Type C-tow is summarized in Table X.

The modulus of elasticity of the bare fiber heat-treated to 1673° K is 213 GN/m^2 (30.9 x 10^6 psi) with an average strain-to-failure of 0.75 percent (sample 16). With copyrolysis and heat treatment to 1673° K, monofilaments composite elastic modulus ranges from 150 GN/m^2 (21.74 x 10^6 psi) to 215 GN/m^2 (31.25 x 10^6 psi). The highest composite modulus after the 1673° K treatment was obtained with oxidized PAN matrix in which the volume fraction matrix was only 7 percent. The strain-to-failure was 0.33 to 0.41 percent reflecting the lower tensile strength obtained in copyrolysed monofilaments.

The best combination of tensile strength, elastic modulus, strain-to-failure, and absence of matrix pyrolysis cracks, was obtained with samples of type 5 for which there was a 12 hour hold at 1273° K during processing. The strain-to-failure was 0.31 to 0.41 percent, which is equivalent to that obtained with flaw-free, monolithic pyrolysed GW-173 rod (Ref. 6). Omitting the 1273° K hold and pyrolysing directly to 1673° K resulted in cracks, and the strain-to-failure with GW-173 matrix was 0.14 to 0.22 percent. With No. 396 pitch, which forms a softer carbon char, the strain-to-failure was 0.16 to 0.26 percent.

Processing to 2873° K caused an increase in elastic modulus with the highest value of 348 GN/m^2 (50.5 x 10^6 psi) obtained with No. 396 pitch.

The real fiber elastic modulus $(E_f)_{real}$ was calculated from the equation below, a rearrangement of the law of mixtures

$$(E_f)_{real} = \left(\frac{L}{A_c \cdot \epsilon} - E_m V_m\right) \Big/ V_f$$

where

E_f = true fiber modulus

L = load

A_c = cross-sectional area of the composite monofilament

ϵ = strain corresponding to load L

E_m = elastic modulus of the matrix

V_m = volume fraction matrix

V_f = volume fraction of fiber

TABLE X. – ELASTIC MODULUS OF COPYROLYSED MONOFILAMENT PRODUCED FROM 1273°K TYPE-C TOW AND VARIOUS MATRICES

Sample No.	Matrix	Composite Heat-Treatment Cycle		Volume (%) Matrix	Elastic Modulus (Fiber Area)		Elastic Modulus (Fiber Plus Matrix)		Strain-to-Failure[a] (%)	$(E_m)_{used}$		$(E_f)_{real}$	
		Cycle	Final Temp (°K)		(GN/m^2)	(psi × 10^6)	(GN/m^2)	(psi × 10^6)		(GN/m^2)	(psi × 10^6)	(GN/m^2)	(psi × 10^6)
16	Epoxy Anhydride (Fiber HTT = 1673°K)	C C-95	1673	0	213	30.9	–	–	0.75 0.95	–	–	–	–
14	Oxidized PAN, single preg, single oxidation	C C-95	1673	7	232	33.6	215	31.25	0.33 0.41	–	–	–	–
5	GW-173 - 60% solution	A I-183 B C-68	1273 1673	51	328	47.6	161	23.32	0.48 0.31	31.0	4.5[b]	296	42.9
13	GW-173 - 70% solution single preg	C C-95	1673	47	256	37.2	132	19.21	0.17 0.22	31.0	4.5[b]	229	33.2
15	GW-173 - 70% solution double preg	C C-95	1673	53	316	45.8	150	21.74	0.14 0.17	31.0	4.5[b]	280	40.7
12	396 Pitch, single preg, matrix not oxidized	C C-95	1673	28	274	39.8	151	21.9	0.16 0.19	13.8	2.0[c]	268	38.9
17	396 Pitch, double preg, matrix not oxidized	C C-95	1673	31	280	40.7	195	28.2	0.20 0.26	13.8	2.0[c]	274	39.8
18	Oxid PAN, single preg, single oxidation	C C-95 C C-97	1673 2873	6	262	38.1	34.7	35.6	0.21 0.30	–	–	–	–
19	GW-173, 70% solution single preg	C C-95 D C-97	1673 2873	45	512	74.3	284	41.2	0.11 0.13	24.1	3.5[b]	493	71.5
20	GW-173 - 70% solution double preg	C C-95 D C-97	1673 2873	54	369	53.5	170	24.6	0.14 0.15	24.1	3.5[b]	340	49.4
21	396 Pitch, single preg matrix not oxidized	C C-95 D C-97	1673 2873	21	471	683	348	50.5	0.17 0.20	13.8	2.0[c]	348	50.5

(a) Calculated from (%) = $\frac{\text{Elastic modulus based on fiber cross section}}{\text{Tensile strength based on fiber cross section}} \times 100$

(b) Reference data for glassy carbon generated from GW-173 (Ref. 5).

(c) Estimated from bulk graphite data.

With Type-C tow processed to 1673° K, the true fiber elastic modulus ranged from 229 to 296 GN/m^2 (33.2 - 42.9) x 10^6 psi, irrespective of matrix, and was equivalent to or slightly better than the value obtained with bare Type-C tow. With a post-copyrolysis heat treatment to 2873° K, the true fiber elastic modulus ranged from 348 to 493 GN/m^2 [(49.4 - 71.5) x 10^6 psi].

In this series, the best combination of tensile strength and modulus was obtained with sample 5 for which there was a long hold at 1273° K. A possible reason for this is the disparity between the carbonization cycles for polyacrylonitrile and GW-173. Polyacrylonitrile is incompletely carbonized at 1273° K. Slight additional weight loss has been observed to 1473° K (Ref. 36), and outgassing of volatile nitrogen is not complete until 1873° K. On the other hand, GW-173 is completely carbonized at 1273° K, exhibiting no substantial change upon heat treatment to higher temperatures. It has an extremely fine closed porosity (22 to 30) x 10^{-10} m (20 to 30 Å) (Ref. 38). Consequently, in the temperature range between 1273° and 1873°K, a slow cycle should be used to allow the nitrogen released from the PAN to diffuse through the matrix.

Because the standard cycle for processing glassy carbon resin requires a prolonged hold at 1173° to 1273° K, limited studies were made on the effect of a similar hold on the properties of bare Type-C tow. Data are given below:

Property	Oxidized Type-C Tow Processed to 1193° K (No Hold)	Oxidized Type-C Tow Processed to 1193° K With a 5.4 x 10^4 sec (15-hr hold)
Wt/Unit Length		
kg/m x 10^{-3}	0.913	0.807
gm/in. x 10^{-3}	(23.2)	(20.5)
Estimated Fiber Cross-Section[a]		
m^2 x 10^{-7}	5.22	4.61
in.^{2} x 10^{-4}	(8.09)	(7.15)
Ultimate Tensile Load		
N, average	886.1	728.6
N, maximum	890.5	740.6
lbf, average	(199.2)	(163.8)
lbf, maximum	(200.2)	(166.5)
Ultimate Tensile Strength		
GN/m^2, average	1.698	1.580
maximum	1.706	1.607
psi x 10^{-3}, average	(245.9)	(229.0)
maximum	(247.2)	(232.8)

[a]Based on a fiber density of 1.76 gm/cm^3 as measured previously (Ref. 6).

These data indicate that polyacrylonitrile undergoes dimensional changes and weight loss when held for a long period at 1193° K; i.e., the outgassing and shrinkage is time dependent as well as temperature dependent. However, the tensile strength of the tow was also decreased, indicating that such a hold might cause a loss of fiber tensile properties. Thus, matrix precursors, such as PAN and pitch, may give somewhat better results if they do not fully densify at 1273° K, and if they do not require the longer hold.

The nature of the fracture surface was investigated by scanning electron microscopy for samples with increasing heat-treatment temperature and tensile strength. With a fiber pretreatment of 873° K followed by copyrolysis and heat treatment to 2273° K, fiber-matrix bonding was excellent, but there is little evidence of crack arrest at the fiber-matrix interface (Figure 8). Fiber elastic-modulus is equivalent to that of the matrix, ~35 GN/m^2 (5×10^6 psi); there is little reinforcement, and the fiber tensile strength is only 0.18 GN/m^2 (26,000 psi). With a fiber pretreatment of 1273° K, fiber texture develops (Figure 9), bonding between fiber and matrix appears poorer, but the fiber tensile strength is 0.38 GN/m^2 (55,000 psi). With a fast copyrolysis cycle to 1673° K (Figure 10), the fiber-matrix bond quality appears to be variable throughout the cross section resulting in stepwise fracture across small fiber-matrix bundles (perpendicular to the fiber axis) with cracks diverted parallel to the filament axis by fiber/matrix debonding. The fiber tensile strength was 0.48 GN/m^2 (70,000 psi). With a slow cycle to 1273° K followed by heat treatment to 1673°K, fiber texture is more developed and interface bonding is intermittent, resulting in a fracture path that is diverted at the filament-matrix interface (Figure 11), and a fiber tensile strength of 1.503 GN/m^2 (218,000 psi). With further heat treatment to 2873° K, fiber structure deteriorates (Figure 12), a coarse texture develops common to the fiber and the matrix, and there is little crack arrest at the interface. The result is a decrease in fiber tensile strength to 0.615 GN/m^2 (89,000 psi). When the Type-C tow is copyrolysed in a softer matrix such as No. 396 pitch, in which the carbonization cycle is more compatible with PAN, fiber deterioration at elevated temperature is not so severe (Figure 13). Debonding occurs at the fiber-matrix interface, and the fiber tensile strength is 0.97 GN/m^2 (140,000 psi).

Further studies with Type-C tow are discussed in Section 4.3, "Process Optimization."

4.2.2 Copyrolysis with Type-D Carbon Fiber Precursor

The second fiber precursor, a 385-filament polyacrlonitrile tow (designated Type D), was selected for copyrolysis studies for two reasons. First, it has a small bundle size, 2.54×10^{-4} m (10 mils) after heat treating at 2873° K, and is thus made more amenable to processing. Second, available information (Refs. 26, 30) indicates that both tensile strength and elastic modulus increases with increasing heat-treatment temperature. With Type-D tow, filaments are dog-bone or Y-shaped in cross section (Figure 14) resulting from the spinning process in which the periphery of the filament hardens and sets more quickly than the interior of the filament (Ref. 38). Upon heat treatment to temperatures above 2073° K, such dog-bone shaped filaments develop greater crystallite size and more preferred orientation than do round filaments (Ref. 33). Round filaments do not become as ordered (Ref. 33) and have a greater tendency to develop interior and surface flaws, with a corresponding reduction in tensile strength (Ref. 23).

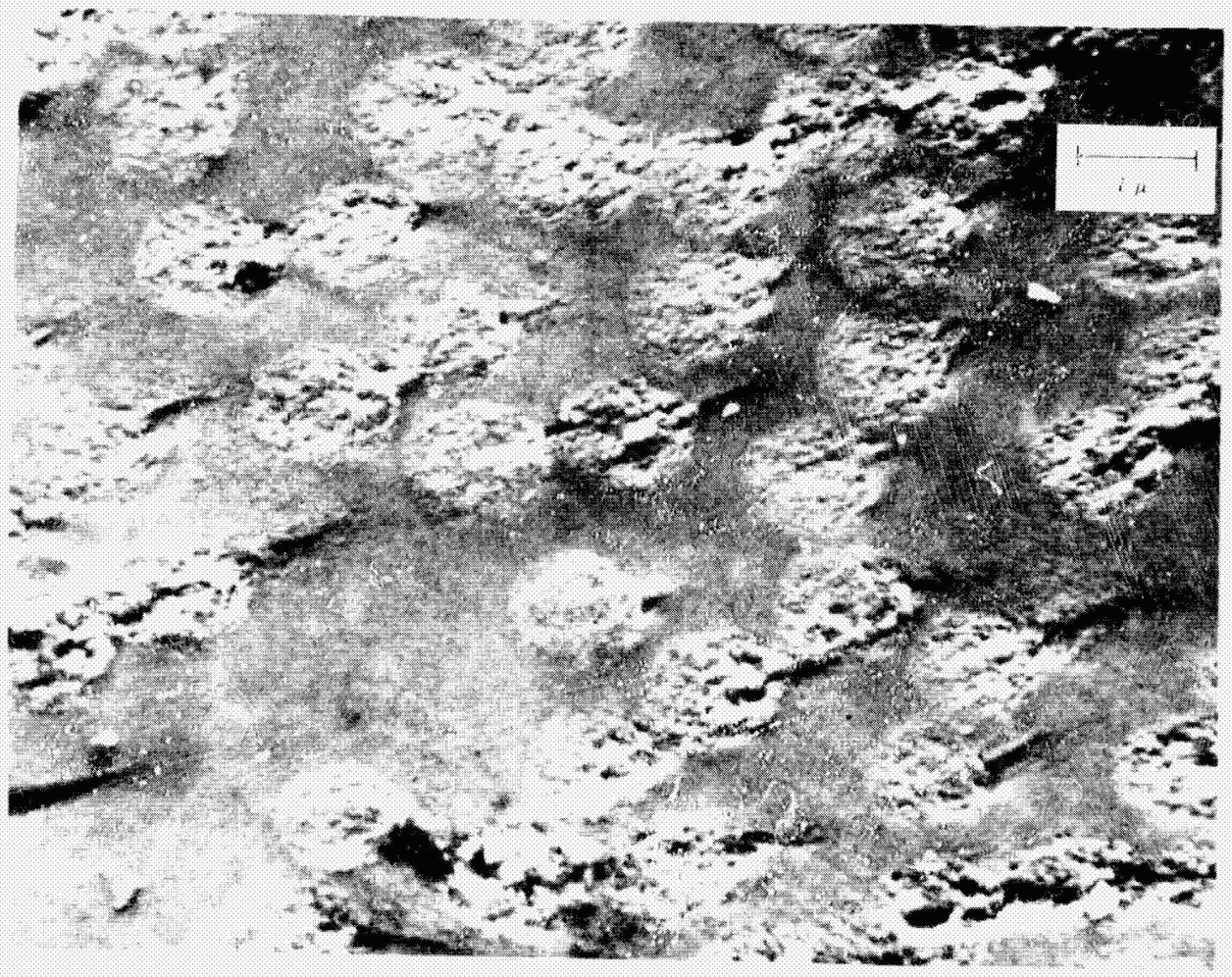

Figure 8. - Fracture Surface of 1873°K Type-C Tow in GW-173. Copyrolysed to 1273°K and Heat-Treated to 2273°K. 3000×. Fiber Tensile Strength = 0.18 GN/m^2 (26 000 psi)

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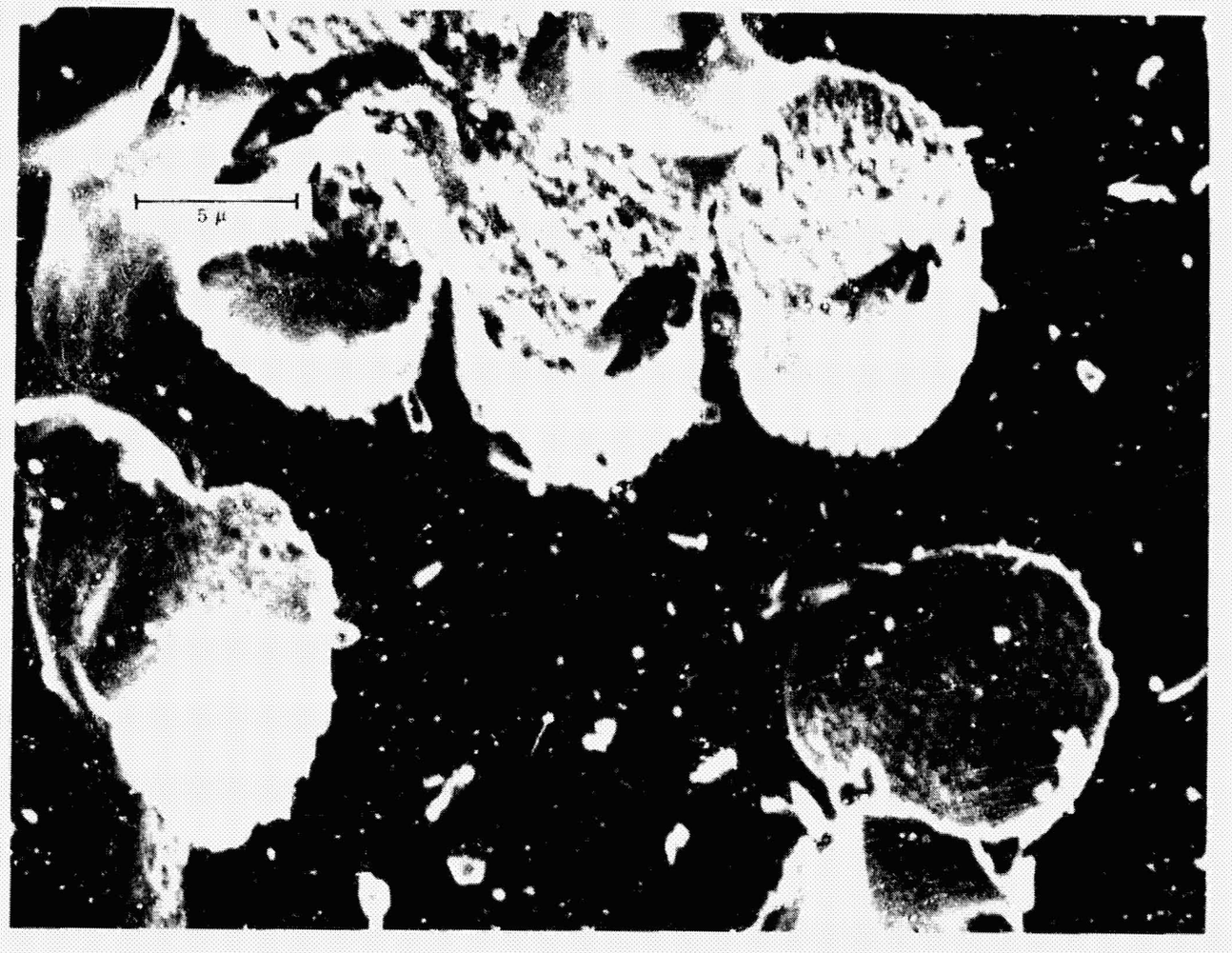

Figure 9. - Fracture Surface of 1273 °K Type C-Tow in GW-173. Copyrolysed to 1273 °K. 1800×. Fiber Tensile Strength = 0.38 GN/m^2 (55,000 psi)

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Figure 10. - Fracture Surface of 1273°K Type-C Tow in GW-173, Rapid Copyrolysis to 1673°K, 2450×. Fiber Tensile Strength = 0.48 GN/m^2 (70,000 psi)

Figure 11. - Fracture Surface of 1273 K Type-C Tow in GW-173. Standard Copyrolysis to 1273 K. 2480×. Fiber Tensile Strength = 1.503 GN/m^2 (218,000 psi)

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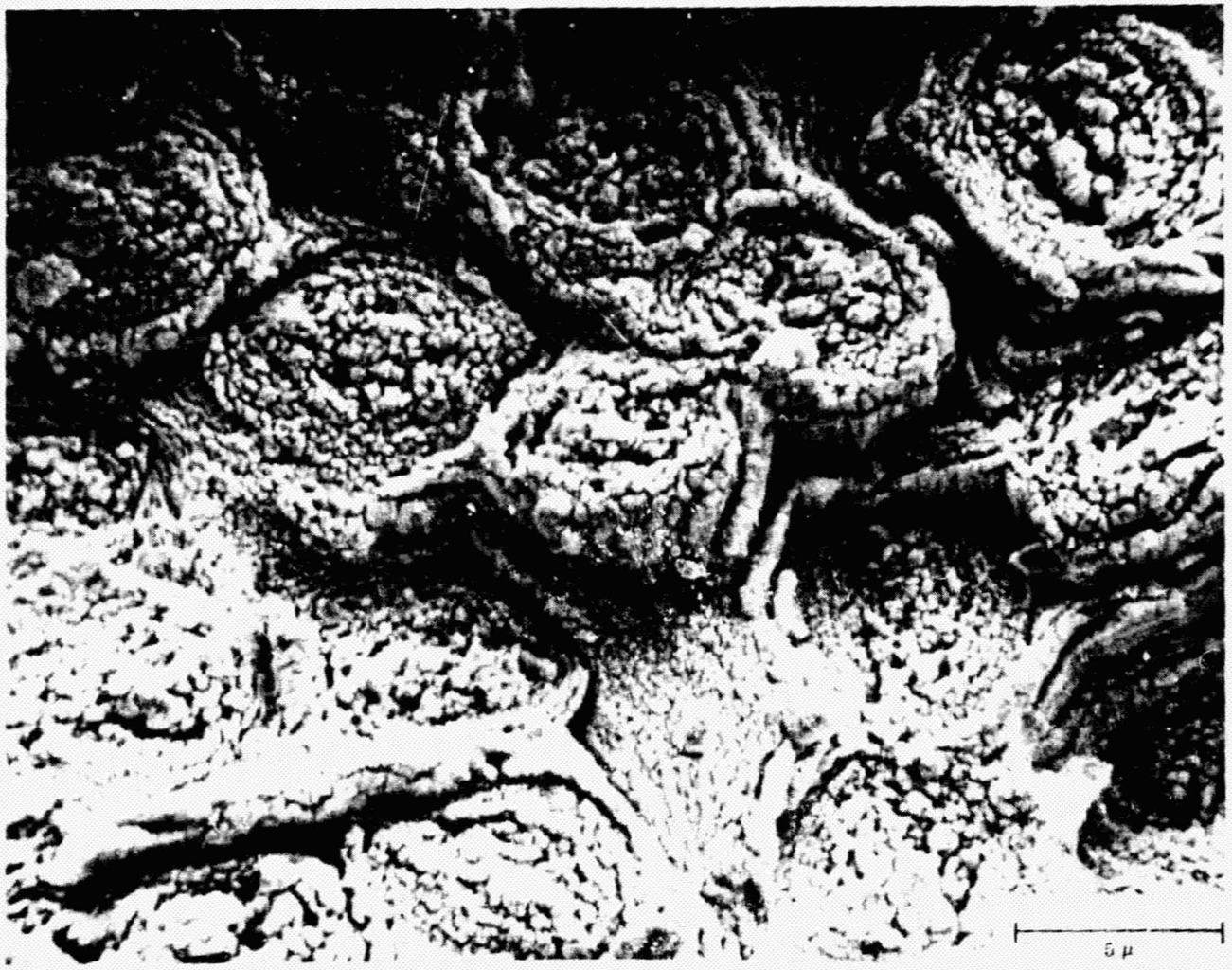

Figure 12. - Fracture Surface of 1273°K Type-C Tow in GW-173, Copyrolysed to 1673°K, Heat-Treated to 2873°K, 6100×, Fiber Tensile Strength = 0.615 GN/m^2 (89,000 psi)

Figure 13. - Fracture Surface of 1273°K Type-C Tow in 396 Pitch, Copyrolysed to 1673°K, Heat-Treated to 2873°K, 5000×, Tensile Strength = 0.97 GN/m^2 (140,000 psi)

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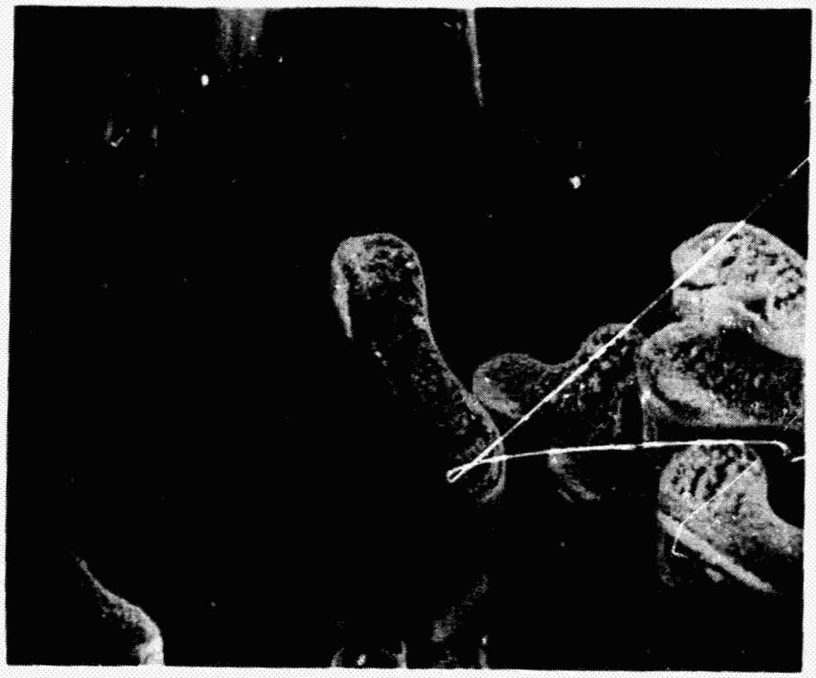

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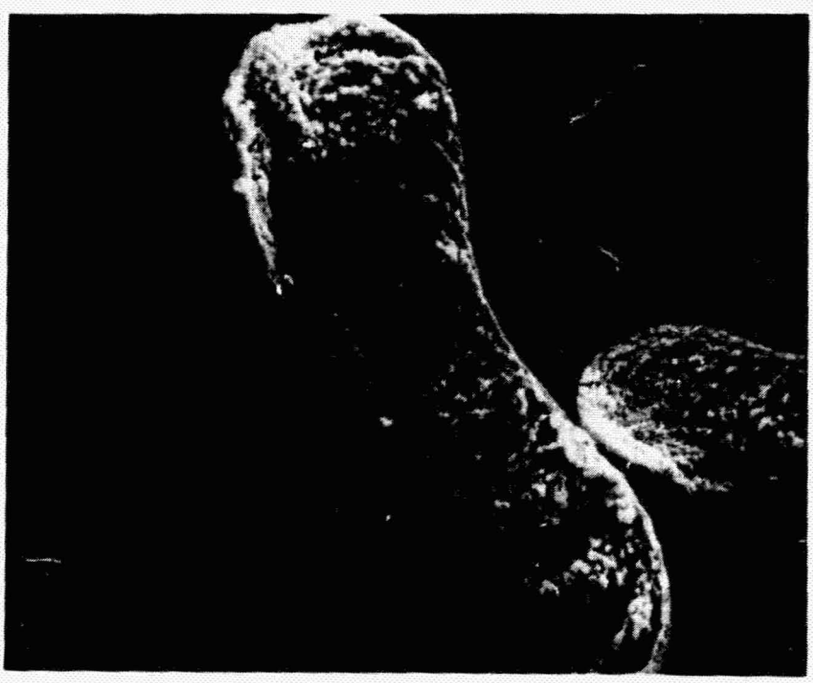

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Figure 14. - Typical Microstructure of Type-D Tow Processed to 2873°K

The properties of bare Type-D tow are listed in Table XI. Density, area cross section, and weight per unit length reach a minimum at 1973° K. Above 2273° K, density increases, and the area cross section as well as the weight per unit length decreases with increasing heat-treatment temperature. Tensile strength reaches a maximum, 2.03 GN/m^2 (294,500 psi), after a heat treatment of 2573°K. Elastic modulus increases with heat-treatment temperature to 499 GN/m^2 (62.4×10^6 psi) after a heat-treatment temperature of 2873°K.

Because tensile strengths obtained after low-temperature copyrolysis with Type-C tow were low, only limited low-temperature experiments were done in this series with Type-D tow. Conditions for most experiments consisted of fiber pretreatment of 1673° K, followed by copyrolysis, and heat treatment to temperatures from 2273° K to 2873° K. Results obtained with HTR resin are summarized in Table XII. With as-oxidized Type-D tow copyrolysed to 1273° K, the maximum fiber tensile strength was 0.356 GN/m^2 (51,600 psi), which was 91 percent of the bare-fiber tensile strength. With as-oxidized Type-C tow, evaluated for purposes of comparison, the maximum fiber tensile strength was 0.197 GN/m^2 (28,600 psi), or 10.9 percent of the bare fiber value.

Both resin concentration in the pregging solution, and final heat-treatment temperature were varied in the next series of experiments using 1673° K Type-D tow. Maximum fiber tensile strength increased with increasing heat-treatment temperature: from 0.802 GN/m^2 (116,300 psi) after a final heat-treatment temperature of 2273° K (sample F), to 1.204 GN/m^2 (174,600 psi) after heat-treatment to 2573° K, sample D, to 1.497 GN/m^2 (217,000 psi) sample X, after a final heat treatment of 2873°K, corresponding to 47.5 percent, 63 percent, and 80.5 percent strength retention, respectively.

Similar results obtained with GW-173 matrix precursor are listed in Table XIII. Fiber tensile strengths increase with heat-treatment temperature reaching a maximum value of 1.427 GN/m^2 (207,000 psi) after a final heat-treatment temperature of 2873° K (sample B), corresponding to a fiber strength retention of 76.5 percent.

Improvement in fiber tensile strength with increasing heat-treatment temperature was also obtained with No. 396 pitch (Table XIV). With as-oxidized Type-D tow, maximum fiber tensile strength was 0.726 GN/m^2 (105,300 psi), equivalent to a strength retention of 38.05 percent (sample K). When as-oxidized Type-D tow was copyrolysed to 2873°K (sample Q), the maximum fiber tensile strength decreased slightly to 0.685 GN/m^2 (99,300 psi). With fiber pretreatment to 1673°K and direct copyrolysis to 2573°K (sample J), the maximum fiber tensile strength was 1.035 GN/m^2 (150,000 psi), i.e., 54.3 percent of the bare-fiber value. Extension of the time to reach maximum temperature, i.e., a 72-hr pyrolysis cycle to 1673°K followed by a short cycle of 2573°K, as in sample M, caused further improvement in the maximum tensile strength to 1.467 GN/m^2 (212,800 psi), 76.9 percent of the bare-fiber value.

Time-temperature effects were similar with a final heat treatment to 2873°K, except that tensile properties were improved in all cases. With a fiber pretreatment of 1673°K, maximum tensile strength was 1.258 GN/m^2 (182,500 psi), sample P. Maximum tensile

TABLE XI. - PROPERTIES OF BARE TYPE-D TOW AS A FUNCTION OF HEAT-TREATMENT TEMPERATURE

Fiber Heat Treatment Condition		Density	Fiber-Cross Sectional Area		Weight per Unit Length	Function	Tensile Strength		Elastic Modulus	
Run No.	Max. Temp (°K)	($kg/m^3 \times 10^3$)	($m^2 \times 10^{-9}$)	($in.^2 \times 10^{-5}$)	($kg/m \times 10^{-4}$)		(GN/m^2)	($psi \times 10^3$)	(GN/m^2)	($psi \times 10^6$)
	543 (Oxidized)	1.40	53.9	8.36	0.756	Average	–	–	12.4	1.8
C-135	1273[a]	1.71	24.8	3.85	0.425	Average Maximum	0.391 0.452	56.7 65.5	75.8	11.0
C-109 C-132	1673[a]	1.67	22.5 22.2	3.48 3.47[b]	0.374	Average Maximum	0.876 0.948	127.0 137.5	250	36.2
C-105	1973[a]	1.50	15.22	2.36	0.229	Average Maximum	0.990 1.051	143.6 152.5	–	–
C-106	2273[a]	1.84	22.1	3.42	0.405	Average Maximum	1.630 1.680	236.3 272.0	–	–
C-114 C-106	2573[a]	1.89 1.79[c]	21.0	3.26	0.398	Average Maximum	1.908 2.030	276.7 294.5	330	48.0
C-113	2873[a]	1.98	18.4	2.85	0.364	Average Maximum	1.86 1.97	270.5 285.6	499	62.4
C-109	3073[a]	2.00	18.0	2.79	0.359	–	–	–	–	–

(a) Fiber first oxidized, then heat-treated to final temperature in inert atmosphere.
(b) Calculated from area fraction determined metallographically.
(c) As reported by Ezekiel (Refs. 25, 31).

TABLE XII. - PROPERTIES OF COPYROLYSED MONOFILAMENTS, TYPE-D AND -C TOW IN HTR MATRIX

Experiment No.	Fiber Type[a]	Run No.	Heat Treatment Temperature (°K)		Matrix[a] (%)	Volume (%) Matrix	Function	Tensile Strength (Fiber Area)		Tensile Strength (Fiber Plus Matrix)		Strength Retention[b] (%)
			Fiber	Composite				(GN/m²)	(psi × 10³)	(GN/m²)	(psi × 10³)	
–	Type D	–	543[c]	1273	33	55.9	Maximum	0.355	51.6	0.157	22.75	91
							Average	0.342	49.6	0.150	21.86	
	Type C		543	1273	33	35.9	Maximum	0.197	28.6	0.127	18.35	10.0
							Average	0.133	19.35	0.103	14.89	
F	Type D	C-112 C-116	1673	1273 2273	33	25.6	Maximum	0.802	116.3	0.521	90.1	49.1
							Average	0.737	106.9	0.571	82.82	
H	Type D	C-112 C-116	1673 –	1273 2273	20	11	Maximum	0.772	111.9	0.082	96.9	47.5
							Average	0.655	95.0	0.579	84.0	
F, H	Type D	C-112 C-116	1673	1273 2273	–	~ 5	Maximum	0.522	75.8	0.509	73.8	32.0
							Average	0.473	68.6	0.428	62.11	
E	Type D	C-112 C-114	1673	1273 2573	20	33	Maximum	0.939	136.2	0.721	104.5	49.5
							Average	0.911	132.1	0.703	101.9	
						11.6	Single Value	0.717	104.0	0.534	92.0	
D	Type D	C-114	1673	2573 (Rapid Cycle)	33	14.4	Maximum	1.204	174.6	1.031	149.6	63.0
							Average	0.959	139.05	0.821	119.1	
						11.8	Maximum	0.924	134.0	0.815	118.2	
							Average	0.867	125.7	0.765	110.9	
A	Type D	C-112 C-113	1673	1273 2873	20	33.3	Maximum	1.061	154.0	0.722	104.76	57.0
							Average	0.967	140.3	0.656	95.22	
						16.7	Single Value	0.821	119.0	0.685	99.4	
X	Type D	VT-69 C 131[d]	1673	1215 2873	30	20	Maximum	1.497	217.0	1.154	167.1	80.5
							Average	1.252	181.9	1.010	146.5	

(a) Percentage refers to resins solids concentration in prepreging bath.

(b) % strength retention = $\frac{\text{Tensile strength (fiber area)}}{\text{Tension strength of reference fiber}} \times 100$.

(c) As-oxidized.

(d) Short cycle. 2.16×10^4 sec (6 hr to temperature).

TABLE XIII. - PROPERTIES OF COPYROLYSED MONOFILAMENTS TYPE-D TOW IN GW-173 MATRIX[a]

Sample No.	Run No.	Fiber Heat Treatment Temp (°K)	Composite Heat Treatment Temp (°K)	Volume % Matrix	Function	Tensile Strength (Fiber Area)		Tensile Strength (Fiber Plus Matrix)		Strength Retention[b] (%)
						(GN/m²)	(psi × 10³)	(GN/m²)	(psi × 10³)	
–	I-215	1673[c]	1273	39.2	Maximum	0.574	83.3	0.343	49.7	87.6
					Average	0.462	67.0	0.276	40.0	
G	I-216 C-116	1673[c]	1273[d] 2273	25.4	Maximum	1.245	180.6	1.110	161.0	76.5
					Average)	0.896	129.9	0.701	101.7	
C	I-216 C-114	1673[c]	1273[d] 2573	10.4	Maximum	1.287	186.7	1.148	166.5	67.4
					Average	1.236	182.1	1.120	162.4	
				29.0	Maximum	1.226	177.8	0.871	126.3	64.2
					Average	1.210	175.5	0.860	124.7	
B	I-216 C-113	1673[c]	1273 2873[d]	50	Maximum	1.427	207.0	0.720	104.4	70.5
					Average	1.409	204.3	0.706	103.1	
				40	Maximum	1.262	183.0	0.757	110.8	67.6
					Average	1.245	180.5	0.747	109.3	
Y	C-133	1273[b]	2873[c]	38.5	Maximum	1.742	252.6	1.071	155.4	93.4
					Average	1.726	250.2	1.061	153.9	
				29	Maximum	1.546	224.2	1.031	149.6	82.8
					Average	1.313	190.4	0.876	127.1	
Z	C-133	1673[b]	2873[c]	74	Maximum	1.643	238.4	1.375	199.4	98.1
					Average	1.480	214.6	1.331	193.1	

(a) Solution of 30% resin solids in methanol

(b) $\frac{\text{Tensile strength (fiber area)}}{\text{Tensile strength of equivalent fiber in epoxy}} \times 100$

(c) Preoxidized at 543°K. 3rd batch oxidation.

(d) Standard 2.592×10^5 sec (72-hr cycle) followed by a 2.16×10^4 (6-hr cycle) to temperature.

TABLE XIV. - PROPERTIES OF TYPE-D TOW IN 396 PITCH MATRIX, DOUBLE PREG

Sample No.	Run No.	Heat Treatment Temperature (°K)		Volume Matrix (%)	Function	Tensile Strength (Fiber Area)		Tensile Strength (Fiber Plus Matrix)		Strength Retention[a] (%)
		Fiber	Composite			(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^3)	
K	C-119[b]	533[c]	2573	43.1	Maximum	0.726	105.3	0.414	60.0	38.05
					Average	0.636	92.2	0.362	52.5	
J	C-119[b]	1673	2573	27	Maximum	1.035	150.1	0.747	108.4	54.3
					Average	0.952	138.1	0.688	99.8	
					Maximum	0.883	128.1	0.708	102.7	46.3
					Average	0.877	127.2	0.699	101.4	
M	C-118[d] C-119[b]	1673	1673 2573	53.4	Maximum	1.467	212.8	0.587	85.2	76.9
					Average	1.120	162.5	0.527	76.4	
Q	C-120[b]	533	2873	47	Maximum	0.685	99.3	0.363	52.7	36.7
					Average	0.671	97.4	0.350	51.7	
P	C-120[b]	1673	2873	33	Single Value	1.258	182.5	0.847	122.9	67.5
				24	Maximum	1.185	171.9	0.871	126.3	63.5
					Average	1.061	153.9	0.809	117.3	
O	C-118[d] C-120[b]	1673	1673 2873	55	Maximum	1.717	249.1	0.816	118.4	90.0
					Average	1.551	225.0	0.704	102.1	
				28	Maximum	1.398	202.8	1.000	145.0	73.3
					Average	1.202	174.3	0.858	124.5	

(a) % Strength Retention = $\frac{\text{Tensile strength (fiber area)}}{\text{Tensile strength of reference fiber}} \times 100$.

(b) Short Cycle – 2.16×10^4 sec (6 hrs) to temperature

(c) As-oxidized Type D Tow, 4th batch.

(d) Extended pyrolysis cycle - 2.78×10^5 sec (72 hr) to temperature.

strength, 1.717 GN/m^2 (249,000 psi), equivalent to a 90-percent strength retention, was obtained with an extended pyrolysis cycle before final heat treatment as in sample O.

With all of the samples in this series, there was considerable variation in matrix pickup within a given batch. Low tensile strength was often associated with low-matrix concentration, e.g., the low average value 0.47 GN/m^2 (68,600 psi) obtained with only 5-percent matrix. Similar variation within a batch was observed with GW-173 (samples B and C), and with No. 396 pitch (samples J, O, and P). With the exception of sample B, higher tensile strength was observed with higher matrix concentration.

Examination by optical microscopy indicated that the low matrix concentration was associated with poor bundle infiltration caused by the high twist in the tow which held the filaments too closely together during impregnation. Before pregging in subsequent experiments (Section 4.3), the tow was untwisted and fluffed by running it over rollers.

4.3 PROCESS OPTIMIZATION, TASK III

The purpose of this task was to optimize the monofilament production process and to evaluate the properties of the composite monofilament produced. The best combinations of materials and processes from Tasks I and II were selected for inclusion in this task. The objective was to obtain the best combination of tensile strength, modulus, and strain-to-failure in a coherent defect-free composite monofilament.

4.3.1 Matrix Improvement

The highest fiber tensile properties obtained in preliminary studies were with Thornel 75 in HTR matrix (Table V, Section 4.1.2). These data showed that tensile-strength increased with increasing heat-treatment temperature. However, the processing conditions had been rather arbitrarily selected (and were designed primarily to determine char yield as a function of heat-treatment temperature) and were not necessarily optimum as regards the resulting monofilament tensile properties.

Consequently, a series of experiments were made in which the most significant parameters were varied and the material produced was tested to determine the best possible processing procedure. The parameters varied were resin concentration in the pregging solution, pyrolysis cycle time, and final heat-treatment temperature.

Results are summarized in Table XV. In the initial experiment (R), short pyrolysis and heat-treatment cycles were used with tows prepegged in a solution of 33-percent HTR resin in methyl ethyl ketone. The average fiber tensile strength after heat treatment to 2873°K was 2.41 GN/m^2 (349,200 psi), equivalent to 100-percent fiber-strength retention, but the composite tensile strength was low, 1.241 GN/m^2 (180,000 psi), because of the large volume fraction matrix (48 percent). In the next experiment (V), the concentration of resin in solution was reduced to 30 percent, and a short pyrolysis cycle was used followed by a long heat-treatment cycle to 2873°K. Maximum fiber tensile

TABLE XV. - PROCESS OPTIMIZATION, THORNEL 75 IN HTR MATRIX PRECURSOR

Experiment No.	Run No.	Heat Treatment Temperature (°K)	Time to Temperature sec ($\times 10^4$)	Time to Temperature (hr)	Resin in Preg Solution (%)	Matrix After Final Processing (Vol %)	Density (g/cc) Composite	Density (g/cc) Matrix	Module Cross Section ($in^2 \times 10^{-8}$)	Module Cross Section ($in.^2 \times 10^{-5}$)	Function	Tensile Test Results[a] Tensile Strength (Fiber Area) (GN/m^2)	Tensile Strength (Fiber Area) ($psi \times 10^3$)	Tensile Strength (Fiber & Matrix) (GN/m^2)	Tensile Strength (Fiber & Matrix) ($psi \times 10^3$)	Strength Retention (%)
As-Cured Monofilament		445	0.72	2	25	36.1	-	-	4.95	7.57	Maximum	2.341	339.9	na		na
											Average	2.137	309.9			
											Minimum	1.923	278.9			
R	C-110	1273	2.5	7												
	C-120	2873	2.9	6	33	48.4	-	-	6.14	9.39	Maximum	2.436	353.3	1.256	182.1	100
											Average	2.407	349.2	1.241	180.0	
V	VT-68	1273	2.9	8	30	22.4	-	-	4.02	6.24	Maximum	2.080	301.6	1.572	228.1	86.7
	C-124	1273	26	72							Average	1.682	244.0	1.286	186.5	
		2873	2.2	6							Minimum	1.225	177.6	0.970	140.7	
S	C-127	1273	5.8	16	25	24.4	1.83	1.86	4.15	6.44	Maximum	1.837	266.5	1.360	197.2	78.4
		2873	2.2	6							Average	1.458	211.5	1.093	158.5	
											Minimum	0.858	124.4	0.658	95.5	
T[b]	C-127	1273	5.8	16	30	39.8	1.80	1.77	5.23	8.11	Maximum	2.278	330.6	1.473	213.6	97.2
		2873	2.2	6							Average	1.990	288.6	1.194	173.2	
											Minimum	1.524	221.1	0.876	127.0	
FF	C-139	1273	5.8	16	30	29.2	1.87	1.92	4.41	6.84	Maximum	1.820	264.0	1.317	191.0	77.6
		3073	2.2	6							Average	1.551	225.0	1.102	160.0	
											Minimum	1.165	169.0	0.841	122.0	

(a) Tensile tests were carried out at a chart speed of 2.1×10^{-5} in./sec (0.05 in./min) using a gage length of 2.54×10^{-2} m (in.).
(b) Elastic modulus was 460 GN/m^2 [$(66.6) \times 10^6$ psi)] calculated on basis of fiber cross-sectional area
302 GN/m^2 (43.7×10^6 psi) calculated on the basis of module cross-sectional area.
Vol. fraction matrix = 34.4% for specific monofilament tested.

strength obtained was 2.08 GN/m^2 (301,600 psi), 89 percent of the as-cured value, and the pyrolysed composite tensile strength was 1.57 GN/m^2 (228,100 psi), somewhat higher than in experiment R because of less matrix content. In the next experiments (S and T), matrix concentration was varied, and the possible effect of combined pyrolysis and heat treatment without intermediate cycling to room temperature was studied. Such combination would save time and elimination of an unnecessary cooldown cycle and might eliminate some differential thermal expansion stresses. With 25-percent resin solids in methyl ethyl ketone and fibers of Type-S, the matrix volume fraction after final heat treatment was 0.244. The maximum fiber tensile strength was 1.837 GN/m^2 (266,500 psi), equivalent to a strength retention of 79 percent, and the composite tensile strength was 1.36 GN/m^2 (197,200 psi). With 30-percent resins solids in the pregging solution, the matrix volume fraction was 0.398. In this case, maximum fiber tensile strength was 2.278 GN/m^2 (330,600 psi), equivalent to a strength retention of 97.2 percent, and the composite tensile strength was 1.47 GN/m^2 (213,600 psi). The composite elastic modulus was 302 GN/m^2 (43.7×10^6 psi).

A plot of tensile strength versus matrix concentration after final processing to 2873°K is shown in Figure 15. Fiber tensile strength increases with increasing matrix concentration, but composite tensile strength does not. Experimental scatter decreases with increasing matrix concentration. The best combination of fiber tensile strength, composite tensile strength, and reproducibility was obtained with a 30-percent solution of HTR resin in MEK and combined copyrolysis and heat treatment to 2873°K, as in the fibers designated T.

Because previous studies (Section 4.1.2) had shown that fiber and composite tensile strength increased with heat-treatment temperature, one experiment was done using heat treatment to 3073°K and 30-percent HTR resin. This produced a matrix concentration decrease from 39.8 percent to 29.2 percent, and a composite density increase from 1.80 g/cc to 1.87 g/cc, but the monofilament tensile properties were significantly reduced. The maximum fiber tensile strength was 1.82 GN/m^2 (264,000 psi), equivalent to 78-percent utilization, and a composite tensile strength of 1.317 GN/m^2 (191,000 psi).

Tensile testing of Type-T samples revealed an unusual fracture mode, suggesting a pseudoplasticity associated with microcracking throughout the composite monofilament. That this was the case can be seen in Figure 16, which shows individual filament breaks throughout the gage length of the specimen. The multiplicity of the filament breaks, which often did not propagate across the immediately adjacent matrix, suggested that the matrix strain-to-failure was equivalent to, or greater than, that for the fiber.

The matrix designated α (Figure 16a) had the appearance of finely nucleated pyrolytic graphite. Cracks were often arrested at the fiber-matrix interface point β, and propagated along the fiber-matrix interface as at point γ. In transverse cross section, individual filaments (δ) were less optically active than the matrix. A tough microcrystalline sheath containing few breaks encapsulated the module. Microcracking was absent in untested samples (Figure 17).

Examination of the load-deflection curves showed that discontinuous failure occurred throughout the series (V, S, and T), but occurred in greater number for the filaments

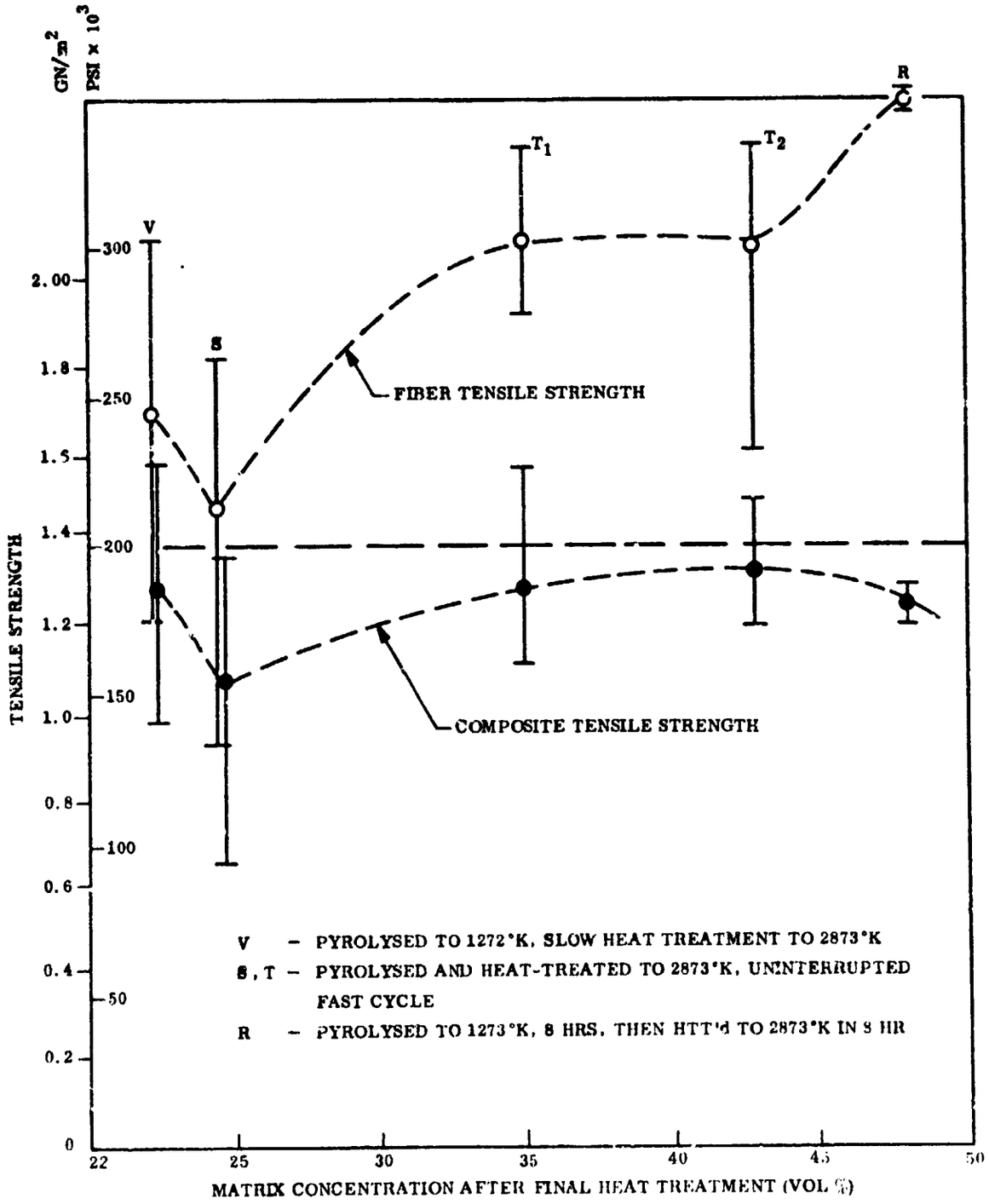

Figure 15. - Effect of Matrix Concentration on Tensile Strength of Monofilaments Produced From HTR Resins, Copyrolysed and Heat-Treated to 2873°K

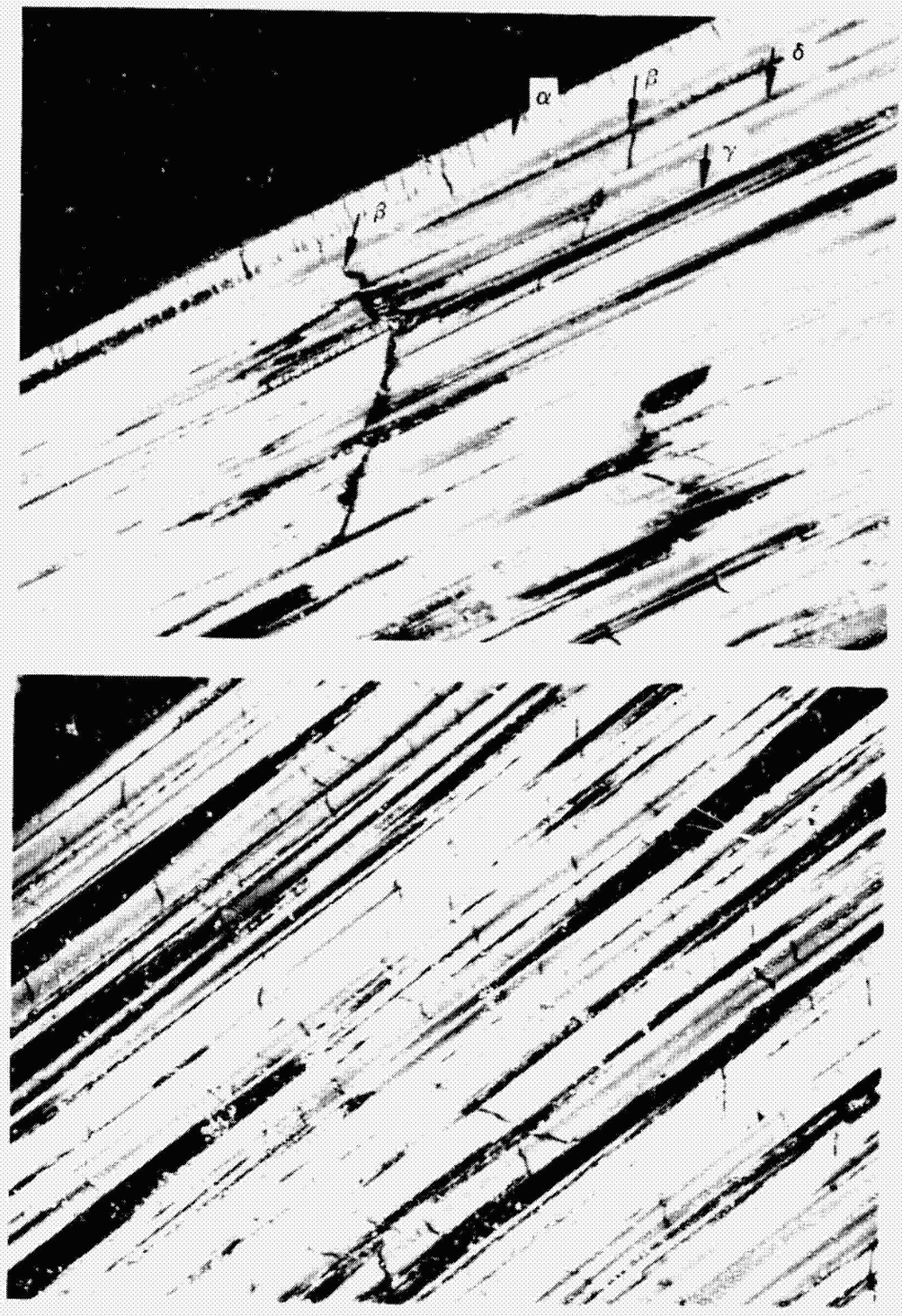

Figure 16. - Samples of Type-T Filament Tested to Failure 1.99 GN/m^2 (288,500 psi) 430×

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Figure 17. - Untested Type-T Monofilament (500×)

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with higher matrix concentration, as in monofilaments of Type-T, suggesting greater fracture toughness when there was a substantial sheath (5×10^{-6} m) around the bundle.

In an attempt to better understand this failure mode, samples having varying matrix concentrations were tested and plotted. It was found that within the range of 34 to 42 volume percent (Figure 15), fiber and composite tensile strength did not vary significantly, but matrix concentration did affect the type of fracture. At the lower matrix concentration (volume percent $\leq$ 35 percent), the failure mode was sometimes catastrophic (i.e., brittle), or the tensile load increased to a maximum value followed by a discontinuous failure at a lower tensile load.

The high composite tensile strength obtained with samples of Type-T, 1.473 GN/m^2 (213,600 psi) together with a strength utilization of 97.3 percent, indicates that the 30-percent resin concentration in the pregging solution and a continuous processing cycle is optimum for Thornel 75 in HTR resin. Additional monofilaments were prepared using the same approach and were shipped under Task IV, Monofilament Production.

4.3.2 Copyrolysis Optimization, Type-C Tow

A bare fiber tensile strength maximum of 2.18 GN/m^2 (316,000 psi) was obtained (Ref. 5) with a final heat-treatment temperature of 1673°K, but at higher heat-treatment temperature the tensile strength decreases (Figure 18). Such decrease in tensile strength with increasing heat-treatment temperature is commonly observed with round PAN monofilaments (Refs. 21, 23, 39, 40) and is apparently associated with the development of flaws and voids at the interior and surface of individual filaments (Ref. 33). Conversely, tensile modulus increases with increasing heat-treatment temperature (Ref. 41), and is related to the degree of preferred orientation (Refs. 42, 43). Consequently, beyond 1273°K fiber strain-to-failure decreases with increasing temperature (Figure 18), and approaches the failure strain of typical pyrolysed resin-based matrices, $\leq$0.41 percent (Refs. 5,6), only after graphitization of the fiber to around 2680°K. Since strain-to-failure of glassy carbon matrices increases with increasing heat-treatment temperature and degree of graphitization (Refs. 6, 44), it was expected that in copyrolysis the best combination of tensile strength, elastic modulus, and strain-to-failure would be obtained with increasing heat-treatment temperature.

However, the optimum temperature and process cycle were yet to be determined. Bare Type-C tow can be processed at fairly rapid heating rates. For example, a rate of 1°K/60 sec is representative (Ref. 45), and Ezekiel (Ref. 39) has stress graphitized such fibers in seconds. However, glassy carbon must be processed more slowly (Ref. 6). Consequently, copyrolysed monofilaments with GW-173 matrix were pyrolysed to 1273°K at a relatively slow rate, $4.6°K \times 10^{-3}$/sec (0.28°K/60 sec), followed by a 4.3×10^4 sec hold at 1273°K, in a standard cycle previously established (Ref. 5) for pyrolysis of monofilaments produced from fully carbonized fiber precursors.

In the preliminary studies (Section 4.2.1), copyrolysis to 1673°K of 1273°K Type-C tow in GW-173 matrix was accomplished in a heat-treatment cycle which was a little more rapid than previously used and which omitted the 1273°K hold, curve C-95 (Figure 19). The resulting fiber tensile strengths averaged 0.448 GN/m^2 (65,000 psi), considerably lower than the 0.752 GN/m^2 (109,000 psi) obtained previously (Table XXXI, Ref. 5) using the standard pyrolysis cycle (see I-211, Figure 19), followed by a second cycle to 1673°K, like C-104.

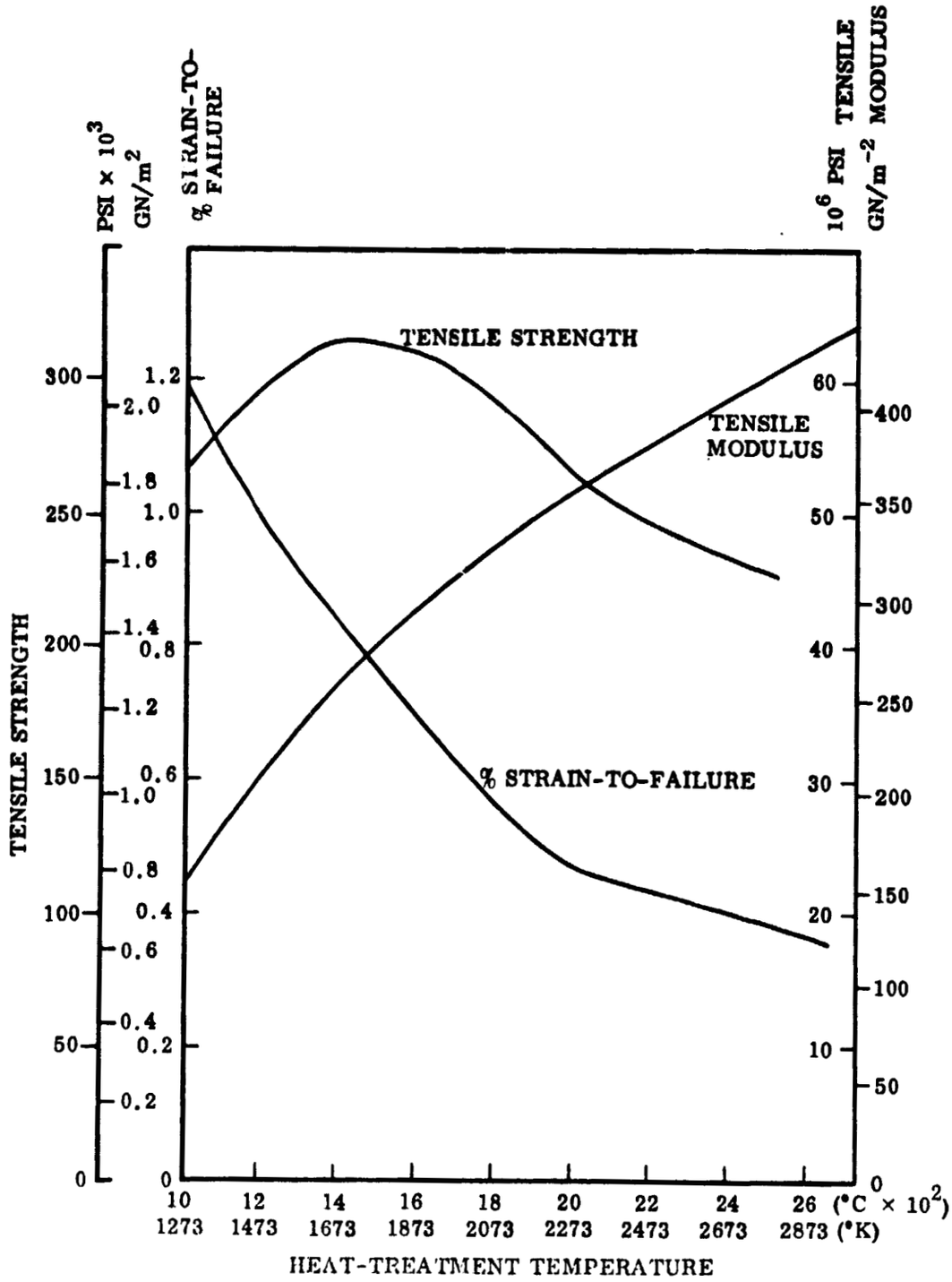

Figure 18.- Properties of Bare Type-C Tow as a Function of Heat-Treatment Temperature (Refs. 6, 41)

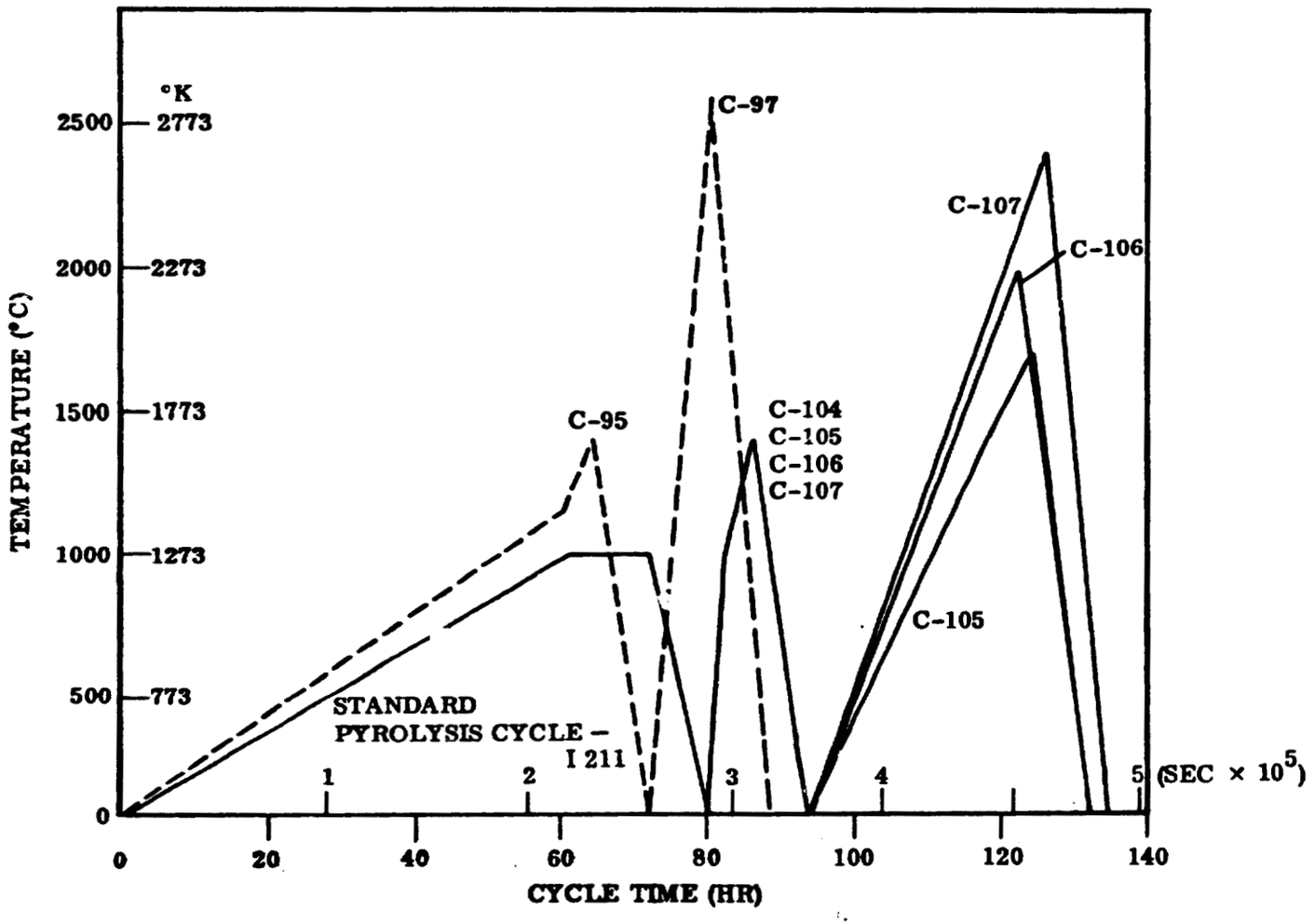

Figure 19.– Copyrolysis and Heat-Treatment Cycles, Process Optimization Studies

Microscopic examination of the more rapidly processed monofilaments revealed that their relative weakness was due to numerous pyrolysis cracks, and that fracture was of the glassy type (Figure 10). Examination of many tensile specimens had shown that such glassy fracture was invariably associated with lower tensile strength and tensile strain.

Copyrolysed monofilaments produced in the previous contract (Ref. 6) were reexamined, and selected samples which appeared to be relatively flaw-free, e.g., free of excessive matrix cracking, were tested. Two specimens were found: one with a tensile strength of 1.031 GN/m^2 (150,000 psi) and the other with 1.503 GN/m^2 (218,000 psi) – values that were higher than the maximum fiber value of 0.847 GN/m^2 (129,000 psi) previously reported (Table XXXI, Row 2, Ref. 3). Examination of these high-strength monofilaments showed that they had a more fibrous nonglassy fracture, that fiber-structure was better developed, and that fiber-matrix debonding occurred during testing (Figure 11).

Elastic modulus was measured on the two types of monofilaments: those rapidly copyrolysed and heat-treated to 1673° K in a combined pyrolysis and heat treatment, and those in which copyrolysis had been carried out with a 12-hr hold at 1273° K (I-211), followed by heat treatment to 1673° K.

Tensile data are reported in Table XVI along with the calculated strain-to-failure. In the more rapid processing, the excessive matrix cracking results in a low monofilament strain-to-failure. In the more extended copyrolysis cycle, both fiber tensile strength and elastic modulus increased, and monofilament strain-to-failure increased correspondingly to values close to the (0.41 ± 0.06 percent) obtained in flaw-free GW-173 matrix (Ref. 5).

TABLE XVI. - EFFECT OF PROCESSING CYCLE ON TENSILE PROPERTIES OF COMPOSITE MONOFILAMENTS PRODUCED FROM 1273° K TYPE-C TOW IN GW-173 MATRIX

Monofilament Processing			Function	Monofilament Tensile Properties				Calculated Monofilament Strain-to-failure (%)
Total Time		Maximum Temperature (°K)		Tensile Strength		Fiber Elastic Modulus		
(sec × 10^5)	(hr)			(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^3)	
2.592	72	1673	Maximum	0.565	82	–	–	0.22
			Average	0.448	65	256	37.2	0.17
3.384	94	1673	Single Values	1.503	218.0	–	–	0.46
				1.031	150.0	326	47.6	0.31

As discussed in Section 4.2.1, the excessive cracking observed in the more rapidly processed monofilaments, might be caused by nitrogen liberated from the PAN, between 1173° and 1673°K, after the GW-173 matrix is fully carbonized and impermeable.

Consequently, the conditions that had been previously used successfully were duplicated as closely as possible. These were: (a) fiber pretreatment of 1273°K, (b) pregging with a solution of 40-percent GW-173 in methanol, followed by (c) copyrolysis to 1273°K in cycle I-211 and heat treatment to 1673°K in cycle C-104. Heat-treatment studies were carried out to higher temperatures, ranging from 1973° to 2573°K, to increase fiber modulus and produce matched fiber and matrix failure strains. To investigate the effect of processing time between 1273° and 1673°K, monofilaments were processed in two ways: pyrolysis to 1273°K followed by direct heat treatment to elevated temperature as in cycles C-105, C-106, and C-107 (Figure 19); or copyrolysis to 1273°K, heat treatment 1673°K, followed by another cycle to maximum temperature.*

The results of these heat-treatment studies are listed in Table XVII. After a heat-treatment to 1273°K, the average fiber tensile strength was 0.554 GN/m (80,300 psi). Heat treatment to 1673°K resulted in improvement to an average value of 0.86 GN/m^2 (124,000 psi). The results do not vary significantly from those previously reported for monofilaments produced in the same way (Ref. 6).

No improvement was obtained in heat-treating to 1973°K, and there is no significant difference between the samples which were first processed to 1673°K, sample 5-[illegible] and those which were heat-treated directly to 1973°K. After multiple heat treatment to 2273°K, the average fiber tensile strength was 0.95 GN/m^2 (137,900 psi), with a maximum value of 1.02 GN/m^2 (147,200 psi). Heat treatment to 2573°K resulted in a slight improvement in maximum fiber tensile strength to 1.11 GN/m^2 (160,400 psi), but was accompanied by greater data scatter. Samples which were first heat-treated to 1673°K (samples designated a) appear to have slightly higher strength than those processed directly to 2273°K or 2573°K (samples designated b).

The effect of heat-treatment optimization is illustrated in Figure 20. At a heat treatment of 1673°K, using a standard cycle with a long hold at 1273°K, the tensile strength is twice what it was with the more rapid processing. At 2273°K, the longer processing time between 1273° and 1673°K produces monofilaments with a maximum fiber tensile strength of 1.02 GN/m^2 (147,000 psi); with the shorter intermediate heat-treatment time, the maximum value is only 0.731 GN/m^2 (106,000 psi).

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*Multiple heat-treatment cycles were used to permit the withdrawal of specimens at selected temperatures and to minimize off-shift operations above 1273°K because the furnaces used did not have automated temperature measurement and controls for use above that temperature. More detailed time-temperature studies above carbonization temperature (1673°K) were not carried out because the time-temperature dependence of graphitization is such that for a given heat-treatment temperature the change in any parameter with time rapidly approaches what appears to be a limiting value characteristic for that temperature, so that additional structural changes are much more readily accomplished by higher temperature heat treatments (Ref. 46).

TABLE XVII. - EFFECT OF HEAT TREATMENT ON MONOFILAMENT PROPERTIES 1273° K – TYPE-C TOW IN GW-173 MATRIX (40% SOLUTION)

Sample Number	Composite Heat Treatment		Vol % Fiber	Cross Section Composite		Function	Load		Tensile Stress (Fiber Area)		Tensile Stress (Fiber + Matrix)	
	Cycle	Final Temp (°K)		($m^2 \times 10^{-7}$)	($in.^2 \times 10^{-4}$)		(Newtons)	(lbf)	(GN/m^2)	($psi \times 10^3$)	(GN/m^2)	($psi \times 10^3$)
	I-211	1273°K	57.2	8.19	12.69	Average	259	58.3	0.554	80.3	0.316	45.9
						Maximum	265	59.5	0.565	81.96	0.323	46.9
5-1	I-211	1273°K	48.5	8.54	13.24	Average	355	79.75	0.856	124.2	0.415	60.2
	C-104	1673°K				Maximum	356	80.0	0.859	124.6	0.416	60.4
5-2a	I-211	1273°K	50.6	7.94	12.31	Average	327	73.5	0.764	110.8	0.411	59.7
	C-104	1673°K				Maximum	347	78.0	0.863	125.2	0.437	63.4
	C-105	1973°K										
5-2b	I-211	1273°K	50.94	7.89	12.23	Average	306	68.75	0.761	110.4	0.387	56.2
	C-105	1973°K				Maximum	345	77.5	0.858	124.4	0.437	63.4
5-3a	I-211	1273°K	48.5	8.14	12.62	Average	373	83.9	0.951	137.9	0.459	66.5
	C-104	1673°K				Maximum	401	90.1	1.020	147.2	0.493	71.5
	C-106	2273°K										
5-3b	I-211	1273°K	51.6	7.65	11.86	Maximum	288	64.8	0.731	106.0	0.378	54.7
	C-106	2273°K				Average	262	59.0	0.665	96.4	0.343	49.7
5-4a	I-211	1273°K	50.0	7.73	11.99	Average	271	60.9[d]	0.702	101.75	0.350	50.8
	C-104	1673°K				Maximum	427	96.0	1.106	160.4	0.352	80.96
	C-107	2573°K										
5-4b	I-211	1273°K	50.0	7.73	11.99	Average	301	67.7[d]	0.780	113.12	0.376	56.46
	C-107	2573°K	50.0			Maximum	352	79.0	0.910	132.00	0.454	65.9

(a) Fibers partially graphitized, pull out of grips during testing.

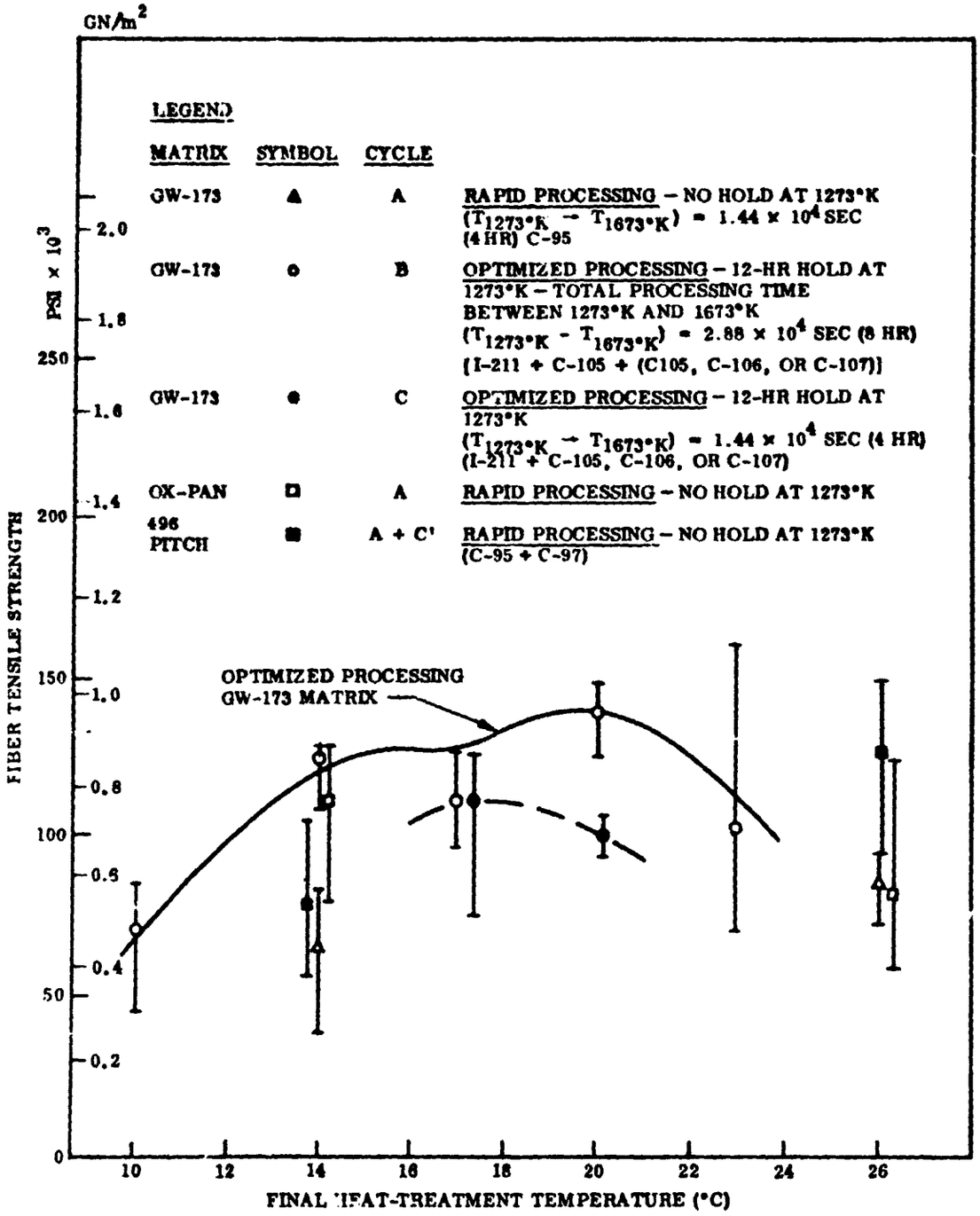

Figure 20.- Comparison of Tensile Strength Obtained With 1273°K Type-C Tow in Various Matrix Precursors and With Various Processing Cycles

With stabilized thermoplastic matrices such as oxidized PAN, and pitch, which are not completely carbonized at 1273°K, and which still undergo molecular rearrangement above that temperature, the long pyrolysis cycle developed for GW-173 may not be necessary. With OX-PAN and a rapid cycle (C-95) to 1673°K, the maximum fiber tensile strength was 0.80 GN/m^2 (116,000 psi), or equivalent to that observed with GW-173 and an optimized long cycle. With a final heat treatment of 2873°K and a graphitizing pitch matrix, maximum fiber tensile strength was 0.97 GN/m^2 (140,000 psi), which was higher than the values obtained with either GW-173 matrix or oxidized PAN matrix. Further improvements in tensile strength might have been obtained with suitable processing in pitch, PAN matrix, or with HTR resin. However, in all cases studied, both bare fiber and composite monofilament tensile strength decreased after a heat treatment above 2273°K, and such a treatment is necessary to develop the desired elastic modulus (Figure 21).

As shown in Figure 21, with both the bare fiber and in copyrolysis, fiber tensile modulus increases with increasing heat-treatment temperature and is independent of the type of matrix. A plot of composite modulus versus matrix concentration, Figure 22, shows that for copyrolysis to either 1673° or 2873°K, the rule of mixtures is obeyed, with a matrix modulus of about 55 GN/m^2 (8 x 10^6 psi), independent of precursor resin, indicated by the common intersection of the curves for both fiber types extrapolated to 100-percent matrix concentration. This value is twice that measured for pure glassy-carbon prepared from GW-173, suggesting that the matrix structure is affected by the presence of fibers during copyrolysis, and the increased stiffness of the composite monofilament with final heat-treatment temperature occurs as a result of changes in the fiber properties only.

The apparent deterioration of strength during copyrolysis of 1273°K Type-C tow in GW-173 matrix can be analyzed in terms of the tensile strength predicted from the ratio of fiber and matrix strain-to-failure using the rationale previously developed (Ref. 6), in which it is assumed that when there is good interfacial bonding between fiber and matrix, the composite monofilament fails, at the strain-to-failure of the matrix (Table XVIII).

Then

$$\sigma_T = \left(\frac{\sigma_f}{\epsilon_f}\right)\epsilon_m = E_f \epsilon_m$$

where σ_T = the predicted fiber tensile strength in the pyrolysed monofilament
E_f = the fiber tensile modulus measured in a more flexible matrix such as epoxy or as-cured resin
ϵ_m = strain-to-failure of the pyrolysed matrix
ϵ_f = fiber strain-to-failure

At a pyrolysis temperature of 1273°K, when the measured fiber tensile strength is 0.55 GN/m^2 (80,300 psi), or 89.0 percent of that predicted while at 1673°K, the average fiber tensile strength is 0.856 GN/m^2 (124,200 psi), corresponding to a decreased strength utilization of 79.8%. At higher heat-treatment temperatures, the values are consistently lower than the predicted values.

Such an inconsistency might have resulted from a failure to develop the fiber elastic modulus in copyrolysis. However, the elastic modulus of copyrolysed monofilaments did not vary significantly from that of bare multifiber bundles (Figure 21).

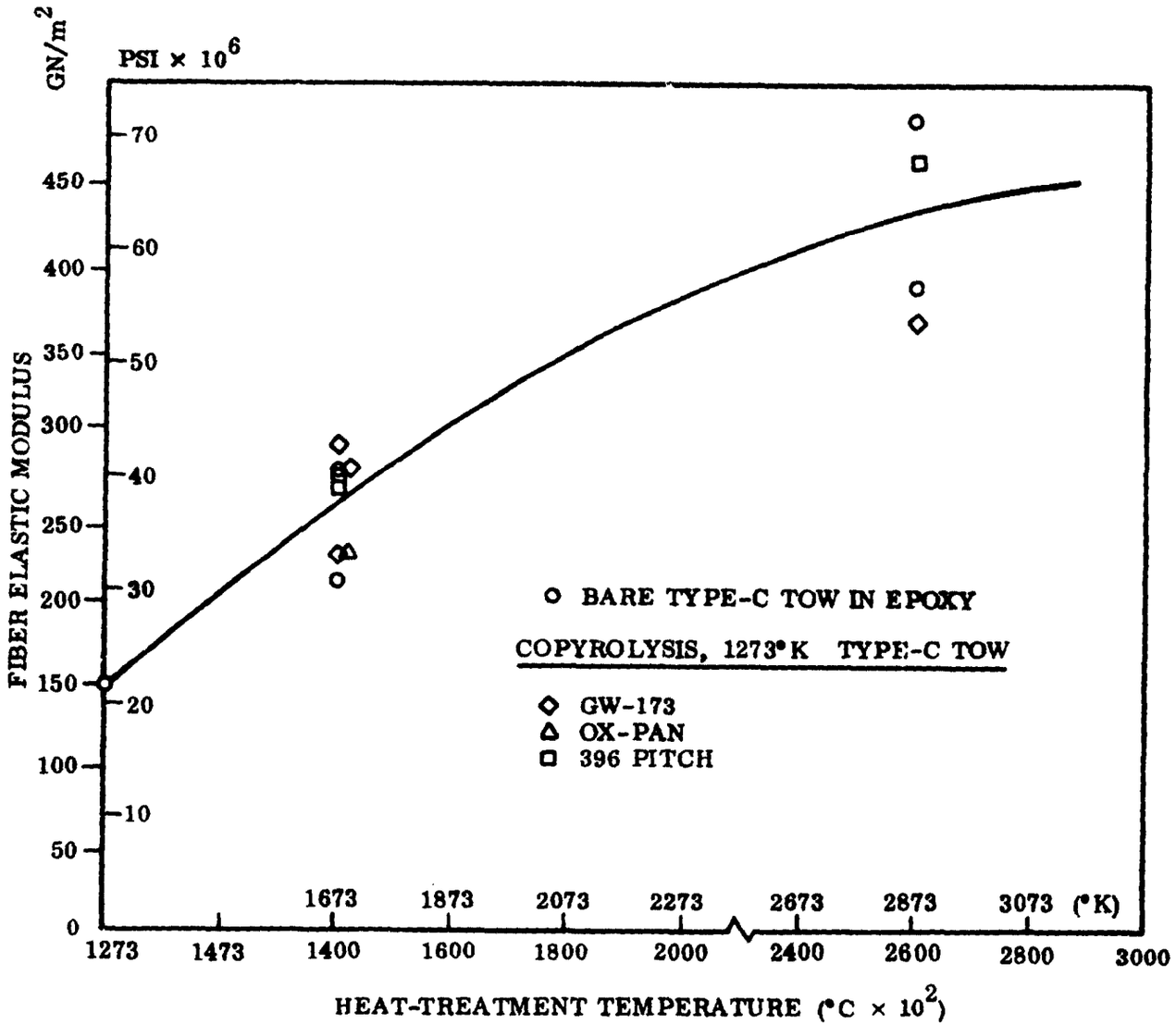

Figure 21.- Elastic Modulus of 1273°K Type-C Tow Copyrolysed in Various Matrices

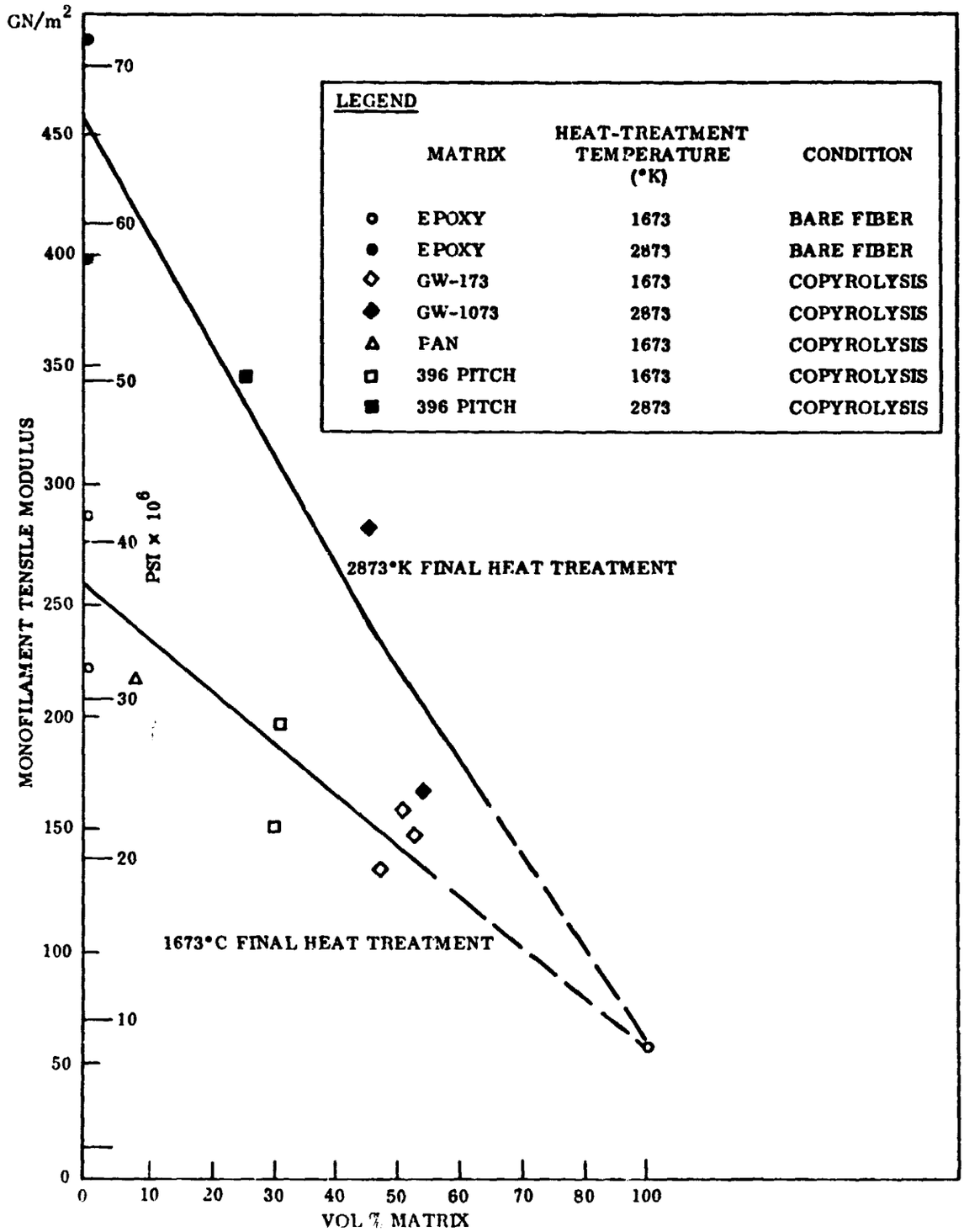

Figure 22.- Monofilament Composite Modulus as a Function of Matrix Concentration

TABLE XVIII. - UTILIZATION OF FIBER TENSILE PROPERTIES
1273° K TYPE-C TOW IN GW-173 MATRIX PRECURSOR

Heat Treatment Temperature (°K)	Bare Fiber Properties				Strain-to-Failure (%)		Composite Monofilaments				Strength Development (%)
	Tensile Strength		Elastic Modulus				Predicted Tensile Strength		Measured Tensile Strength		
	(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^6)	ϵ_f	ϵ_m	(GN/m^2)	(psi × 10^3)	(GN/m^2)	(psi × 10^3)	
1273	1.82	263.1	152	22.0	1.19	0.41	0.62	90.2	0.554	80.3	88.0
									0.665	82.0	90.0
1673	2.18	316.0	259	37.5	0.842	0.415	1.07	155.6	0.856	124.2	79.8
								203.0	0.869	124.6	80.1
1973	1.965	285.0	331	48	0.60	0.42	1.38	201.6	0.769	119.9	55.9
									0.862	125.3	62.1
2273	1.84	266.0	386	56	0.48	0.415	1.62	238.0	0.961	127.9	57.9
									1.020	147.2	61.8
2573	1.66	240.2	400	58	0.41	0.42	1.66	240.2	0.702	101.8	42.4
									1.106	160.4	65.8

Another possible explanation of low tensile-strength results is that the strain-to-failure of the copyrolysed monofilaments is lower than that predicted from the value of the individual constituents; i.e., high-temperature heat-treatment caused the formation of flaws which weakened the structure.

Both microscopic and macroscopic effects occurred. For example, when 1273°K Type-C tow was pregged with GW-173, and heat-treated to 2873°K, there was an apparent deterioration in fiber texture. Scanning electron microscopy of fracture surface of a sample which had a tensile strength at 0.615 GN/m^2 (89,000 psi) (Figure 12) showed the development of a coarse granular structure in which the filaments are not readily distinguishable from the matrix and in which there was little crack interruption at the fiber-matrix interface. The measured elastic modulus was 512 GN/m^2 (74.3×10^6 psi), equivalent to a strain-to-failure of 0.12 percent.

Under the same heat-treatment conditions in a pitch matrix, fiber texture was less degraded, there was interruption of the fracture path at the fiber matrix interface, and the fiber tensile strength measured was 0.965 GN/m^2 (140,000 psi). (See Figure 13.) The elastic modulus was 471 GN/m^2 (68.3×10^6 psi) and the strain-to-failure 0.205 percent.

With Type-C tow in all matrix precursors, there was a problem with alignment of individual filaments. The larger number of filaments (10,000) and the lack of twist in the tow made it difficult to maintain collimation during processing. Further, some filaments would orient themselves at various angles to the bundle axis, particularly at the periphery of the tow. These misoriented filaments were found to be the origin of the transverse matrix cracks, formed during copyrolysis, and act as stress concentrators.

The effect of failure to maintain collimation is shown in Figure 23, in which many filaments are misaligned, forming a matrix-rich region with matrix cracks normal to the tow axis. When the pregging operation was carried out more carefully, collimation was retained, and large misorientations did not occur (Figure 24). However, cracks are visible at higher magnification (Figure 25).

This failure to maintain collimation combined with the large bundle diameter, 1.5×10^{-3} m (60 mils), frequently resulted in copyrolysed monofilaments which were kinked and warped. When such monofilaments were tested, low tensile-strength measurements resulted, 0.35 GN/m^2 (50,000 psi).

No further work was done with Type-C tow, for the above reasons and because results with Type-D tow were more promising. In comparison with Type-D tow, the Type-C tow had the following disadvantages:

- Deterioration in tensile-strength with increasing heat-treatment temperature
- Large bundle diameter resulting in poor processability.

It did have an apparent advantage in that it was less difficult to impregnate and wet than the Type-D tow, but this advantage was offset by the limit on the maximum tensile strength attainable.

To summarize, with bare oxidized Type-C tow, a tensile strength maximum is reached at 1673°K, but maximum elastic modulus is not reached until a heat-treatment temperature

35×

150×

Figure 23. - Effect of Poor Filament Collimation in Type-C Tow, Copyrolysed in GW-173 Matrix to 1273°K

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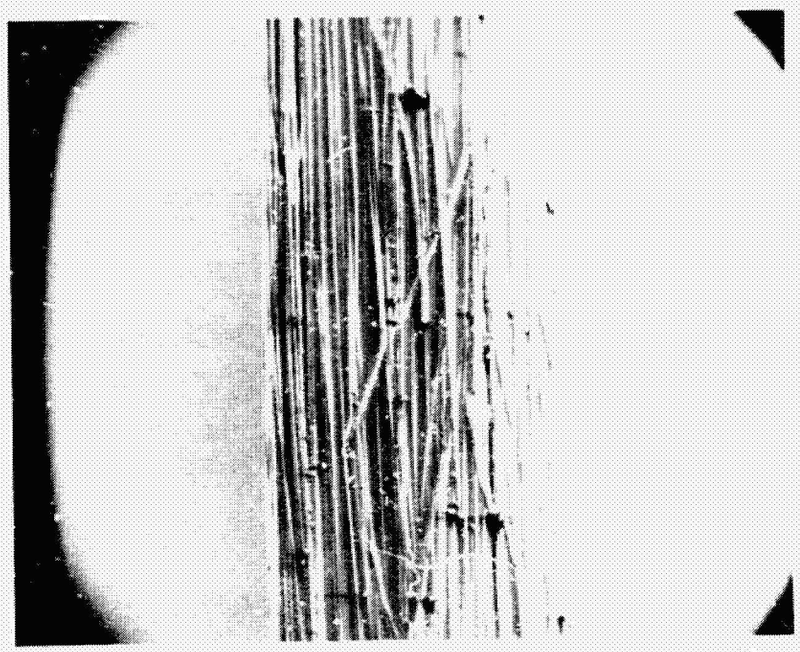

35×

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Figure 24. - Improved Collimation of Filaments in Type-C Tow, Copyrolysed in GW-173 Matrix to 1273°K

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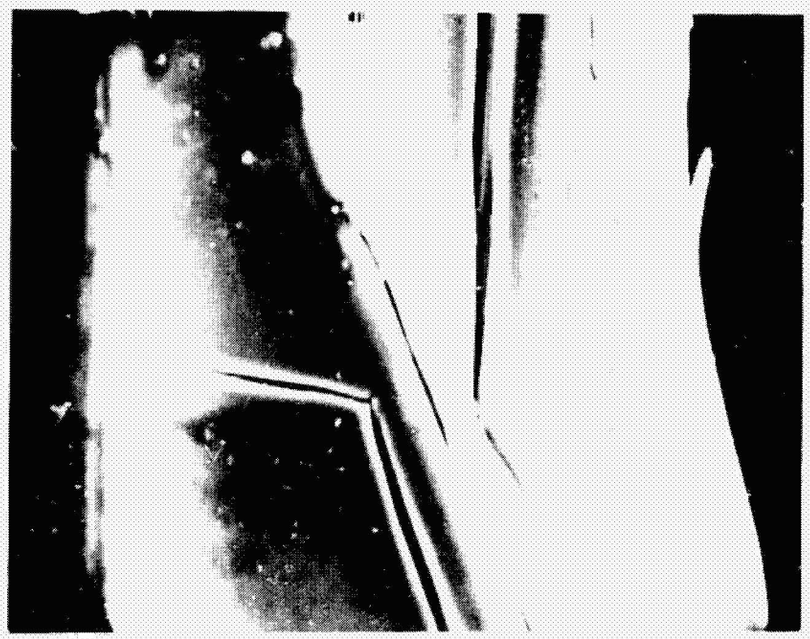

1500×

Figure 25.- Small Matrix Cracks Occurring During Pyrolysis of Type-C Tow (1273°K Type-C Tow in GW-173 Matrix, Copyrolysed to 1273°K)

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of 2873°K. In copyrolysis, with GW-173 matrix, the maximum monofilament tensile strength is obtained at 2273°K when fiber and matrix strain-to-failure are nearly similar. At 2873°K, there is a definite decrease in tensile strength in all matrix precursors probably caused by the development of microscopic flaws within individual filaments, and the enlargement of macroscopic flaws in the copyrolysed bundle.

4.3.3 Copyrolysis Optimization, Type-D Tow

In the preliminary studies with Type-D tow, a major problem was bundle infiltration and poor filament wetting, caused by the high twist on the tow and close packing of the filaments after oxidation. Two methods of alleviating this problem were tried: (a) mechanical processing of the tow to loosen it and spread it, and (b) further study of the effect of fiber pretreatment of 1273°K and 1673°K. The lower temperature pretreatment was studied because of an observed greater resin pickup with lower temperature heat treatment in preliminary studies with Type-C tow.

All optimization studies were done with oxidized Type-D tow treated as indicated above, pregged with HTR or GW-173 resin, copyrolysed and heat-treated to the desired final temperature of 2873°K or 3073°K. Since preliminary studies had shown that with the bare Type-D tow, and in copyrolysis, tensile strength increases with increasing heat-treatment temperature, the last copyrolysis experiments were done at 2873°K and 3073°K.

Results of optimization studies are summarized in Table XIX.

The best results were obtained with 1673°K Type-D tow pregged with HTR resin, copyrolysed and heat-treated to 2873°K, in the overnight continuous cycle developed with Thornel 75 and HTR resin (Section 4.3.1). The composite tensile strength was 1.491 GM/m^2 (216,300 psi), equivalent to 100-percent utilization of bare fiber tensile strength, and the maximum fiber tensile strength was 2.405 GN/m^2 (348,800 psi). The fiber elastic modulus was 427 GN/m^2 (61.9 × 10^6 psi), and the composite monofilament modulus 293 GN/m^2 (42.5 × 10^6 psi). Since this specimen had the highest tensile strength obtained by any copyrolysis process investigated, monofilaments of this type were shipped under Task IV, Monofilament Production. Results were poorer with a lower temperature, 1273°K pretreatment. The maximum fiber tensile strength obtained after copyrolysis and heat treatment to 2873°K was 1.130 GN/m^2 (164,000 psi), sample CC. In a second batch, CCA, the maximum fiber tensile strength observed was 0.993 GN/m^2 (144,000 psi). The average values 0.841 GN/m^2 (122,000 psi) and 0.807 GN/m^2 (117,000 psi) are within the limits of experimental variation which is 0.180 GN/m^2 (26.1 psi). Heat treatment to 3073°K caused a slight improvement in fiber tensile strength to a maximum value of 1.296 GN/m^2 (188,000 psi).

With GW-173 matrix, the maximum fiber tensile strength, 1.742 GN/m^2 (252,600 psi), a strength retention of 93.4 percent was obtained with a fiber pretreatment of 1273°K, sample Y. With a pretreatment of 1673°K, maximum fiber tensile strength was 1.644 GN/m^2 (238,400 psi), equivalent to a composite strength of 1.375 GN/m^2 (199,400 psi). The fiber elastic modulus was 299 GN/m^2 (43.3 × 10^6 psi). Fibers of Type Z were selected for shipment because their strength approached the value of 1.379 GN/m^2 (200,000 psi). Higher fiber tensile strength, a maximum of 1.742 GN/m^2 (252,600 psi), equivalent to a strength retention of 93.4 percent, was obtained with a fiber pretreatment of 1273°K, but because the matrix concentration was higher, the composite tensile strength was only 1.07 GN/m^2 (155,400 psi).

Table XIX. – COPYROLYSIS WITH TYPE-D TOW, PROCESS OPTIMIZATION SUMMARY

Experiment No.	Pyrolysis Run No.	Heat Treatment: Temperature (°K) Fiber	Heat Treatment: Temperature (°K) Composite	Heat Treatment: Total Time (10^4 sec)	Heat Treatment: Total Time (hr)	Matrix Precursor	Composite Monofilament: Avg Matrix Content (%)	Density (gm/cc)	Cross-Sectional Area (10^{-8} m^2)	Cross-Sectional Area (10^{-5} in.^{2})	Function	Tensile Strength: Fiber (GN/m^2)	Tensile Strength: Fiber (10^3 psi)	Tensile Strength: Composite (GN/m^2)	Tensile Strength: Composite (10^3 psi)	Strength Retention[d] (%)	No. of Tests
BB[a]	C-134	167 (5)	2,873	8.64	24	HTR	36.1	1.80	2.84	4.41	Maximum	2.405	348.8	1.491	216.3	100	
											Minimum	2.111	306.1	1.309	189.8		
											Average	2.255	327.0	1.438	208.6	100	5
											Std Dev.	0.110	15.9	0.068	12.8		
CC	C-138	1,273 (5)[c]	2,873	8.64	24	HTR	12.7	1.94	1.51	2.34	Maximum	1.130	164.0	0.986	143.0	60.6	
											Minimum	0.648	94.0	0.510	84.0		
											Average	0.838	121.6	0.745	108.0	45.1	6
											Std. Dev.	0.179	25.9	0.150	21.7		
CC-A	C-138	1,273 (7)[c]	2,873	8.64	24	HTR	18.7	1.95	2.22	3.44	Maximum	0.993	144.0	0.800	116.0	53.2	
											Minimum	0.531	77.0	0.421	61.0		
											Average	0.807	117.0	0.654	94.8	43.2	
											Std. Dev.	0.181	26.2	0.148	21.5		
EE	C-139	1,273 (7)[c]	3,073	8.64	24	HTR	26.9	1.97	2.49	3.86	Maximum	1.296	188.0	1.000	145.0		
											Minimum	0.510	74.0	0.317	46.0		
											Average	1.020	148.0	0.752	109.0		5
											Std. Dev.	0.323	46.8	0.288	41.7		
Y	C-133	1,273 (5)[c]	1,273 2,873	25.9 2.16	72 6	GW-173	38.5	1.87	2.95	4.57	Maximum	1.742	252.6	1.071	155.4	93.4	
											Average	1.725	250.2	1.061	153.9		3
											Std. Dev.	0.028	4.07	0.017	2.5		
Y	C-133	1,273 (5)[c]	1,273 2,873	25.9 2.16	72 6	GW-173	29.0	1.87	2.72	4.22	Maximum	1.546	224.	1.031	149.6	82.5	
											Average	1.313	190.4	0.876	127.1		2
											Std. Dev.	0.330	47.8	0.210	31.9		
Z[b]	C-133	1,673 (5)[c]	1,273 2,873	25.9 2.16	72 6	GW-173	13.5	[illegible]	2.11	3.27	Maximum	1.644	238.4	1.375	199.4	[illegible]	
											Average	1.55	224.9	1.331	193.1		5
											Std. Dev.	0.094	13.6	0.048	7.0		

(a) Elastic modulus was 426 GN/m^2 (61.9 × 10^6 psi) calculated on the basis of fiber area
293 GN/m^2 (42.5 × 10^6 psi) calculated on the basis of composite area.
Vol fraction matrix = 33.5%.

(b) Elastic modulus was 299 GN/m^2 [(43.3) × 10^6 psi)] calculated on the basis of fiber cross-sectional area.
264 GN/m^2 [(38.2) × 10^6 psi)] calculated on the basis of module cross-sectional area.

(c) Refers to batch lot number for oxidation.

(d) $\left(\frac{\text{Measured tensile strength}}{\text{Reference fiber strength (Table XI)}}\right) \times 100$.

The results of optimization studies are shown comparatively in Figure 26. Optimization consisted of: (a) improvement in maintaining tension during the oxidation cycle, (b) untwisting the tow after oxidation to improve bundle impregnation, and (c) the use of combined pyrolysis and heat treatment to reduce thermal stresses resulting from snrinkage and thermal expansion mismatches.

With HTR matrix precursor, optimization resulted in more than doubling fiber tensile properties from an average value of 1.0 GN/m^2 (145,000 psi) to an average of 2.26 GN/m^2 (327,000 psi) and a maximum of 2.41 GN/m^2 (349,000 psi) using 1673°K Type-D tow and combined pyrolysis and heat treatment to 2873°K. With GW-173, matrix maximum fiber tensile strength was 1.742 GN/m^2 (252,600 psi) obtained with a pretreatment of 1273°K.

With both matrix precursors, fiber tensile strength increases with matrix concentration for both 1273°K and 1673°K Type-D tow (Figure 26). At comparable matrix volume fractions, results are higher for copyrolysed monofilaments produced from 1673°K Type-D tow than with 1273°K Type-D tow, irrespective of matrix precursor. Thus, if the filament bundle can be adequately infiltrated, a 1673°K pretreatment is preferable.

The elastic modulus increase with heat-treatment temperature for both bare Type D tow and copyrolysed monofilaments is shown in Figure 28. The tensile strength and modulus both increase with temperature, but in such a way as to cause an initial decrease in fiber strain -to-failure to a value of 0.5 percent or less after processing to 1673°K, i.e., a strain-to-failure compatible with matrix precursors which have similarly low failure strains.

Results obtained with Type-D in GW-173 matrix were analyzed in terms of fiber and matrix strain-to-failure (Table XX). The strength retention increased with increasing heat-treatment temperature and process optimization, approaching 93 percent of the as-cured value after a heat treatment of 2873°K when fiber-and matrix strains are equal and the process has been fully optimized. Once the process had been optimized, fiber collimation was readily attainable and monofilament lengths free of defects could be processed to 2873°K without the formation of flaws (Figures 29 and 30).

Type-D tow is preferable for the following reasons:

- Increase of both tensile strength and elastic modulus with heat-treatment temperature, reaching a maximum of 2873°K.
- Small bundle size, more suitable for meeting the program objective of a 2.54×10^{-4}m (10 mil), or less, monofilament diameter.
- Smaller number of filaments per tow (384 for Type-D tow compared with 10,000 for Type-C) which simplify the collimating needed to eliminate flaws(occurring where fibril deviates substantially from being parallel to the monofilament axis).
- Processability to high temperatures (2873°K) without the formation of flaws and without decrease in tensile strength.
- Approach of fiber failure strain to that of typical resin-base matrices ($\leq$0.5 percent), permitting 93-percent utilization of fiber properties in the pyrolysed composite monofilament.
- With HTR resin, a more graphitizable matrix, tensile strength of the pyrolysed composite monofilament was greater than that obtained with the bare fiber.

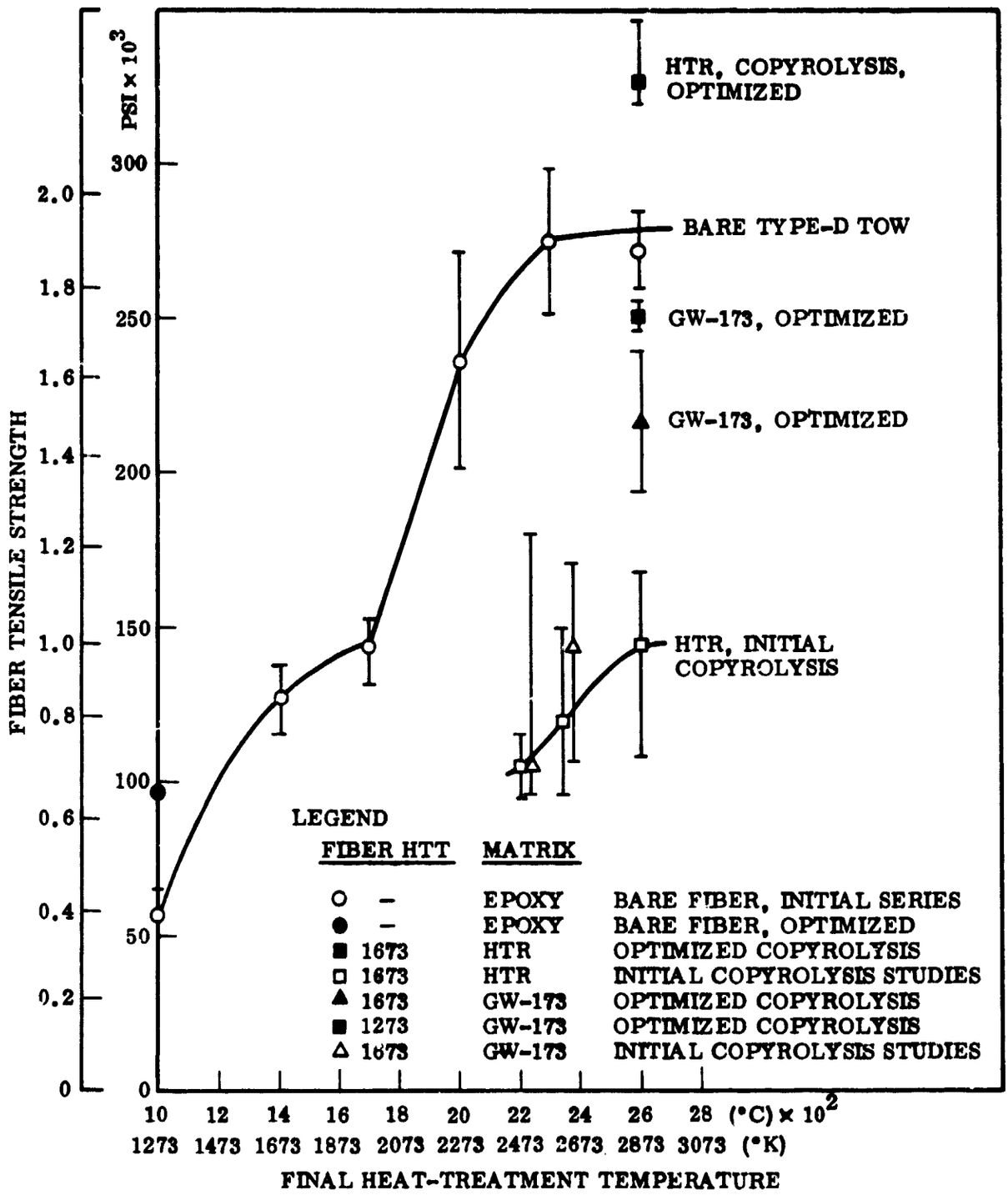


Figure 26. - Process Optimization, Copyrolysis With Type-D Tow

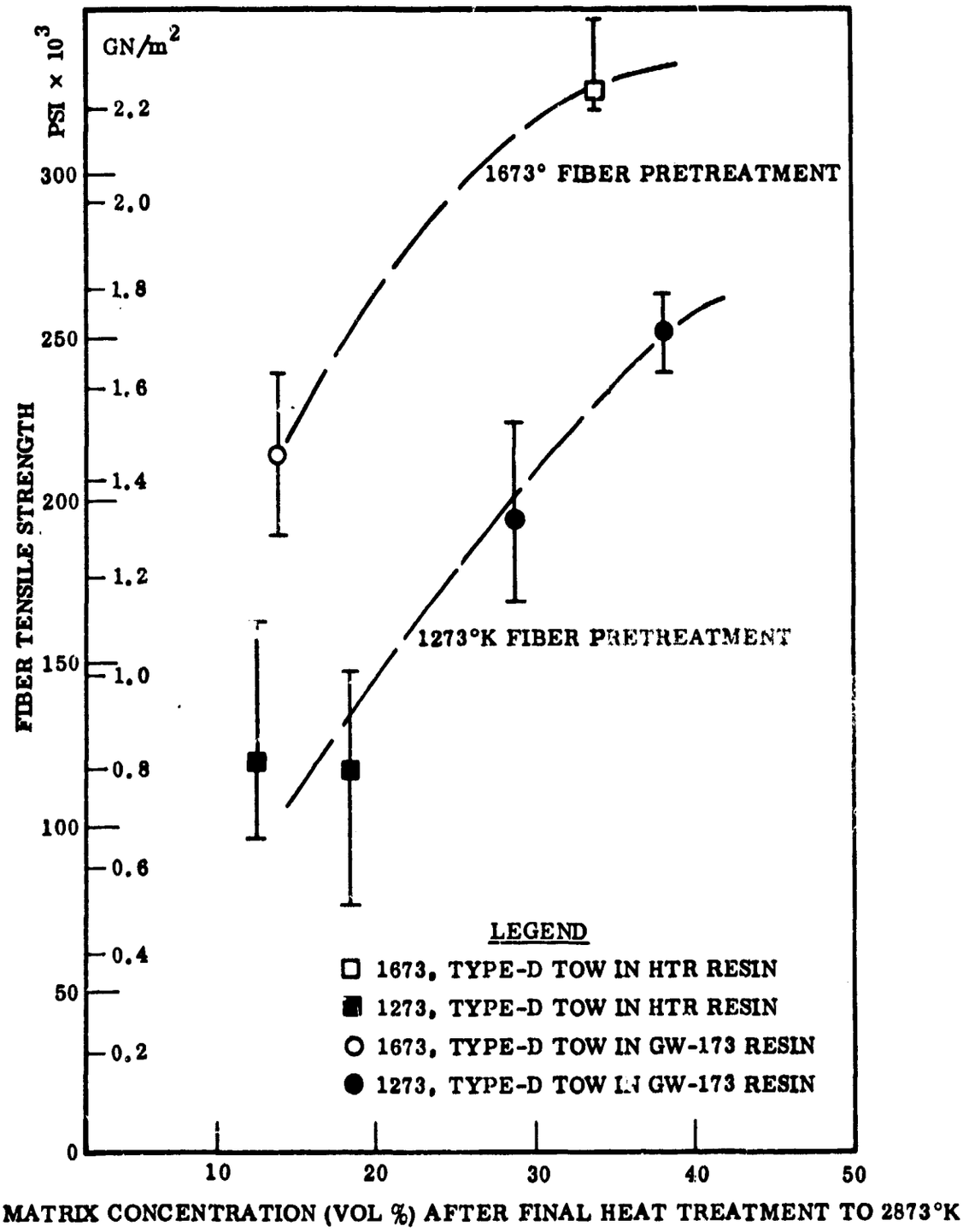


Figure 27. - Effect of Matrix Concentration on Tensile Strength of Copyrolysed Monofilaments, Type-D Tow in Various Matrices

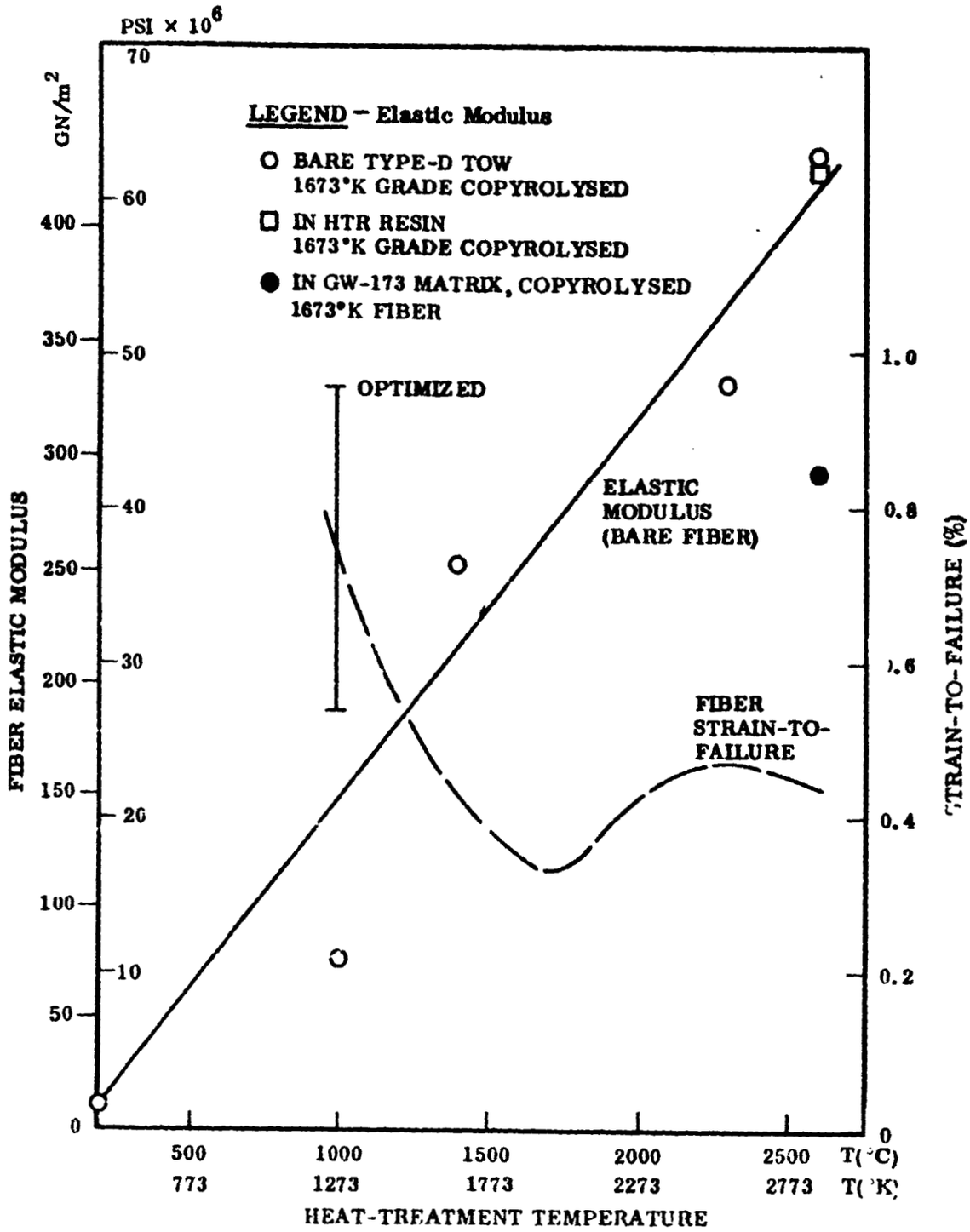


Figure 28. - Properties of Type-D Tow as a Function of Heat-Treatment Temperature

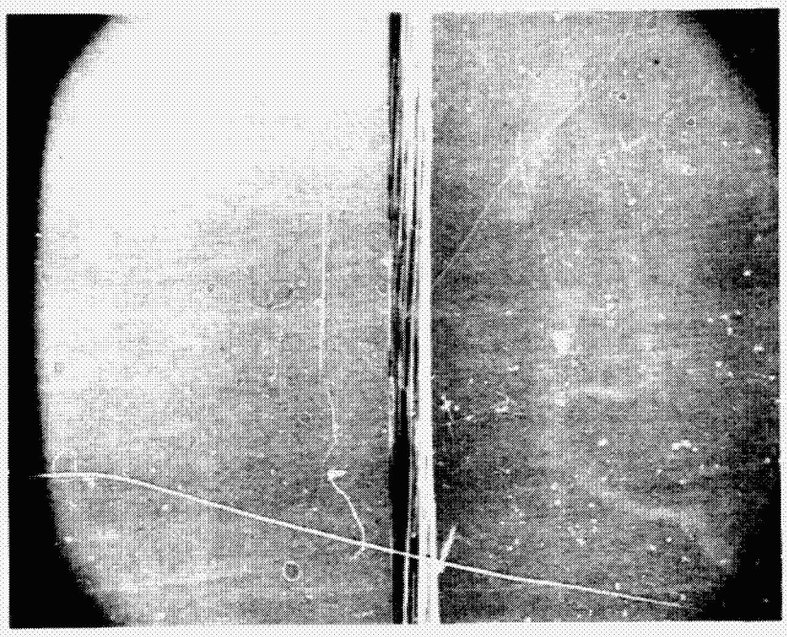
Table XX. – UTILIZATION OF FIBER PROPERTIES 1673°K TYPE-D TOW COPYROLYSED IN GW-173 MATRIX

Final Heat-Treatment Temperature (°K)	Function	Tensile Strength of As-Cured Fiber (σ_f)		Tensile Strength of Pyrolysed Monofilament		Strain-to-Failure (%)		Predicted Tensile Strength (σ^T)[a]		Predicted Value (%)
		(GN/m^2)	($psi \times 10^3$)	(GN/m^2)	($psi \times 10^3$)	Fiber (ϵ_f)	Matrix (ϵ_m)	(GN/m^2)	($psi \times 10^3$)	
2,273[b]	Average	1.630	236.3	0.896	129.9[b]	0.42	0.425	1.629	236.3	34.8
	Maximum	1.680	272.0	1.245	180.6			1.875	272.0	66.4
2,573[b]	Average	1.908	276.7	1.256	182.1[b]	0.56	0.435	1.482	214.9	84.7
	Maximum	2.030	294.5	1.287	187.7			1.573	228.1	81.9
2,873[c]	Average	1.865	270.5	1.726	250.2[c]	0.43	0.44	1.865	270.5	92.5
	Maximum	1.969	285.6	1.742	252.6			1.969	285.6	88.4

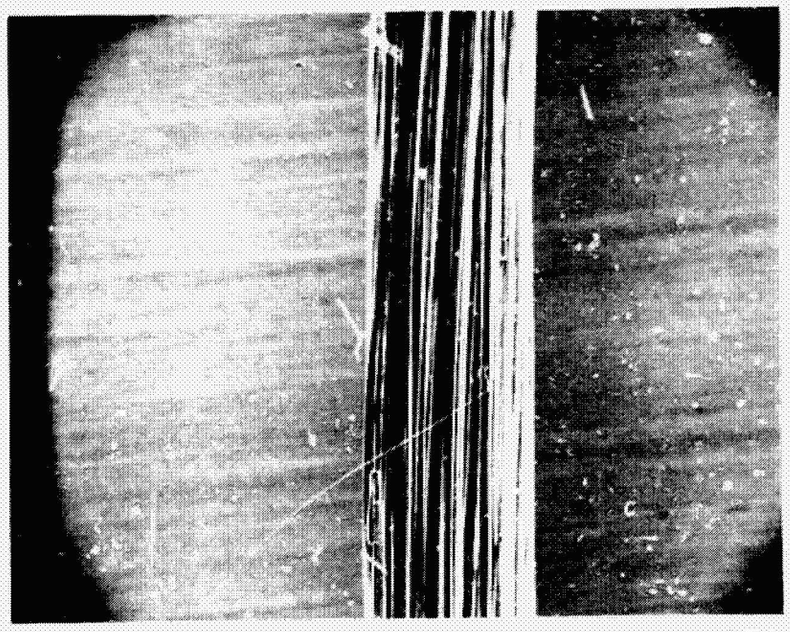
(a) Predicted Tensile Strength $= \sigma^T = \sigma_f \cdot (\epsilon_m/\epsilon_f)$.

(b) Results obtained prior to optimization.

(c) Results obtained after optimization.



35×



150×

Figure 29. - Bundle Collimation, 1673 °K Type-D Tow, in HTR Resin, Copyrolysed to 2873 °K

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1500×

Figure 30. - Surface of 1673 K Type-D Tow in HTR Resin, Copyrolysed to 2873 K, 1500×

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Type-D tow has one disadvantage – filaments are not as readily wetted as Type-C tow, so that bundle impregnation tends to be somewhat inconsistent. However, this was corrected, at least in part, by mechanical separation of individual filaments, resulting in substantial improvements in monofilament properties. Further improvements might have been achieved by chemical treatment to etch the surfaces of the filaments used.

4.4 MONOFILAMENT PRODUCTION

Because of time limitations and the long process schedules required in some cases – for example, 4.86×10^5 sec (135 hr) were required to copyrolyse and heat-treat Type-C tow in GW-173 matrix to 2873°K under optimum conditions – process optimization and monofilament production runs were in some cases made concurrently. Consequently, in the latter optimization studies, composite monofilaments were produced in sufficient quantities for shipment provided that they met the following acceptance criteria.

Criteria for acceptance were a composite tensile strength of 1.38 GN/m^2 (200,000 psi) or greater and a composite modulus of about 280 GN/m^2 (40×10^6 psi). The composite monofilament diameter required was 2 to 15 mils. Lengths of 0.2 to 1 m were acceptable, and a round configuration for the composite monofilament was preferred. Monofilaments were produced in approximately 0.3-m lengths.

Properties of the composite monofilaments shipped are listed in Table XXI. Monofilaments designated T, W, and DD were a series of runs produced from Thornel 75 in HTR resin using the optimized processing cycle, i.e., with 30-percent HTR resin in methyl ethyl ketone solution and combined pyrolysis and heat treatment in a continuous 8.65×10^4 sec (24 hr) cycle to 2873°K. Monofilaments designated T were used for characterization studies, i.e., evaluation of size effects, types of fracture failure, and elastic modulus. The maximum composite tensile strength of Type-T was 1.495 GN/m^2 (216,800 psi); the composite elastic modulus was 302 GN/m^2 (43.7×10^6 psi).

Fibers of Type-W and Type-DD were two lots produced subsequently to Type-T. With each succeeding run, the average tensile strength increased and the data scatter decreased; i.e., the standard deviation decreased. The average composite tensile strength of fibers of Type-W was 1.403 GN/m^2 (203,600 psi) ± 0.081 GN/m^2 (11,800 psi). The average composite tensile strength of fibers of Type-DD was 1.449 GN/m^2 (210,200 psi) ± 0.068 GN/m^2 (9,800 psi). The maximum composite tensile strength obtained by matrix improvement and conventional pyrolysis was with Thornel 75 and HTR resin (monofilaments designated W), in which the maximum tensile strength obtained was 1.511 GN/m^2 (219,200 psi).

Fibers of Type-BB were the best of composite monofilaments produced by copyrolysis. These were produced from 1673°K Type-D tow in HTR matrix, copyrolysed and heat-treated to 2873°K. The maximum composite tensile strength was 1.532 GN/m^2 (222,200 psi). The composite elastic modulus was 293 GN/m^2 (42.5×10^6 psi).

Fibers of Type-Z were the best of the copyrolysis series produced from Type-D tow in GW-173 matrix. The maximum composite tensile strength was 1.375 GN/m^2 (199,400 psi); the composite elastic modulus was 264 GN/m^2 (38.2×10^6 psi).

TABLE XXI. PROPERTIES OF COMPOSITE MONOFILAMENTS, MONOFILAMENT PRODUCTION

Monofilament Designation	Fiber Type	Matrix Type	Final Heat Treatment Temperature (°K)	Monofilament Density (gm/cc)	Vol. % Matrix	Composite Monofilament Diameter		Function	Tensile Strength				Electric Modulus			
									Fiber		Composite		Fiber		Composite	
						(10^{-5} m)	(mils)		(N/m^2)	(10^3 psi)	(GN/m^2)	(10^3 psi)	(GN/m^2)	(10^6 psi)	(GN/m^2)	(10^6 psi)
T	Thornel 75	HTR	2873	1.80	34 to 43 39.8 Average	25.0	10.2	Maximum	2.279	330.6	1.495	216.8				
								Average	2.178	315.9	1.371	198.9	460	66.6	302	43.7
								Minimum	1.995	289.3	1.263	183.2				
								Standard Deviation	0.119	17.3	0.092	13.4				
W	Thornel 75	HTR	2873	1.80	30.3	25.2	9.9	Maximum	2.187	314.1	1.511	219.2	–			
								Average	2.023	293.4	1.403	203.6	–	–	–	–
								Minimum	1.880	272.7	1.304	189.2				
								Standard Deviation	0.110	16.5	0.081	11.8				
DD	Thornel 75	HTR	2873	1.76	31.9	24.0	9.56	Maximum	2.234	324.0	1.496	217.0				
								Average	2.144	311.0	1.449	210.2	–	–	–	–
								Minimum	1.960	272.7	1.367	198.2				
								Standard Deviation	0.150	21.8	0.068	9.8				
Z	1673°K Type D Tow	GW-17J	2873	1.98	13.5	16.0	6.42	Maximum	1.644	238.4	1.375	199.4				
								Average	1.555	224.9	1.331	193.1	290	43.3	204	30.2
								Minimum	1.423	206.4	1.273	184.7				
								Standard Deviation	0.094	13.6	0.048	7.0				
BB	1673°K Type D Tow	HTR	2873	1.80	36.1	19.05	7.50	Maximum	2.405	348.3	1.532	222.2				
								Average	2.255	327.0	1.434	208.0	426	61.8	293	42.3
								Minimum	2.110	306.1	1.392	202.0				
								Standard Deviation	0.110	15.9	0.058	12.8				
GG	Thornel 75	GW-173	1273	–	37.0	25.1	9.88	Maximum	1.411	204.6	0.867	125.6				
								Average	1.227	179.4	0.777	112.8				
								Minimum	0.728	105.3	0.456	66.2				
								Standard Deviation	0.259	37.6	0.163	23.6				

Early in the program, the best technology developed in the antecedent contract was used to produce one lot of monofilament, as requested by the NASA-project monitor. This lot, designated GG, was produced from Thornel 75, pregged with 30-percent GW-173 in methanol and pyrolysed to 1273°K in the standard 2.59×10^5 sec (72 hr) cycle. The maximum composite tensile strength was 0.887 GN/m^2 (128,600 psi).

Composite monofilaments with varying gage lengths were tested to determine the possible effect of flaws such as matrix cracks perpendicular to the filament axis formed at discrete intervals along monofilament length, since such cracks are commonly found in conventional pyrolysis (Ref. 6).

With HTR resin, which has a high char yield and does not produce macroscopic flaws during pyrolysis and heat treatment, the measured tensile strength is relatively independent of gage length (Table XXII). There was greater variation within given gage length than there was between specimens of different gage lengths; i.e., gage length had no significant effect. With the Type-GG specimens, which formed pyrolysis cracks, gage length had a significant effect. With the shorter gage length, both maximum and average composite tensile strength increased from 0.887 and 0.777 GN/m^2 (128,600 and 112,800 psi) in the standard specimen to 1.092 and 1.070 GN/m^2 (158,400 and 155,200 psi), respectively, in the shorter specimen, indicating that as the number of flaws per gage length increases, the tensile strength decreases.

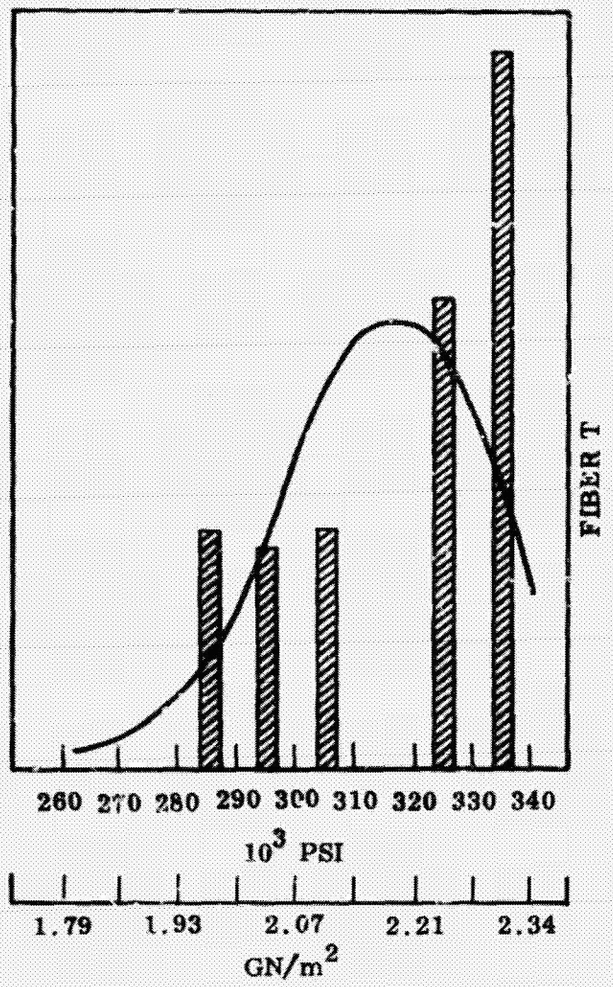
The effect of matrix optimization to reduce pyrolysis cracking is shown by histograms of the individual tensile results (Figure 31). With the technology developed previously [Ref. 6] (Thornel 75 in GW-173 matrix, Type-GG monofilament), the data scatter is broad and a single low value – 0.456 GN/m^2 (66,200 psi) probably associated with excessive matrix cracking or with damage – significantly reduces the average tensile strength. Data scatter with Type-T monofilament (Thornel 75 in HTR matrix) is much less pronounced and the histogram is narrower, thus reflecting greater reproducibility.

To summarize, matrix modification using high-char-forming HTR resin combined with process optimization resulted in carbon-carbon monofilaments free of deleterious cracks and with composite tensile strength greater than 1.38 GN/m^2 (200,000 psi) and an elastic modulus of 264 GN/m^2 (38×10^6 psi) or greater. The fiber diameter ranged from $(16.0 \text{ to } 25.9) \times 10^{-5}$ m (0.00642 to 0.0102 inches). Monofilaments produced from Thornel 75 roving had a twist to them and were not round in cross section. Monofilaments produced from Type-D tow were round in cross section.

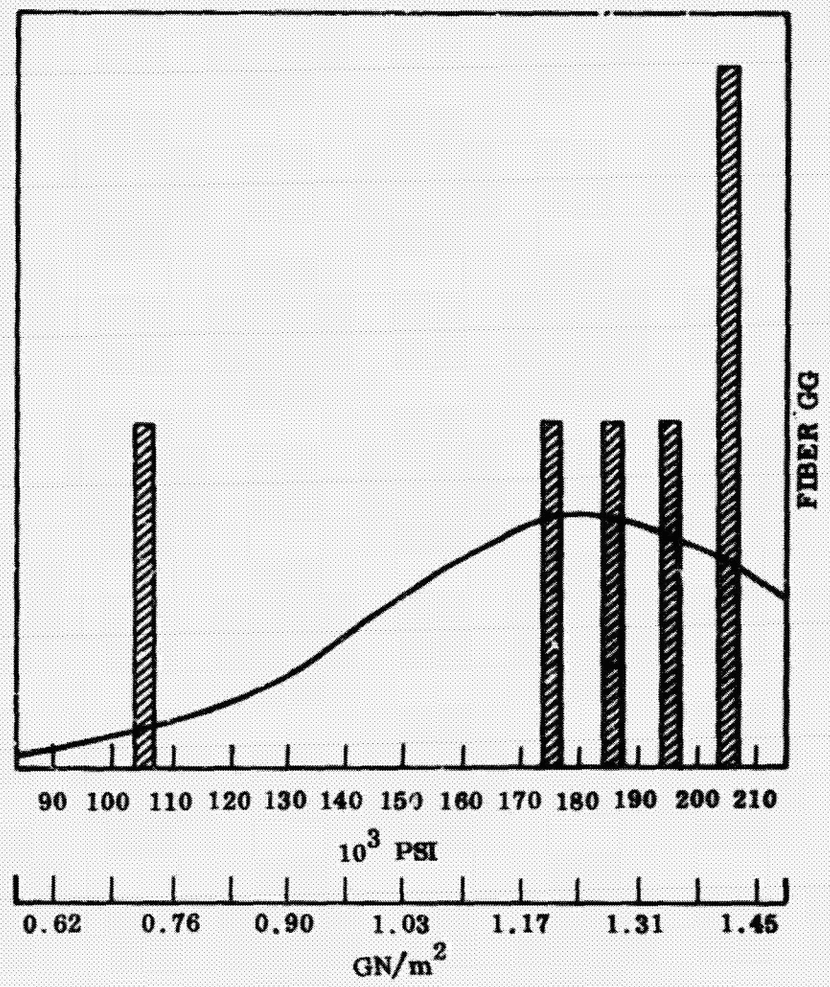
TABLE XXII. EFFECT OF GAGE LENGTH ON MEASURED TENSILE STRENGTH

Monofilament Designation	Matrix	Gage Length (m)	No. of Tests	Function	Tensile Strength Fiber Area		Tensile Strength	
					(GN/m^2)	($psi \times 10^3$)	(Fiber + Matrix) (GN/m^2)	(Fiber + Matrix) ($psi \times 10^3$)
T	HTR	1.27×10^{-2}	3	Maximum	2.279	330.6	1.495	216.8
				Average	2.170	314.7	1.349	195.6
				Minimum	1.995	289.3	1.263	183.2
				Standard Deviation	0.154	22.3	0.126	18.4
T	HTR	2.54×10^{-2}(a)	3	Maximum	2.278	330.4	1.473	213.6
				Average	2.188	317.4	1.359	197.1
				Minimum	2.008	291.3	1.287	186.7
				Standard Deviation	0.156	22.6	0.185	26.9
T	HTR	5.08×10^{-2}	2	Maximum	2.208	320.3	1.448	210.0
				Average	2.173	315.1	1.420	206.0
				Standard Deviation	0.050	7.3	0.055	8.0
T	HTR	All Spec.	8	Maximum	2.279	330.6	1.495	216.8
				Average	2.177	315.8	1.371	198.9
				Minimum	1.995	289.3	1.263	183.2
				Standard Deviation	0.119	17.2	0.093	13.5
GG	GW-173	0.625×10^{-2}	2	Maximum	1.738	252.1	1.092	158.4
				Average	1.703	247.2	1.070	155.2
				Standard Deviation	0.051	7.4	0.032	4.65
GG	GW-173	2.54×10^{-2}(a)	7	Maximum	1.411	204.6	0.887	128.6
				Average	1.237	179.4	0.777	112.8
				Minimum	0.726	105.3	0.456	66.2
				Standard Deviation	0.259	37.6	0.163	23.6

(a) Standard gage length.



a. Histogram of Tensile Strength Values Obtained With Fiber T, Thornel 75 in HTR Matrix



b. Histogram of Tensile Strength Obtained With Fiber GG, Thornel 75 in GW-173 Matrix

Figure 31. - Distribution of Fiber Tensile Strength Measurements in Two Composite Monofilaments

Section 5

GENERAL DISCUSSION

It had been previously found (Ref. 6) in the fabrication of high tensile strength, high-elastic modulus carbon composite monofilaments by resin impregnation of multifiber bundles followed by pyrolysis, that the properties of the pyrolysed matrix precursors can seriously reduce the properties of the composite monofilaments. Two problem areas were found: (1) the inherently low strain-to-failure of most pyrolysed matrices, and (2) the development of pyrolysis cracks in the matrix induced by dissimilar shrinkage between fiber and matrix during pyrolysis.

Two approaches to overcoming these problems were suggested. These were: (1) matrix modification to increase char yield and strain-to-failure, and (2) minimization of differential shrinkage cracks by the development of a process, designated copyrolysis, in which the partially processed carbon fiber precursors are impregnated with suitable matrix precursors and then both are pyrolysed and heat-treated together to produce a fully carbonized monofilament.

Both approaches were used successfully; i.e., pyrolysis cracking could be eliminated either by the use of high-char forming HTR resins or by copyrolysis. Mismatch between fiber-and-matrix strain-to-failure preventing full utilization of fiber tensile strength has been overcome by increasing matrix strain-to-failures from 0.31 to 0.47 percent and by using high-strength, high-modulus carbon fibers such as Thornel 75 with a strain-to-failure of the same magnitude – 0.5 percent.

In matrix modification studies, six matrix precursors were investigated either in conventional pyrolysis or copyrolysis. Conventional pyrolysis was used only with thermosetting resins which have a high char yield and cause little matrix cracking. The high average composite tensile strength obtained in conventional pyrolysis was with Thornel 75 in HTR matrix. After process optimization, the highest average composite tensile strength was 1.449 GN/m^2 (210,200 psi), equivalent to a fiber tensile strength of 2.144 GN/m^2 (311,000 psi). The composite elastic modulus of monofilaments of this type was 302 GN/m^2 (43.7 x 10^6 psi), equivalent to a fiber elastic modulus of 460 GN/m^2 (66.6 x 10^6 psi).

In copyrolysis, the highest tensile properties were obtained with a polyacrylonitrile fiber, Type-D tow, preheat-treated to 1673°K, impregnated with HTR resin and heat-treated to 2873°K, when fiber and matrix strain-to-failure were the same. After copyrolysis optimization, the average composite tensile strength was 1.438 GN/m^2 (208,600 psi), equivalent to a fiber tensile strength of 2.255 GN/m^2 (327,000 psi). The composite elastic modulus was 293 GN/m^2 (42.5 x 10^6 psi), equivalent to a fiber elastic modulus of 426 GN/m^2 (61.9 x 10^6 psi).

Table XXIII summarizes the utilization of fiber tensile strength of Thornel 75 after pyrolysis and heat treatment of two matrix precursors: (1) GW-173, a modified phenolic with a char yield of 70 percent, and (2) in HTR matrix a highly cross-linked

TABLE XXIII. - UTILIZATION OF FIBER TENSILE PROPERTIES OF THORNEL 75[a] IN TWO MATRIX PRECURSORS

Fiber Designation	Final Heat Treatment Temperature (°K)	Matrix		Function	Tensile Strength Pyrolysed and Heat Treated Fiber[a] (Fiber Area)		Strain-To Failure (%)	Predicted Tensile Strength[c] (Fiber Area)		% of Predicted Value	Composite Tensile Strength					(E_m) Used	
		Type	Vol. % After Final Heat Treatment								Measured		Predicted[f]		Percent of Predicted		
					(GN/m²)	(10³ psi)	(ϵ_m)[b]	(GN/m²)	(10³ psi)		(GN/m²)	(10³ psi)	(GN/m²)	(10³ psi)		(GN/m²)	(10³ psi)
GG	1273	GW-173	37.0	Average	1.237	179.4	0.31[e]	1.538	223.2	80.4	0.777	112.8	1.073	155.7	72.4	55.0	8.0[g]
				Maximum	1.411	204.6	0.41[d]	2.137	310.0	66.0	0.887	128.6	1.418	205.8	62.4		
HH	1160	HTR	58.2	Average	1.681	243.8	0.36[e]	1.787	259.2	94.0	0.702	101.8	0.894	127.8	78.5	55.0	8.0 est
				Maximum	1.852	268.6		1.877	272.2	98.7	0.773	112.1			86.5		
I	2573	HTR	58.4	Average	2.250	326.4	0.45[e]	2.234	324.0	100.0	0.938	136.1	1.125	163.2	83.4	60.0	8.7 est
				Maximum	2.322	336.8		2.346	340.2	99.0	0.967	140.2			85.9		
R	2873	HTR	48.5	Average	2.407	349.2	0.47[e]	2.333	338.4	100.0+	1.241	180.0	1.383	202.1	89.1	62.5	9.07
				Maximum	2.436	353.3		2.450	355.3	99.4	1.256	182.1			90.1		
T	2873	HTR	39.8	Average	2.178	315.9	0.47[e]	2.333	338.4	93.4	1.371	198.9	1.580	229.2	86.8	62.5	9.07
				Maximum	2.279	330.6		2.450	355.3	93.1	1.495	216.8			94.6		
W	2873	HTR	30.3	Average	2.023	293.4	0.47[e]	2.333	338.4	86.7	1.403	203.6	1.763	256.6	79.7	62.5	9.07
				Maximum	2.166	314.1		2.450	355.3	88.4	1.511	219.2			84.8		
DD	2873	HTR	31.9	Average	2.144	311.0	0.47[e]	2.333	338.4	91.9	1.449	210.2	1.773	253.7	81.7	62.5	9.07
				Maximum	2.234	324.0		2.450	355.3	91.2	1.496	217.0			84.4		
S	2873	HTR	24.4	Average	1.459	211.6	0.47[e]	2.333	338.4	62.5	1.093	158.5	1.908	276.8	57.2	62.5	9.07
				Maximum	1.837	266.5		2.450	355.3	75.0	1.360	197.2			71.2		

(a) ϵ_f = bare fiber strain-to-failure = 0.60% for Thornel 75.

(b) ϵ_m = matrix strain-to-failure.

(c) δ_T = predicted tensile strength = $\frac{\epsilon_m}{\epsilon_f}\delta_f$ where δ_f = bare-fiber strength, $(\delta_f)_{avg}$ = 2.482 GN/m² (360,000 psi). $(\delta_f)_{max}$ = 2.606 GN/m² (378,000 psi).

(d) ϵ_m = strain-to-failure of monolithic matrix = 0.41 for glassy carbon matrix produced from GW-173 resin (Ref. 5).

(e) $(\epsilon_m)_c$ = strain-to-failure of matrix in composite estimated from ratio of monofilament tensile strength to monofilament elastic modulus as determined on three types of monofilaments processed to reference temperature (Ref. 41).

(f) σ_c = $E_c \cdot \epsilon_c = (E_f V_f + E_m V_m)(\epsilon_m)_c$.

(g) From Fig. 22 (p. 60).

thermosetting resin with a char yield of 90 percent. Predicted tensile strength of each monofilament after pyrolysis or graphitization were calculated in the following manner, utilizing the rationale previously developed (Ref. 5). An efficiency factor, F, was calculated from the ratio of the matrix strain-to-failure, ϵ_m, to the fiber, ϵ_f strain-to-failure. The predicted tensile strength, σ_T, is given by the product of the efficiency factor times the tensile strength of the bare fiber determined in epoxy or the as-cured matrix precursor.

With GW-173 matrix, the strain-to-failure of the pyrolysed monolithic matrix is 0.41 ± 0.06 percent (Ref. 6), but when processed in composite monofilament form, the presence of pyrolysis cracks reduces the effective failure strain to 0.30 percent or less. Calculated on this basis, 80.4 percent of the predicted tensile strength was obtained with monofilaments of type GG. If the matrix strain-to-failure were 0.41 percent, only 66 percent of the fiber tensile strength theoretically obtainable was utilized.

When processed in monolithic form, HTR resin forms a hard glasslike carbon. However, when processed to high temperatures (2873°K) in contact with graphite fibers, a fine granular graphitic phase nucleates at the fiber surface, having the appearance of a pyrolytic graphite (Figure 16). Matrix strain-to-failure was therefore estimated from composite data, assuming that the failure strain measured in the composite is equivalent to the matrix strain-to-failure. Then, in the series of monofilaments designated HH, I, and R, the matrix strain-to-failure increases with heat-treatment temperature from 0.36 percent to 0.45 percent, to 0.47 percent with increasing heat-treatment temperature of 1160°K, 2578°K, and 2873°K, respectively, i.e., with degree of graphitization.

Fiber tensile strength, both predicted and measured, increases with heat-treatment temperature. When Thornel 75 was pregged with HTR resin and pyrolysed to 1160°K, the maximum fiber tensile strength was 1.852 GN/m^2 (268,600 psi). After pyrolysis and heat treatment to 2573°K, the maximum fiber tensile strength observed was 2.322 GN/m^2 (336,800 psi), equivalent to a composite tensile strength of 0.967 GN/m^2 (140,200 psi), and 99-percent utilization of the fiber tensile strength. Examination of the fracture surface showed a fibrous texture and excellent bonding, as shown by the replication of the crenulated filament surface and adherence of matrix fragments to filament surfaces (Figure 32). After pyrolysis and heat treatment to 2873°K, the maximum fiber tensile strength was 2.436 GN/m^2 (353,300 psi), equivalent to a composite tensile strength of 1.241 GN/m^2 (180,000 psi) and 99.4 utilization of the fiber tensile strength. The nature of the fracture was fibrous (Figure 33). Small discontinuities, α, occur in the matrix where it is packed between the filaments. Such discontinuities may account for the pseudoplasticity observed with monofilaments of this type. Full utilization of fiber tensile properties is confirmed by the presence of a single microfibril at point β. Such fibrils are regions of stacked graphite layers forming high-density regions within the graphite filament and are observed when individual filaments pull apart in tension.

As examination of the data in Table XXIII indicates, strength utilization in monofilaments of Thornel 75 in HTR matrix heat treated to 2873°K is dependent on matrix concentration. Fiber strength utilization increases with matrix concentration and reaches a maximum at 50-percent matrix (Figure 34). At a low matrix volume fraction, 0.244, fiber tensile strength was only 1.459 GN/m^2 (211,600 psi), equivalent to 62.5-

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Figure 32. - Fracture Surface of Thornel 75 in HTR Matrix, Heat-Treated to 2573°K, 4000×, Fiber Tensile Strength = 2.322 GN/m^2 (336,800 psi)

Figure 33. - Fracture Surface of Thornel 75 in HTR Matrix Heat-Treated to 2873 K, 4000×, Fiber Tensile Strength = 2.440 GN/m^2 (353,300 psi)

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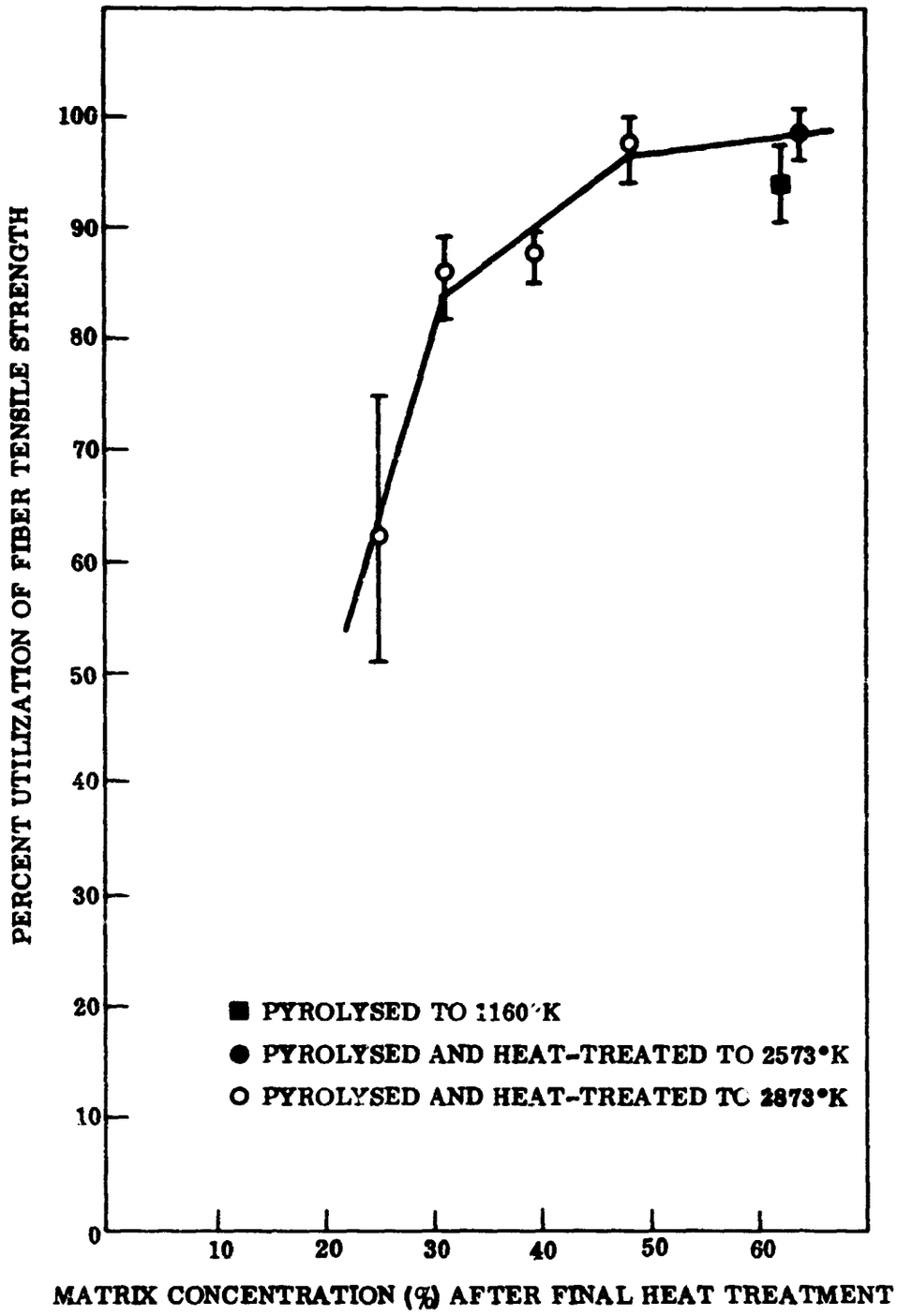

Figure 34. - Utilization of Fiber Tensile Properties, Thornel 75 in HTR Matrix, Various Heat Treatments

percent utilization of the bare fiber tensile strength and a composite tensile strength of 1.093 GN/m^2 (158,500 psi). Microscopic examination of the monofilament of this type, S, showed poor bundle infiltration and matrix cracking at the monofilament surface. At intermediate matrix concentration of 30.3 percent, average fiber tensile strength was 2.023 GN/m^2 (293,400 psi), equivalent to a strength utilization of 86.7 percent and a composite tensile strength of 1.403 GN/m^2 (203,600 psi). Examination of the micrograph in cross section showed excellent fiber-matrix bonding and a sheath of matrix around the filament bundle (Figure 35). At higher matrix concentration, 48.5 percent, the average fiber tensile strength was 2.407 GN/m^2 (349,200 psi), equivalent to a strength utilization greater than 100 percent and a composite tensile strength of 1.241 GN/m^2 (180,000 psi). Examination of the monofilaments showed complete bundle infiltration and excess matrix at the filament surface.

Composite tensile strength, σ_c, can be predicted from the properties of the monofilament constituents as follows:

$$\sigma_c = E_c \cdot \epsilon_c = (E_f V_f + E_m V_m) \epsilon_c$$

where

E_c = the predicted composite modulus

ϵ_c = the strain-to-failure in the composite

F_f = elastic modulus of the bare fiber,
= 517 GN/m^2 (75×10^6 psi) for Thornel 75

V_f = fiber volume fraction

E_m = matrix modulus

V_m = volume fraction matrix

The elastic modulus of HTR matrix in monofilament pyrolysed and heat-treated to 2873°K was calculated from the measured composite and fiber tensile moduli as follows:

$$(E_{HTR})_{2873°K} = \frac{E_c - E_f V_f}{V_m}$$

and was found to equal 62.5 GN/m^2 (9.07×10^6 psi). Similarly, the tensile strength of HTR in the monofilament after heat treatment to 2873°K is given by

$$(\sigma_{HTR})_{2873°K} = E_m (\epsilon_m)_c = 0.293 \text{ GN/m}^2 \text{ (42,600 psi).}$$

Unlike other matrix precursors previously evaluated (Ref. 6), the tensile strength of HTR when processed in the composite is sufficiently strong to make an effective contribution to composite monofilament properties.

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Figure 35. - Cross Section of Type-W Monofilament. Polarized Light, 1000×

Predicted and measured composite tensile strengths are listed in columns 9 and 10 of Table XXIII. With GW-173 matrix, the measured tensile strength is 89 percent of that calculated on the basis of a matrix strain-to-failure of 0.41 percent, but 100 percent when the estimated strain-to-failure is reduced to 0.31 percent to account for matrix cracking. With HTR matrix, correlation between measured and predicted values improves with heat-treatment temperature. The effect of volume fraction matrix on measured and predicted composite tensile strength at the optimum heat-treatment temperature of 2873°K is shown in Figure 36. Predicted composite tensile strength increases with volume fraction fiber. Experimental results approach predicted values at fiber volume fraction of 50 to 68 percent, i.e., increase with volume fraction fiber. Maximum composite tensile strength is reached at fiber volume fractions between 60 and 70 percent.

At more than 70-percent fiber, actual composite tensile strength decreased rapidly. As previously discussed, this decrease in monofilament tensile strength is due to poor filament impregnation, and inadequate fiber-matrix bonding throughout the module cross section so that there is poor load transfer between fiber and matrix. Moreover, where there is poor filament impregnation, the monofilament bundle is more susceptible to damage and there is greater data scatter with low values associated with such damage.

Copyrolysis experiments were carried out using two types of fiber precursors, both generated from polyacrylonitrile. One, designated Type-C tow,* had filaments which are round in cross section; the other, designated Type-D tow, had filaments which had a dog-bone shape. Although it was not clear to us when the studies were initiated, this filament cross section significantly affects the fiber tensile properties which can be obtained by graphitization. The manner in which the filament is spun affects the filament cross section, its structure, degree of preferred orientation, porosity, and microheterogeneity. Type-C tow* is produced from copolymer of polyacrylonitrile and methyl methacrylate by wet spinning (Ref. 38). When wet-spun fibers are round in cross section, the spinning conditions are such that the diffusion rate of solvent inward to diffusion rate outward is equal, and the resultant fibers have a high specific volume and high internal surface area. Such fibers have a microheterogeneity of the order of 1 to 10 nanometers, an amorphous texture, and a significant volume of open pores in the 10^2 to 10^4 nanometer range, detectable by mercury porosimetry. As shown by Le Maistre and Diefendorf (Ref. 33), a radial structure develops in Courtelle filaments, Figure 37, with a fully stabilized sheath at the outer surface. Voids developed at the interior when pyrolysis was carried out at too rapid a rate. Such flaws are responsible for a deterioration in fiber tensile strength (Ref. 23). Increasing heat-treatment temperature enhances the radial structure, causes a straightening of the basal planes parallel to the fiber axis, and reduces the interfibrillar coupling present in the lower-temperature intermediate-modulus carbon fibers. Furthermore, the radial microstructure causes residual stresses to develop upon cooling from the heat-treatment temperature; it accentuates decoupling (Ref. 33) and reduces fiber strain-to-failure.

This deterioration in properties with high-temperature heat-treatment was observed by us both with bare fibers and copyrolysis. The maximum bare fiber tensile strength obtained with Type-C tow was 2.17 GN/m^2 (316,000 psi) which was reached after carbonization at 1673°K, but the fiber strain-to-failure was 0.842 percent, and the elastic modulus was only 259 GN/m^2 (37.5×10^6 psi). After graphitization at 2873°K, the tensile strength degraded to 1.606 GN/m^2 (233,000 psi), the elastic modulus was 331 GN/m^2 (60×10^6 psi), and the strain-to-failure was 0.39 percent.

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*Type-C tow, obtained from Rolls-Royce, Ltd., England is nominally a type of Courtelle tow manufactured by Courtauld, Ltd., England.

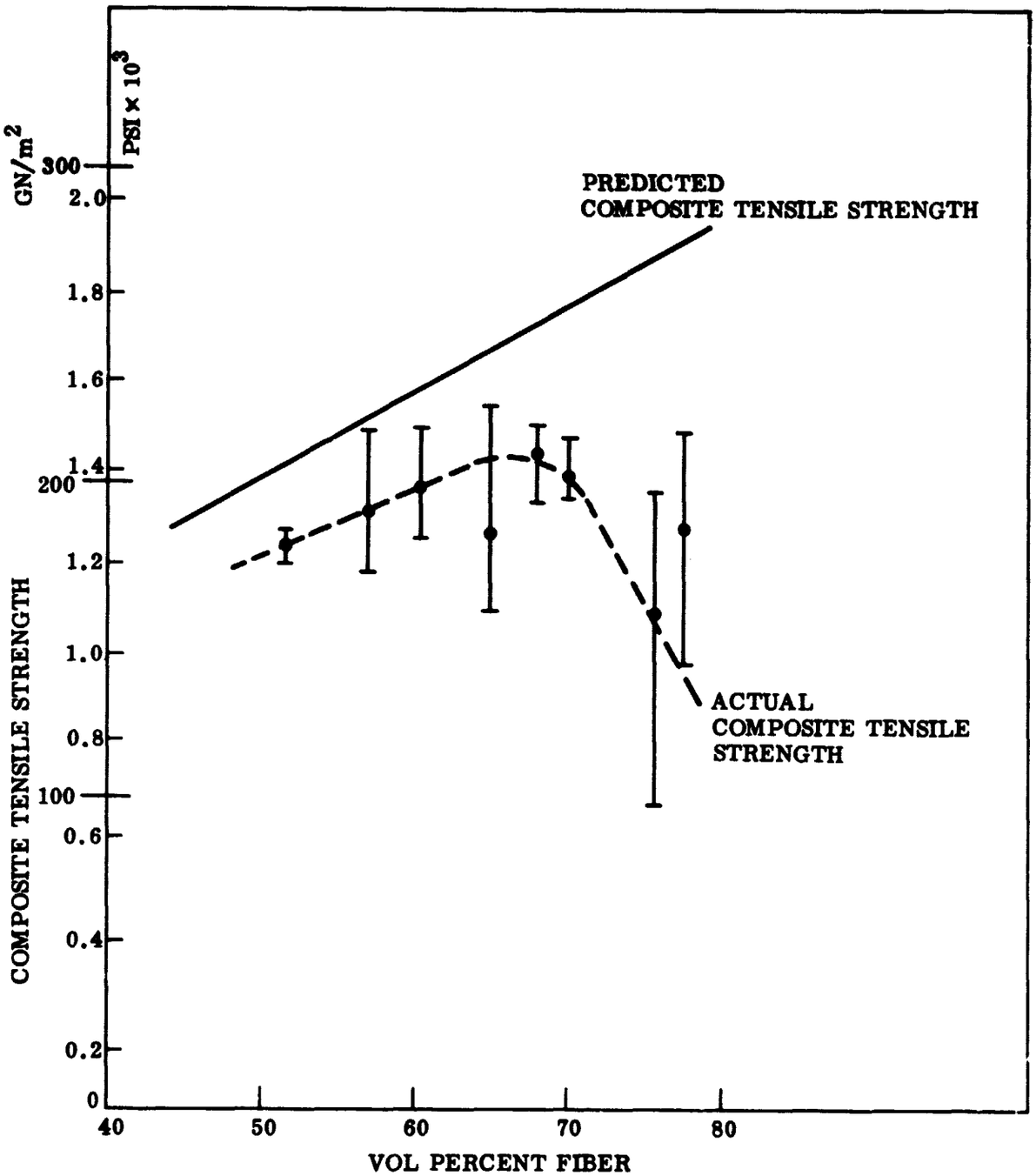


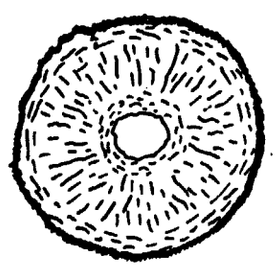
Figure 36. - Effect of Matrix Concentration on Predicted and Measured Composite Tensile Strength, Thornel 75 in HTR Matrix, Heat-Treated to 2873°K

a. Fully Stabilized Courtelle

Basal planes have a preferred orientation parallel to the outer surface and the exterior is more ordered than the interior.

b. Slowly Carbonized at a Heating Rate of 0.833°K/60 sec to 1273°K

The outer stabilized skin retains the onion microstructure, while a radial microstructure is observed to form in the unstabilized core.



c. Carbonized at Rapid Rates (400°K/60 sec).

Voids and defects develop at the center of the fiber.

Figure 37. - Schematic Microstructure of Courtelle-Type Monofilament (Ref. 33)

In copyrolysis experiments, the objective was to develop both fiber tensile strength and elastic modulus, while minimizing the deleterious effects of matrix shrinkage. Copyrolysis experiments with Type-C tow were carried out in various matrix precursors using fiber pretreatments ranging from 473 to 1273°K. It was found that a pretreatment temperature of 1273°K was necessary to develop the fiber texture and preferred orientation associated with optimum tensile strength and elastic modulus. With copyrolysed monofilaments produced from Type-C tow, it was found that the diameter of individual filaments was larger when pyrolysed in the matrix than when pyrolysed as base fiber; i.e., the matrix was inhibiting pore collapse during pyrolysis and the development of preferred orientation necessary to develop optimum tensile properties.

Consequently, copyrolysis optimization studies with Type-C tow were done with a fiber pretreatment of 1273°K. The results of such optimization were discussed in detail in Subsection 4.3.

Utilization of fiber tensile strength of 1273°K Type-C tow in two matrix precursors is indicated in Table XXIV. In GW-173 matrix after slow pyrolysis to 1673°K, the maximum fiber tensile strength is 0.859 GN/m^2 (124,600 psi) equivalent to 80-percent realization of the fiber tensile strength. The maximum composite tensile strength was 0.416 GN/m^2 (60,400 psi), and the composite elastic modulus was 150 GN/m^2 (21.74 x 10^6 psi). Slight improvements are obtained by heat treatment to 2573°K; the maximum composite tensile strength was 0.552 GN/m^2 (80,060 psi), and the composite elastic modulus was 207.3 GN/m^2 (30.07 x 10^6 psi), equivalent to a strength utilization of 66.8 percent. After heat treatment to 2573°K, the composite elastic modulus was 207.3 GN/m^2 (30.07 x 10^6 psi). Examination of the fracture-surface shows a very nodular coarse fiber structure (Figure 12). Failure to realize the predicted fiber tensile strength after high-temperature heat-treatment may be associated in part with matrix cracking but may also be associated with flaws developing in the fiber as a result of copyrolysis, since the gases produced within the PAN fiber must diffuse not only to the filament surface but through the matrix as well. Radial cracking within the filaments may have been accentuated by multiple processing cycles.

Better results were obtained in pitch matrix. After copyrolysis to 1673°K, maximum fiber tensile strength was 0.730 GN/m^2 (106,000 psi); the composite tensile strength was 0.507 GN/m^2 (73,600 psi), and the composite elastic modulus was 192.4 GN/m^2 (27.9 x 10^6 psi). After heat treatment to 2873°K, maximum fiber tensile strength was 0.965 GN/m^2 (140,000 psi), composite tensile strength was 0.760 GN/m^2 (110,000 psi), and elastic modulus was 348 GN/m^2 (50.5 x 10^6 psi). Examination of the fracture surface of this type of monofilament (Figure 13) showed the radial microstructure described by LeMaistre and Diefendorf (Ref. 33).

Type-C tow had two major disadvantages: (1) development of maximum tensile elastic modulus could be obtained only by heat treatment at 2873°K which caused a deterioration in tensile strength, and (2) large bundle diameter which resulted in poor processability enhancing a tendency to develop macroscopic defects. The high-temperature deterioration in tensile strength is inherent in this type of precursor fiber and results from microvoids and lenticular flaws introduced into the precursor fiber during spinning. The porosity and high surface area of Type-C tow probably accounts for the excellent bonding between fiber and matrix observed with low-temperature ($T < 1273°K$) fiber pretreatments. Such bonding, however, results in a brittle fracture and low composite tensile strength.

TABLE XXIV. - UTILIZATION OF FIBER TENSILE PROPERTIES, COPYROLYSIS OF 1273°K TYPE-C TOW IN TWO MATRIX PRECURSORS

Property	GW-173 Resin		396 Pitch		GW-173 Resin		396 Pitch	
Final Heat HTT (°K)	1673		1673		2573		2873	
Matrix Vol. Fraction (%)	51.5		30.5		50.0		21.0	
	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum
Fiber Tensile Strength								
(GN/m^2	0.866	0.869	0.550	0.730	0.702	1.106	0.807	0.967
($psi \times 10^3$)	124.2	124.6	79.9	106.0	101.8	160.4	117.0	140.2
Matrix Strain-To-Failure	0.415		0.3 est(a)		0.43		0.40 (est(a)	
Predicted Tensile Strength(b)								
(GN/m^2)	1.072		0.776		1.656		1.606	
($psi \times 10^3$)	155.6		112.5		240.2		233.0	
Percent Utilization of Fiber Tensile Strength	79.8	80.0	71.0	94.2	42.4	66.8	50.2	60.2
Composite Tensile Strength								
(GN/m^2)	0.415	0.416	0.382	0.507	0.350	0.552	0.635	0.760
($psi \times 10^3$)	60.2	60.4	55.5	73.6	50.8	80.06	92.1	110.2
Composite Elastic Modulus								
(GN/m^2)	150.0		192.4		207.3		348.0	
($psi \times 10^3$)	21.74		27.9		30.07		50.5	
Composite Strain-To-Failure	0.27	0.27	0.16	0.19	0.16	0.26	0.18	0.22
Process Cycle	Slow (See Fig. 19) (I-211, C-101)		Fast (See Fig. 19) (C-95)		Slow (See Fig. 19) (I-211, C-104, C-107)		Fast (See Fig. 19) (C-95, C-97)	

(a) Estimated from bulk graphite data.

(b) Calculated from $\delta_T = \frac{\epsilon_m}{\epsilon_f} \delta_f$ ≡ bare fiber tensile strength as indicated in Table XVIII.

Further improvements might have resulted from modified fiber pretreatments, slower copyrolysis, stretch graphitization, and the use of HTR resin. However, since Type-D tow did not have these disadvantages, further copyrolysis experiments were done with it. Type-D tow* is produced from polyacrylonitrile homopolymer and has a dog-bone configuration. Fibers with a dog-bone configuration are normally produced by dry-spinning. In dry-spinning, one-directional diffusion of the solvent results in rapid solidification of the outer layer followed by additional contraction and collapse to noncylindrical shapes. The dog-bone configuration is obtained when the rate of surface evaporation is much greater than the diffusion of solvent from the interior. The resulting fiber has an outer sheath which is more oriented. The radial texture seen in Courtelle does not develop because the surface-to-volume ratio is higher. Voids at the fiber interior do not develop as readily, and a structure like that illustrated in Figure 38 is formed after complete stabilization. This texture is shown in Figure 14. With this fiber, both tensile strength and elastic modulus increase with increasing heat-treatment temperature. With bare Type-D tow, after heat treatment at 2873°K, the tensile strength obtained initially was 1.86 GN/m^2 (270,000 psi), the elastic modulus was 449 GN/m^2 (62.4×10^6 psi), and a strain-to-failure was 0.43 percent.

Limited low-temperature copyrolysis experiments were done with Type-D tow because preliminary results indicated that such treatment would be no more effective than they were with Type-C tow. For example, as-oxidized stabilized Type-D tow impregnated with HTR resin and copyrolysed to 1273°K had a fiber tensile strength of 0.356 GN/m^2 (51,600 psi). Additional copyrolysis experiments were done with Type-D tow preheat-treated to 1273°K or 1673°K, followed by resin impregnation, pyrolysis, and heat treatment to temperatures ranging from 2273° to 3073°K. As indicated by data reported in Tables XII, XIII, and XIV, tensile strength increased with final heat-treatment temperature to 2873°K in three matrix precursors. Maximum fiber tensile strength of 1673 K Type-D tow pyrolysed and heat treated to 2873°K was 1.497 GN/m^2 (217,000 psi) in HTR matrix, 1.427 GN/m^2 (207,000 psi) in GW-173 matrix, and 1.717 GN/m^2 (249,100 psi) in 396 pitch matrix. These values corresponded to composite tensile strengths of 1.154 GN/m^2 (167,100 psi) in HTR matrix, 0.720 GN/m^2 (104,400 psi) in GW-173 matrix, and 0.816 GN/m^2 (118,400 psi) in pitch matrix.

Optical examination of the monofilaments indicated that bundle impregnation and failure to obtain adequate wetting was associated with lower tensile strengths; a plot of tensile strength versus matrix concentration indicated that fiber tensile strength increased with matrix concentration (Figure 39). Poor bundle infiltration made the monofilaments more susceptible to damage; there was poor load transfer throughout the monofilament, and low tensile strength resulted. Bundle impregnation was improved by untwisting the yarn and spreading the fibers prior to impregnation.

The highest values obtained in three matrix precursors after process optimization are given in Table XXV. In HTR matrix, the average fiber tensile strength was 2.254 GN/m^2 (327,000 psi), which was higher than the values obtained with bare fiber prior to process optimization which consisted of better control of tension during oxidation and improvement in bundle infiltration. (According to Ezekiel, References 25, 26,

*Trade name, Dralon T, produced by Bayer-Farbenfabriken, Germany.

Figure 38. - Schematic Microstructure of Fully Graphitized Type-D Tow. The microstructure illustrates the typical wrap-around basal orientation of fully stablized and graphitized fibers

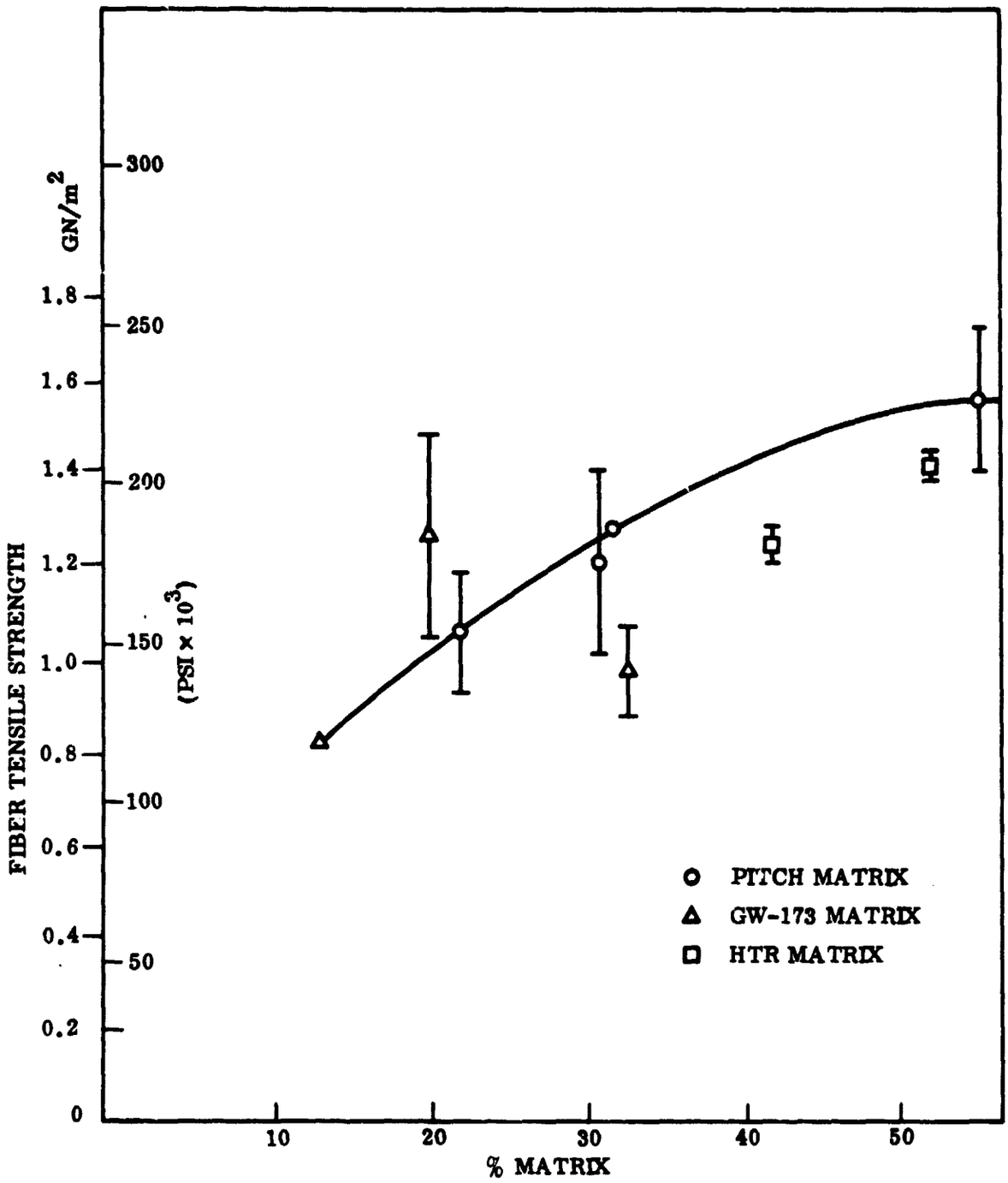


Figure 39. - Effect of Matrix Concentration on Fiber Tensile Strength – 1673°K Type-D Tow Copyrolysed to 2873°K in Various Matrices

TABLE XXV. UTILIZATION OF FIBER TENSILE PROPERTIES, COPYROLYSIS OF 1673°K TYPE-D TOW IN HTR MATRIX

Property	HTR Resin		GW-173 Resin		396 Pitch	
Fiber Designation	BB		Z		0	
Final HTT (°K)	2873		2873		2873	
Matrix Vol. Fraction	36.1		13.5		55.0	
	Average	Maximum	Average	Maximum	Average	Maximum
Monofilament Tensile Strength						
(GN/m^2)	2.255	2.405	1.551	1.644	1.551	1.717
(psi × 10^3)	327.0	348.8	224.9	238.4	225.0	249.1
Strain-to-Failure of Matrix (%)	0.47		0.435		0.4	
Predicted Fiber	1.865	1.969	1.865	1.969	1.732	1.832
Tensile Strength[a]	270.5	285.6	270.5	285.6	251.6	265.7
Percent Utilization of Fiber Tensile Strength	100	100	83.1	83.4	89.4	93.7
Composite Tensile Strength						
(GN/m^2)	1.438	1.532	1.331	1.375	0.704	0.816
(psi × 10^3)	208.6	222.2	193.1	199.4	102.1	118.4
Composite Elastic Modulus						
(GN/m^2)	293.0		264.0			
(psi × 10^3)	42.5		38.2			
Composite Strain-To-Failure	0.49	0.52	0.50	0.55		

(a) Estimated from $(\epsilon_m/\epsilon_f) \cdot \delta_f$, where δ_f = 1.865 - 1.969 GN/m^2 (270,500 to 285,600 psi).

failure to prevent the fibers from sticking together during oxidation and graphitization results in poor fiber tensile strength.) The average composite tensile strength was 1.438 GN/m^2 (208,600 psi), and the composite modulus was 293 GN/m^2 (42.5 x 10^6 psi). Results were lower in GW-173 matrix. Fiber tensile strength was 1.531 GN/m^2 (224,900 psi), equivalent to 83 percent of the value predicted, and the composite tensile strength was 1.331 GN/m^2(193,100 psi). Composite elastic modulus was 264 GN/m^2 (38.2 x 10^6 psi). In pitch matrix, the fiber tensile strength was 1.551 GN/m^2 (225,000 psi), equivalent to 89.4 percent utilization of fiber tensile strength, assuming a matrix strain-to-failure of 0.4 percent. Calculated on the basis of composite area, the tensile strength was lower, 0.704 GN/m^2 (102,100 psi), because of the high matrix concentration.

Type-D tow had the following advantages as a fiber precursor: (1) smaller bundle diameter made for easier processability with less tendency to develop macroscopic cracks due to poor fiber collimation; (2) the filament cross-section is such that pyrolysis gases can escape more readily during carbonization, and both tensile strength and elastic modulus increase with increasing heat-treatment temperature.

Bundle impregnation problems and filament wetting are encountered with Type-D tow Twofold improvement was accomplished by untwisting the tow prior to impregnation (Figure 26). Possibly further improvements could have been accomplished by chemical treatment of the fiber to increase the wettability.

To summarize, in both conventional and copyrolysis experiments, best results were obtained with a matrix with a high char yield and improved strain-to-failure, i.e., with HTR matrix. In copyrolysis, best results were obtained with Type-D tow in which both tensile strength and modulus increase with increasing heat-treatment temperature and in which the bundle size is small enough to facilitate ease of handling and to minimize the formation of flaws.

Section 6

CONCLUSIONS

Fabrication of large-diameter carbon composite monofilaments with high-strength and high-modulus by resin impregnation of multifiber carbon tows or rovings followed by pyrolysis has been limited by two factors which affect the properties of the composite monofilament. These are: (1) the inherently low strain-to-failure of most pyrolysed matrices which prevent the full utilization of the fiber reinforcing potential, and (2) the development of shrinkage cracks induced in the matrix by differential shrinkage between fiber and matrix during pyrolysis which further reduce matrix strain-to-failure and, consequently, composite tensile properties.

These problems have been overcome by matrix modification to improve matrix char yield and strain-to-failure and by the use of copyrolysis in which partially processed carbon-fiber precursors are pregged with suitable matrix precursors and pyrolyzing and heat-treating them together.

The best results with conventional pyrolysis was with Thornel 75 in high-temperature thermosetting resins (HTR) with a high char yield (90 percent) which was graphitizable when processed in the carbon composite monofilament. Improvement in strain-to-failure from 0.31 percent after pyrolysis to 1273°K to 0.47 percent was obtained after graphitization at 2873°K. The highest composite tensile strengths were obtained with fiber volume fractions of 60 to 70 percent. The highest average composite tensile strength was 1.449 GN/m^2 (210,200 psi). The range of values obtained after process optimization was 1.511 GN/m^2 (219,200 psi) to 1.337 GN/m^2 (194,000 psi). The composite elastic modulus of monofilaments of this type was 302 GN/m^2 (43.7 x 10^6 psi), equivalent to a fiber elastic modulus of 460 GN/m^2 (66.6 x 10^6 psi). The composite strain-to-failure was 0.47 percent.

In copyrolysis, the best results were obtained with Type-D-tow, a polyacrylonitrile fiber precursor in which both tensile strength and elastic modulus increase with heat-treatment temperature. Best results were obtained with a fiber pretreatment of 1673°K, followed by impregnation with HTR resin and combined pyrolysis and heat-treatment to 2873°K when fiber and matrix strain-to-failure were the same. After copyrolysis optimization, the average composite tensile strength was 1.438 GN/m^2 (208,600 psi), and the range of values was 1.393 GN/m^2 (202,000 psi) to 1.532 GN/m^2 (222,200 psi). The composite elastic modulus was 293 GN/m^2 (42.5 x 10^6 psi), equivalent to fiber-elastic modulus of 426 GN/m^2 (61.9 x 10^6 psi). Monofilaments produced with HTR matrix were free of excessive flaws and defects.

With matrix precursors with lower char yield (70 percent), such as GW-173, a modified phenol formaldehyde, better results were obtained with copyrolysis than with conventional pyrolysis. With Thornel 75 pyrolysed to 1273° K in GW-173, the average composite tensile strength was 0.777 GN/m^2 (112,800 psi), and the monofilament was not free

of pyrolysis cracks and defects. Using this matrix with 1673°K Type-D tow and copyrolysing and heat-treating to 2873°K produced a carbon composite monofilament with an average composite tensile strength of 1.331 GN/m^2 (193,100 psi) and a maximum value of 1.375 GN/m^2 (199,400 psi). Composite elastic modulus was 264 GN/m^2 (38.2 x 10^6 psi), equivalent to a fiber elastic modulus of 299 GN/m^2 (43.3 x 10^6 psi).

Section 7

RECOMMENDATIONS FOR FUTURE WORK

These studies have shown that the best tensile properties can be achieved in pyrolysis of graphitized filament or with partially carbonized filaments when high char-forming resins are used and heat treatment is carried out to temperatures to equalize fiber-and-matrix strain-to-failure.

Further improvements could be accomplisned by (1) continuous processing to minimize fiber damage from handling; (2) use of high-char-forming resins with higher-strength, higher-modulus fibers as they become available; i.e., with strengths of the order cf 2.758 GN/m^2 (400,000 psi) and elastic moduli of the order of 552 GN/m^2 (80×10^6 psi); and (3) further development of the copyrolysis technique using Type-D tow and HTR resin.

Areas which merit further study are:

- The oxidation process, using a continuous process and varying the tension to determine the effect of degree of stretch on tensile properties
- Time-temperature relationships in carbonization and copyrolysis with possible emphasis on longer processing cycles to minimize the formation of flaws within the carbon-fiber precursors
- Improvement in wetting of Type-D tow by chemical treatments and improved impregnation procedures
- Stress graphitization of copyrolysed monofilaments to increase both tensile strength and elastic modulus to values higher than those attainable without such stretching

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Appendix A

NOMENCLATURE

A_f = fiber cross-sectional area

A_m = matrix cross-sectional area

d spacing = interlayer distance

d_c = density of composite monofilament

d_f = density of fiber

d_m = density of matrix

E_c = elastic modulus of composite monofilament

E_f = true fiber elastic modulus

E_m = elastic modulus of the matrix

L = load

L_c = crystallite size, c-direction

V_f = volume fraction fiber

V_m = volume fraction matrix

w_c = unit length weight of composite monofilament

w_f = unit length weight of bare fiber

w_m = unit length weight of matrix

ϵ_f = fiber strain-to-failure, bare fiber

$(\epsilon/_m)_c$ = strain-to-failure of matrix in the composite

ϵ_m = matrix strain-to-failure

σ_c = ultimate tensile stress in the composite

σ_f = tensile stress in the fiber

σ_m = tensile stress in the matrix

σ_t = predicted tensile strength