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Properties of Textile Grade Ceramic Fibers

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Abstract

The availability of textile grade ceramic fibers has sparked great interest for applications in composite reinforcement and high temperature insulation. This paper summarizes the properties of various small diameter textile grade ceramic fibers currently available. Room temperature mechanical and electrical properties of the fibers are discussed for three cases: ambient conditions, after heat aging in argon, and after heat aging in wet air. Dow Corning (R) HPZ Ceramic Fiber, a silicon nitride type fiber, is shown to have improved retention of mechanical and electrical properties above 1200C.

Introduction

The utility of ceramic fibers for reinforcement of ceramic matrix composites (CMC) is well established. The extensive research on a variety of composite systems is worldwide in scope and has produced some outstanding high temperature composite materials. The high strength and excellent toughness of these systems is a direct result of the mechanical properties of the reinforcing fibers. Commercially available fibers such as Ceramic Grade (CG) Nicalon (R) fiber, Nextel (R) 480, and SCS-6 offer a composite fabricator a range of desirable properties to work with. It is also well recognized that in many of these systems, the reinforcing fiber is a limitation due to thermal decomposition and/or loss of mechanical properties at the elevated temperatures that are encountered during composite fabrication or end-use conditions.

The purpose of this paper is to review the properties of some commercial fiber materials and compare these to a new fiber recently introduced by Dow Corning. The paper will be broken down into two sections: first, some general information about HPZ fiber, and then some more specific mechanical and electrical properties of various textile grade ceramic fibers. This discussion will be limited to the class of small diameter, textile grade ceramic fibers generally considered to be most desirable for CMC reinforcement. The data presented is limited to direct fiber tests and is not composite data. The author feels that these comparisons are useful for initial evaluation of fiber properties and material selection. We also recognize that such comparisons do not predict composite performance. Ongoing studies of fiber-matrix compatibility and fiber interfaces are necessary to fully determine performance of composites.

General Information about HPZ Ceramic Fiber

HPZ Ceramic Fiber is made via a polymer precursor route. This unique, amorphous silicon nitride-type fiber has been developed as part of a DARPA/Air Force contract. The processing chemistry and characterization of this material have been the subject of several publications and will not be covered here. Silane monomers manufactured by Dow Corning (Figure I) are reacted to form a preceramic polymer which is then extruded through a spinnerette at temperatures ranging from 100-300C. The resulting uncured polymer fiber (green fiber) is then cured to a fully crosslinked, non-melting form. The cured fiber is then pyrolyzed to yield the ceramic fiber. During pyrolysis, various flue gases (CO, CH_4, SiO, etc.) are given off.

HPZ was officially introduced to the marketplace at the SAMPE show in April. It is available in developmental quantities and has a useful balance of mechanical and electrical properties. Typical properties are shown in Table I. The filament diameter has an oval cross-section that is calculated by taking the geometric average of the major and minor axes. As a developmental product, properties typically quoted cover a range of values. As you can see from Figure II, over the last two years we have been able to almost double the average tensile strength of the fiber through a series of process and procedural improvements. While no guarantees are made with regard to continuing this rate of improvement, suffice it to say that we are constantly working on improving fiber properties and that the values achieved today may be improved upon in the future.

Figure III is a typical range of tensile strength values from one particular lot of HPZ fiber. Each data point represents an individual filament tensile test (recall that HPZ is currently supplied in 500 filament tows). The range of values falls between a low of over 200 ksi to a high of about 650 ksi with an average tensile strength of 417 ksi. Such a spread of values is typical for ceramic fibers and other relatively brittle ceramic material.

As we'll see in the following section, HPZ maintains a large percentage of its mechanical and electrical properties at elevated temperatures. It has been proven elsewhere that this behavior can be attributed to the stability of the Si-N-C chemistry and that the oxygen in the fiber primarily resides near the surface of the fiber. A composition depth profile (Figure IV) produced with a scanning Auger microscope reveals that at the surface there is roughly 37% oxygen and 40% carbon, but at a depth of less than 700 nanometers, these concentrations have dropped to 5% and 12% respectively.

HPZ Ceramic Fiber is available in both 100g and 250g spools. The 250g spool contains nearly 1.5 miles of continuous tow (Figure V). The fiber is also available in several weave styles (8HS and Plain weave). Weavers who have handled HPZ for us have remarked that the fiber handles at least as well as mid-modulus carbon fibers. The fiber is supplied with a PVA sizing that can be removed by either a double hot water wash, or a 30 minute/600C/air exposure. Both of these methods will effectively remove the sizing without any effect on the mechanical or electrical properties.

As a class, non-oxide fibers such as HPZ have a higher strength than oxide fibers. Since non-oxide fibers typically have a lower density, they are considerably stronger than oxide fibers on a specific strength basis. Figure VI illustrates this nicely. The small circled area shows the range of properties currently possible with laboratory prepared HPZ. The excellent combination of specific strength and modulus of T-300 carbon fiber (as an example of carbon fibers) is shown by its location in the upper right quadrant of the chart. Clearly, we would like to improve the properties of ceramic fibers to equal the room temperature properties of the graphite fibers, and have the properties retained at very high temperatures in air.

<u>Room Temperature Properties</u>

Table II illustrates the mechanical and electrical properties of several textile grade ceramic fibers considered in this paper. Structural and compositional information is presented in Table III. Of the fibers in this list, only Dow Corning (R) HPZ Ceramic Fiber is likely to be new to this audience. The reader should note that unless otherwise specified, fiber tensile data is for single filament testing at 1" length, tensile modulus values are calculated using machine compliance corrections, and that electrical measurements are made at 10 Ghz (x-band) at room temperature.

Obviously, it is the elevated temperature performance of ceramic fibers that is critical for the majority of applications where they are considered for use. Although some workers only consider oxidizing conditions to be of interest, we felt that inert, non-oxidizing conditions are useful since they represent conditions encountered during some composite fabrication processes and some use conditions (For example, the interior of a fully dense CMC may contain a very low partial pressure of oxygen). A two hour, 1400C flowing argon heat soak became a somewhat standard test condition during early studies within our program. This condition was initially chosen because Nicalon fiber was almost completely destroyed by such treatment. As shown in Figure VII, both Nicalon and Tyranno almost totally lose their reinforcing properties after such a thermal treatment. These studies, as well as work by others, show that this is a result of massive decomposition that occurs with loss of CO and SiO. As is also reported elsewhere, the oxide fibers generally weaken somewhat due to grain growth. In the case of HPZ fiber, it has been determined that the chemistry and the amorphous structure are very stable at 1400C. However the strength of the fiber is sensitive to minute levels of impurities. Recently we have tested a number of samples that retain fully 100% strength and maintain >300 ksi after a 2 hour soak at 1400C. No other fiber tested has shown such excellent inert atmosphere stability.

Similar argon agings have been carried out at lower temperatures. Generally, these studies show trends that are consistent with studies reported in the literature. Figure VIII shows the large weight losses that occur with Nicalon and Tyranno as CO evolves at higher temperatures. Note however, that the High Volume Resistivity (HVR) Nicalon fiber does remain reasonably stable for 65 hours at 1100C. As expected, the more stable chemistry of Nextel fiber shows only the weight loss associated with organic sizing present on the tows. Similarly, HPZ fiber shows the sizing burnoff and finally the loss of some surface oxygen at 1300C.

The electrical properties of the fibers essentially reflect the changes in bulk chemistry occurring. Figures IX and X show that the dielectric behavior of Nicalon and Tyranno change significantly as the chemistry changes due to loss of CO. In sharp contrast, HPZ and Nextel are electrically very stable as a result of the much more stable chemistry of these fibers.

Since certain applications require that fibers are exposed to air at elevated temperatures, it is important to examine heat aging under oxidizing conditions. We selected 100 hours at 1000C as a representative condition. Flowing wet air (humidified at RT) was selected for its aggressiveness. In the study illustrated in Figure XI, we found that SiC-type fibers CG Nicalon, HVR Nicalon, and Tyranno lost strength in sequence as expected based on our findings in the inert atmosphere. Thus, the retained strength was (in order) CG Nicalon, HVR Nicalon and Tyranno. Once again, the titanium present in Tyranno did not aid stability under these conditions. Another surprise was the significant strength loss of the oxide fibers under oxidizing conditions. Apparently, some grain growth occurs even at 1000C in air causing a strength loss. Of the commercial fibers, only CG Nicalon retains >200 ksi strength.

Although it was expected that a silicon nitride fiber such as HPZ would show good oxidative stability, the results were still somewhat surprising. Within the normal error of the tensile test, no change in strength was observed during this experiment. Other work at Dow Corning at 1100C has also shown excellent strength retention for periods up to at least 15 hours.

As illustrated by the data, HPZ ceramic fiber strength is unaffected by a 100 hour oxidative treatment. Multiple batches and repeat runs show no loss of strength although some evidence of surface oxidation is observed. At higher temperatures, for instance, this surface oxidation can lead to fusion of the individual filaments within the tow bundle. Such fusion creates a very brittle, weak tow when treated at room temperature. Paul Sawko (NASA Ames) has studied fiber tow oxidation over a range of temperatures as illustrated in Figure XII. This data was generated by tensile testing fiber tows at room temperature after a 2 hour soak in air. This data nicely shows that while only HPZ fiber retains strength well in 1200C heat soaks, the strength reduction caused by fiber fusion does degrade strength at higher temperatures. Thus, in tow form, the usable temperature of HPZ fiber in free air appears to be 100-200C higher than for other non-oxide materials, but is still limited to about 1200-1300C. Note that the HPZ sample used in this experiment was from the earlier stages of our program. The denier here is only 400, while today's fiber has 1000 d. Also the starting fiber strength is about 200 ksi, and current values are around 400 ksi. Newer material would start at about 8 kg/denier and be expected to follow the same trend.

Although room temperature tests after heat soaks can be useful in judging the performance of a fiber, actual properties at various temperatures are necessary to effectively design composites for high temperature use. Workers at Penn State University have developed equipment and procedures for elevated temperature tensile testing of single filaments in air. One uniqueness of this technique is the capability for testing at greater than 1400C. Figure XIII shows the results of one test series. As reported previously, the oxide based fibers are generally lower strength at room temperature and maintain strength reasonably well to about 800C. Above 800C the strength degrades rapidly until at 1200C there is sufficient deformation to prevent testing at higher temperatures. In contrast, non-oxide fibers are considerably stronger at room temperature and generally maintain strength well up to about 1200C in fast fracture tests of this type. Above 1200C, Tyranno fiber loses strength rapidly, presumably due to its high oxygen content, while only Nicalon and HPZ hold useable strength levels at 1400C. Even at 1450C, the HPZ fiber has greater than 100 ksi strength. Elevated temperature modulus data (Figure XIV) generally parallels the same behavior, although here the excellent stability of HPZ's microstructure and fiber chemistry is even more apparent as evidenced by the superior modulus retention.

Conclusions

1) Non-oxide fibers have good room temperature strength and modulus, generally much higher than for oxide fibers.

2) CG Nicalon and HPZ are the only fibers to retain useable tensile strength and modulus above 1300C.

3) HPZ fiber exhibits good retention of mechanical properties after oxidation at 1000C for 100 hours. This is the only material showing no strength loss under such conditions.

4) The handling properties of HPZ are similar to mid-modulus carbon fibers.

DOW CORNING® HPZ CERAMIC FIBER

Typical Properties

• Composition (Wt. %)	Si	57%
	N	28%
	C	10%
	O	5%
• Amorphous Structure		
• Diameter	10-12 microns	
• Tensile Strength	420 ksi (2.9 GPa)	
• Tensile Modulus	28 Msi (193 GPa)	
• Density	2.4 g/cc	
• DK	6.1	
• LF	0.06	
• Heat Capacity	0.68 J/g C	
• Coeff. of Thermal Ex (20-1100°C)	4.1 ppm/C	

Table I : HPZ Ceramic Fiber - Typical Properties

FIBER PROPERTIES

Fiber	Diameter	Tensile Strength	Modulus	DK	LF
CG NICALON	15	400	28-30	9.5	1.0
HVR NICALON	15	350	26-28	6.4	0.05
LVR NICALON	15	425	26-28	>20	>10
C-Coated NICALON	15	425	28-30	-	-
TYRANNO	8	450	22	7.8	1.0
HPZ	10-12	420	28-32	6.1	0.06
NEXTEL 480	8-10	220	30-32	6.4	0.05

Table II : Comparable Fiber Properties

FIBER CHARACTERISTICS

Fiber	Composition	Density (g/cc)	Structure
CG NICALON™	Si-C-O	2.55	nanocrystalline SiC/ amorphous
HVR NICALON	Si-C-O	2.35	nanocrystalline SiC/ amorphous
LVR NICALON	Si-C-O	2.35	nanocrystalline SiC/ amorphous
C-Coated NICALON	Si-C-O	2.55	nanocrystalline SiC/ amorphous
TYRANNO®	Si-O-C-Ti	2.40	amorphous
HPZ	Si-N-C-O	2.40	amorphous
NEXTEL® 480	$Al_2O_3/SiO_2/B_2O_3$	3.10	crystalline, mullite

Table III : Fiber Characteristics

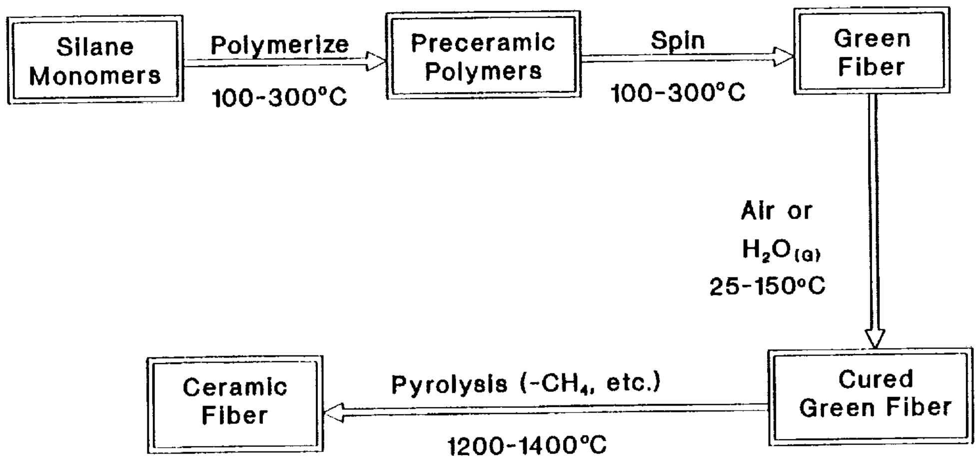


Figure I : Process Schematic - Polymer Precursor Route

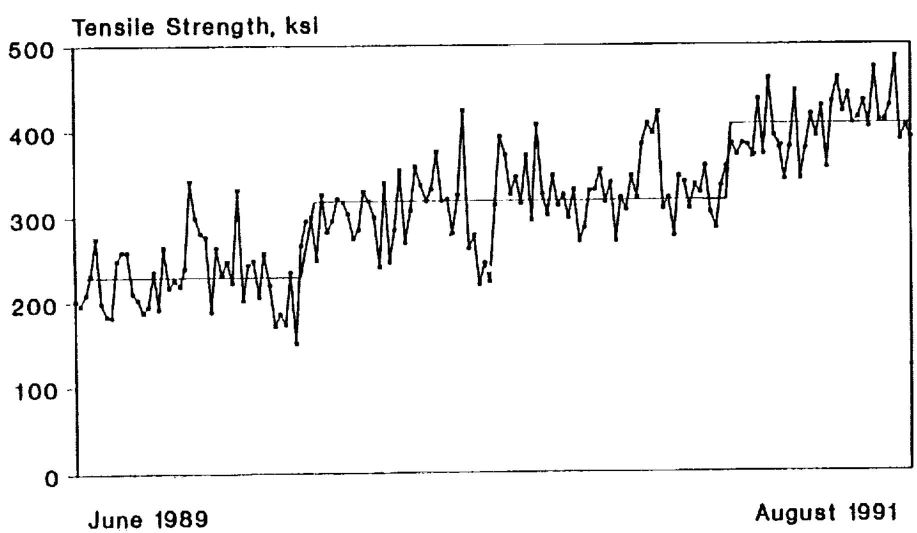


Figure II : HPZ Ceramic Fiber - Tensile Improvements

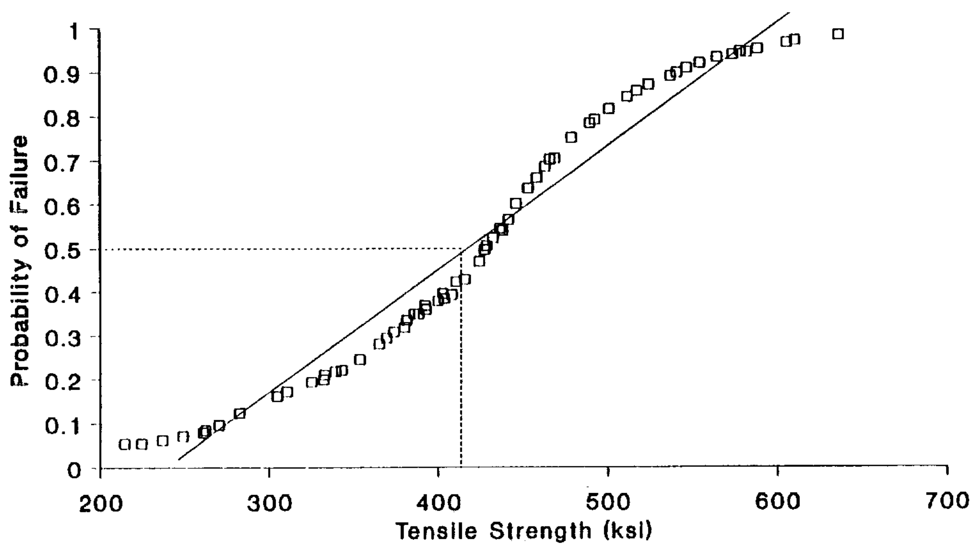


Figure III : Failure Probabilities

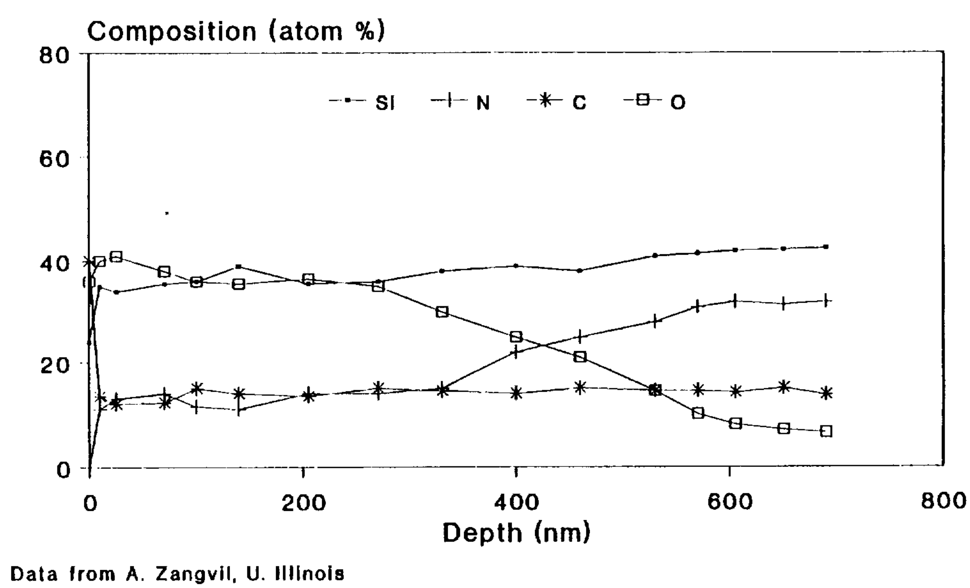


Figure IV : Compositional Depth Profile

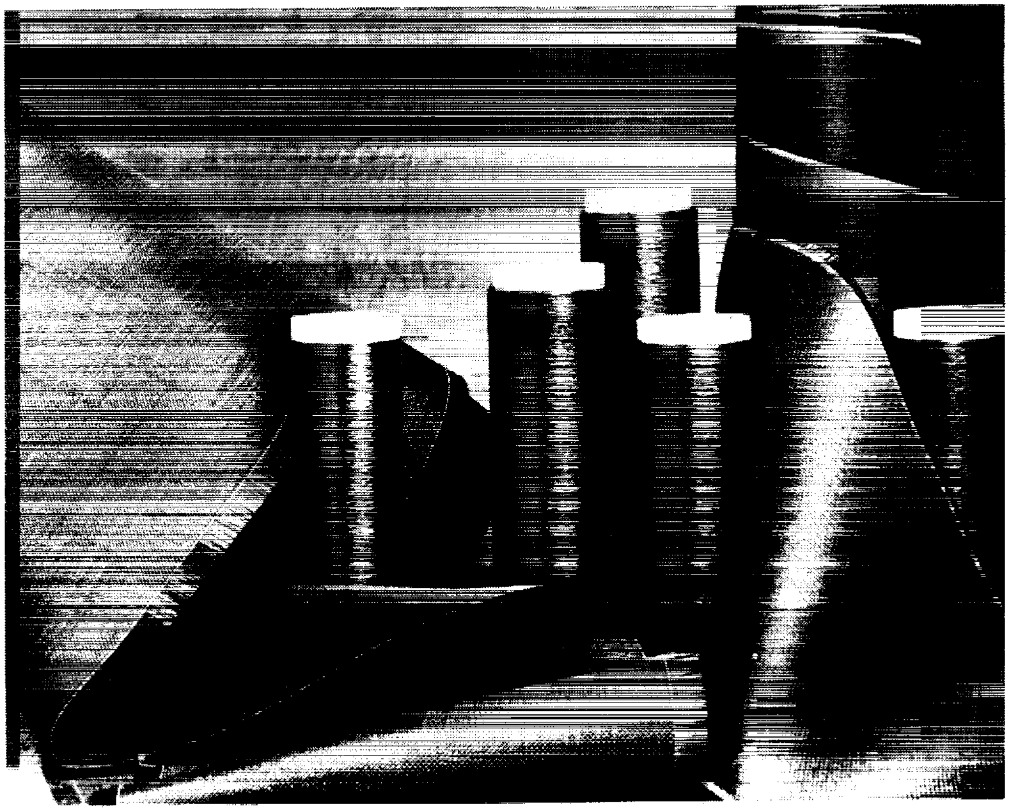


Figure V : HPZ spools and woven cloth

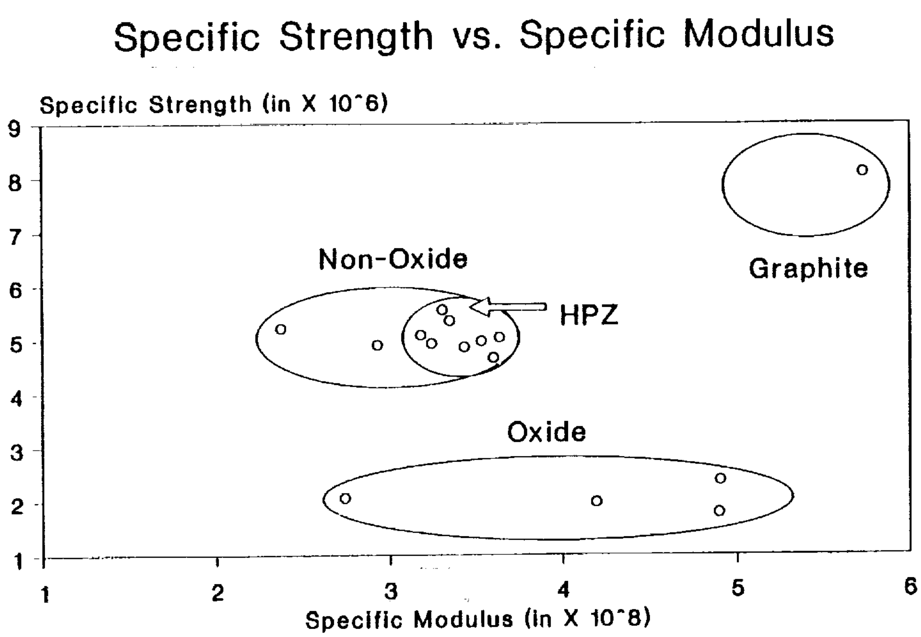


Figure VI : Continuous Fiber Comparisons

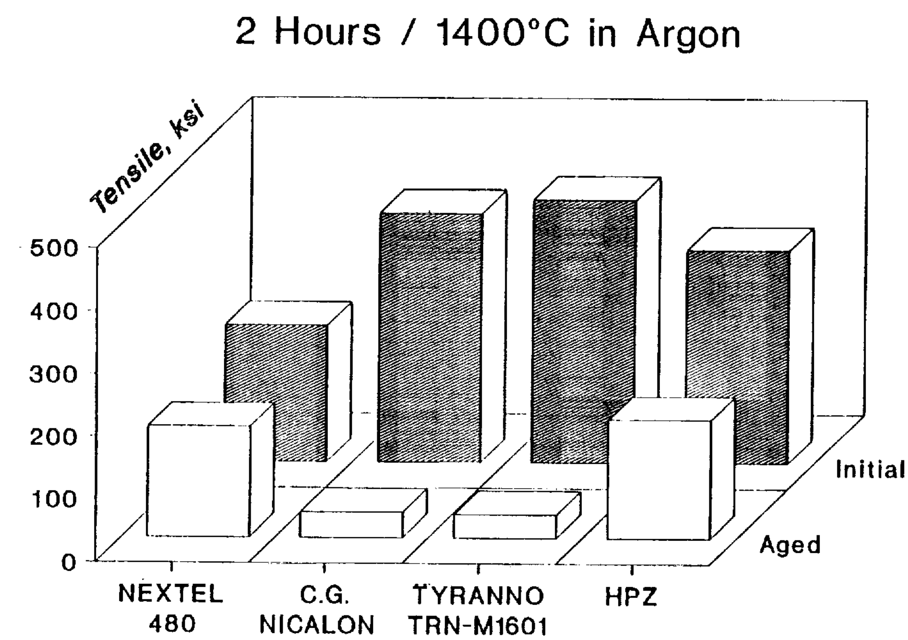


Figure VII : Inert Aging Comparisons

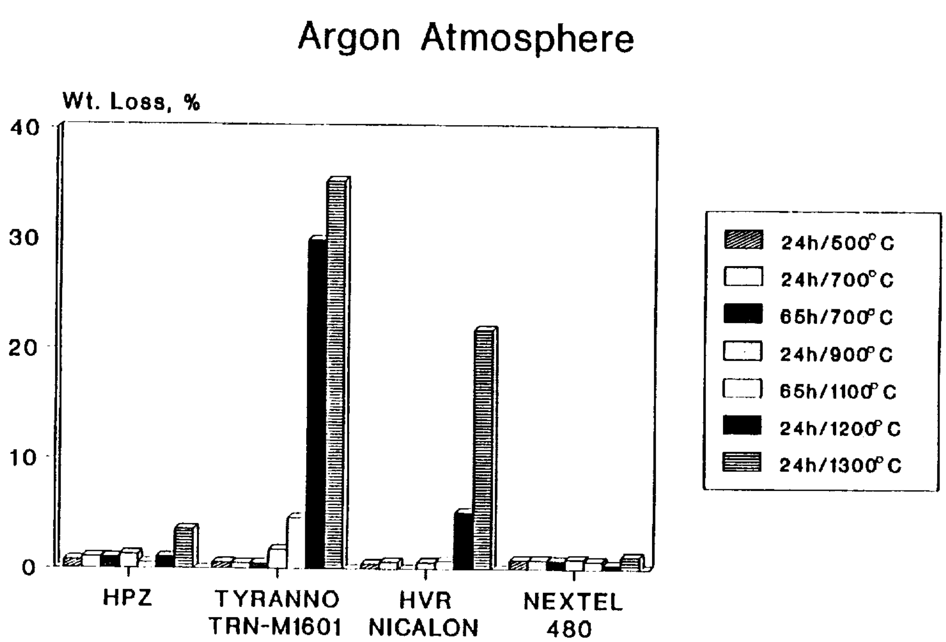


Figure VIII: Aging Effect on Fiber Weight

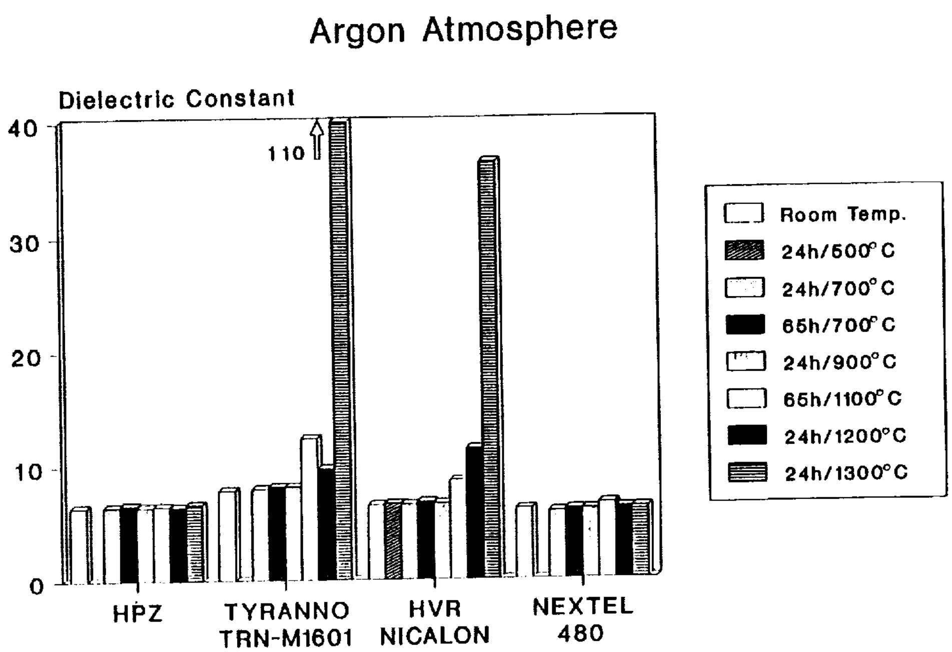


Figure IX : Aging Effect on Fiber DK

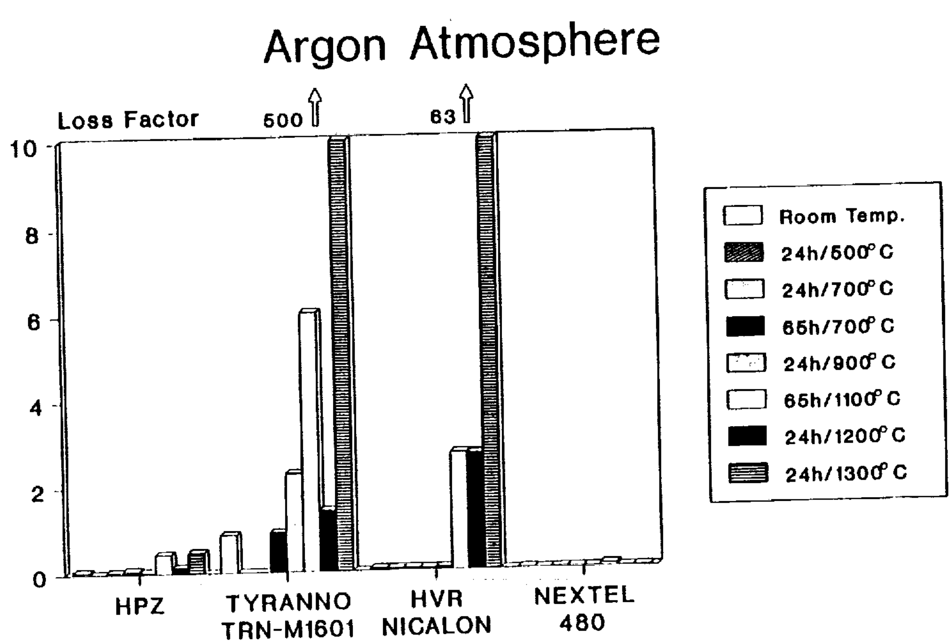


Figure X : Aging Effect on Fiber LF

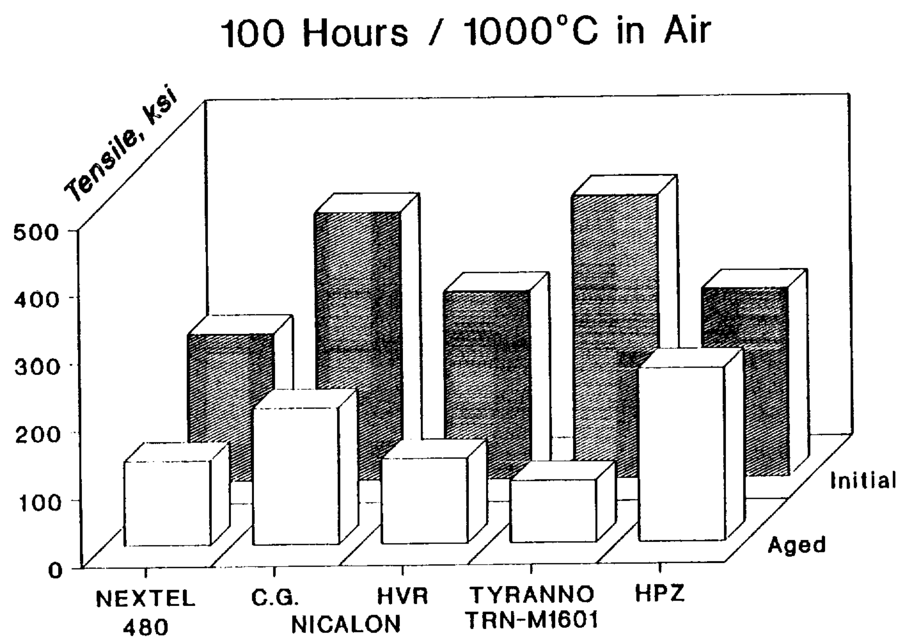


Figure XI : Fiber Oxidation Results

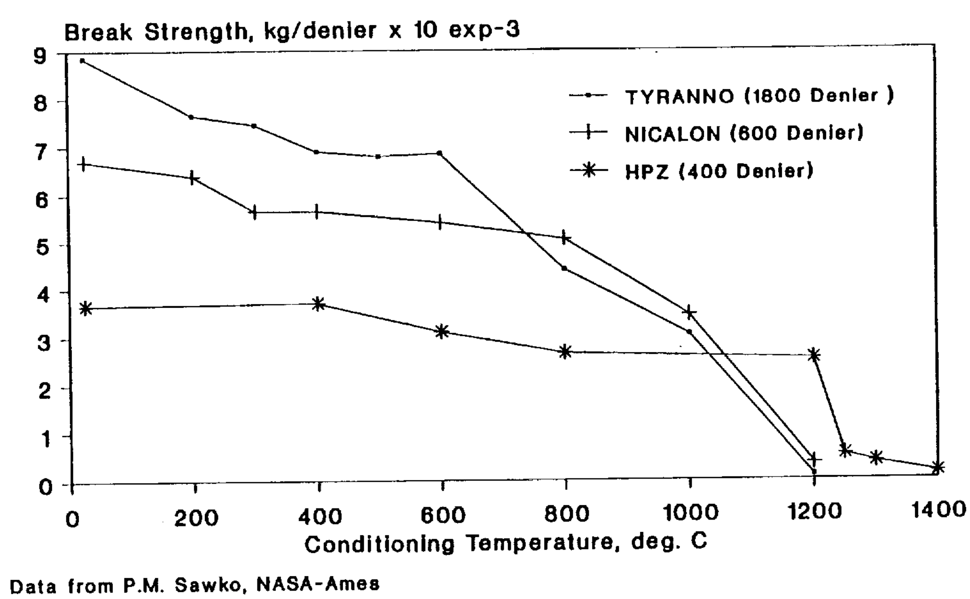
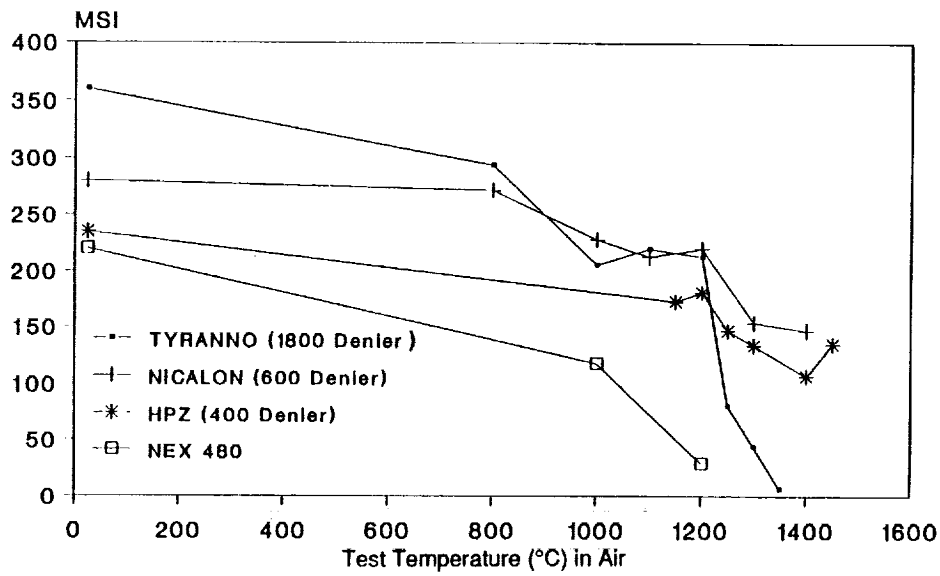
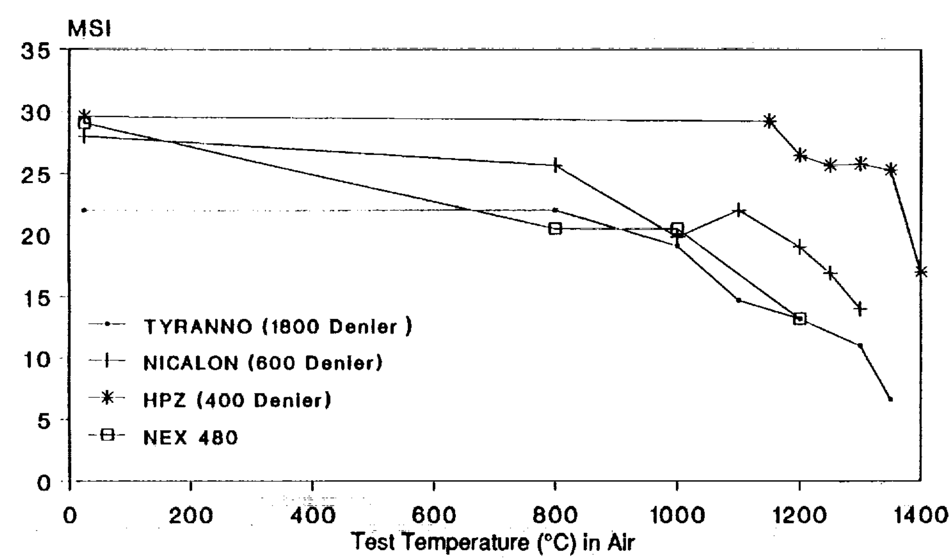


Figure XII : Effect of Conditioning Temperature on Break Strength



Data from R. Tressler, Penn State

Figure XIII: Fiber Tensile Strength - At Temperature In Air



Data from R. Tressler, Penn State

Figure XIV : Fiber Tensile Modulus - At Temperature In Air